Fluorinated anions

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UNIVERSITY OF DURHAM

A THESIS
entitled

FLUORINATED ANIONS

submitted by

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(Graduate Society)

A candidate for the degree of Doctor of Philosophy

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To Mom and Dad,

Family, and Friends.

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Finally I should like to thank my family for their continuing support and Margaret for help in the thesis production.

MEMORANDUM:

The work described in this thesis was carried out in the University of Durham between October 1986 and September 1989. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

The work has been presented, in part, by the author at:

Postgraduate Heterocyclic Symposium, Nottingham, July 1988;

12th. International Symposium on Fluorine Chemistry, Santa Cruz, California, U.S.A., August 1988;

Graduate Symposium, Durham, April 1989.

Note:

Throughout this work an 'F' in the center of a ring is used to denote that all unmarked substituents are to fluorine.

Fluorinated Anions

by M. P. Greenhall

Abstract

Each of my four main areas of work is concerned with the formation and further reactions of organic fluorinated anions.

a) We have investigated the fluoride ion induced reactions of 2H-pentafluoropropene with some perfluoro-aromatic compounds, forming a series of aryl substituted carbon acids and their corresponding carbanions. Also included is a study of an unusual product that was formed with pentafluoronitrobenzene as the aromatic substrate.

b) Some fluorinated dienes have been generated from the fluoride ion induced reactions of dimethylacetylenedicarboxylate with a series of cyclic fluorinated alkenes. With perfluorocyclohexene, a variable temperature n.m.r. investigation indicated that one of the products was fluxional at room temperature. Products derived from perfluorocyclopentene were then further reacted with mono- and bi-functional nucleophiles forming some new products including some interesting polycyclic compounds.

c) We have studied the fluoride ion induced reactions of malononitrile and phenylsulphonylacetonitrile with a range of polyfluorinated aromatic and heteroaromatic systems. This study has yielded a series of stable fluorinated organic caesium salts which could be crystallised. Acidification of these salts yielded a series of conjugate acids and some acidity measurements were made. Analysis of n.m.r. data has shed some light on the n.m.r. consequences of tautomerisation which was observed in some of the conjugate acids. A highly unusual carbon-13 n.m.r. concentration effect was studied for several pyrimidyl salts in perdeuteroacetone solution.

d) The reaction of bifunctional carbon acids with fluorinated dienes has been used to develop a route to new pentadienyl anions, cyclopentadienes, and cyclopentadienyl anions. FAB mass spectroscopy has proved to be an important tool in the study of our anionic species. Some unusual thermal isomerisation behaviour of the new cyclopentadienes has also been observed and investigated.

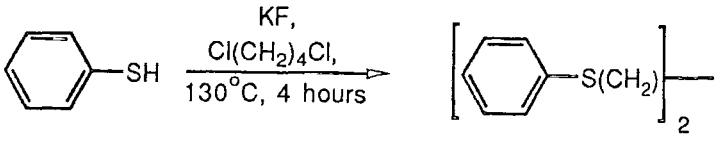
Contents

Chapter 1 - General Introduction

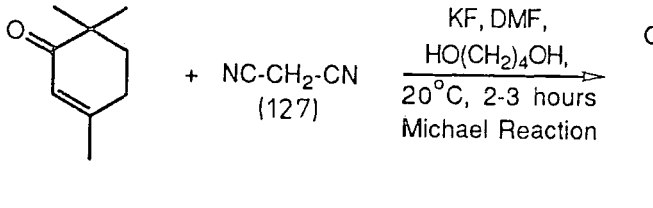
The ability of fluorine to replace hydrogen in most organic systems creates the wide ranging field of fluorocarbon chemistry. With fluorocarbons found only rarely in nature, this relatively new area of study is entirely synthetic. This introduction will not discuss the foundations of fluorocarbon chemistry as these have been extensively discussed and reviewed elsewhere, for examples see refs.[1-6]

1.1 Fluoride Ion as a Base

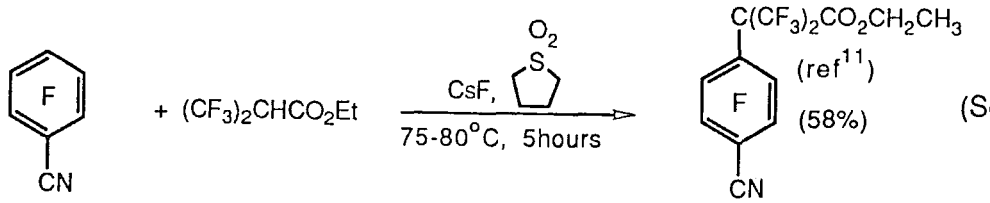
The role of fluoride ion as a base in organic synthesis has been reviewed.[7] The base strength of an ionic fluoride is dependent on the solvent in which it is dissolved, on the amount of water that is present, and on the counter cation. These contributing factors help to explain the inconsistencies of the reported basicities of fluorides. Many early reports, based upon the use of alkali metal fluorides dissolved in protic solvents such as alcohols or diols, considered fluorides to be behaving as weak bases. Conversely, aprotic solvent solutions of tetra-alkylammonium fluorides have been reported to be comparable to organomagnesium or even organolithium reagents on the basis of their ability to generate carbanions from such weak carbon acids as $(CH_3)_2SO$, CH_3CN, CH_3NO_2 and fluorene.[7,8] The addition of the cation complexing 18-crown-6 to KF-benzene or KF-CH_3CN systems may improve the fluoride solubility by at least a factor of ten, improving both fluorides basic and nucleophilic properties.[7] Reactions involving KF or CsF in aprotic media may be considered to involve a significant amount of reaction at the surface of undissolved fluoride.[9] Thus fluoride may be used to effect a wide range of base-assisted reactions (For some examples see scheme 1.1.a-c). In the final example fluoride ion presumably deprotonates the ester substrate forming an intermediate resonance stabilised anion which then reacts with the aromatic substrate. In principle the approach may



(ref[9]) (92%) (Scheme 1.1.a)



(ref[10]) (56%) (Scheme 1.1.b)



(ref[11]) (58%) (Scheme 1.1.c)

be extended to fluorinated saturated systems, *e.g.* monohydrofluorocarbons, which are known to be particularly strong carbon acids [Indeed nonafluoroisobutane is the strongest saturated carbon acid yet discovered (pK_a[12] *ca* 11 which compares well with species with extensive α,β-unsaturation, *e.g.* CH_3NO_2 pK_a[13] 10)].

1.2 Fluoride Ion as a Nucleophile

It is well known that fluoride ion functions best as a nucleophile in polar aprotic solvents,[1] although much early work used glycols as solvents. Under most conditions the general order of reactivity of the alkali metal fluorides is CsF > KF > NaF > NH_4F > LiF,[2] *i.e.* the fluoride with the lowest lattice energy is the most efficient fluorinating agent.

1.2.1 Displacement of halogen at saturated carbon

Heating is often required to effect reaction between a metal fluoride and a halogenated alkane, with best results often being obtained in the absence of solvents, or with polar solvents such as N-methyl-2-pyrrolidone (which dissolves approximately three percent potassium fluoride at 190-200°C).[6] The use of silver fluoride has the advantage of requiring relatively mild reaction conditions for sensitive compounds such as halogenoesters without disturbing the ester groups (for examples scheme 1.2.a-c).

(Scheme 1.2.a)

$Cl_3C\text{-}CCl_2\text{-}CCl_3$ —KF, 195°C, N-methyl-2-pyrrolidone→ $F_3C\text{-}CCl_2\text{-}CF_3$ (*ca* 69%) ref[14]

(Scheme 1.2.b)

$C(CH_2Br)_4$ —KF, $O(CH_2CH_2OH)_2$, 175-180°C, 200-210°C→ $C(CH_2F)_4$ (57-60%) ref[15]

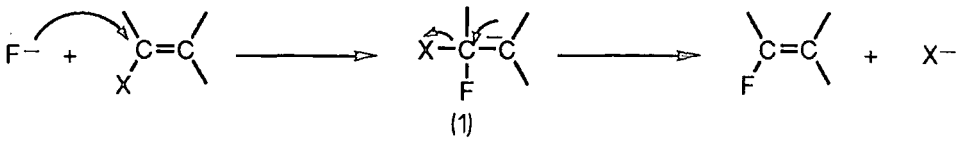
(Scheme 1.2.c)

$Br(CH_2)_6CO_2C_2H_5$ —AgF, 60°C→ $F(CH_2)_6CO_2C_2H_5$ (34%) ref[16]

1.2.2 Displacement of halogen at sp^2 or sp hybridised carbon

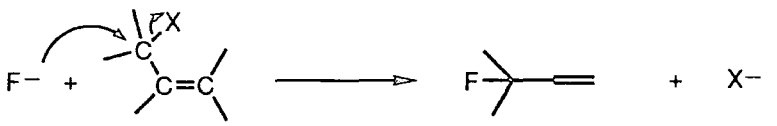
There are three processes that can lead to displacement of halide ion by fluoride ion in unsaturated systems[1] (Figs. 1.3.a-c), these are: a) addition elimination; b) allylic or benzylic substitution; c) nucleophilic substitution with rearrangement. Alternatively

(Fig. 1.3.a)



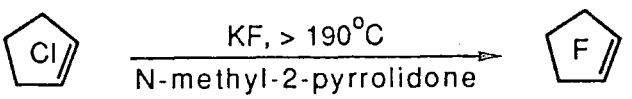
(1)

(Fig. 1.3.b)



(Fig. 1.3.c)

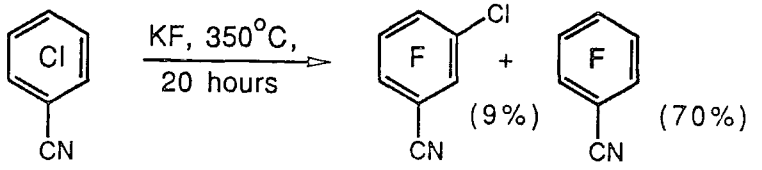
anion (1) may be trapped by an electrophilic species yielding fluoro- or polyfluoro- alkylated products (or vinylic products if an acetylenic substrate is used) (See chapters two and three). In some cases anion (1) is stable and may be observed (See section 1.3). An excellent example of perfluorination *via* process (c) is illustrated in scheme 1.4.[14] Halogenated aromatic compounds may



(Scheme 1.4)

(72%)

often be fluorinated *via* nucleophilic aromatic substitution, for example scheme 1.5.[17]



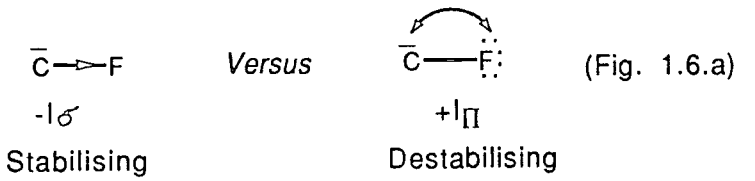
(Scheme 1.5)

1.3 Fluorinated Carbanions

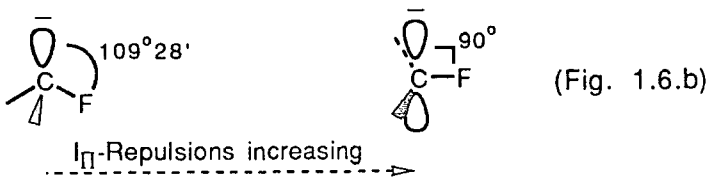
1.3.1 Stabilities of fluorinated carbanions

a) *Fluorine bonded directly to the carbanionic site*

The effect of a fluorine atom bonded directly to a carbanionic site can vary from modest stabilisation (compared to hydrogen) to strong destabilisation depending upon the geometrical situation. The more planar the carbanion the greater is the destabilising influence.[6] This phenomenon arises through conflict between a stabilising σ-inductive effect ($-I\sigma$) and a destabilising π-inductive effect ($+I\pi$) (Fig. 1.6.a). The latter stems from



(Fig. 1.6.a)



(Fig. 1.6.b)

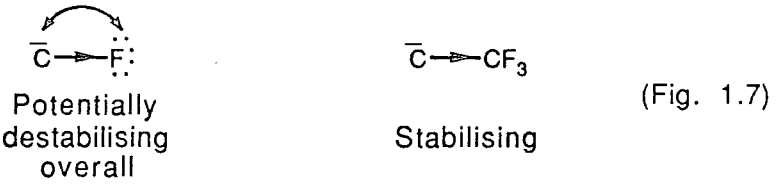
repulsive interaction between filled p-orbitals on the halogen and the filled outer orbital of the attached carbon. Because $I\pi$ repulsion is at a maximum for planar systems (Fig. 1.6.b) α-fluorinated carbanions prefer to adopt pyramidal forms.[6] Maximisation of fluorine $I\pi$ repulsion in planar systems accounts for: the observation that *para*-fluorophenol is less acidic than phenol;[6] for the deactivating influence of para fluorines in aromatic systems undergoing nucleophilic substitution;[6] and the highly unstable nature of fluorinated acetylenes such as fluoroethyne and especially difluoroethyne (see ref.[1]).

Another factor which must be considered in the context of carbanionic stabilities is B-strain[18] which is the reduction in

unfavourable repulsions when an sp^3 carbon atom changes to an essentially sp^2 hybridisation. However work on haloforms[18] has shown this factor to be relatively small.

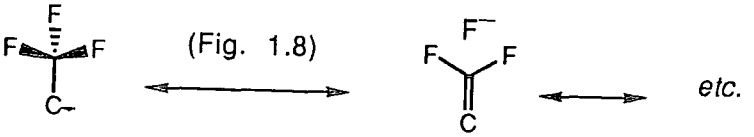
b) *Fluorine bonded adjacent to the carbanionic site*

Fluorine atoms situated β- to the carbanionic site are always stabilising with respect to hydrogen.[6] Indeed stabilisation increases as the number of β-fluorines increases at the expense of hydrogen.[6] With Iπ repulsions absent and steric factors considerably diminished the dominant effect will be inductive stabilisation (Fig. 1.7).

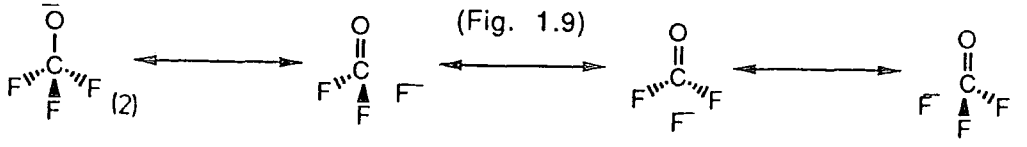


(Fig. 1.7)

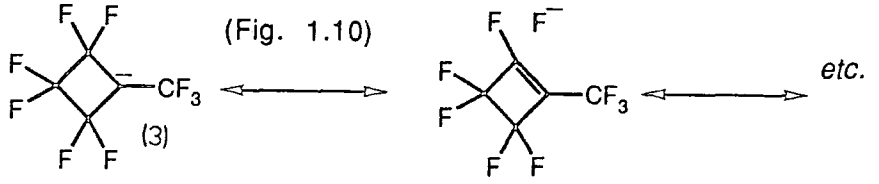
In 1950 it was proposed[19] that an additional resonance effect (negative hyperconjugation, see fig.1.8) was required to account for the measured dipole moment and relative reactivity data of certain trifluoromethyl substituted aromatic compounds. Molecular



orbital calculations can be used to predict bond angles and bond lengths of hyperconjugating species, and in the case of the trifluoromethoxide ion (2)[20] are close to the experimental X-ray determinations. In this ion (Fig. 1.9) C-F bond lengths are found to be exceptionally long while the C-O bond length is unusually short. Also each fluorine atom carries more negative charge (an extra 0.2e) than might be otherwise be predicted. Inexplicably the F-C-F bond angles were found to be very small at *ca* 102^0.



Recently the molecular and electronic structure of a salt of ion (3) (Fig. 1.10) has been reported.[21] The C-C bond distances to



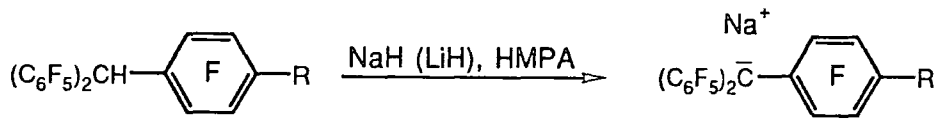
the planar carbanionic centre are short and the C-F bonds on the CF_2 groups are long, providing some evidence for fluorine negative hyperconjugation. Recently work by Rahman and Lemal,[22] studying the rotation-inversion barrier in α-fluoroamines using variable temperature n.m.r., has demonstrated the effect of negative hyperconjugation in neutral species (negative hyperconjugation raises the barrier to C-N rotation).

Although there is little evidence from reaction kinetics studies for the effect of negative hyperconjugation,[23,24] the theory now seems to rest on a solid foundation.[22]

1.3.2 Formation of fluorinated carbanions

a) *By base induced deprotonations*

A notable example of the formation of a fluorinated carbanion was reported by Vlasov and Yakobson[25] (Scheme 1.11). A correlation



Where R = OCH_3, CH_3, H, F, Cl, Br, CF_3 and other variants (Scheme 1.11)

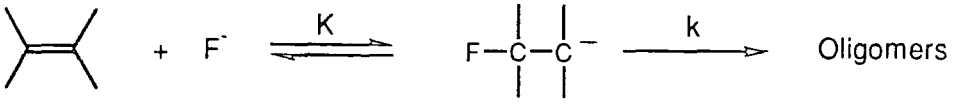
was proposed between the change in the chemical shifts of the *para* fluorine atoms upon ionisation with the pK_a of the molecule (with higher pK_a values for larger chemical shift changes). When 'R' equals fluorine a *ca* 24ppm upfield shift is reported upon ionisation. From an analysis of fluorine n.m.r. data it was suggested that in the systems where 'R' was electron donating (OCH_3, CH_3) the substituted phenyl ring resides more out of the carbanionic plane than when 'R' is of an electron withdrawing nature.

By a comparison of reactions with hydroxide the following acidity order for nitrile and trifluoromethyl substituted carbon acids has been determined[26] (Fig. 1.12).

$(CF_3)_2CH_2 \leq F_3C\text{-}CHF\text{-}CN << CF_3CH_2CN$ (Fig. 1.12)

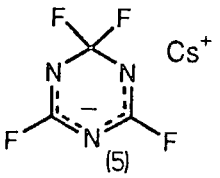
b) *By reaction of an alkene with fluoride ion*

The generation of perfluoroalkyl anions by the reaction of fluoride ion with fluorinated alkenes is well known.[27] However, such anions (4) are rarely long-lived since they promote oligomerisation reactions of the corresponding alkene



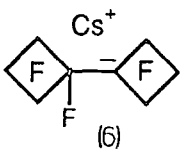
(Scheme 1.13) (4)

(Scheme 1.13). Only in cases where K is large and / or k is small will anion (4) be long-lived, hence observable. There are now a number of examples of stable fluorinated carbanions including, from these laboratories, σ-complexes such as salt (5)[28] (Fig. 1.14.a), cyclic anions such as salt (6)[29] (Fig. 1.14.b), other tertiary perfluorocarbanions[30,31] [For example salt (7), fig. 1.14.c] and from other laboratories species such as allyl anion (8)[32] (Fig. 1.14.d). The chemical shift data for



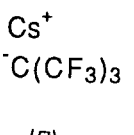
(5)

(Fig. 1.14.a)



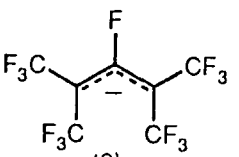
(6)

(Fig. 1.14.b)



(7)

(Fig. 1.14.c)



(8)

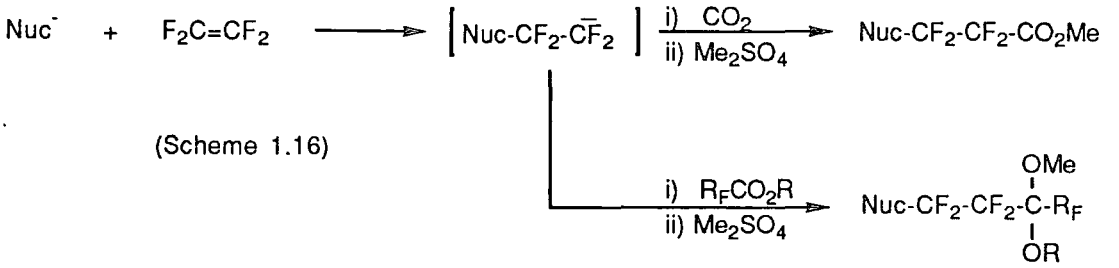
(Fig. 1.14.d)

perfluoro-*t*-butyl caesium (7) are remarkable for the fact that the carbon bearing negative charge is associated with an upfield shift from appropriate model compounds (bromo-derivatives), but the adjacent carbon is associated with a downfield shift. The same downfield shift is reflected in the ^{19}F n.m.r. spectrum for the site adjacent to charge.[31,32] It is argued[31] that the observed substantial low-field shifts for positions adjacent to the carbanionic centre provide some evidence for the previously discussed concept of negative hyperconjugation (Fig. 1.15).

(Fig. 1.15)

c) *By reaction of an alkene with other nucleophiles*

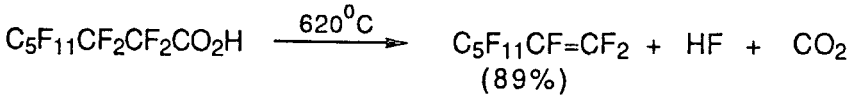
Krespan and coworkers[34,35] have employed a wide variety of nucleophiles (including cyanide, azide, phenoxide and even chloride) in reactions with terminal fluorinated alkenes. The resulting carbanionic species were then trapped by carbon dioxide or by fluorinated esters followed by methylation (For example see scheme 1.16).



(Scheme 1.16)

d) *Decarboxylation Reactions*

Pyrolysis (sometimes mild) of fluorinated carboxylic acids or of their anions will yield products derived from their respective carbanions (either through loss of fluoride forming an alkene or by reaction with an electrophile)[2] (See[36] scheme 1.17).



(Scheme 1.17)

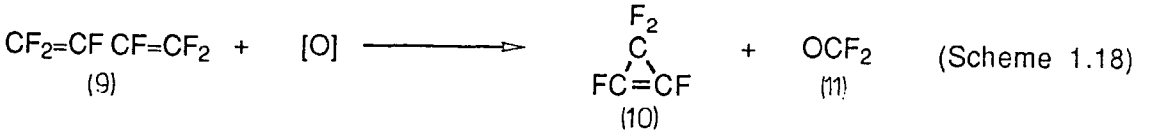
1.4 Fluorinated Cycloalkenes, Dienes, and Related Systems

1.4.1 Introduction

This section discusses the syntheses and some limited aspects of the chemistry of fluorinated cycloalkenes, dienes, and related systems. This discussion will be restricted to the more highly unsaturated systems, other systems have been described in the literature (For example[37]) and elsewhere (For example[138]).

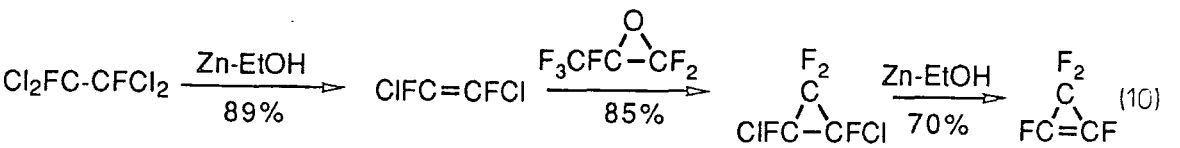
1.4.2 Tetrafluorocyclopropene (10)

Tetrafluorocyclopropene (10), the smallest unsaturated cyclic fluorocarbon, was first isolated by Stuckey and Heicklen[38] as an oxidation product of 1,3-perfluorobutadiene (9). Mercury sensitised photolysis of mixtures of diene (9), and oxygen yielded compound (10) as a minor product. However, compound (10) and difluorophosgene (11) were found as the major products in the reaction of diene (9) and atomic oxygen (formed by *in situ* photolysis of nitrous oxide) (Scheme 1.18). Mercury sensitised



(Scheme 1.18)

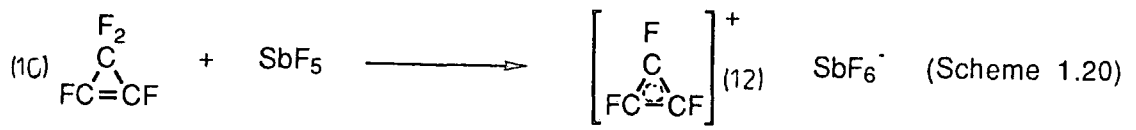
decomposition of compound (10) led to tetrafluoroallene, tetrafluoromethylacetylene and tetrafluoroethene. Similar products have recently been reported from the infrared multiphoton-induced isomerisation of compound (10).[39] Sargeant and Krespan[40] have published a more convenient dehalogenation route to compound (10) (Scheme 1.19).



50-55% overall yield

(Scheme 1.19)

Tetrafluorocyclopropene (10) is a colourless, flammable, toxic, explosive[40] gas (bp *ca* -13°C). The lower explosive limit is approximately 3% in air. Reaction with strong Lewis acids (antimony pentafluoride, or boron trifluoride) produced white precipitates consistent with the salts of perfluorocyclopropenium ion (12) (Scheme 1.20).



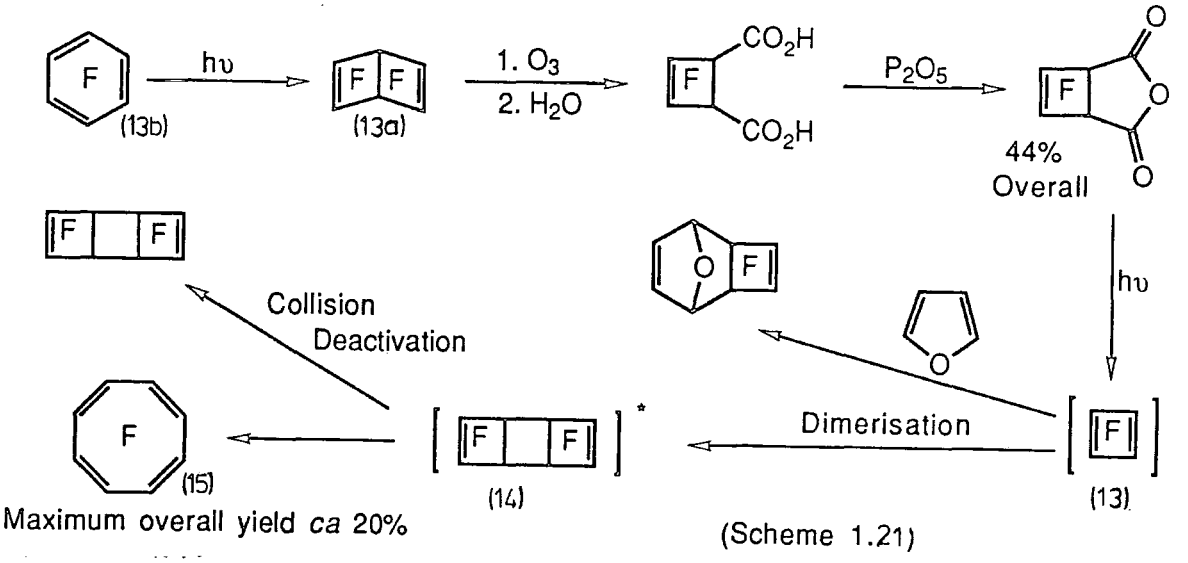
(Scheme 1.20)

1.4.3 Fluorinated Cyclobutadienes

a) *Tetrafluorocyclobutadiene (13)*

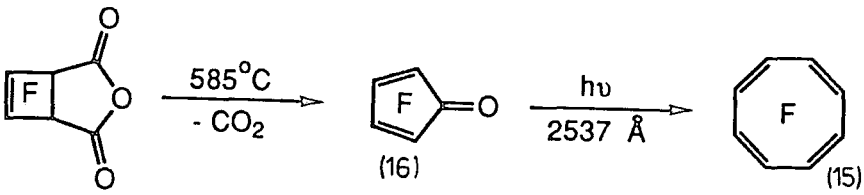
Tetrafluorocyclobutadiene (13) like its hydrocarbon counterpart is predicted to be antiaromatic in nature. Gerace, Lemal, and Ertl[41] have generated what they believed to be the short lived compound (13); its existence being revealed by its corresponding

trapping products. Their route (Scheme 1.21) is based upon the Dewar valence isomer (13a) of hexafluorobenzene which was itself prepared by vapour phase photoisomerisation of hexafluorobenzene (13b). Their procedure involved ozonolysis, hydrolysis, dehydration, and finally, vapour phase photolysis yielding the transient compound (13) (Scheme 1.21).



(Scheme 1.21)

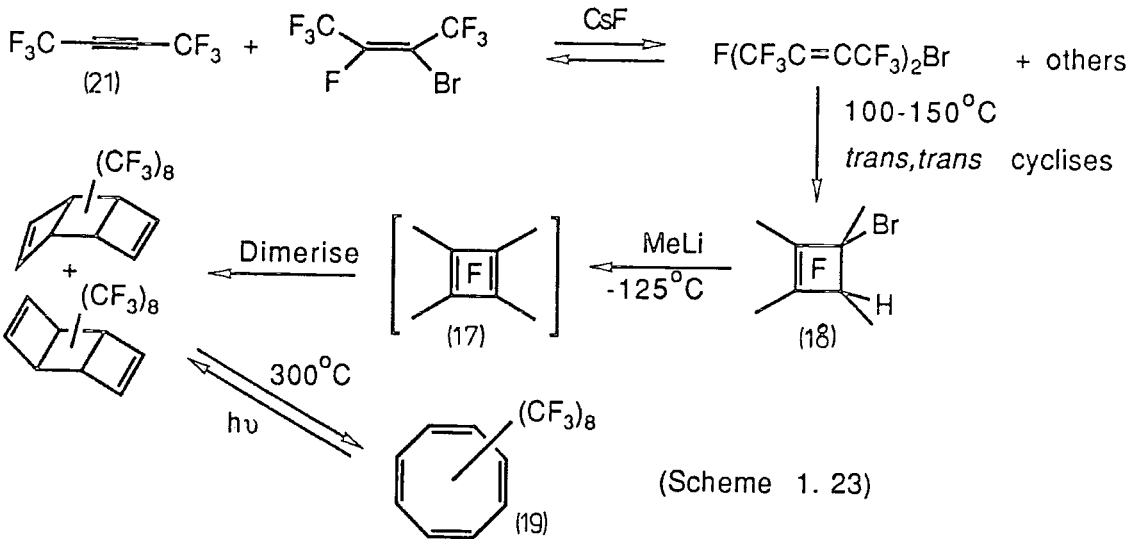
Cyclic Diene (13) may be trapped with furan, or may be allowed to dimerise. If the activated dimer (14) is not collision deactivated by inert gas it may ring open to octafluorocyclo-octatetraene (15). It is also noteworthy[42] that the vapour phase photolysis of tetrafluorocyclopentadienone (16) smoothly yields the cyclic tetraene (15). This may also involve tetrafluorocyclobutadiene (13) as an intermediate (Scheme 1.22).



(Scheme 1.22)

b) *Tetrakis(trifluoromethyl)cyclobutadiene* (17)

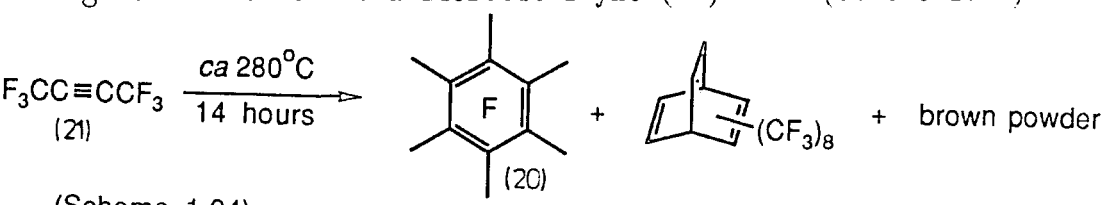
Several routes to diene (17) have been reported (for example[43-46]). In an early report[47] diene (17) was formed *via* the low temperature dehydrobromination of alkene (18) (Scheme 1.23). On warming dimerisation of the diene occurs. Heating the dimers to 300°C produces perfluoro-octamethylcyclo-octatetraene (19).



(Scheme 1. 23)

1.4.4 Hexakis(trifluoromethyl)benzene (20)

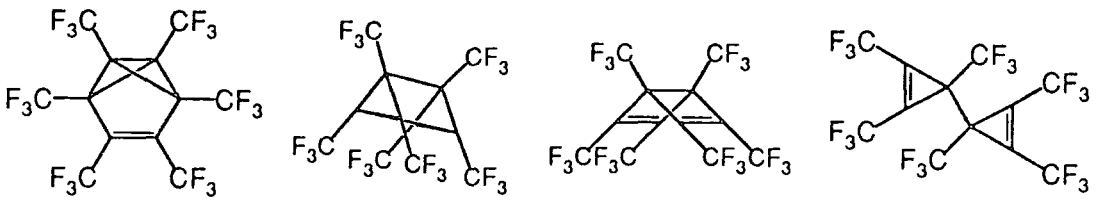
Compound (20) was first reported as a product of the thermal oligomerisation of hexafluorobut-2-yne (21)[48,49] (Scheme 1.24).



(Scheme 1.24)

(3.5g, pure) (0.4g, pure)

The valence isomer chemistry of compound (20) has been reported by Haszeldine and coworkers,[50] with three valence-bond isomers (20a, 20b, 20c) (Figure 1.25) being formed *via* the room temperature u.v. irradiation of compound (20). Grayston and Lemal,[51] have reported the final member in this the first complete set of benzene valence isomers (20d). Although isomer (20d) was synthesised from acyclic precursors it may be aromatised to compound (20) at 360°C, or photolysed to give a mixture of all five valence isomers.

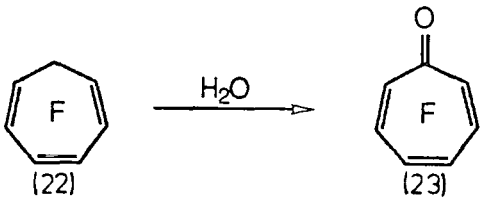


(20a) (20b) (20c) (20d)

(Fig. 1.25)

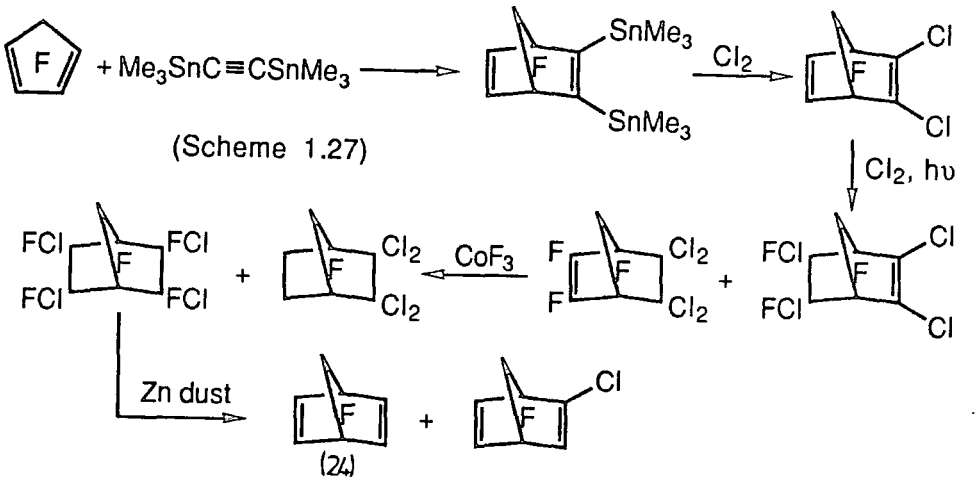
1.4.5 Octafluorocyclohepta-1,3,5-triene (22)

Octafluorocyclohepta-1,3,5-triene (22) and its hydrolysis product hexafluorotropone (23) were first reported in 1972.[52] Triene (22) was prepared from cyclohepta-1,3,5-triene *via* fluorination (cobalt trifluoride), followed by dehydrofluorination, substitution of fluorine by hydrogen using sodium borohydride, followed by further dehydrofluorination. The overall yield is not quoted, but is presumably low. Triene (22) was found to be extremely susceptible to hydrolysis giving tropone (23) (Scheme 1.26).

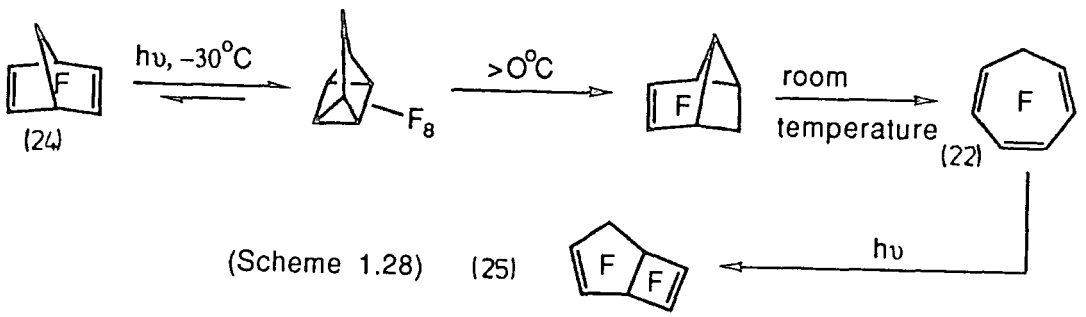


(22) (23) (Scheme 1.26)

Using the valence isomer chemistry of perfluoronorbornadiene (24) (Preparation,[53] see scheme 1.27) Dailey and Lemal[54] have devised

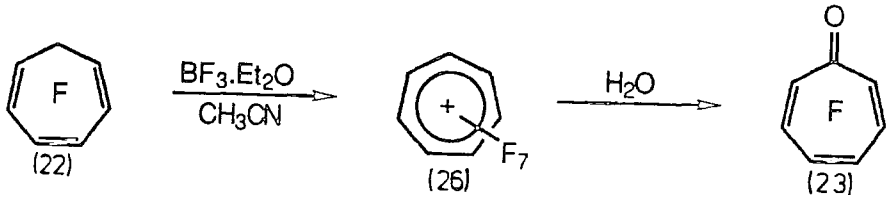


an elegant route to triene (22) (Scheme 1.28). Ultraviolet irradiation of triene (22) causes rapid isomerisation to the



bicyclic diene (25). When treated with boron trifluoride etherate in acetonitrile triene (22) yielded a species whose ^{19}F n.m.r. was a sharp singlet at δ-99.5ppm. That this species was the

perfluorotropylium ion (26) was confirmed by its immediate hydrolysis to the hexafluorotropone (23) (Scheme 1.29)

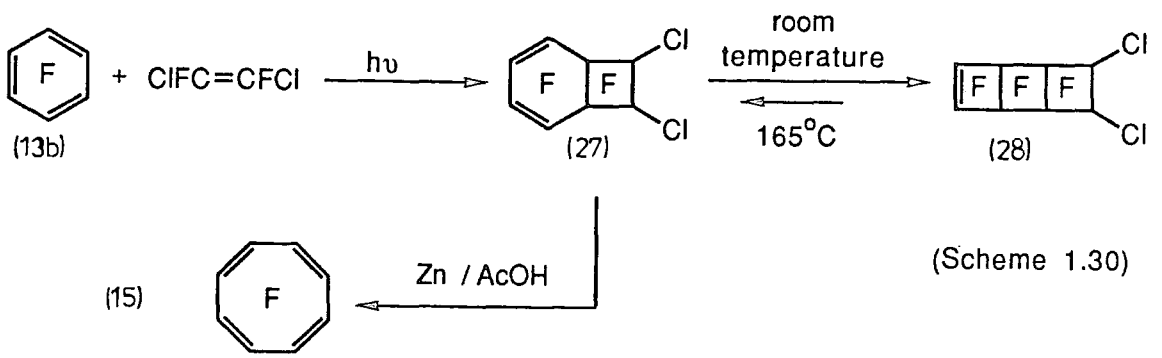


(Scheme 1.29)

1.4.6 Fluorinated Cyclo-octatetraenes

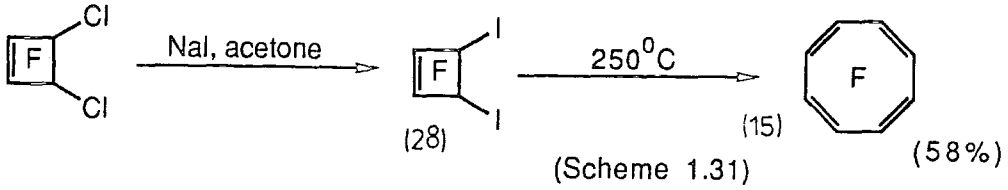
a) *Octafluorocyclo-octatetraene* (15)

The synthesis of octafluorocyclo-octatetraene (15) was first reported by Lemal and coworkers in 1975[41] with an approximately 20% optimised overall yield (See section 1.4.3.a). In 1980 a closely related route was reported by Lemal and coworkers involving the photolysis of tetrafluorocyclopentadienone (16) (See section 1.4.3.a) (yield was not quoted). Both of the above syntheses involve two vapour phase photolyses which proved difficult to scale up to the tens of gram scale. In 1980 Lemal and coworkers[55] approached the synthesis with a view to overcoming scaling problems. Their route (Scheme 1.30) involved only one photochemical step which could be conducted with hundreds of grams of a neat liquid mixture. Under the reaction conditions initially



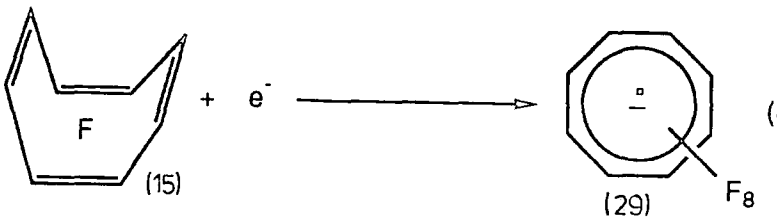
(Scheme 1.30)

formed bicyclic (27) isomerises to the tricyclic (28). The tricyclic (28) may be almost quantitatively thermally reopened to bicycle (27). Reductive dechlorination of bicyclic (27) yields tetraene (15). Also in 1980, Haszeldine and coworkers[56] reported a synthesis of tetraene (15), based on the static pyrolysis of 3,4-di-iodo-1,2,3,4—tetrafluorocyclobutene (28) (Scheme 1.31).



(Scheme 1.31)

Both cyclo-octatetraene and octafluorocyclo-octatetraene (15) adopt a tub conformation, the fluorinated analog being slightly more flattened.[57] Lemal and coworkers[58] investigated whether or not the radical anion of tetraene (15) can assume planarity and become aromatic like its hydrogen containing analog[59] (Scheme 1.32). Attempts to observe tetraene (15) radical anion by reduction of the neutral compound with alkali metals met with failure. However, the radical anion (29) was observed by ESR at 145K in 2-methyltetrahydrofuran solution, following γ-irradiation of the sample in the glassy state at 77K. The observed equivalence of the eight fluorines suggested a planar D_{8h} structure. 1,2-η and 1,2,3,6-η complexes of tetraene (15) with iron and platinum have been reported.[60]

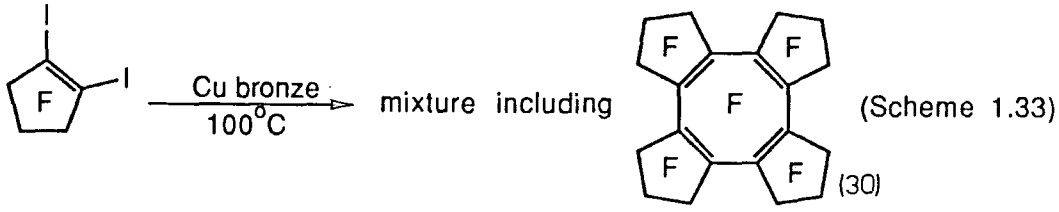


(Scheme 1.32)

b) *Perfluoro-octamethylcyclo-octatetraene* (19)
(See section 1.4.3.b)

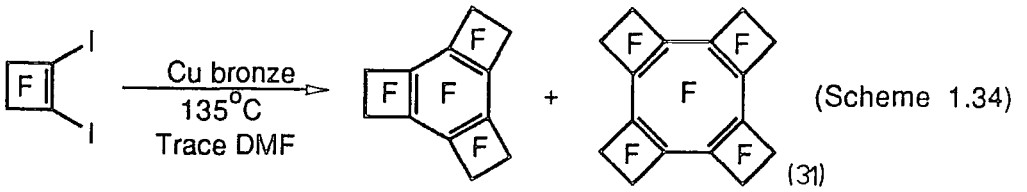
c) *Perfluoropolycyclo-octatetraenes*

In 1971 Camaggi reported[61] the synthesis of tetraene (30) (Scheme 1.33). X-ray studies reveal that tetraene (30) again adopts a tub



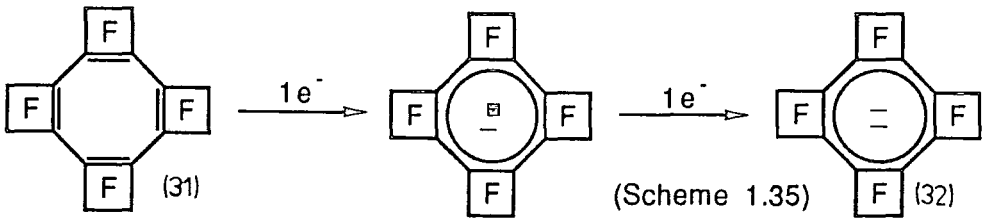
(Scheme 1.33)

conformation.[62] It is therefore noteworthy that tetraene (31) (Synthesis,[63] Scheme 1.34) is reported to have a planar



(Scheme 1.34)

conformation.[64] The eight-membered ring bond lengths are all very similar (± 0.036Å) indicating that the system is delocalised, hence antiaromatic. Photoelectron spectroscopy[65] suggests that tetraene (31) retains its planar conformation in the gas phase. Tetraene (31) is one of the most powerful organic oxidants known,[66] showing two reversible one step reductions (Scheme 1.35). Dianion (32) is a 10π-aromatic system.



(Scheme 1.35)

1.5 Non-Fluorinated Pentakis Substituted Cyclopentadienes

1.5.1 Introduction

This section discusses the syntheses and some of the properties of cyclopentadienes and cyclopentadienyls which bear, usually multiply, electron withdrawing substituents.

1.5.2 Nitriles

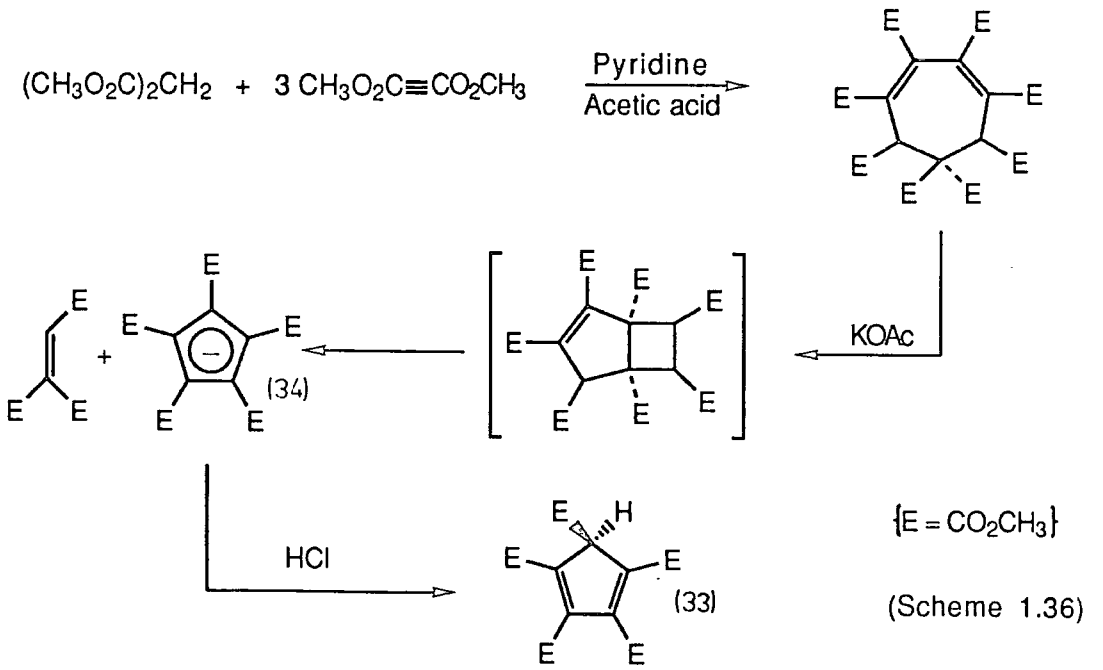
Webster[67] has reported that all of the possible cyanocyclopentadienides have been made by the stepwise cyanation of cyclopentadiene with cyanogen chloride. The first three cyano groups were introduced with the aid of sodium hydride (promoting cyclopentadienyl anion formation), the fourth and fifth with the aid of aluminium chloride (the Lewis acid activates the cyanogen chloride). In an earlier report[68] Webster detailed a different route to the tetrakis- and pentakis- cyanated anions from acyclic precursors. Webster also reported that potassium pentacyanocyclopentadienyl was exceedingly thermally stable, surviving heating to 400°C in air. The pentacyanacyclopentadienide anion is also a very weak base, with

spectrophotometry detecting no protonation by perchloric acid in acetonitrile. This leads to a calculated pK_a, of the conjugate acid in water, of less than minus eleven: making it the strongest carbon acid known.[69]

Other workers[70] have prepared tetracyanocyclopentadienide salts which have been subsequently converted into halogeno-, nitro-, and acetyl derivatives by the appropriate electrophilic reagents.

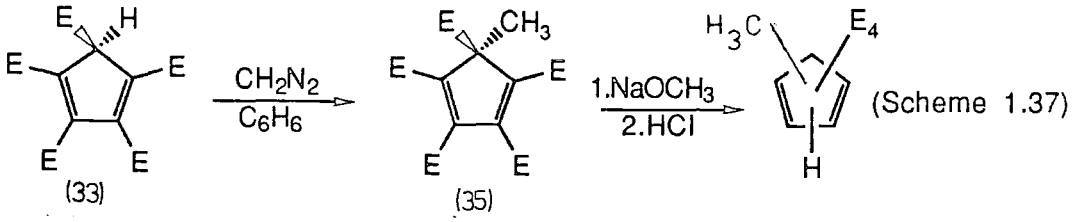
1.5.3 Pentamethoxycarbonylcyclopentadiene (33)

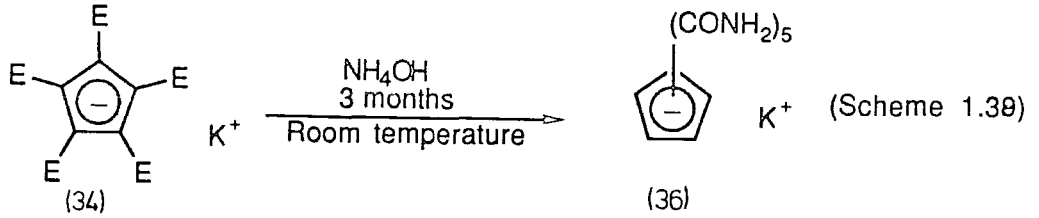
Cp derivative (33) was first reported by Diels.[71,72] Further work[73-75] has confirmed Diels' assignment and has reanalysed the reaction intermediates (Scheme 1.36). Cp derivative (33) is a



(Scheme 1.36)

powerful carbon acid, being at least as strong as hydrochloric acid.[75] An aqueous solution of cp derivative (33) dissolves metallic iron with the evolution of hydrogen and with the formation of the corresponding ferrous salt. As with, for example, the pentamethoxycarbonyl-,[76] tetracyano-,[70] and dicyanodiethyoxycarbonyl- analogs,[70] anion (34) is much too stable to rearrange to the corresponding ferrocene. Cookson and coworkers[75] also report the formation and subsequent hydrolysis of the C-methyl derivative (35) (Scheme 1.37). The formation of 5-chloro and 5-bromo dienes is reported, as is that of the

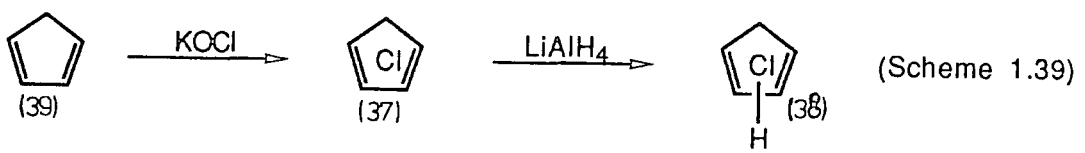




pentamide (36) (Scheme 1.38). A series of papers by Bruce and coworkers (See[77] and references therein) reports the chemistry of the pentakis(carbomethoxy)cyclopentadienyl moiety.

1.5.4 Hexachlorocyclopentadiene (37) and pentachlorocyclopentadiene (38)

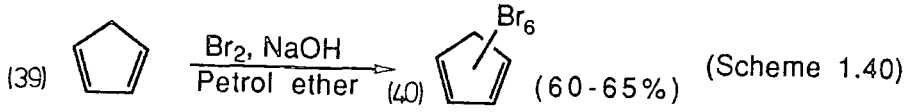
Cp derivative (37) was reported in 1930[78] as the product of the treatment of cyclopentadiene (39) with potassium chlorate(I) (Scheme 1.39). Cp derivative (37) does not readily dimerise.[79]



Cp derivative (37) when either: a) reduced with lithium aluminium hydride at -50 ^{0}C;[78] b) catalytically hydrogenated;[78,80] c) reduced with stannus chloride in acetone,[80] yields pentachlorocyclopentadiene (38). Cp derivative (38) does reversibly dimerise in a Diels-Alder fashion. All attempts to convert the anion derived from cp derivative (38) using transition metal halides to perchlorocyclopentadienyl complexes failed.[81] However, the first perhalo- and oxidatively stable metalocene, decachloroferrocene, has been reported to be formed[82] by a series of repetitive metalation exchange-halogenation reactions of 1,1'- dichloroferrocene.

1.5.5 Hexabromocyclopentadiene (40)

The synthesis of hexabromocyclopentadiene (40) was also initially reported in 1930[78,83] (Scheme 1.40).

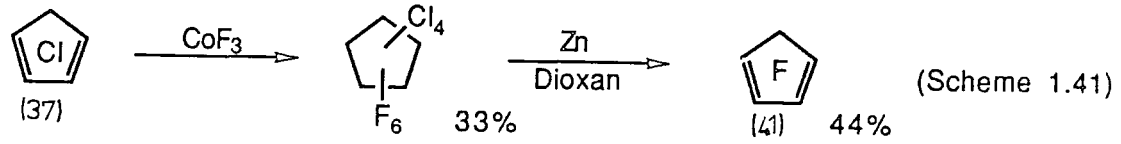


(Scheme 1.40)

1.6 Fluorinated Cyclopentadienes and Cyclopentadienyls

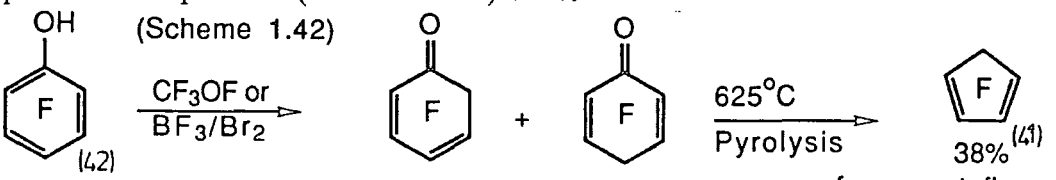
1.6.1 Hexafluorocyclopentadiene (41)

The first synthesis of cp derivative (41) was reported in 1963[84] (Scheme 1.41). With recycling of fractions up to a 42% overall



(Scheme 1.41)

yield is obtainable. Other routes have been presented.[85,86,88] Lemal and coworkers[86] have reported a notable route to cp derivative (41) starting with the six membered ring of pentafluorophenol (Scheme 1.42) (42).



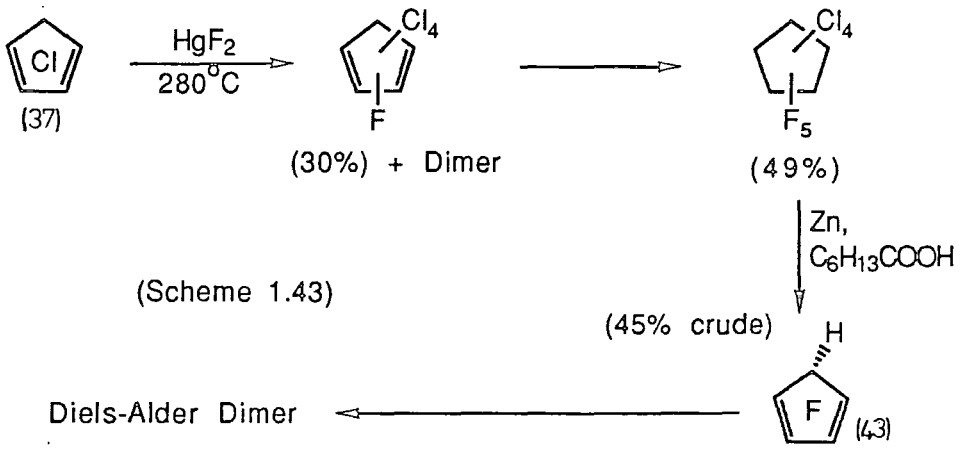
(Scheme 1.42)

from pentafluorophenol

Hexafluorocyclopentadiene (41) (bp 29°C) was the first perfluoro-1,3-diene to undergo a Diels-Alder type of dimerisation when stored either in the vapour phase, or as a liquid under a nitrogen atmosphere.[85]

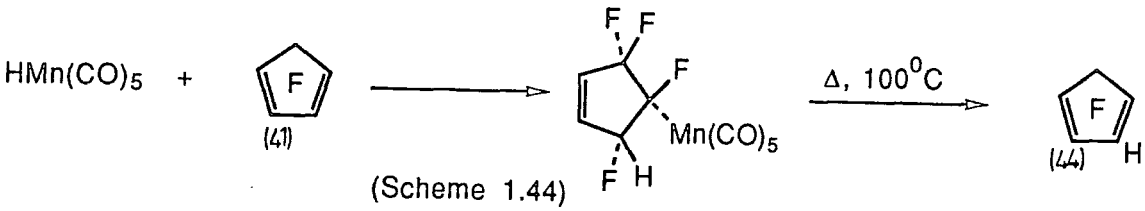
1.6.2 1,2,3,4,5-Pentafluorocyclopentadiene (43)

Paprott and coworkers[89-91] have prepared cp derivative (43) starting from hexachlorocyclopentadiene (37) (Scheme 1.43). An



(Scheme 1.43)

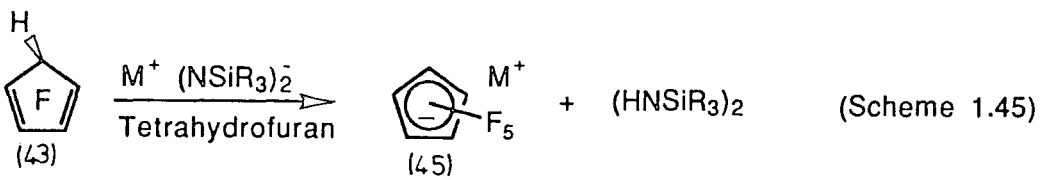
isomer of cp derivative (43), most probably 1,3,4,5,5-
-pentafluorocyclopentadiene (44) has been reported[92] (Scheme 1.44).



(Scheme 1.44)

1.6.3 Pentafluorocyclopentadienyl Anion (45)

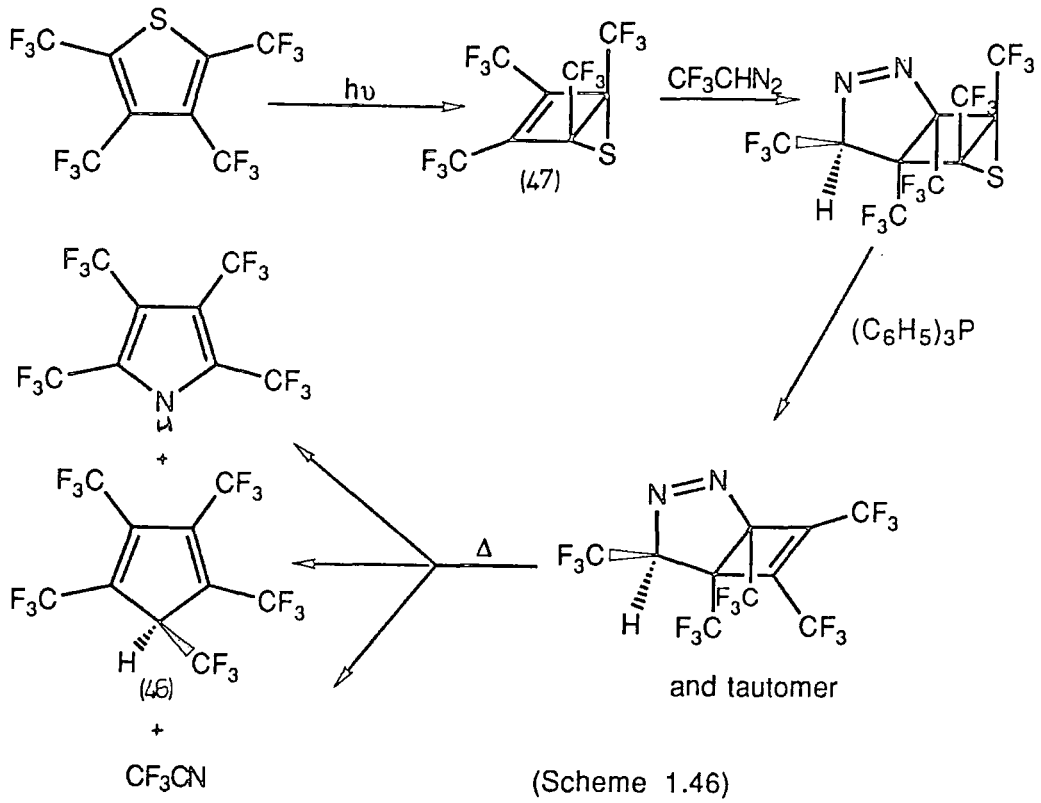
Metalation of the proton in cp derivative (43), preferably with $[M^+ N(SiR_3)_2^-]$ affords anion (45)[50] (Scheme 1.45). Tetrahydrofuran solutions of the metal salts are unstable. The lithium salt decomposes within minutes at -110°C, the sodium salt within hours at -78°C, the thallium and caesium salts decompose at -30°C. $\{Na^+[18\text{-crown-}6]C_5F_5^-\}$ in tetrahydrofuran is the most stable salt reported, being observed at 22°C for a few hours. The typical decomposition reaction is loss of metal fluoride coupled with polymerisation.



(Scheme 1.45)

1.6.4 Pentakis(trifluoromethyl)cyclopentadiene (46)

In 1980 Lemal and Laganis reported[69] a low yielding synthesis of cp derivative (46) involving tetrakis(trifluoromethyl)-
-(Dewar)thiophene (47) (Scheme 1.46). Cp derivative (46) is an

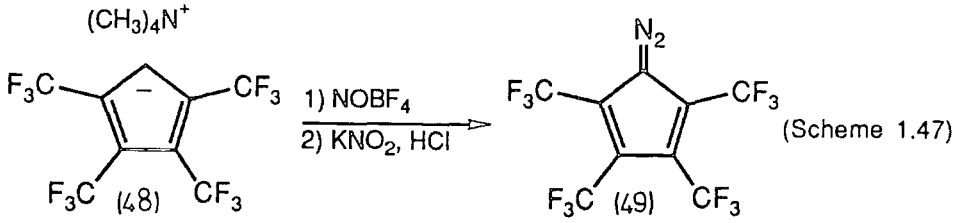


(Scheme 1.46)

extraordinarily powerful carbon acid (pK_a less than minus two), exceeding nitric acid in strength despite its lack of conjugating substituents. This strong acidity is in marked contrast to 1,2,3,4,5-pentafluorocyclopentadiene (43) (pK_a 12.8 to 15.5). This large difference in acidity is a further demonstration of the electronic dual nature of fluorine dependant on whether the carbon atom next to fluorine is saturated (See section 1.3.1). Cp derivative (46) is a volatile liquid, freely soluble in water, the neat liquid attacking even silyated glass containers.

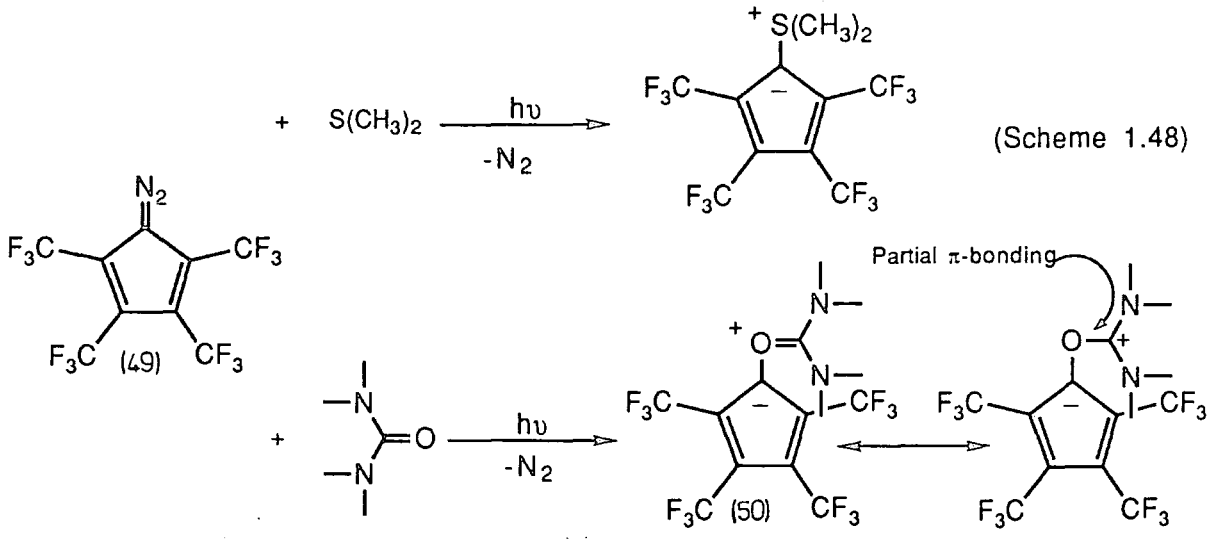
1.6.5 1.2.3.4-Tetrakis(trifluoromethyl)cyclopentadienide (48)

In 1983, Janulis, and Arduengo[87] used a variant of the above synthesis (Diazomethane was used as the 1,3-dipole, then the corresponding cyclopentadiene was neutralised and counterion exchanged to give the tetramethylammonium salt) to prepare salts of 1,2,3,4-tetrakis(trifluoromethyl)cyclopentadiene (48) which were then converted to 5-diazo-1,2,3,4-tetrakis(trifluoromethyl) cp derivative (49) (Scheme 1.47). Although thermally stable



(Scheme 1.47)

(unchanged after heating to 190°C in chlorobenzene), cp derivative (49) undergoes a photochemical loss of nitrogen to give a highly reactive electrophilic carbene. This carbene may be trapped by conducting the photolysis of cp derivative (49) in the presence of nucleophiles, forming ylides (for example, Scheme 1.48). The ylide (50) was the first stable carbonyl ylide to be reported.[93]

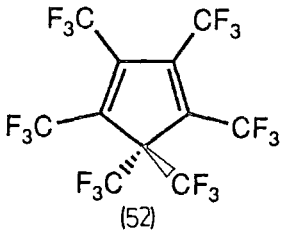


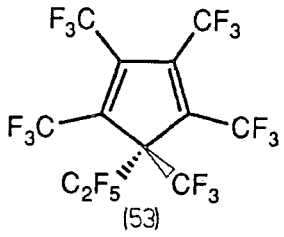
(Scheme 1.48)

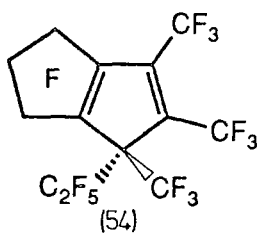
The chemical and thermal stability of this ylide allowed x-ray crystallographic analysis. It appears that there is partial π-bonding between the carbonium centre and oxygen, while the oxygen cyclopentadienylide linkage appears as a single σ-bond.

1.6.6 Syntheses from Hexafluorobut-2-yne (21)

Chambers and Jones[94] have reported the presence of cyclopentadienes (52, 53, and 54) (Figure 1.49) in the complex mixtures derived from the fluoride ion induced co-oligomerisations of hexafluorobut-2-yne (21) with hexafluoropropene, octafluorobut-2-ene, and octafluorocyclopentene, respectively.

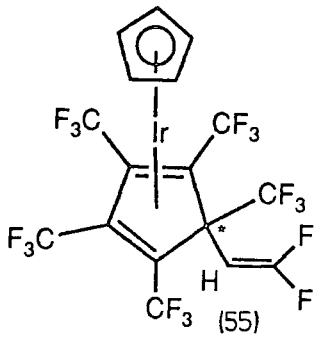

(52)


(53)


(54)

(Fig. 1.49)

It has been reported[95] that the reaction between $(\eta\text{-}C_5H_5)Ir(CO_2)$ and hexafluorobut-2-yne (21) at 160°C gives complex (55) (Fig. 1.50) in low yield. The mechanism of formation of complex (55)


(55)

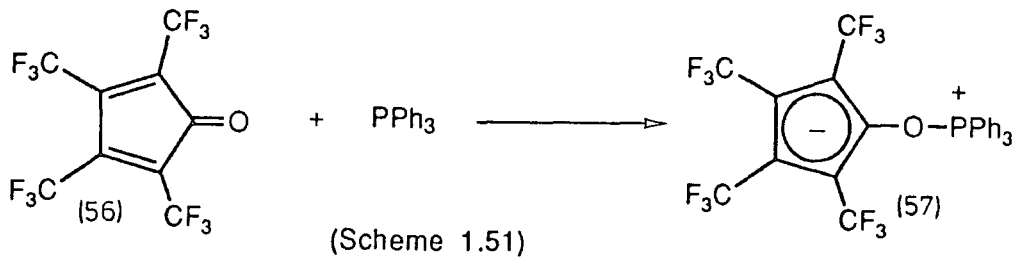
(Figure 1.50)

Stereochemistry about * uncertain

may involve the initial generation of an Ir-H species followed by insertion of three hexafluorobut-2-yne (21) units.

1.6.7 Tetrakis(trifluoromethyl)cyclopentadienone (56)

Dienone (56) was first reported by Dickson and Wilkinson[96] *via* the reaction of hexafluorobut-2-yne (21) with dicarbonylchlororhodium at *ca* 150°C under a high pressure of carbon monoxide. The resistance of dienone (56) to dimerisation disguises the fact that it is an extremely reactive molecule. Dienone (56) will react with tetramethylethene, cyclohexene and many more dienophiles in the inverse electron demand Diels-Alder reaction.[97] The reaction of dienone (56) with triphenylphosphine yields the ylide tetrakis(trifluoromethyl)cyclopentadienone--triphenylphosphorane (57)[98] (Scheme 1.51).

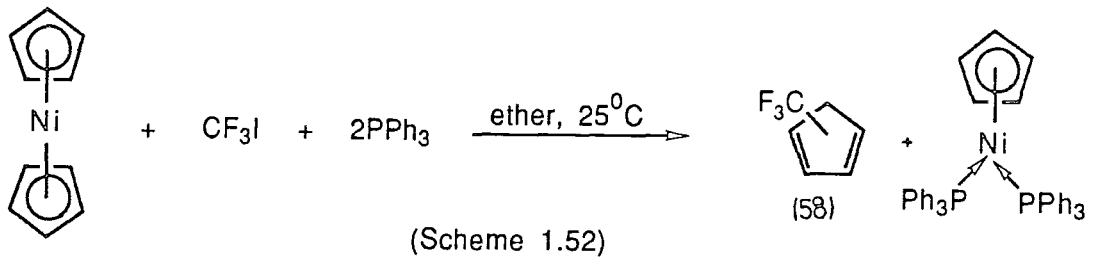

(56) (57)

(Scheme 1.51)

1.6.8 Tetrafluorocyclopentadienone (16) (See section 1.4.3.a)

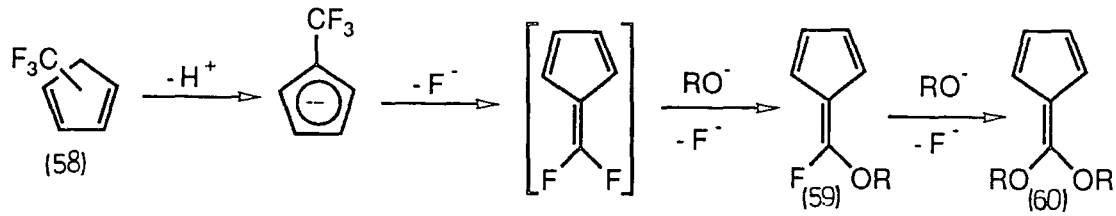
1.6.9 Trifluoromethylcyclopentadiene (58)

Ollson and Wennerstrom[99] have reported the synthesis of trifluoromethylcyclopentadiene (58) (Scheme 1.52). Cp derivative



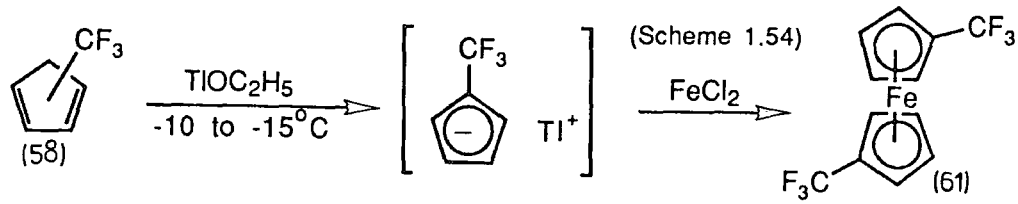
(Scheme 1.52)

(58) was isolated in a 70:30 mixture of the 1- and 2- isomers. The reaction of cp derivative (58) with alkoxide initially yields 6-fluoro-6-alkoxyfulvene (59). Further reaction gives the 6,6-dialkoxyfulvene (60) (Scheme 1.53).



(Scheme 1.53) R = CH_3, C_2H_5

Bis(trifluoromethyl)ferrocene (61) has been prepared by the reaction of the thallium salt of diene (58) with ferrous chloride (Scheme 1.54).[100] E.S.C.A. measurements on ferrocene (61)



illustrate the strong electron withdrawing effect of trifluoromethyl groups, causing an increase of the binding energy for the iron inner shell electrons.

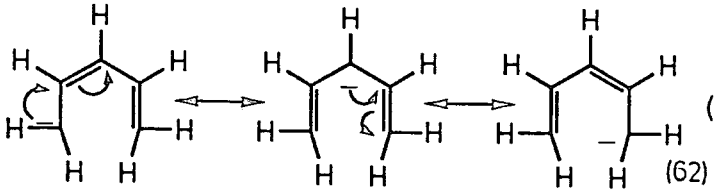
1.7 The Pentadienyl-Cyclopentenyl Rearrangement

1.7.1 Introduction

Allyl, pentadienyl, and heptatrienyl anions can in principle undergo electrocyclic rearrangements.[101] The pentadienyl-cyclopentenyl rearrangement has particular relevance to our route to polysubstituted cyclopentadienes and cyclopentadienyls. The electrocyclic reaction of the *pentadienyl anion* $\rightleftharpoons$ *cyclopentenyl anion* is relatively unimportant in all carbon systems, and has not yet been verified in the case of the parent compound. However, in the heterocyclic series, where up to five carbon atoms of the pentadienyl anion are replaced by heteroatoms, a whole multitude of ring closures and ring openings can be classified as 1,5-electrocyclisation reactions.[101]

1.7.2 Overall reaction for the pentadienyl anion (theoretical)

The pentadienyl anion (62) has six electrons in 5 parallel p-orbitals. The resonance structures (Figure 1.55) illustrate the charge distribution over carbon atoms 1, 3, and 5. The electrocyclic ring closure, requiring a U configuration of the open chain species, is associated with a transformation of the terminal sp^2-hybridised centers into tetrahedral carbon atoms. The remaining four π-electrons emerge as an allyl anion.

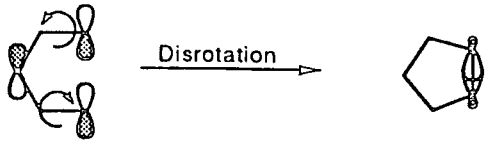


(Fig. 1.55)

(62)

1.7.3 Orbital control

Woodward and Hoffmann[102] found that the inspection of the HOMO (highest occupied molecular orbital) symmetry to be the simplest treatment accounting for the steric course of electrocyclic reactions. Figure 1.56 shows that the terminal bonds must rotate

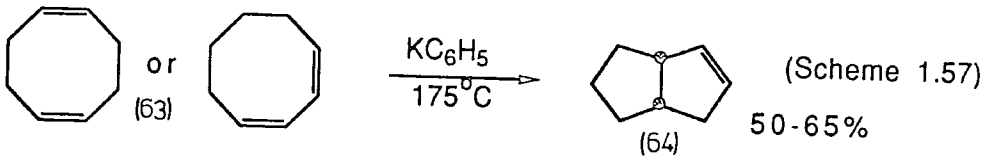


(Fig. 1.56)

in opposite directions inorder to achieve phase consistent overlap of the terminal orbitals forming the new σ-bond.

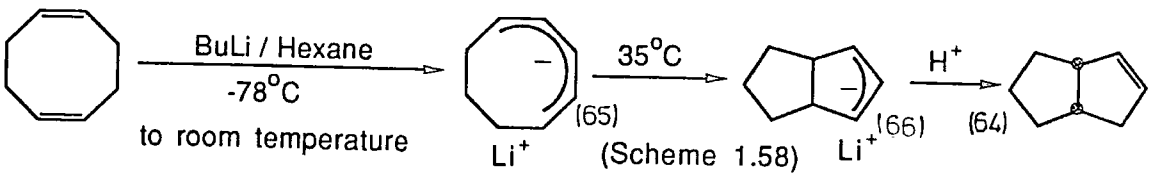
1.7.4 Cyclo-octadienes

Although not observed in the parent case of *pentadienyl anion* $\rightleftharpoons$ *cyclopentenyl anion* the base catalysed isomerisation of [(1,3-), (1,5)]cyclo-octadienes (63) to cis-bicyclo[3.3.0]oct-2-ene (64) has been reported[103] (Scheme 1.57). Further work[104,105] led to the conclusion that this was



(Scheme 1.57)

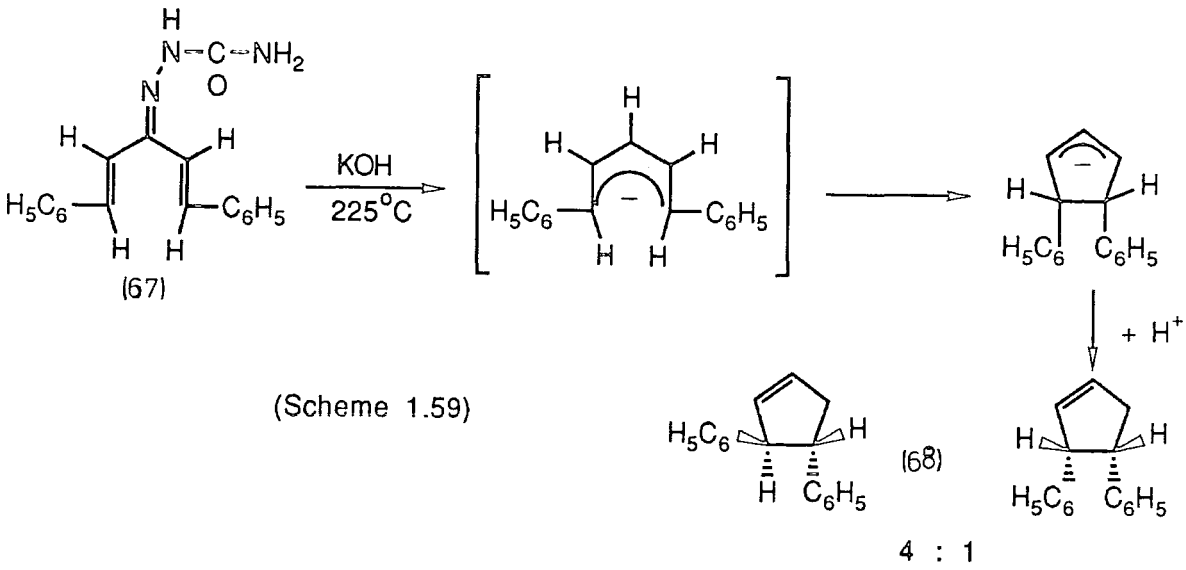
indeed the first example of the pentadienyl-cyclopentenyl inter conversion. Bates and McCombs[105] reported the generation and n.m.r. spectral properties of cyclo-octadienyllithium (65). The first order cyclisation of anion (65) to bicycle (66) (Scheme 1.58) was also recorded, the half life was found to be 80 minutes at 35°C.



(Scheme 1.58)

1.7.5 Known all carbon chain examples

In the cyclisation of *open-chain* pentadienyl anion a ring strain energy of *ca* 7Kcalmol^{-1} is built up.[106] Furthermore, the conversion to the rigid cyclopentenyl anion causes an increase in entropy during the cyclisation. A single unexplained example[101] of such a cyclisation is the conversion of semicarbazone (67) into cyclopentenes (68) with 12% yield (Scheme 1.59).[107] However, no

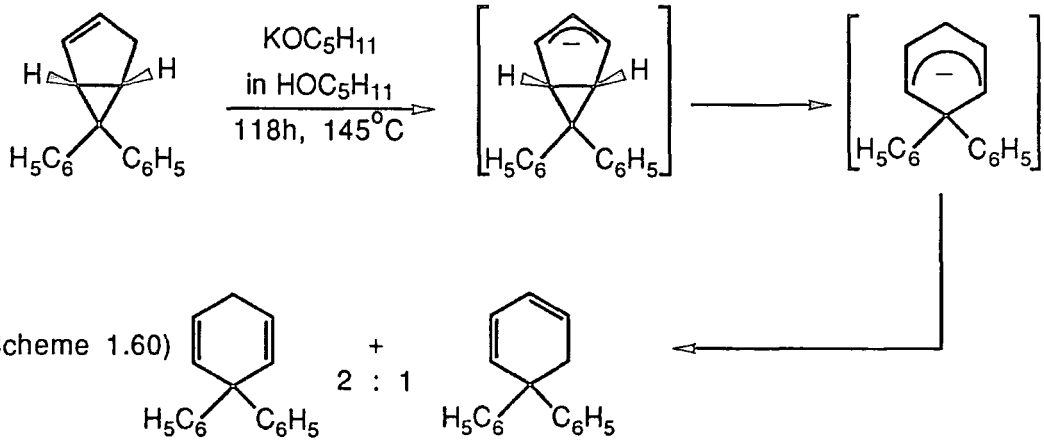


(67) (68)

(Scheme 1.59)

reaction was observed when 1,5-diphenyl-1,4-pentadiene was heated with butyllithium at 190°C.

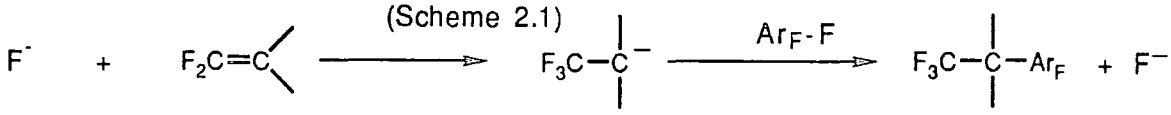
Ring openings are known in non-heterocyclic systems. In scheme 1.60 we see an anionic ring opening which clearly profits from the release of the cyclopropane ring strain.[108]



(Scheme 1.60)

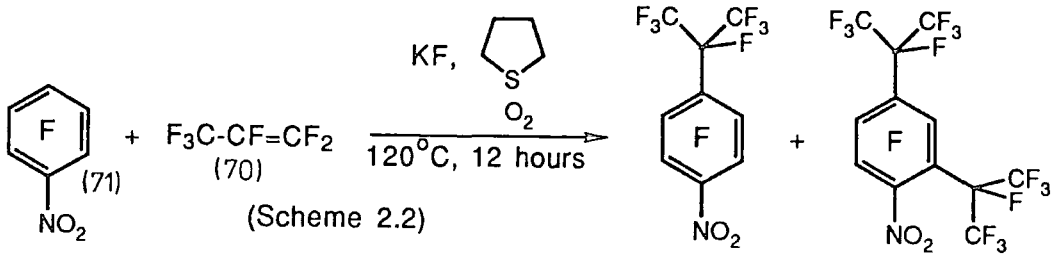
2.1 Introduction

The reactions of perfluoro-olefins with fluoride ion are synthetically useful, and one of the applications of this process is in the preparation of polyfluoroalkyl-substituted aromatic compounds. Such reactions (For example scheme 2.1) proceed *via* the initial formation of a perfluorocarbanion. Subsequent attack of this nucleophilic species upon a polyfluoroaromatic substrate yields a polyfluoroalkyl substituted product. The substrate



usually requires some activation to nucleophilic aromatic substitution. Indeed hexafluorobenzene does not normally react with perfluoro-olefins in the presence of fluoride ion.[109,110]

The reaction of hexafluoropropene (70) with pentafluoronitrobenzene (71) is well known[110] (Scheme 2.2). In



(Scheme 2.2)

a preliminary study M.J. Seabury (these laboratories)[111] observed the formation of an unexpected product in the analogous reaction of 2H-PFP (69) with pentafluoronitrobenzene (71) and fluoride ion. This reaction together with other reactions of 2H-PFP (69) with aromatic substrates will be discussed in this chapter.

2.2 2H-Pentafluoropropene (2H-PFP) (69)

2.2.1 Preparation

2H-PFP (69) was prepared by a literature method[112] (Scheme 2.3).

(Scheme 2.3)

$$CF_3\text{-}CF{=}CF_2 \;(70) + H_3COH \xrightarrow[100^oC,\ 270mins]{\text{Benzoyl peroxide (Free radical initiator)}} F_3C\text{-}CF(H)\text{-}CF_2\text{-}CH_2\text{-}OH \quad (72)\ (85\%)$$

$$F_3C\text{-}CF(H)\text{-}CF_2\text{-}CH_2\text{-}OH \xrightarrow[ii)\ NaOH]{i)\ K_2Cr_2O_7} F_3C\text{-}CF(H)\text{-}CF_2\text{-}CO_2Na \quad (73)\ (70\%)$$

$$CF_3\text{-}CH{=}CF_2 \;(69)\ (91\%) + CO_2 + NaF \xleftarrow{\text{Pyrolysis}} F_3C\text{-}CF(H)\text{-}CF_2\text{-}CO_2Na$$

2.2.2 Some Known Reactions of 2H-PFP (69) with Nucleophiles

The reactions of several nucleophiles with 2H-PFP (69) have been reported[113,114] (Scheme 2.4), with products arising from the substitution of a fluorine atom by the nucleophile *via* an addition-elimination mechanism. Reaction of 2H-PFP (69)

$$nuc^- + CF_3CH{=}CF_2 \;(69) \xrightarrow{\text{ether}} \underset{H}{\overset{F_3C}{\rangle}}C{=}C\langle^{nuc}_{F} + \underset{H}{\overset{F_3C}{\rangle}}C{=}C\langle^{F}_{nuc} + F^-$$

(Scheme 2.4) (nuc = NHR_2, ^-SR, $HPMe_2$)

with a slight excess of caesium fluoride in moist tetrahydrothiophen-1,1-dioxide at 75°C gave alkane (74),[113] presumed to be formed *via* carbanion (75) (Scheme 2.5). Anion (75)

$$CF_3CH{=}CF_2 \;(69) \xrightarrow{F^-} F_3C\text{-}\bar{C}H\text{-}CF_3 \;(75) \xrightarrow{H_2O} F_3C\text{-}CH_2\text{-}CF_3 \;(74)$$

(Scheme 2.5)

has also been observed in the gas phase[115,116] (Scheme 2.6).

(Scheme 2.6)

$$(CF_3)_2C{=}N_2 \xrightarrow{\text{electrons}} (CF_3)_2C: \xrightarrow{PH_3 \text{ or } CH_3CN} (CF_3)_2CH^- \quad (75)$$

2.2.3 Reaction of 2H-PFP (69) with Antimony Pentafluoride

It has been reported[117] that the treatment of 2H-PFP (69) with a deficiency of antimony pentafluoride yielded dimer (76). The following rationalisation was proposed (Scheme 2.7). Subsequently

(Scheme 2.7)

$$F_3C\text{-}CH{=}CF_2 \xrightarrow{SbF_5} [CF_2\text{-}CH\text{-}CF_2]^+ \xrightarrow[SbF_6^-]{F_3C\text{-}CH{=}CF_2} CF_2{=}CH\text{-}CF_2\text{-}CH(CF_3)_2$$

(69) (77) (76)

it was reported[118] that treatment of 2H-PFP (69) with an excess of antimony pentafluoride yielded allyl cation (77) (Scheme 2.8), observed by fluorine and carbon-13 n.m.r..

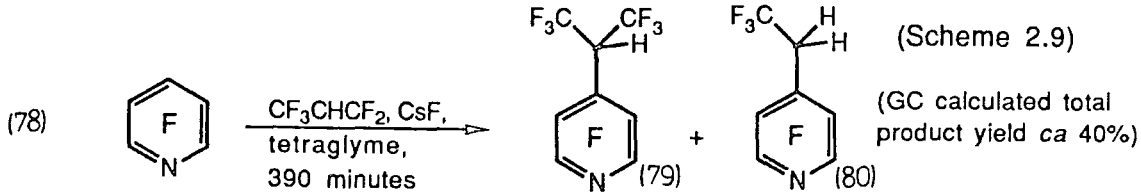
$$F_2C{=}CH\text{-}CF_3 \xrightarrow[\text{excess}]{SbF_5} \left[F_2C \overset{H}{\underset{(77)}{\diagup\!\diagdown}} CF_2 \right]^+ \left[Sb_nF_{5n+1}\right]^- \quad \text{(Scheme 2.8)}$$

(69)

2.3 Some Fluoride Induced Reactions of 2H-PFP (69)

2.3.1 With pentafluoropyridine (78)

The reaction was conducted in an atmosphere of 2H-PFP (69), with caesium fluoride, in tetraglyme, at room temperature. A mixture of two principal products, separable only by gas chromatography, and a brown tar were obtained (Scheme 2.9). Compound (79) is a

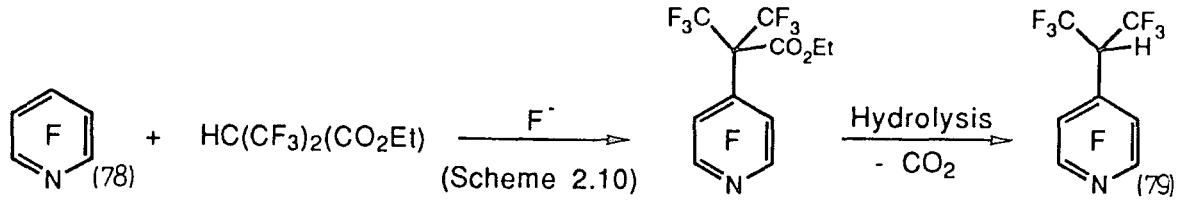


(Scheme 2.9)

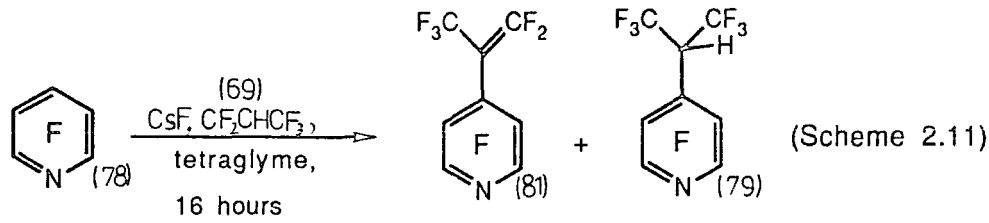
(GC calculated total product yield *ca* 40%)

ca 3 : 1

known compound, prepared using an alternative route[11] (Scheme 2.10).



It must be noted that our products differed from those reported in the previous investigation[111] (Scheme 2.11) [Compound (81) is formed by the elimination of the elements of hydrogen fluoride from compound (79)]. We can only conclude that our system was

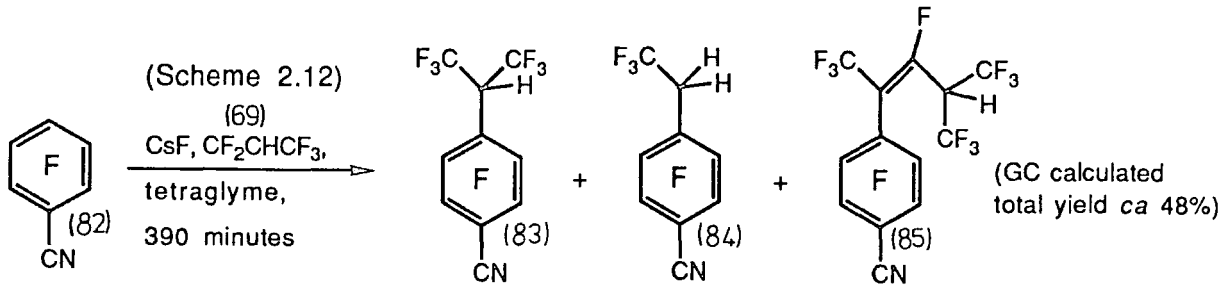


ca 8 : 1

not as anhydrous as that of the previous investigation, which is puzzling. The formation of compounds of the type (80) will be discussed in section 2.6.

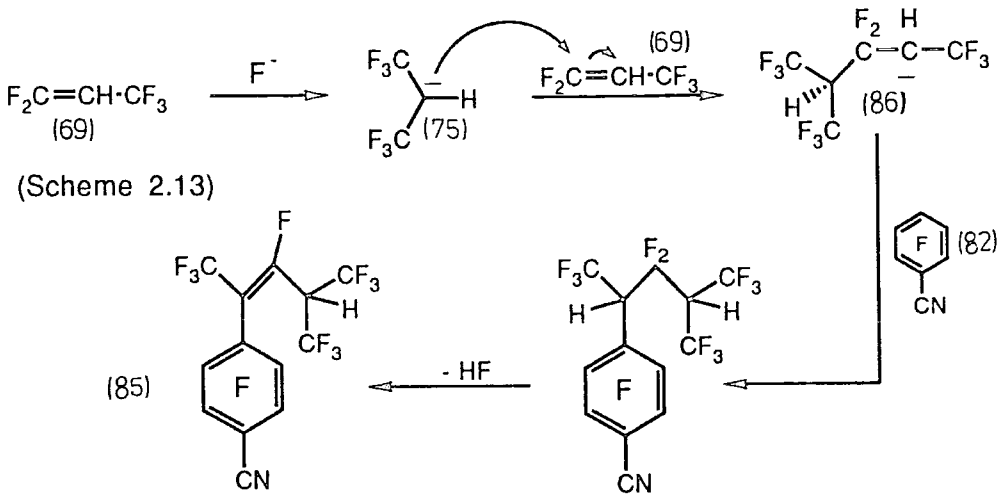
2.3.2 With pentafluorobenzonitrile (82)

Three products were isolated from the reaction between pentafluorobenzonitrile (82) and 2H-PFP (69) (Scheme 2.12) in addition to tar formation. Compounds (83 and 84) are analogous



ca 7 : 3 : 1

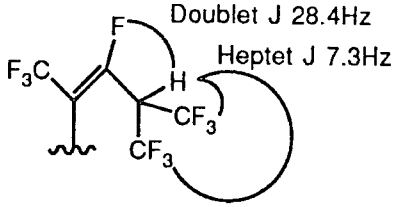
to compounds (79 and 80), but compound (85) is clearly formed by the nucleophilic aromatic substitution of 2H-PFP dimer anion (86) into pentafluorobenzonitrile (82) (Scheme 2.13). The proton n.m.r. spectrum of compound (85) is particularly revealing,

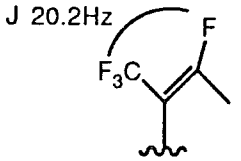


(Scheme 2.13)

exhibiting a doublet of heptets (Fig. 2.14.a). The alkene configuration was assigned using the large (typically cisoid[119]) $^{5}J_{(CF_3\text{-}F)}$ coupling constant (Fig. 2.14.b).

(Fig. 2.14.a)

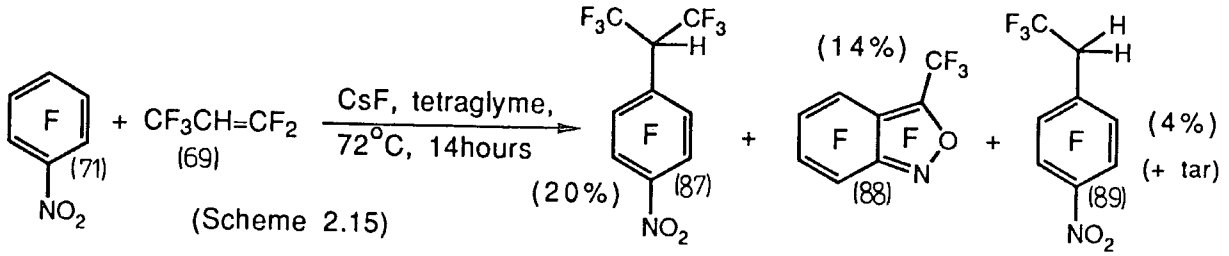




(Fig. 2.14.b)

2.3.3 With pentafluoronitrobenzene (71)[111]

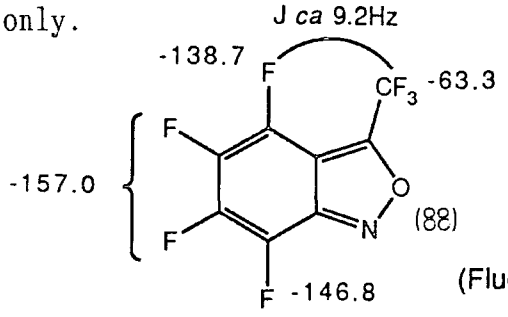
The title reaction was reported[111] to yield a complex mixture, the three principle volatile components being compounds (87, 88, and 89) (Scheme 2.15). Compounds (87 and 89) are analogous to the



(Scheme 2.15)

products derived in the preceding sections. However, compound (88) was a new and unexpected product (See section 2.7). We have repeated this reaction with similar results. Isolation of compound (88) followed by characterisation confirmed the earlier assignment (^{19}F n.m.r. data is shown in fig. 2.16. Elemental analysis, an accurate mass measurement and carbon-13 n.m.r. were

all consistent with the assignment). A significant number of low yielding components were also observed,[111] however this investigation has concentrated upon the three major components only.



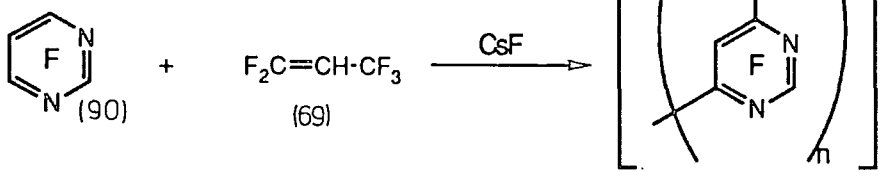
(Fig. 2.16)

(Fluorine n.m.r. chemical shifts in ppm)

2.3.4 Other fluoride ion induced reactions of 2H-PFP (69)

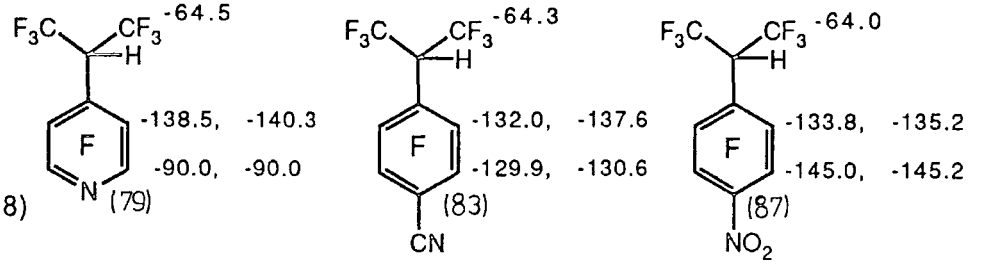
Octafluorotoluene proved insufficiently active to react with 2H-PFP (69) under our conditions. It is interesting to note[11] that the corresponding 2H-hexafluoroisopropyl product was obtained using the route outlined for pentafluoropyridine (78) in scheme 2.10. Conversely tetrafluoropyrimidine (90) proved to be too reactive to yield useful products, with gelation occurring after stirring for one hour, presumably as a result of polymer formation (Scheme 2.17).

(Scheme 2.17)



2.4 Fluorine N.m.r. Spectra of Compounds (79, 83, and 87)

The ^{19}F n.m.r. spectra of compounds (79, 83, and 87) illustrate the existence of restricted rotation of the $HC(CF_3)_2$ group leading to the magnetic non-equivalence of the aromatic fluorine atoms



(Fig. 2.18)

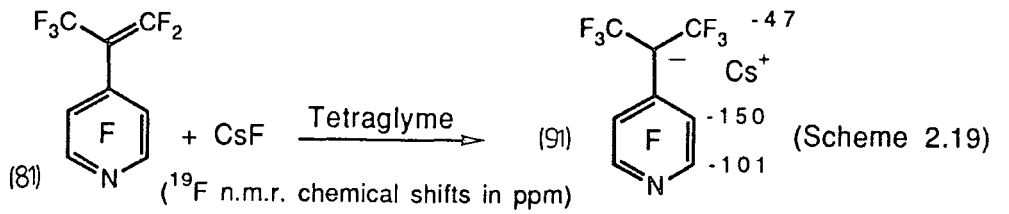
Observed Coalesence Temperature	*ca* 360K	*ca* 385K	*ca* 391K
Literature ref.	*ca* 393K[11]	—	*ca* 393K[111]

(Fig. 2.18). Warming induces rotation of the isopropyl group leading to the coalescence of the aromatic fluorine resonances.

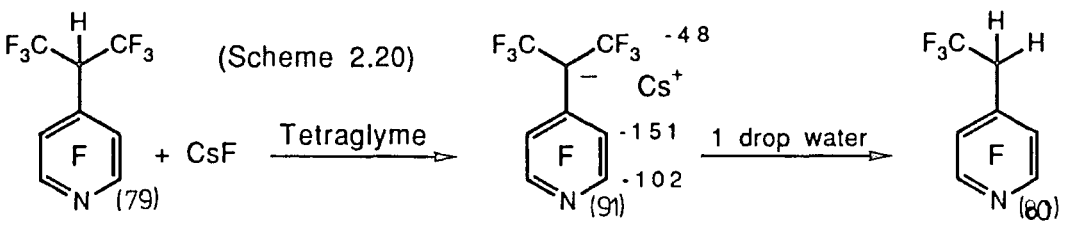
2.5 Formation of anions

2.5.1 Hexafluoroisopropyl anions

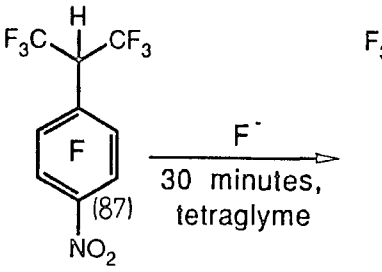
Seabury reported[111] that the reaction of compound (81) with caesium fluoride in tetraglyme solution yielded the stable salt (91) (Scheme 2.19). We have observed the formation of stable



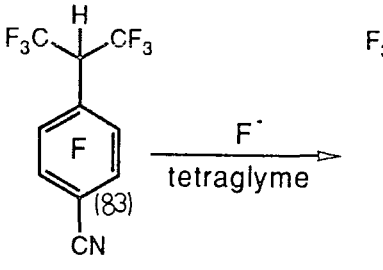
salt (91) by the reaction of a large excess of caesium fluoride with compound (79). However, if a drop of water is added ^{19}F n.m.r. resonances consistent with compound (80) appear (Scheme 2.20) (see section 2.6 for discussion). In a similar manner we



have used fluoride ion to deprotonate compounds (87 and 83) yielding the anions (93 and 94) (Scheme 2.21.a,b).

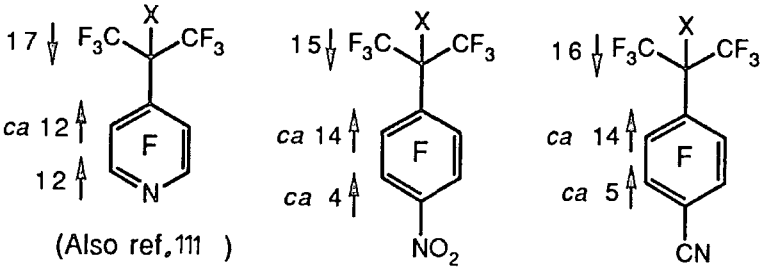


(Scheme 2.21.a)



(Scheme 2.21.b)

The ^{19}F n.m.r. chemical shift changes that occur upon ionisation are illustrated in fig. 2.22 (an uparrow represents an upfield shift upon ionisation). Large downfield shifts are observed at sites adjacent to charge (see section 1.3.2.b), with upfield shifts for the ring fluorine atoms.

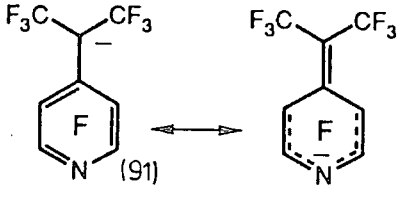


(Also ref. 111)

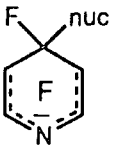
(Fig. 2.22)

(Changes marked " *ca* " are mean values due to the magnetic inequivalence of sites in the carbon acids)

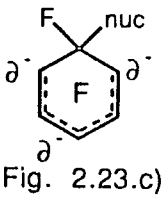
The activating influence of fluorine atom substitution with respect to nucleophilic aromatic substitution in phenyl and pyridyl systems has been investigated.[120,121] Anions such as anion (91) (Fig. 2.23.a) could be considered as models for the transition states of such substitution reactions (Fig. 2.23.b).



(Fig. 2.23.a)



(Fig. 2.23.b)



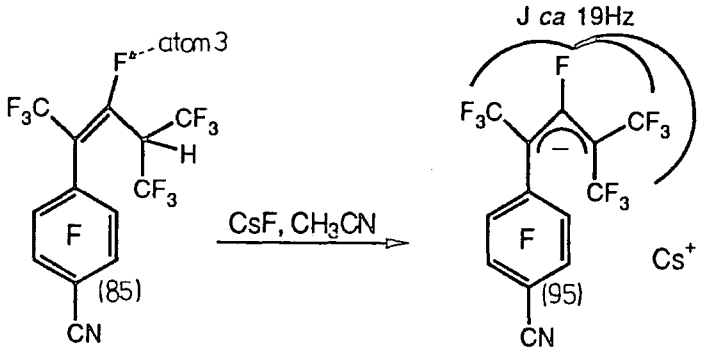
(Fig. 2.23.c)

The influence of *ortho* and *meta* fluorine substitution in the phenyl and pyridyl systems was reported to be strongly activating while that of *para* substitution was found to be slightly

deactivating with respect to hydrogen.[111] These effects have been rationalised[120-122] by a consideration of transition state carbanionic stabilities (for *ortho*, *meta*, and *para*) (Fig. 2.23.c) and ion-dipole effects (for *ortho*). It is noteworthy that in the pyridyl system (91) we see a similar fluorine n.m.r. chemical shift change for the *ortho* and *meta* sites roughly in accord with nucleophilic aromatic substitution activating abilities. However, lacking data for other aromatic systems this correlation can only be regarded as tentative (See also pyridyl systems in chapter 4).

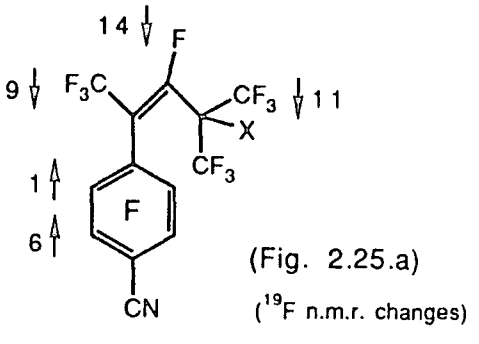
2.5.2 Anion derived from compound (85)

The addition of caesium fluoride to a solution of compound (85) in acetonitrile produced a species whose fluorine n.m.r. spectrum was consistent with that of anion (95) (Scheme 2.24). Fluorine atom 3 appears to couple to all three CF_3 groups with a coupling constant of *ca* 19Hz. The ^{19}F and ^{13}C n.m.r. chemical shift

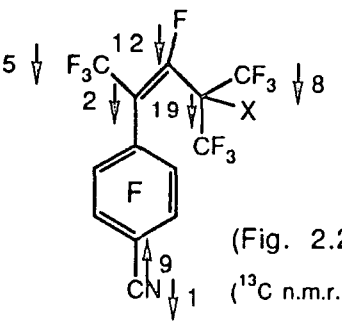


(Scheme 2.24)

changes that occur upon ionisation are indicated in fig 2.25.a and 2.25.b respectively, with downfield shifts occurring in the potentially allylic side chain, and upfield shifts at the ring fluorine atoms.



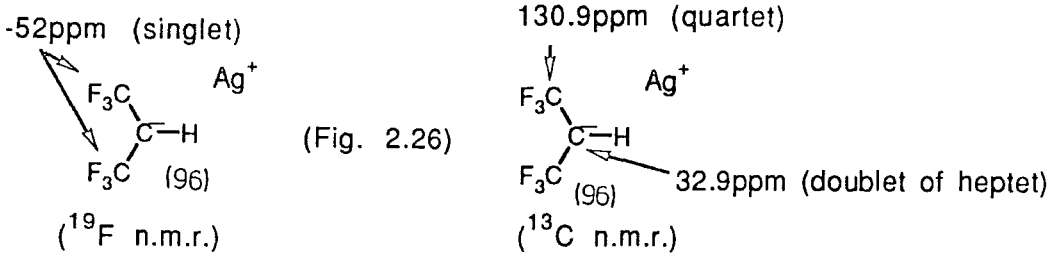
(Fig. 2.25.a)
(^{19}F n.m.r. changes)



(Fig. 2.25.b)
(^{13}C n.m.r. changes)

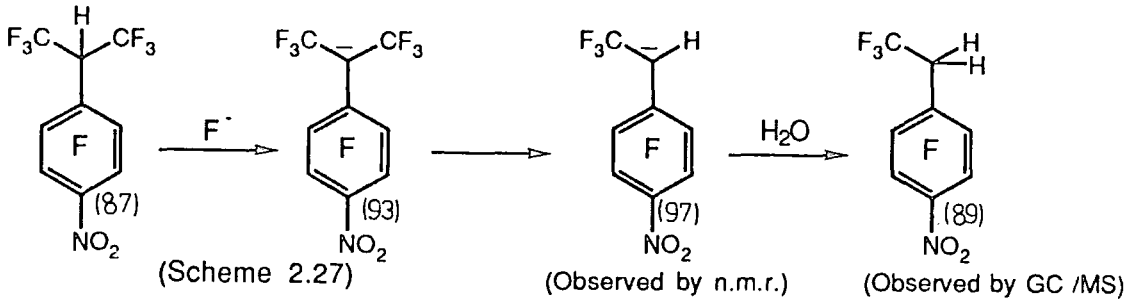
2.5.3 Anion derived from 2H-pentafluoropropene (69)

Using caesium fluoride as a fluoride ion source we were not successful in our attempts to observe the salt $[(CF_3)_2CH^-]\ Cs^+$. However, using silver fluoride we observed ^{19}F and ^{13}C n.m.r resonances that were consistent with salt (96) in tetraglyme solution (Fig. 2.26) (the proton resonance was not visible) [*c.f.* caesium fluoride dimerises hexafluoropropene, but silver fluoride forms relatively stable $(CF_3)_2C(F)Ag^{123}$]



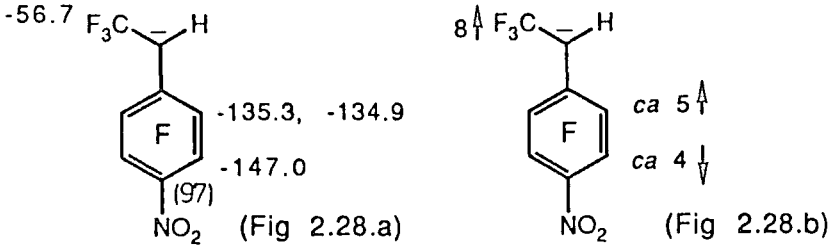
2.6 Formation of Trifluoroethyl Derivatives (80, 84, and 89)

In each of the preceding reactions of 2H-PFP (69) with aromatic substrates we have observed products of the type $Ar\text{-}CH_2CF_3$. We have also noted the formation of compound (80) from compound (79) in the presence of fluoride ion and water (section 2.5.1). In addition we have observed the slow formation of salt (97) from a pure sample of compound (87) in the presence of fluoride ion (Scheme 2.27). Fig 2.28.a shows the fluorine n.m.r. chemical

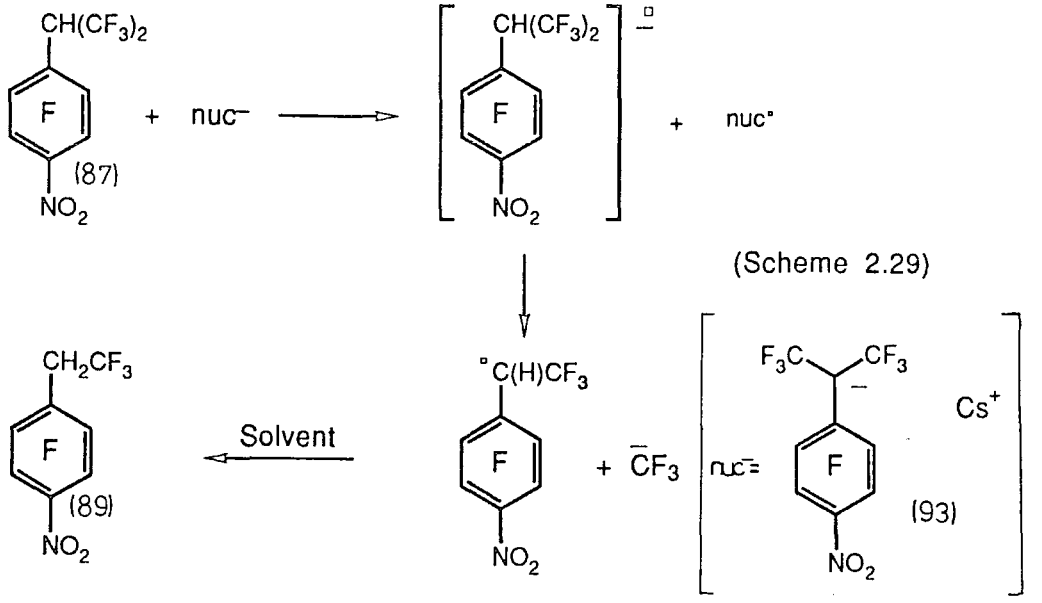


(Scheme 2.27) (Observed by n.m.r.) (Observed by GC /MS)

shifts tentatively assigned to ion (97) and fig 2.28.b shows the chemical shift changes produced upon ionisation.



In Seaburys' preliminary investigation[111] a tentative electron transfer process was proposed to account for the formation of a trifluoroethyl derivative (Scheme 2.29) (This is similar to that proposed for the substitution reactions of nitrobenzyl



(Scheme 2.29)

halides[124]). It is reasonable to expect that such a process will be enhanced by the addition of water [increasing the concentration of electron accepter compound (87) with respect to electron donor salt (93)]. We have demonstrated the electron transfer nature of the conversion by the formation of compound (89) (observed by ^{19}F n.m.r. and GC / MS) in the electrochemical reduction of compound (87).

2.7 Investigation into the Mechanism of Formation of Perfluoro-3-methyl-2,1-benzisoxazole (88)

2.7.1 Experimental Evidence - Reactions of Compounds (87) and (89)

a) *Pure compound* (87) *with fluoride ion*

As was discussed in section 2.6 a pure sample of compound (87) reacts with caesium fluoride to yield anion (93) and subsequently anion (97). GC analysis of the worked up solution indicated only a trace of isoxazole derivative (88).

b) *Effect of pentafluoronitrobenzene* (71)

In the presence of pentafluoronitrobenzene (71) compound (88) is the major GC detected product, followed by compounds (87) and (89). Hence pentafluoronitrobenzene (71) clearly plays an important role in the formation of compound (88).

c) *Effect of pentafluorobenzonitrile* (82)

Replacing the pentafluoronitrobenzene (71) impurity with pentafluorobenzonitrile (82) had a considerable effect upon the ratios of the products formed (see table 6.1). With pentafluoronitrobenzene (71), compound (88) has the largest GC integral, but with pentafluorobenzonitrile (82) compound (89) has a GC integral nearly nine times larger than that of compound (88). Hence pentafluorobenzonitrile (82) is clearly not enhancing the formation of compound (88) as pentafluoronitrobenzene (71) appears to.

d) *Effect of solution concentration upon reaction of compound* (87) *with fluoride ion*

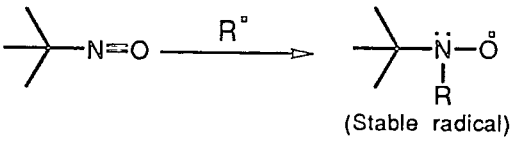
An intramolecular reaction would be expected to be largely unaffected by the solution concentration. However, the relative concentration of compound (88) in the worked up reaction mixtures was found to be highly dependant on the mass of solvent used. Concentrated reaction mixtures yielded high compound (88) concentrations [relative to compounds (87 and 89)], whereas low concentration reaction mixtures yielded lower ratios of compound (88) relative to compounds (87 and 89) (see table 6.2). This result suggests that the rate determining step is intermolecular in nature.

e) *Compound* (89) *under reaction conditions*

The reaction of trifluoroethyl derivative (89) with pentafluoronitrobenzene (71) and fluoride ion yielded no significant volatile products. Hence it can be deduced that compound (89) is not on the mechanistic pathway to compound (88).

f) *Effect of a free radical trap*

Adding 2-methyl-2-nitrosopropane dimer should inhibit a free radical reaction by forming a stable nitroxide radical from radical species (Scheme 2.30). Some reduction in the relative



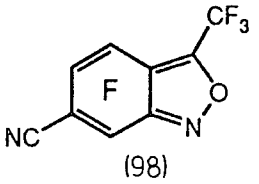
(Scheme 2.30)

concentration of isoxazole derivative (88) was observed (*ca* 50%, table 6.3) in the presence of the radical trap. However this experiment can not be considered to be conclusively for or against free radical participation in the isoxazole forming reaction.

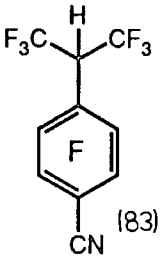
g) *Attempt to form a substituted isoxazole derivative*

An attempt was made to form the substituted isoxazole derivative (98) (Fig. 2.31.a) by the reaction of compound (83) (Fig. 2.31.b)

(Fig. 2.31.a)



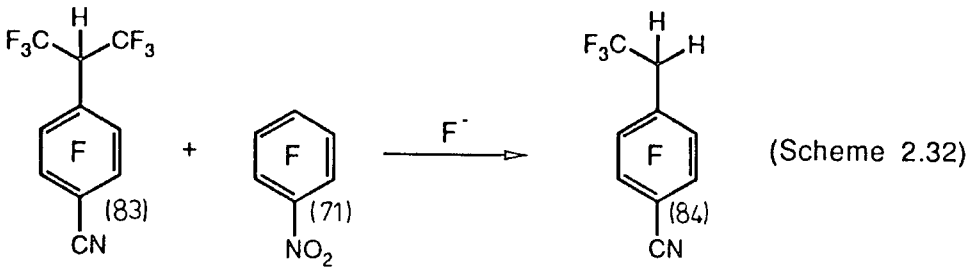
(98)



(83)

(Fig. 2.31.b)

with pentafluoronitrobenzene (71) and fluoride ion. However, compound (98) was not observed in the product mixture (Scheme 2.32). The principal product was found to be trifluoroethyl derivative (84).



(Scheme 2.32)

2.7.2 Summary of deductions on the nature of the cyclisation

From the experimental observations we can deduce that:

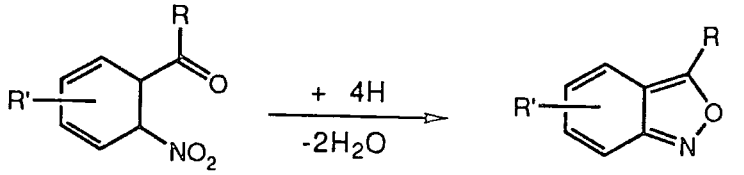
i) isopropyl derivative (87) is an intermediate but trifluoroethyl derivative (89) is not;

ii) pentafluoronitrobenzene (71) is required (but possibly not as a one electron accepter otherwise we might anticipate that pentafluorobenzonitrile (82) would promote the reaction);

iii) the rate determining step is intermolecular.

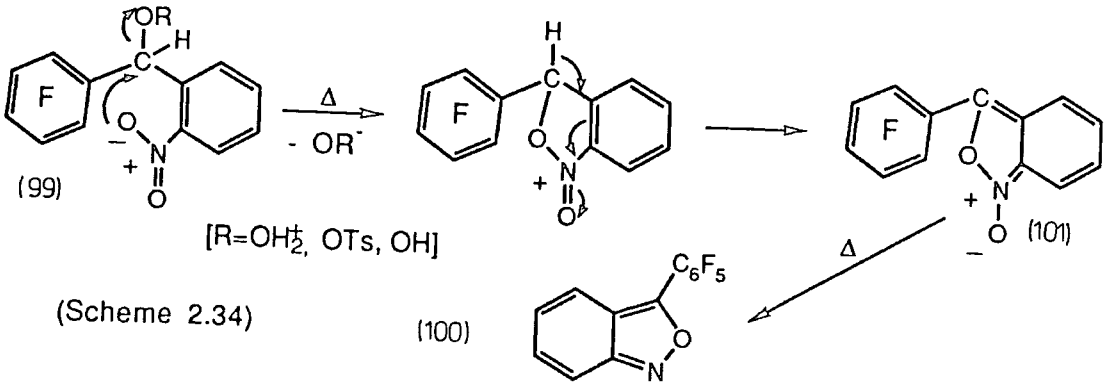
2.7.3 2,1-Benzisoxazoles (Anthranils)

The formation of 2,1-benzisoxazoles has been reviewed.[125] 2,1-Benzisoxazoles are often formed by reduction of *ortho*-nitroso or *ortho*-nitro benzyl carbonyls (for example see scheme 2.33).



(Scheme 2.33)

It is reported[126] that pyrolysis of compound (99) (Scheme 2.34) yielded compound (100), believed formed by the initial elimination of $^{-}$OR. N-oxide (101) was also shown to decompose partly to compound (100) on pyrolysis. Such a mechanism can clearly not



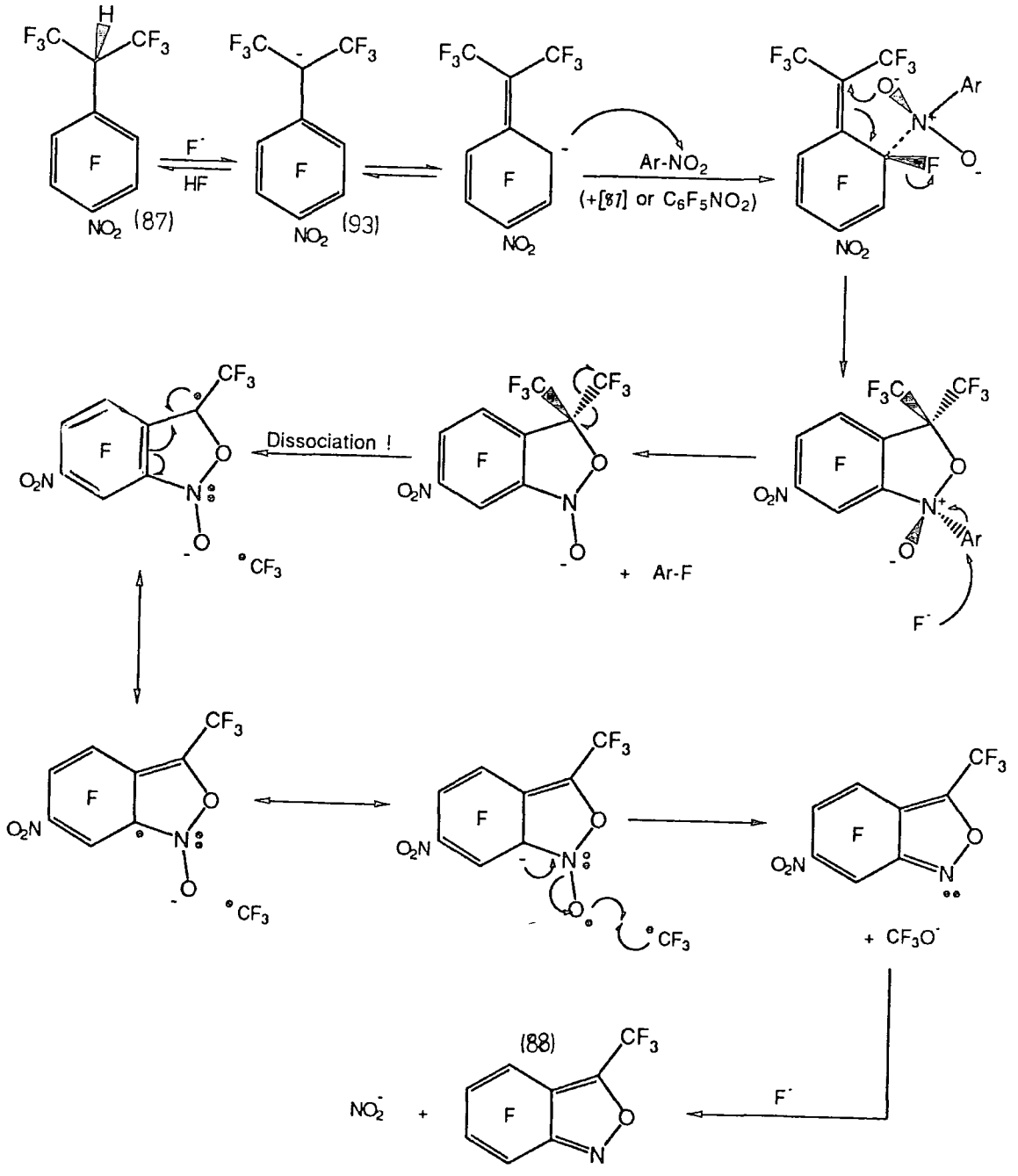
(Scheme 2.34)

account for our apparently intermolecular reaction.

2.7.4 Proposed Mechanism of Formation of Compound (88)

Seabury[111] proposed an initial intramolecular rearrangement to give an *ortho*-substituted nitroalkyl derivative, which then cyclised. We have discounted this mechanism, again due to the apparent intermolecular nature of the reaction. To account for our observations we feel that the most likely mechanism is that outlined in scheme 2.35. The first step is the formation of

(Scheme 2.35)

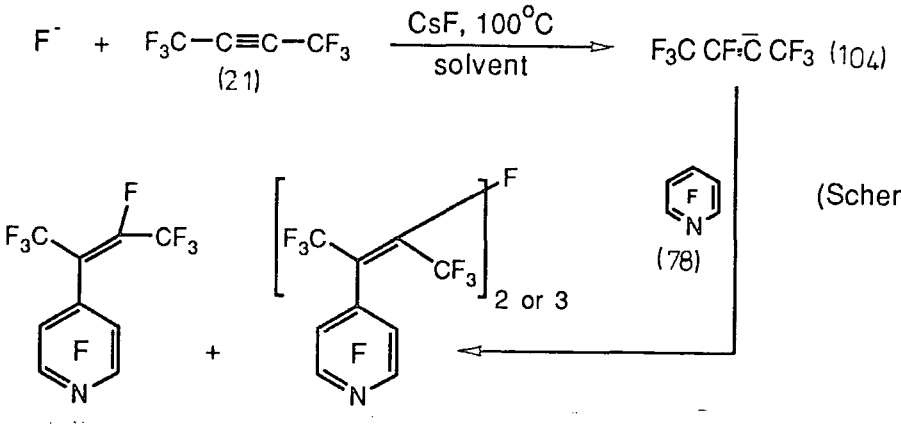


anion (93) (*ca* 98% by n.m.r.). This then reacts preferentially in the *ortho*-position with a nitro-aromatic. Nitro-aromatic anion (93) will be deactivated to nucleophilic attack itself as a result of its negative charge, hence the presence of neutral pentafluoronitrobenzene should greatly enhance this step. Ring closure with displacement of fluoride followed by displacement of the aromatic group, as Ar-F, leads to the formation of the required ring skeleton. At this point we must invoke a homolytic cleavage yielding a CF_3 radical, which migrates, combines with oxygen, and is lost as CF_3O^- (CF_3O^- will dissociate to give difluorophosgene and fluoride ion). Finally at some point during the reaction the ring nitro group must be displaced by fluoride ion so that the final product is compound (88).

Chapter 3 - Fluoride Ion Induced Reactions of Dimethylacetylenedicarboxylate (105)

3.1 Introduction

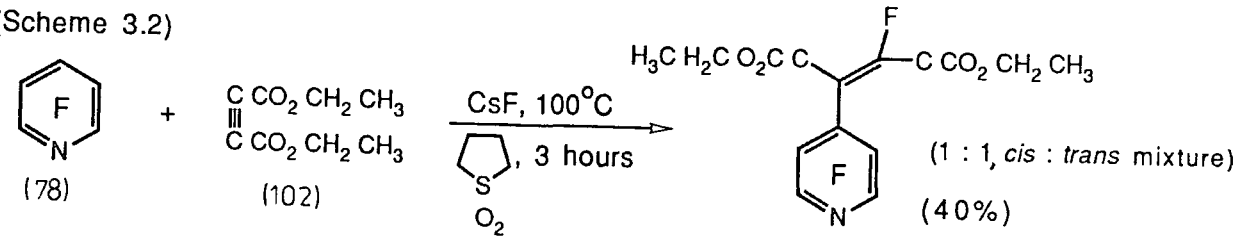
In the same way that fluoride ion will react with alkenes forming alkyl anions, the reaction of fluoride ion with acetylenes may form intermediate vinyl anions.[1] The reaction of hexafluorobut-2-yne (21), caesium fluoride and perfluorinated aromatic substrates has been studied[127-129] (Scheme 3.1). The corresponding chemistry using diethylacetylenedicarboxylate (102)



(Scheme 3.1)

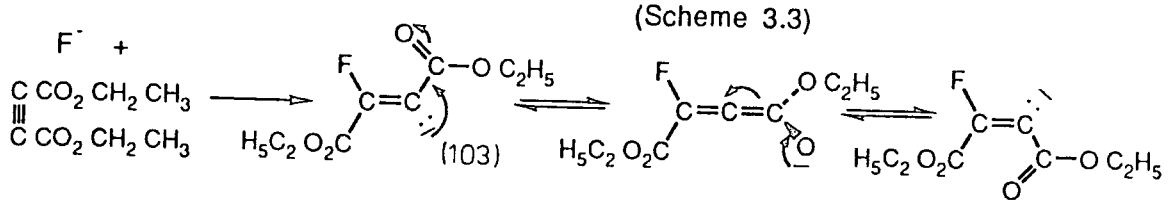
as the acetylene with pentafluoropyridine (78) has also been reported[128,130,131] (Scheme 3.2). The formation of *cis* and *trans*

(Scheme 3.2)



products has been rationalised[128] by the isomerisation of the intermediate carbanion (103) (Scheme 3.3). No such interconversion mechanism exists for anion (104) (Scheme 3.1) which proceeds to exclusively form *trans* products.

(Scheme 3.3)

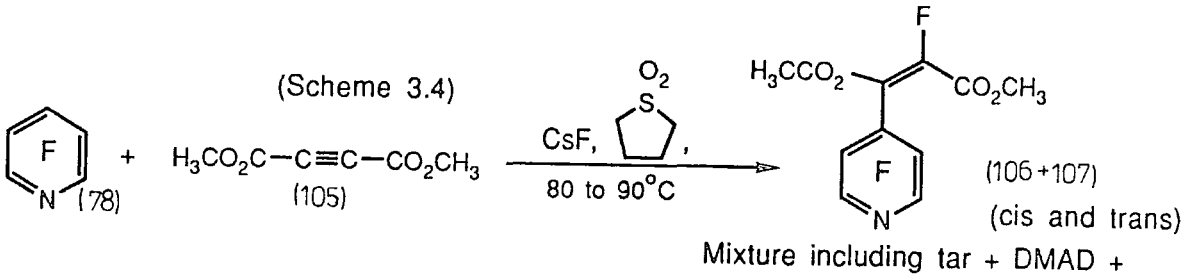


We have investigated some of the reactions of dimethylacetylenedicarboxylate (DMAD) (105) and fluoride ion with pentafluoropyridine (78) and also with several cyclic fluorinated alkenes.

3.2 With Pentafluoropyridine (78)

The reaction of DMAD (105) with pentafluoropyridine (78) yielded a mixture of tar, compounds (106 and 107; in ratio 3 : 2 by fluorine n.m.r.) and residual DMAD (105). A temperature of 80 to 90°C was chosen in accordance with the earlier diethylacetylenedicarboxylate work (See section 3.1). This mixture proved difficult to separate and the impure products (Scheme 3.4) were characterised by n.m.r. (^1H, ^{19}F) and by mass spectroscopy.

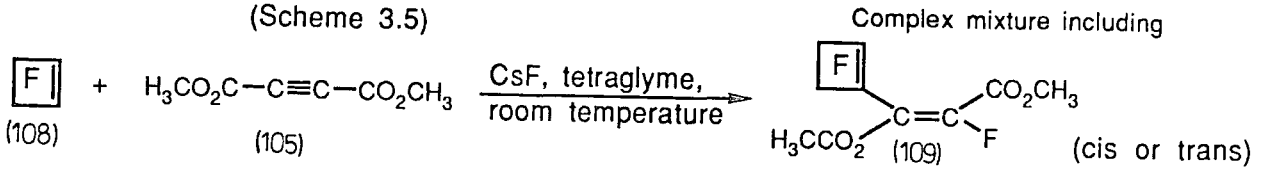
(Scheme 3.4)



3.3 With Perfluorinated Cycloalkenes

3.3.1 With perfluorocyclobutene (108) (Scheme 3.5)

(Scheme 3.5)

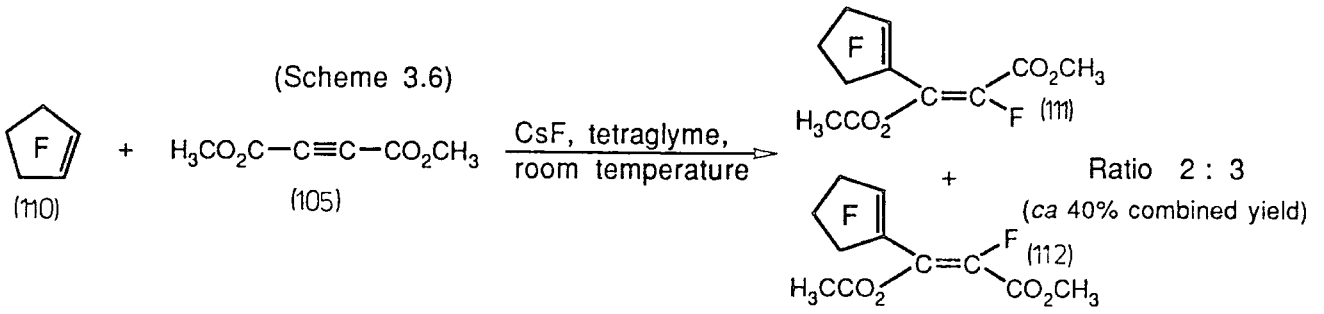


Although no products could be isolated from the reaction mixture GC / MS indicated the presence of perfluorocyclobutene oligomers and tentatively of a small quantity of compound (109). We can deduce that at room temperature the fluoride ion induced oligomerisation of cycloalkene (108) proceeds more rapidly than the formation and reaction of a fluoro-butenylide anion.

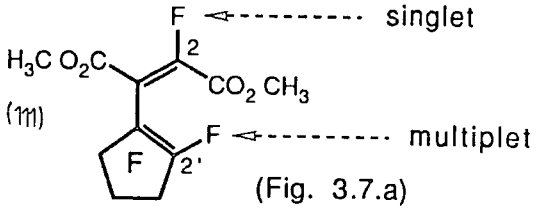
3.3.2 With perfluorocyclopentene (110)

Perfluorocyclopentene (110) is known to be less reactive with respect to dimerisation and oligomerisation in the presence of fluoride ion than is perfluorocyclobutene (108). Hence it was not surprising when reaction of perfluorocyclopentene (110) with DMAD (105) in the presence of fluoride ion afforded a useful yield of monosubstituted products (Up to 40% of a *cis / trans* mixture). (Scheme 3.6). The minor isomer readily crystallised from the

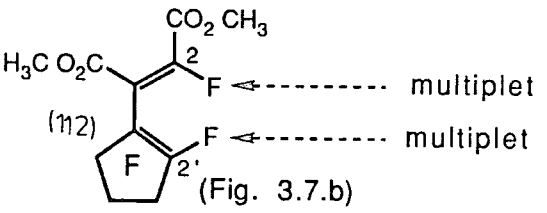
(Scheme 3.6)



mixture and has been tentatively assigned as the *trans* isomer (111) based upon the lack of a possible fluorine n.m.r. F2-F2' coupling (See fig 3.7.a in comparison to fig. 3.7.b). The major isomer was not isolated from the mixture but based upon mass spectroscopy and n.m.r. was assigned as the *cis*-isomer (112) (Fig. 3.7.b).



(Fig. 3.7.a)

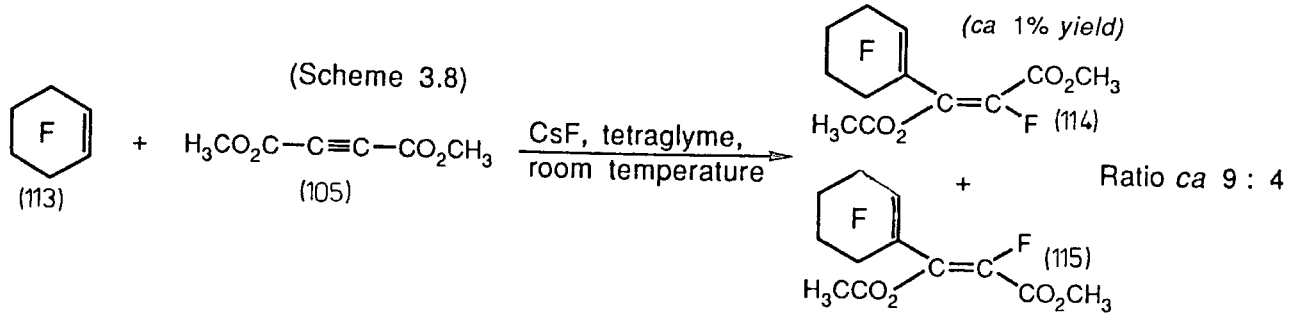


(Fig. 3.7.b)

3.3.3 With perfluorocyclohexene (113)

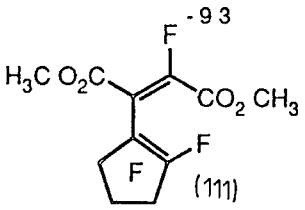
The reaction of perfluorocyclohexene (113) with DMAD (105) in the presence of fluoride ion yielded only a small quantity of a mixture of the desired monosubstituted products (Scheme 3.8).

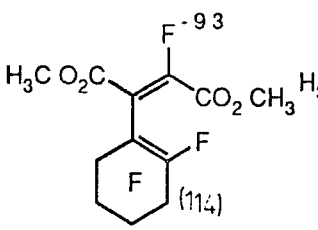
(Scheme 3.8)



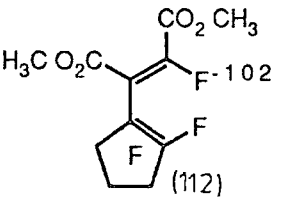
The major isomer crystallised from the worked up mixture and was assigned as the *trans*-isomer (114), the minor isomer was assigned as the *cis* isomer (115). The assignments were based upon a comparison of vinylic ^{19}F n.m.r. chemical shifts of compounds (111, 112, 114, and 115) (Fig. 3.9).

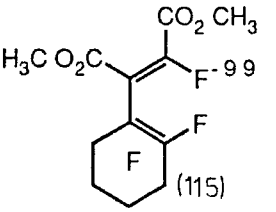
Trans compounds





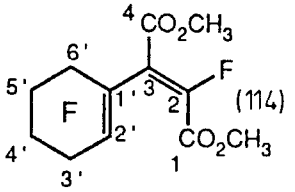
Cis compounds





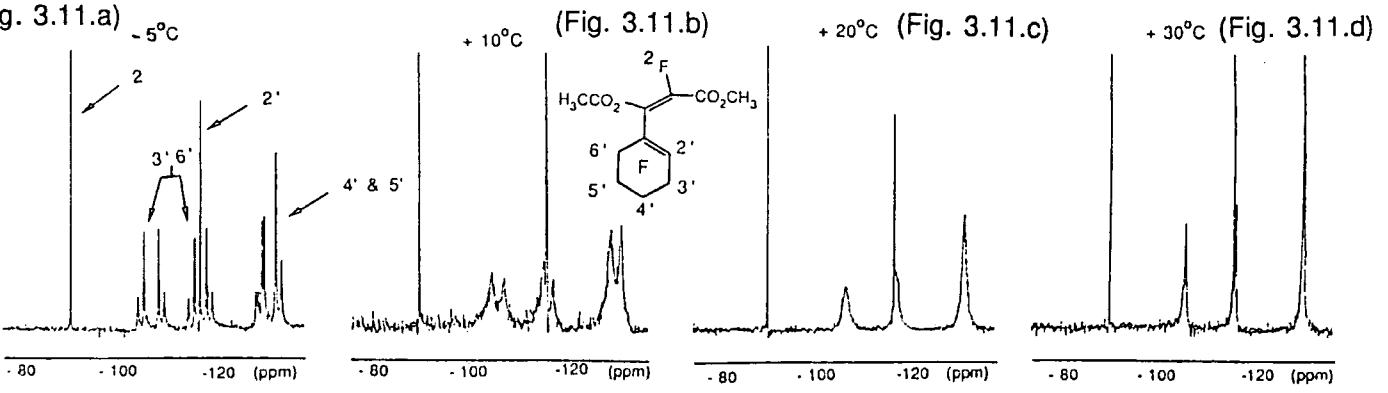
(Fig. 3.9) (Fluorine n.m.r. data in ppm)

The *trans*-isomer (114) exhibited an unusual fluorine n.m.r. spectrum with very broad difluoromethylene resonances in the 3', 4', 5', and 6' sites at room temperature (Fig. 3.10). A variable

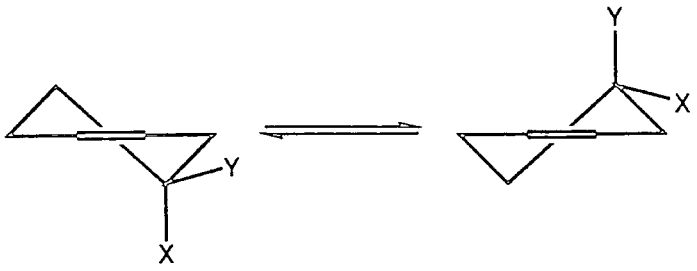


(Fig. 3.10)

temperature experiment indicated that at low temperatures (-5^{0}C) the spectrum consisted of sharp AB type multiplets (Fig. 3.11.a) (a highly coupled none averaged spectrum), at higher temperatures (10-20^{0}C) coalescence occurred (Figs 3.11.b, 3.11.c) and at higher temperatures still (30^{0}C) each difluoromethylene resonance became sharp (Fig. 3.11.d). We have attributed the temperature



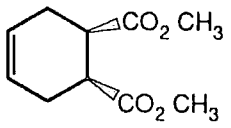
dependence to an interconversion between two half-chair conformations with substituents changing from axial sites to equatorial sites (Fig. 3.12). A similar temperature dependence

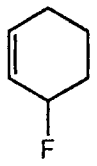


(Fig. 3.12)

has been observed in a series of cyclohexenes,[132-134] although the coalescence temperatures are typically less than -130°C (*eg* fig. 3.13). It may be that it is the bulky transoid 2-substituent in

(Fig. 3.13)





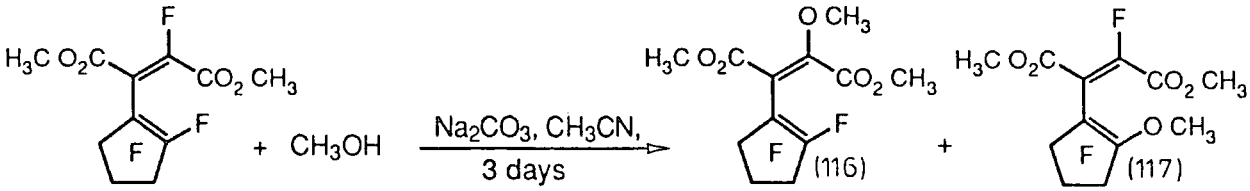
Coalesence Temperature (°C)	-135.5	-151.8	-150 → -164

compound (114) that is making the ring interconversion a much higher energy process. At room temperature the *cis*-isomer (115) gave sharp simple fluorine n.m.r. resonances indicating that the exchange is already rapid in this system, hence the configuration of the 1'-substituent is important in the exchange process. We have discounted rotation of the C1'-C3 bond (Fig 3.10) as a cause of the exchange as this would almost certainly greatly influence the n.m.r. resonance of F2' which is observed to give a sharp n.m.r. signal at all of the temperatures investigated.

3.4 Some Reactions of Compounds (111 and 112)

3.4.1 With methanol

No reaction was observed between neutral methanol and compounds (111 and 112). However, addition of sodium hydrogen carbonate yielded two products (Scheme 3.14). Compound (116) was not



(111,112)

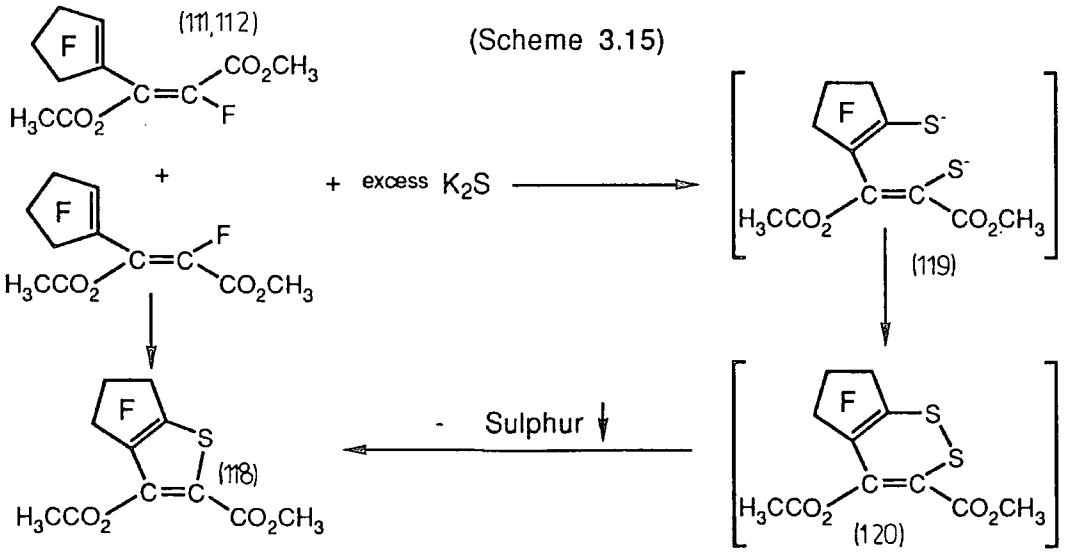
(Scheme 3.14)

(Ratio 5 :6) (*ca* 90% crude yield)

isolated but was identified by mass spectroscopy and n.m.r., whereas compound (117) was isolated as a solid and was fully characterised. From the product ratios we can deduce that the endocyclic site is slightly more reactive to basic methanol than is the endocyclic site.

3.4.2 With potassium sulphide

The reaction of sulphide ion with fluorinated alkenes is well known.[135-137] The reaction of a small excess of sulphide with a mixture of compounds (111 and 112) yielded a low melting point solid which was identified as thiophene derivative (118) (Scheme 3.15) and a small quantity of another white solid which was believed to be elemental sulphur. Compound (118) was fully characterised, notably with fluorine n.m.r. showing three distinct resonances.



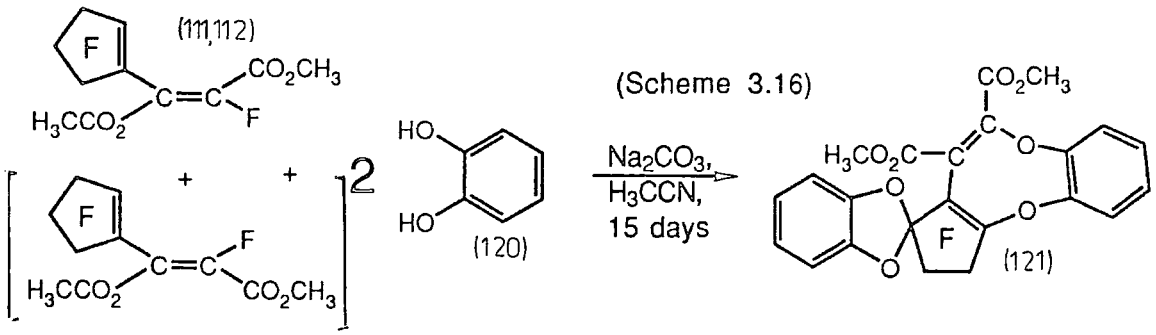
We believe that there may be two routes to compound (118):

a) *via* nucleophilic displacement of each vinylic fluorine atom by different sulphur atoms forming dianion (119) with subsequent oxidation yielding dithiete (120), which extrudes sulphur to yield thiophene (118);

b) *via* overall displacement of both vinylic fluorine atoms by the same sulphur atom yielding thiophene (118) directly.

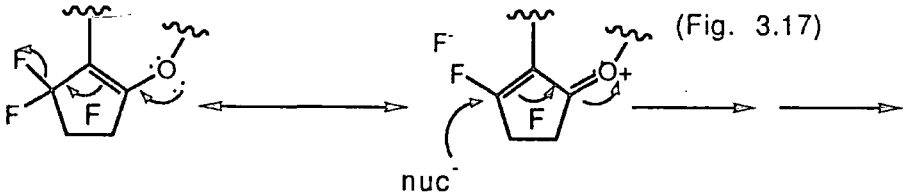
3.4.3 With catechol (120) and sodium carbonate

The reaction of a mixture of compounds (111 and 112) with two equivalents of catechol (120) in the presence of sodium carbonate produced *spiro*-benzodioxocin derivative (121) (Scheme 3.16). The



(Scheme 3.16)

dioxocin ring is clearly formed by the nucleophilic displacement of fluoride from both vinylic sites. The oxygen lone pairs (Fig. 3.17) can then activate the indicated methylene fluorine atoms to nucleophilic substitution leading ultimately to the formation of the *spiro* ring. The product (121) was fully characterised (^{13}C

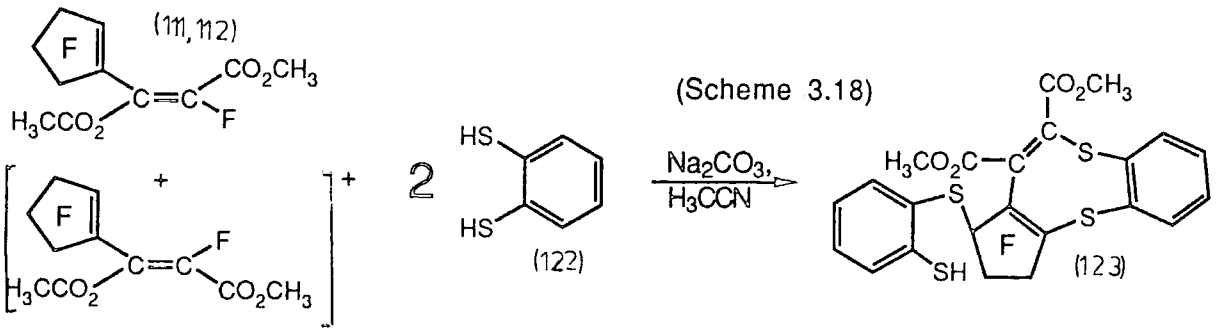


(Fig. 3.17)

n.m.r. was not completely assigned owing to the complexity of the molecule). It was notable that the fluorine n.m.r. spectrum consisted of only two equal intensity singlets.

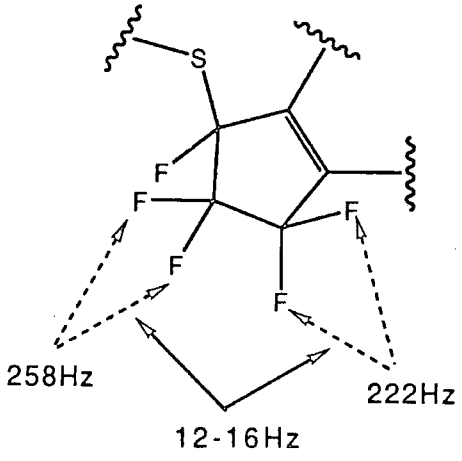
3.4.4 With 1,2-benzenedithiol (122) and sodium carbonate

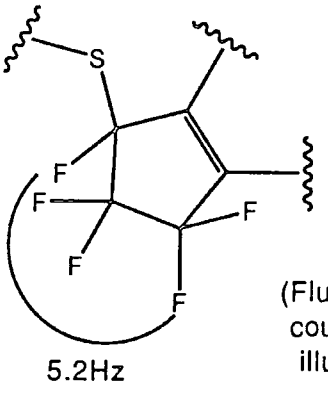
Having made the catechol derived compound (121) we next attempted to prepare the analogous 1,2-benzenedithiol derivative. After a reaction time of three days fluorine n.m.r. indicated that the reaction had reached completion. Analysis of the worked up product revealed that we had lost both vinylic fluorine atoms, indicating that we had formed a benzodithiocin ring, however we observed a total of five fluorine atoms in each molecule. Mass spectroscopy (including an accurate mass measurement) and elemental analyses were consistent with the molecular formula $C_{23}H_{15}F_5S_4O_4$ corresponding to compound (123) (Scheme 3.18) where only one of the methylene fluorine atoms has been replaced.



(Scheme 3.18)

The intra-ring fluorine n.m.r. couplings are illustrated in fig. 3.19, which clearly support the proposed substitution pattern.



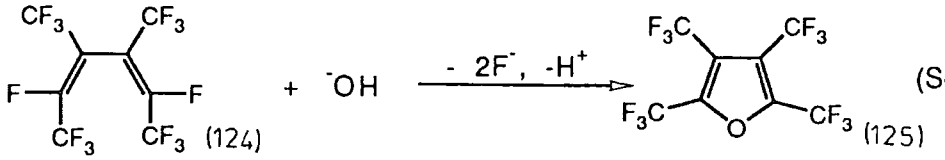


(Fig. 3.19)

(Fluorine n.m.r. couplings are illustrated)

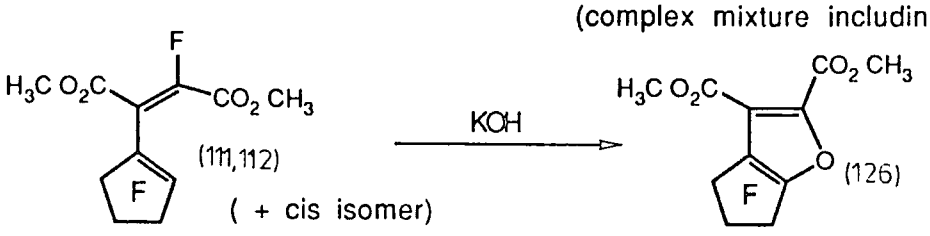
3.4.5 With potassium hydroxide

It has been reported[138] that the reaction of diene (124) with potassium hydroxide yielded perfluorotetramethylfuran (125) (Scheme 3.20). We have attempted a similar reaction using our



(Scheme 3.20)

mixture of compounds (111 and 112) (Scheme 3.21). We obtained a complex mixture, GC/MS analysis of which indicated the possible



(Scheme 3.21)

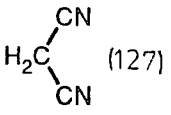
presence of compound (126) (M^+, 322). There was also some evidence for the presence of trimethoxy derivatives (116 and 117) presumably formed by methoxide ion (displaced from esters by hydroxide) reacting with compounds (111 and 112).

Chapter 4 - Bifunctional Carbon Nucleophiles with Fluorinated Aromatic Systems

4.1 Introduction

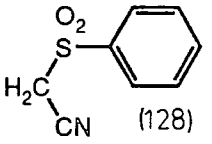
Further to recent work on perfluorocarbanions (Section 1.3.2.b) we have investigated some of the reactions and properties of fluorinated aromatic and fluorinated heteroaromatic systems which bear a negatively charged substituent.

We have paid particular attention to salts derived from a) malononitrile (127), and b) phenylsulphonyl acetonitrile (128) (Fig. 4.1).



(127)

a) malononitrile



(128)

a) phenylsulphonylacetonitrile

(Fig. 4.1)

4.2 Procedure for Preparing the Salts and their Conjugate Acids

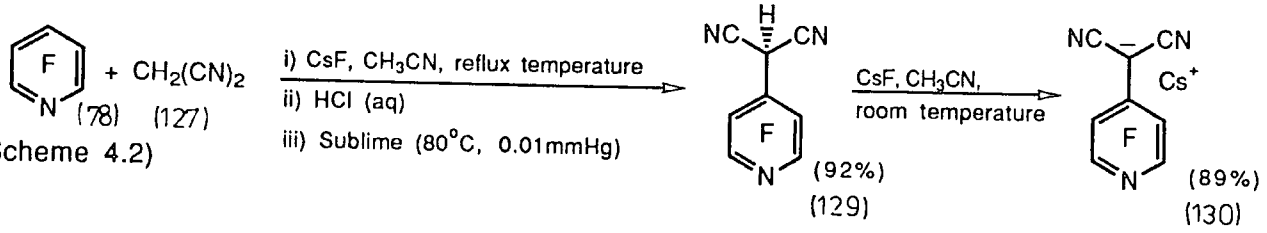
The overall reaction may be summarised as illustrated below.

$$X(CN)CH_2 + Ar_F \xrightarrow{M^+ F^-} [Ar_FC(X)CN]^- M^+ \xrightarrow{H^+} Ar_FCH(X)CN$$

[Where X = CN (127) or $PhSO_2$, M = K or Cs, and Ar_F = a fluorinated aromatic]

4.2.1 Synthesis of a salt and its conjugate acid

The preparation of malononitrile derivative (129) and salt (130) are illustrated in scheme 4.2. In this example it was found



(78) (127)

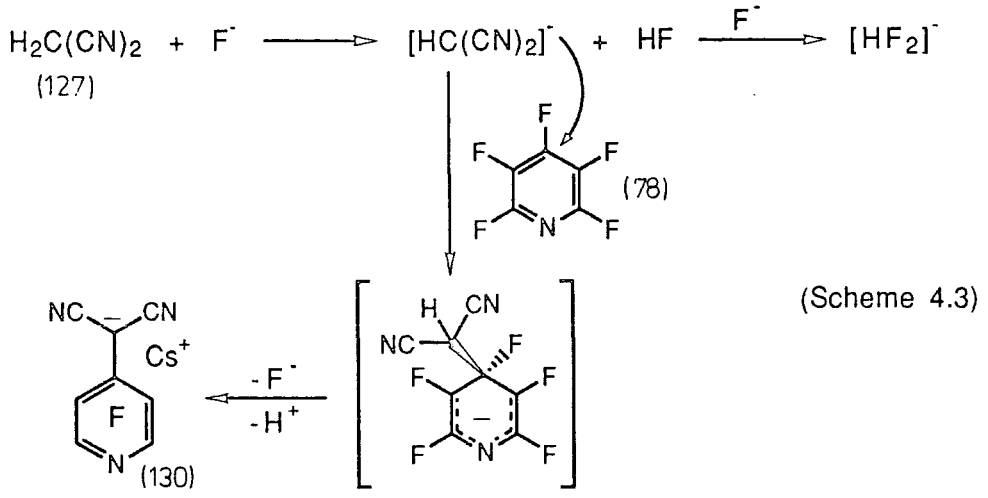
(92%) (129)

(89%) (130)

(Scheme 4.2)

preferable to first isolate compound (129) with a further reaction with caesium fluoride generating salt (130).

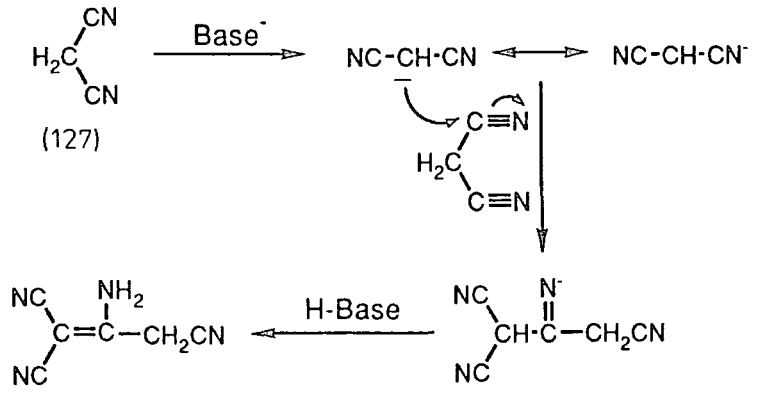
In all cases we have used fluoride ion as a base in order to promote a nucleophilic aromatic substitution reaction (Scheme 4.3).



(Scheme 4.3)

4.2.2 The choice of fluoride ion as a base

Fluoride ion has been reported[7] to be a sufficiently strong base to effect reactions of this type (For example[11] see section 2.3.1). Also there can be no side products formed from the nucleophilic substitution of fluoride ion into the aromatic rings (fluoride ion would be both the entering and the leaving group), which might be a problem with other nucleophilic bases. Using fluoride ion as a base we have not observed any evidence for the base catalysed self condensation of malononitrile (Scheme 4.4) which often accompanies malononitrile reactions.[139]



(Scheme 4.4)

4.2.3 N.m.r. analysis of the products

Perdeuteroacetone was chosen as the n.m.r. solvent because both the salts and their conjugate acids dissolve well, while the salts often had poor solubility in the more usual chloroform. Where the quantity of the product permitted, proton, fluorine, and carbon-13 n.m.r. spectra were acquired as appropriate.

4.3 Salts and Conjugate Acids Derived From Malononitrile

4.3.1 Substituted malononitrile salts

Using this methodology a series of substituted malononitrile salts has been prepared and studied (See table 4.1).

4.3.2 Conjugate acids

Acidification of the salts using hydrochloric acid usually yielded the corresponding conjugate acids (See table 4.2). It may be noted that some of the structures are written as tautomers with protonation at nitrogen (For discussion see section 4.3.10) The conjugate acids can be seen to be much stronger acids than malononitrile itself [*c.f.* malononitrile $pK_a \simeq 11.1$ in dimethylsulphoxide (DMSO) solution;[159] $HC(CN)_3$ $pK_a \simeq 0$[13]]. The enhancement of the equilibrium acidities of carbon acids by polyfluoroaryl substituents has been reported (for example:[140] CH_3CN pK_a 31.3; $C_6F_5CH_2CN$ pK_a 17.5).

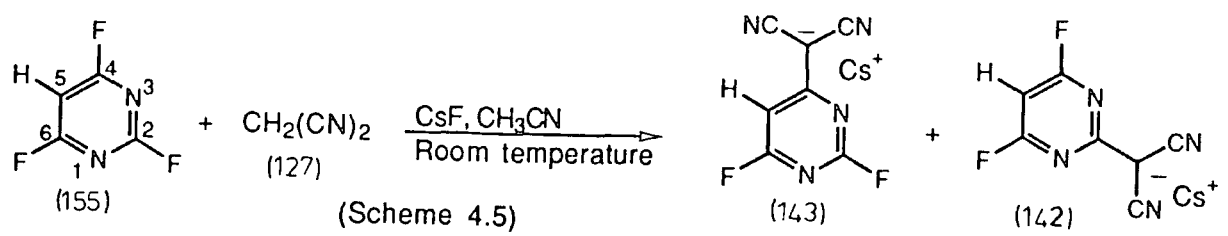
4.3.3 N.m.r. determination of the site of substitution

The site of substitution was determined using fluorine n.m.r. involving a consideration of:

a) the number of n.m.r. resonances observed, giving an indication of the degree of symmetry in the fluorine atom substitution pattern;
b) the spectra of other derivatives of the substrate;
c) the spectra of the substrate;
d) characteristic coupling constants (for example: perfluoro--phenyl;[141] -pyridyl[142] (^{19}F and ^{13}C); -pyrazyl;[143] -*iso*-quinyl;[144] or-napthyl[145])
e) (a), (b), and (d) were also considered for the ^{13}C n.m.r. spectra where available.

4.3.4 Reactions yielding mixtures

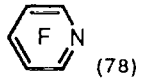
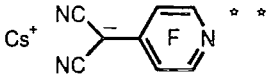
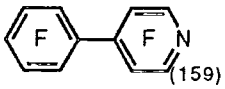
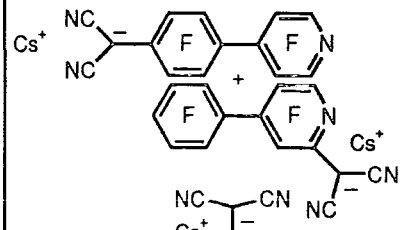
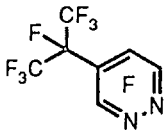
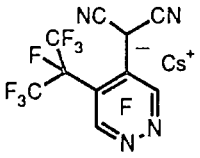
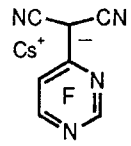
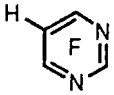
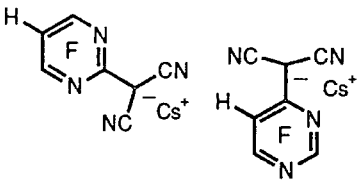
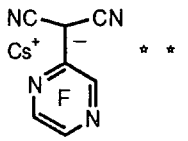
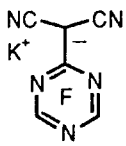
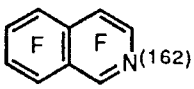
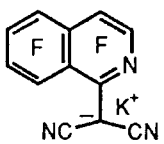
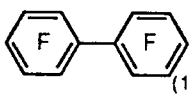
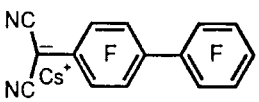
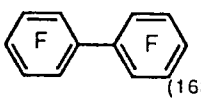
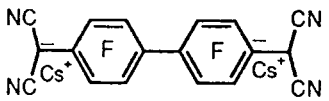
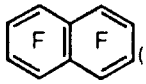
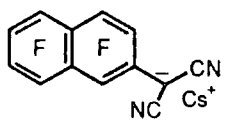
a) *with* 2,4,6-*trifluoropyrimidine* (155)



(Scheme 4.5)

ca 5 : 6

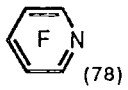
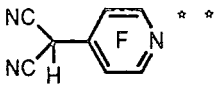
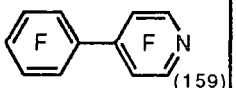
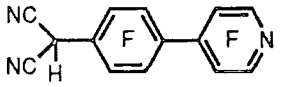
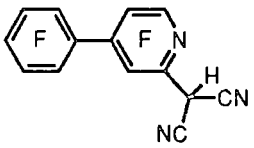
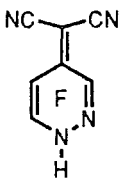
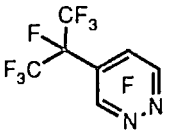
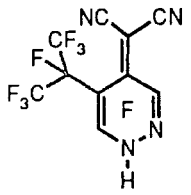
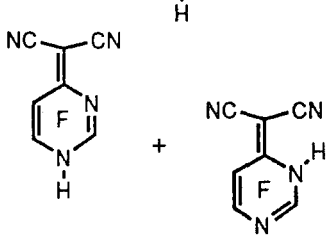
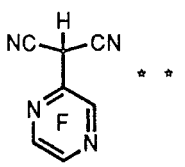
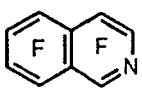
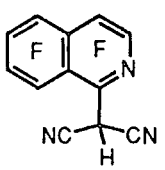
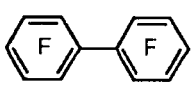
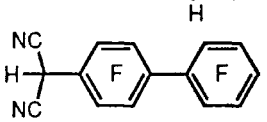
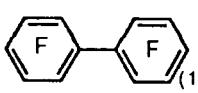
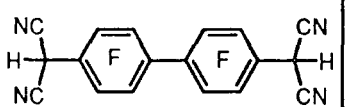
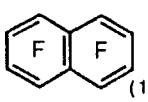
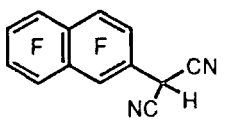
Table 4.1

Substrate	Salt Product(s)	Number	Yield*
 (78)	 **	(130)	80%
 (159)		(132) (134)	56% 7%
 (158)		(136)	80%
 (157)		(138)	*ca* 95%
 (156)		(140)	72%
 (155)		(142) (143)	42% 35%
 (160)	 **	(145)	30%
 (161)		(146)	91%
 (162)		(148)	*ca* 68%
 (163)		(150)	*ca* 89%
 (163)		(152)	*ca* 96%
 (164)		(154)	*ca* 94%

* Yields are calculated from the parent aromatic compound

** *via* conjugate acid

Table 4.2

Substrate	Conjugate Acid(s)	Number	Yield*
 (78)	 **	(129)	89% pK_a 1.6
 (159)	 + 	(131) (133)	76% 45%
 (158)		(135)	61% pK_a 2.9
 (157)		(137)	78% pK_a 3.2
 (156)		(139) (141)	9%
 (160)	 **	(144)	68% pK_a 3.2
 (162)		(147)	64%
 (163)		(149)	60%
 (163)		(151)	47%
 (164)	*** 	(153)	67% pK_a 3.0

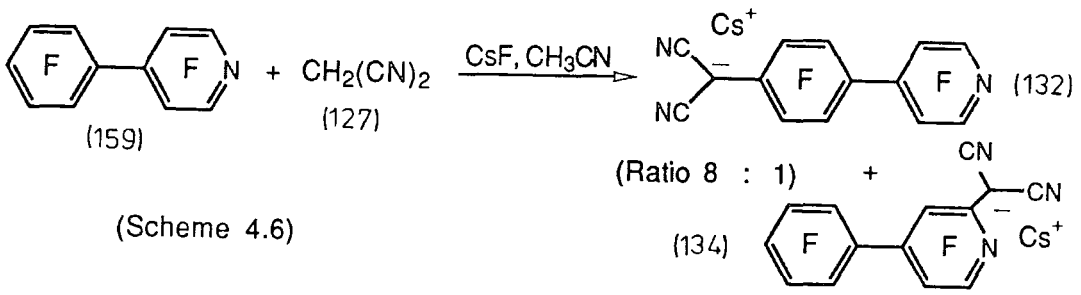
* Yields are calculated from the corresponding salt

** Yield calculated from the parent aromatic compound

*** pK_a measured in aqueous acetone (15%) due to low solubility in water

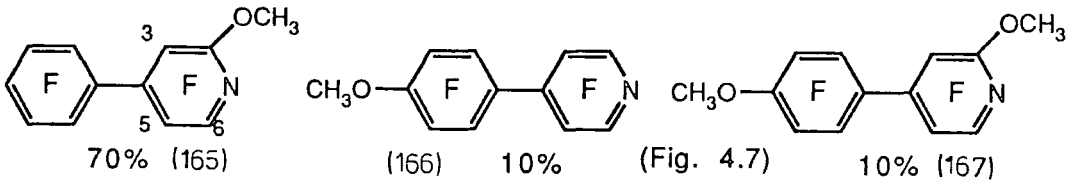
The replacement of hydrogen for fluorine in position five has a dramatic effect upon the site of nucleophilic substitution.[146] Similarly with tetrafluoropyrimidine (156) (Table 4.1) we observed substitution only at site four. However, with compound (155) we observed over 50% substitution at site two, with the remainder at site four. The resulting isomeric salts were separated by recrystallisation from water.

b) *With 4-phenylpyridine* (159)



(Scheme 4.6)

It is notable that substitution occurs predominantly at the *para* site of the pentafluorophenyl ring rather than at the *ortho* sites of the tetrafluoropyridyl ring (Scheme 4.6). In contrast it has been reported[147] that the reaction of compound (159) with a one molar equivalent of sodium methoxide in methanol yielded compounds (165, 166, and 167) in the ratio 7 : 1 : 1 (Fig. 4.7). It has

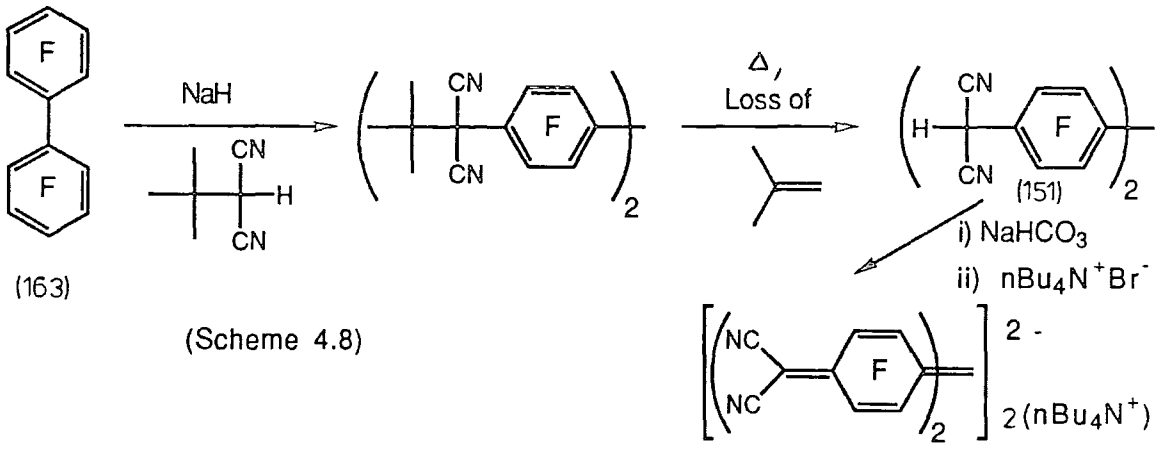


also been reported that in the reaction of compound (159) with the anions $\{[(\pi\text{-}C_5H_5)Fe(CO_2)]^-$ and $[Re(CO)_5]^-\}$ the only products obtained were low yields (17 and 25% respectively) of compounds derived from 4'-substitution into the phenyl ring.[148] Hence it appears that soft nucleophiles (transition metal complexes, malononitrile anion) preferentially attack the phenyl ring, while harder nucleophiles (methoxide, hydroxide,[147] ammonia[147]) preferentially attack the pyridyl ring. For salt (134) and its conjugate acid (133) assignment of the 3 and 5 position fluorine resonances was aided by comparison with the chemical shifts and coupling constants reported for compound (165).[147]

4.3.5 Previously reported compounds or salts

a) $(nBu_4N^+)_2$ *analog of salt* (152)

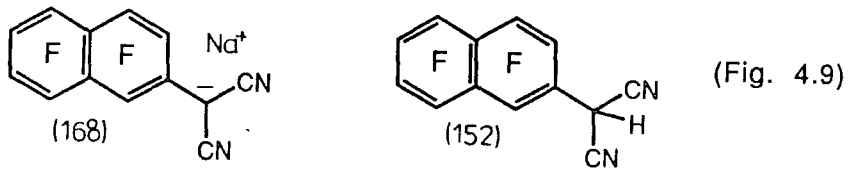
The above salt was prepared by a less direct method by Wheland and Martin[149] (Scheme 4.8).



(Scheme 4.8)

b) *β-Heptafluoronaphthylmalononitrile* (153) *and its* Na^+ *salt* (168)

These compounds (Fig. 4.9) were prepared by the sodium hydride induced reaction between malononitrile and perfluoronaphthalene, as part of an investigation into a series of β-heptafluoronaphthyl containing carbanions.[150]



(Fig. 4.9)

c) *Pentafluorophenylmalononitrile*

Pentafluorophenylmalononitrile was first reported[151] in 1962 and has subsequently been reported as the product of the reaction between hexafluorobenzene and the sodium salt of malononitrile in hexamethylphosphoramide solution.[152] We have found no evidence for reaction between hexafluorobenzene and malononitrile under our conditions.

d) *Some notable examples of related air / water stable systems*

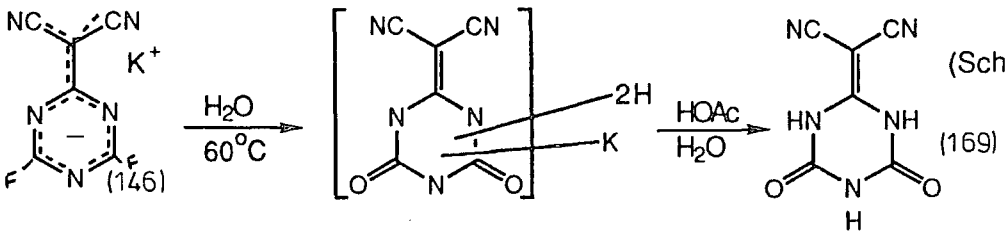
Hartzler[153] has reported stable sodium and potassium salts of $[O_2NC_6H_4C(CN)_2]^-$, while more recently Dixon and co-workers[154] have reported the crystal and molecular structure of the stable charge transfer salt $[Fe(C_5Me_5)_2]^+[C(CN)_3]^-$. The stable cyclic dianions $\{C_3[C(CN)_2]_3\}^{2-}$ and $\{C_4[C(CN)_2]_4\}^{2-}$ have been prepared by the sodium hydride induced reaction of malononitrile with halogenated cyclic alkenes.[155,156]

4.3.6 Effect of counter ion on n.m.r. spectra

Low concentration (*ca* 0.2M in perdeuteroacetone) spectra of the caesium and potassium salts of salt (146) (See table 4.1 or scheme 4.10) were very nearly identical to each other. Hence we can conclude that at such concentrations the metal cation has little effect upon the observed anionic n.m.r. spectra.

4.3.7 Stability of the salts

The salts have been stored as dry solids for prolonged periods without showing any signs of decomposition. The hydrolytic stability of many of the salts has been demonstrated by the use of recrystallisation from hot water as a purification procedure. A notable exception is the hydrolysis of salt (146) which occurred at approximately 60°C in aqueous solution (Scheme 4.10). After

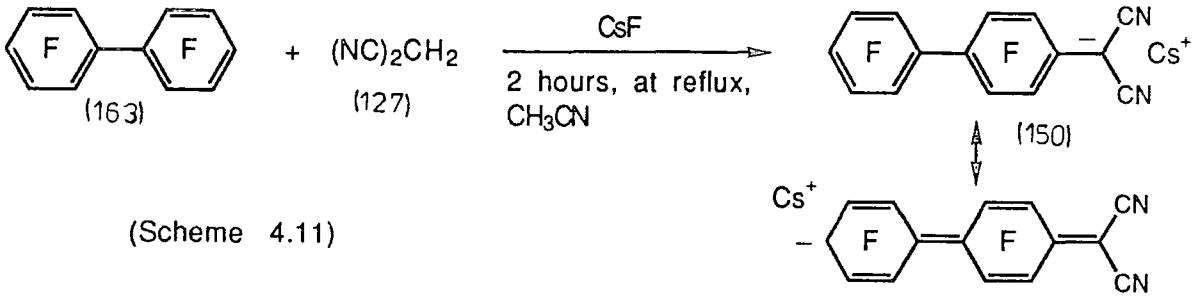


(Scheme 4.10)

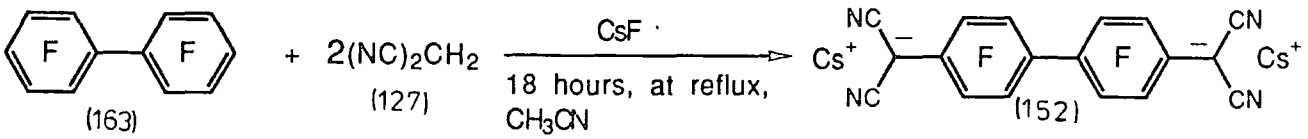
multiple acidic recrystallisations the hydrolysis product was isolated as the new derivative (169). It is remarkable that an F-triazine derivative is even stable in cool aqueous solution given the known extreme susceptibility of F-triazine and its derivatives to hydrolysis.[157]

4.3.8 Multiple substitution reactions

Multiple substitution has been observed only in the case of perfluorobiphenyl (163). With one equivalent of malononitrile[127] in acetonitrile, perfluorobiphenyl (163) forms only the monosubstituted malononitrile salt (150) after two hours at reflux temperature. To form the disubstituted salt (152) requires eighteen hours at reflux temperature with two equivalents of malononitrile. The decrease in reactivity of the second site is clear evidence for charge transmission through the aromatic rings (Scheme 4.11). We have not found any evidence for disubstitution



(Scheme 4.11)

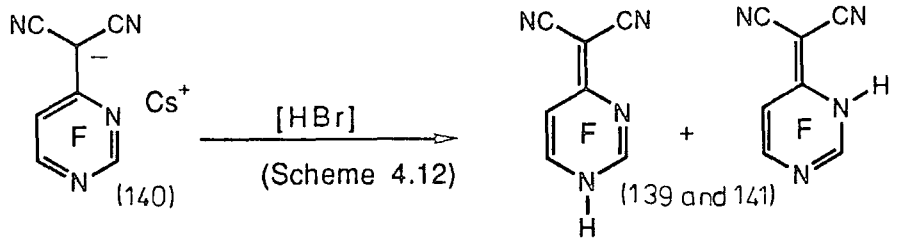


in any of the other systems, particular efforts being made in the case of the triazine and naphthalene systems.

4.3.9 Stability of the conjugate acids

Samples of the conjugate acids discolour if they are exposed to air for prolonged periods. This was particularly evident for the pyridazine and pyrimidine derivatives (135, 137, 139, and 141) (See table 4.2).

Although the pyrimidine derivatives (139 and 141) could be observed by fluorine n.m.r. in aqueous hydrochloric acid solution they could not be isolated from such solutions. Reaction with trimethylsilyl bromide produced compounds (139 and 141) which were isolated in low yield by sublimation (presumably traces of water were present yielding hydrogen bromide as the acidic species) (Scheme 4.12).



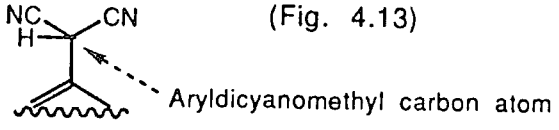
No attempt was made to prepare the conjugate acid of triazine salt (146) due to the previously mentioned extreme susceptibility of F-triazine derivatives to hydrolysis.

4.3.10 Tautomerism in the conjugate acids

It may be noted that in table 4.2 some of the conjugate acids were written with protonation at carbon, while others were written in a tautomeric form with protonation at nitrogen (compounds 135, 137, 139, and 141). Protonation at nitrogen was easily distinguishable from protonation at carbon due to:

a) very broad N-H infrared absorptions (2300 to 3100cm^{-1}) compared to relatively sharp C-H absorptions (2910 to 2945cm^{-1});
b) N-H ^{1}H n.m.r. resonances are broad with δ > 11ppm compared to C-H with sharp resonances at δ 4.8 to 6.6ppm;
c) for N-H there are no Overhauser enhancements or proton-carbon spin couplings visible in the ^{13}C n.m.r. spectra;
d) variation of ^{13}C chemical shifts (see section 4.5).

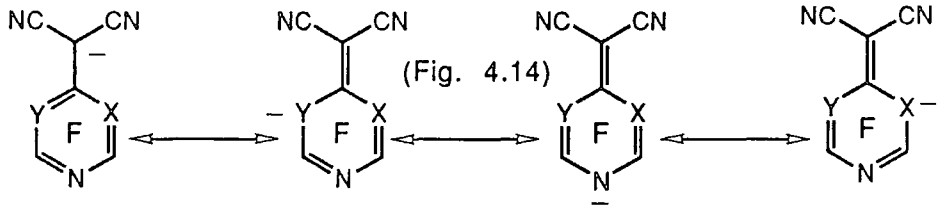
In order to account for the tautomerism we must consider both the acidity of the aryldicyanomethane proton (See fig. 4.13) and the basicity of the ring nitrogens.



(Fig. 4.13)

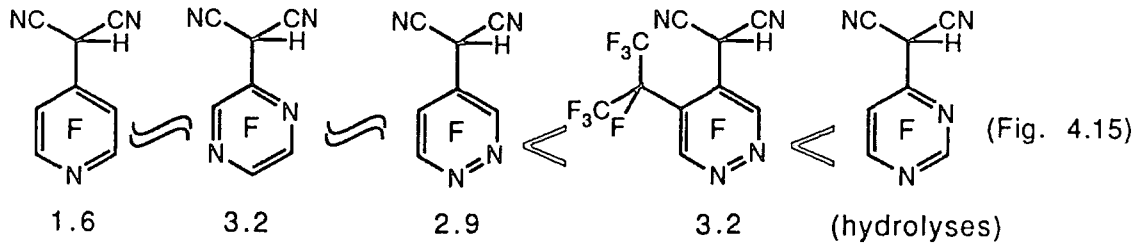
i) *acidity of the aryldicyanomethane proton*

The relative acidity of the aryldicyanomethane proton will be influenced by the ability of the substituents to stabilise a negative charge in the corresponding carbanion. It is known that fluorine atoms are destabilising when adjacent to sp^2 hybridised carbon atoms which bear a negative charge (Section 1.3.1.a). Hence, anions with canonical forms bearing fluorine atoms (rather than charge stabilising ring nitrogen or perfluoroalkyl groups) at negatively charged sites will be destabilised (Fig.4.14).



(Fig. 4.14)

Hence X = Y = C-F is predicted to be less stable (*i.e.* the conjugate acid is a weaker acid) than X = C-F, Y = N.
Using this somewhat simplistic criterion we have ranked some of the compounds in order of predicted carbon acidity, along with measured pK_a values, in fig. 4.15.

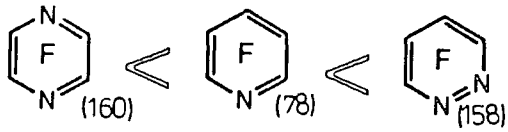


(Fig. 4.15)

We can see that there is no correlation between predicted carbon acidity and measured acidity. Hence we need to take into account that some of the compounds are protonated at nitrogen rather than at carbon.

ii) *Basicity of ring nitrogens*

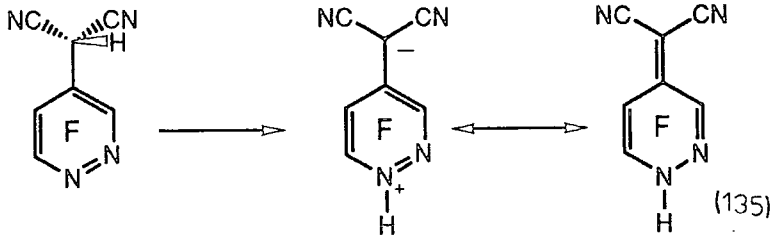
Experimental observations[158] indicate that the ring nitrogen basicity order for some of the parent compounds is as shown



(Fig. 4.16)

(no data for tetrafluoropyrimidine)

in fig.4.16. A combination of a strong carbon acid and strong ring nitrogen basicity may lead to tautomerism (Scheme 4.17).



(Scheme 4.17)

(135)

4.3.11 FAB mass spectra

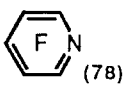
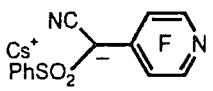
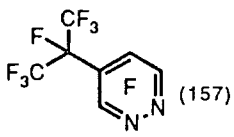
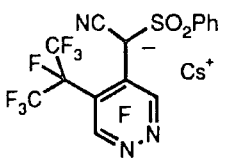
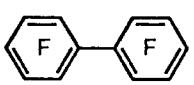
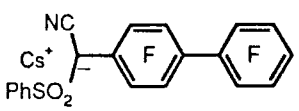
FAB mass spectra have been obtained for some of the salts (salts 130, 138, 140, 142, 143, and 146). The anionic spectra clearly show the parent anion mass, helping to confirm the identity of the salts. The cationic spectra often show Cs^+ (m/e 133), $(Cs_2F)^+$ (m/e 285), and $[Cs_2\ (Anion)]^+$.

4.4 Salts and Conjugate Acids Derived From Phenylsulphonylacetonitrile (128)

4.4.1 Salts

Several salts which are derived from the base induced reaction of phenylsulphonylacetonitrile (128) with fluorinated aromatics have been prepared and studied (Table 4.3).

Table 4.3

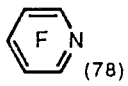
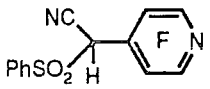
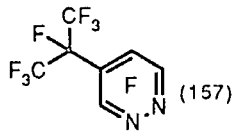
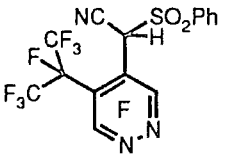
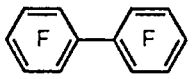
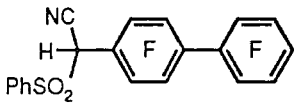
Substrate	Salt Product	Number	Yield*
 (78)		(170)	67%
 (157)		(172)	89%
 (163)		(174)	46%

* Yields are calculated from the parent aromatic compound

4.4.2 Conjugate Acids

Treatment of the salts shown in table 4.3 with hydrochloric acid yielded the conjugate acids shown in table 4.4.

Table 4.4

Substrate	Conjugate Acid	Number	Yield*
 (78)		(171)	53%
 (157)		(173)	77%
 (163)		(175)	68%

* Yields are calculated from the corresponding salt

4.4.3 Stability of the salts and the corresponding conjugate acids

Both the salts and the conjugate acids are stable and may be stored for long periods without discolouration or decomposition.

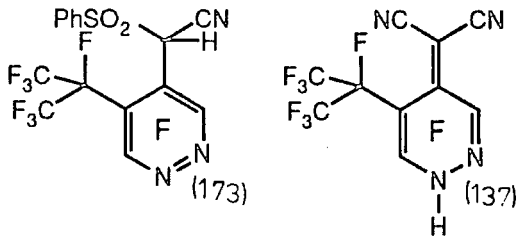
4.4.4 Tautomerism in the conjugate acids

The three conjugate acids investigated were all found to be carbon acids (See table 4.5 and section 4.3.10). It is interesting

Table 4.5

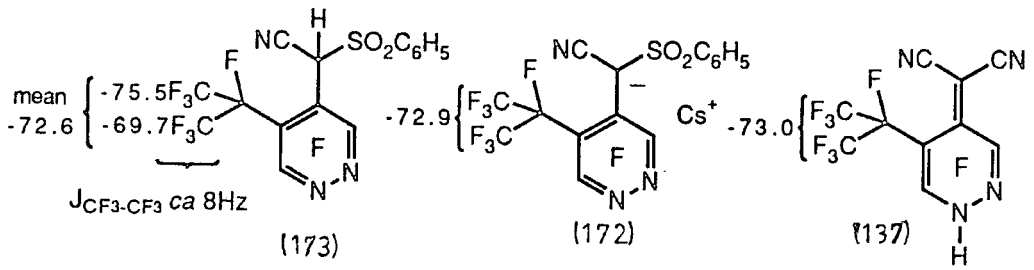
Compound	$\delta(^1H)$ (ppm)	^{13}C $[^1J(C\text{-}H)]$ (Hz)
(171)	6.6	149.3
(173)	6.9	*ca* 150
(175)	6.6	148.7

to note that compound (173) (Fig. 4.18) exists in the C-H form while compound (137) exists in the N-H form. This may be due to compound (173) having a lower carbon acidity than compound (137) [*c.f.* $PhSO_2CH_2CN$ ($pK_a \simeq 12.0$) is a weaker carbon acid than $CH_2(CN)_2$ ($pK_a \simeq 11.1$) (in dimethylsulphoxide solution)[159]].



(Fig. 4.18)

4.4.5 N.m.r. spectra of compounds (173 and 137)

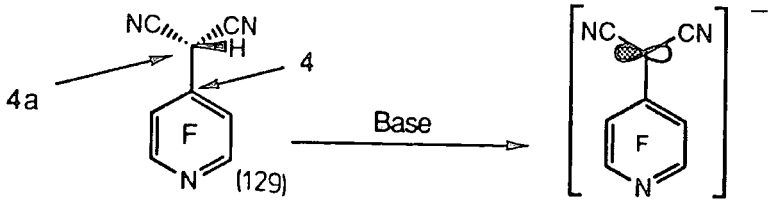


(Fig. 4.19) (Chemical shifts in ppm)

It was observed that the trifluoromethyl groups in compound (173) (Fig. 4.19) gave separate ^{19}F n.m.r. resonances. The CF_3 groups of compounds (172 and 137) appear to be magnetically equivalent (these species possess a plane of symmetry). The magnetic non-equivalence leads to an intertrifluoromethyl coupling of *ca* 8Hz in compound (173).

4.5 Comparison of N.m.r. Spectra of the Salts and Conjugate Acids

Carbon-13 n.m.r. spectra have been acquired for the salts and their conjugate acids in perdeuteroacetone solution. Although complete assignment has not proved possible in all cases, assignment has been made of the carbon atoms that are near to the nitrile group(s). A comparison of the changes in ^{13}C n.m.r. chemical shifts at particular sites between the salts and their conjugate acids has been used to investigate the n.m.r. consequences of tautomerisation. Considering compound (129) (Scheme 4.20), carbon atom (*4a*) must be sp^3 hybridised with the



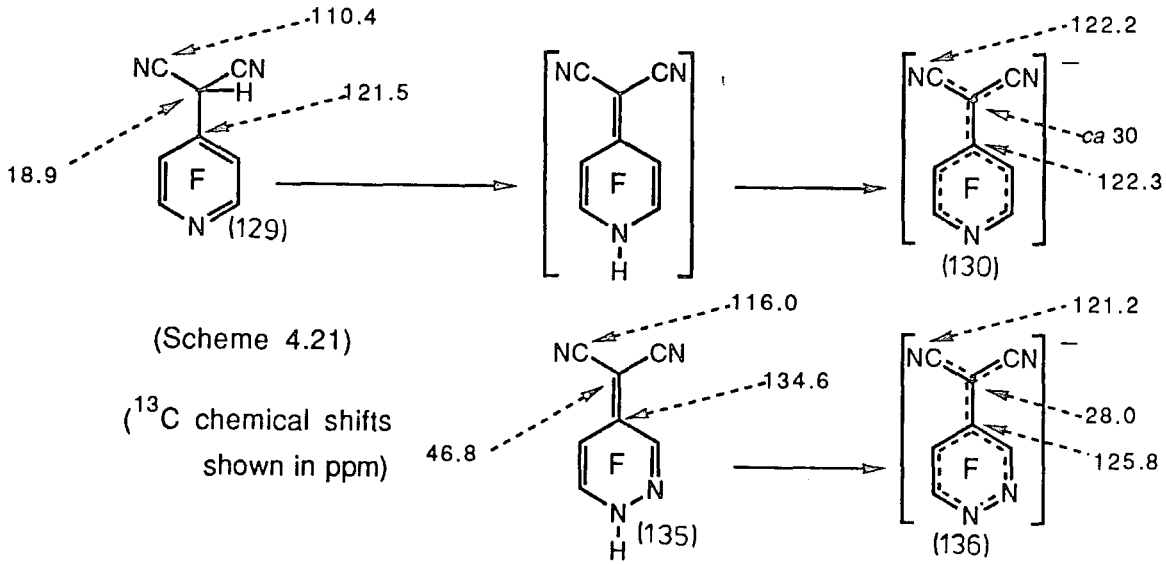
(Scheme 4.20)

nitrile groups lying out of the ring plane. If after anion formation the site becomes sp^2 hybridised the nitrile groups may now lie in the same plane as atoms (4) and (4a), potentially lying in the ring plane. Therefore the ^{13}C n.m.r. spectra would be influenced by both the acquisition of charge and by a geometry change upon ionisation. The geometry of the tautomeric nitrogen acids does not change so drastically upon ionisation, hence acquisition of charge will be the principle influence upon their ^{13}C n.m.r. spectra.

We have attempted to quantify the component of the ^{13}C chemical shift change upon anion formation that corresponds to such a change in geometry:

i.e. we have assumed:

Total chemical shift change = Change due to geometry change + Change due to negative charge



(Scheme 4.21)

(^{13}C chemical shifts shown in ppm)

Scheme 4.21 shows some of the ^{13}C n.m.r. chemical shifts for compounds (129 and 135) and salts (130 and 136). The chemical shifts for corresponding sites in the anions can be seen to be very similar. However, there are much larger differences in the case of the neutral compounds (129 and 135). We have attributed these larger chemical shift differences to the change from tetrahedral to planar geometry in compound (135). We have assigned these chemical shift changes as empirical 'geometry change terms' (table 4.6). Subtracting these chemical shift

changes from those which occur upon the ionisation of a carbon acid may allow the direct comparison of charge related chemical shift changes for both the nitrogen and carbon acids.

Table 4.6 (for the malononitrile derived systems only)

Resonance position	Downfield correction term for sp^3 to sp^2 hybridisation (ppm)
nitriles	5.6
carbon adjacent to nitriles	27.9
ring substitution site	13.1

4.5.1 Comparison of ^{13}C n.m.r. nitrile resonances

Table 4.7 lists the chemical shifts of the nitrile resonances for the conjugate acids (-H) and for the anions (-M) that we have investigated. It is interesting to note that upon anion formation the nitriles move downfield, presumably due to an enhanced electron current in the nitrile π-system. Also listed are the downfield chemical shift changes of the nitrile resonances that were observed upon anion formation [Δ(H → M)] (M = K or Cs).

Table 4.7 (Downfield chemical shift changes are taken as positive)

Parent system	Conjugate acid	-H (ppm)	-M (ppm)	Δ(H → M) (ppm)	Δ(H → M) - 5.6 (ppm)
Malononitrile derived compounds					
F-pyridine	(129)	110.4	122.2	11.8	6.2
F-pyridazine	(135)	116.0	121.2	5.2	
F-*i*-propylpyridazine	(137)	115.8	121.6	5.8	
F-pyrimidine	(139 & 141)	114.1	120.6	6.5	
F-pyrazine	(144)	110.9	122.3	11.4	5.8
F-triazine	(---)	-----	119.0	----	
F-*i*-quinoline	(147)	111.7	123.3	11.5	5.9
F-naphthalene	(153)	111.2	124.8	12.6	7.0
F-biphenyl (mono)	(149)	111.1	123.2	12.1	6.5
F-biphenyl (di)	(151)	111.0	124.5	13.5	7.9
F-4-phenylpyridine (*para*)	(131)	111.0	123.3	12.3	6.7
Phenylsulphonylacetonitrile Derived Compounds					
F-pyridine	(171)	111.2	123.5	12.3	
F-*i*-propylpyridazine	(173)	111.2	123.0	11.8	
F-biphenyl (mono)	(175)	111.8	124.7	12.9	

a) Considering the malononitrile derived compounds

It may be noted that for the tautomeric compounds (135, 137, 139, and 141) $\Delta(H \rightarrow M)$ values are very much smaller than for the carbon acids. If we subtract the geometry correction term previously calculated for nitriles (5.6ppm) from the carbon acid values they become similar to those of the nitrogen acids (we are correcting for the carbon acids sp^3 geometry). Hence for the nitrile resonances we can say:

i) the model seems to work, *ie* the anions are rehybridised (the dicyanomethyl carbon is sp^2 hybridised);

ii) the chemical shift change due to the geometry change is *ca* 5 to 6ppm downfield (as in table 4.6);

iii) the chemical shift change due to anion formation is *ca* 5 to 8ppm downfield (as for the malononitrile derived compounds in table 4.7).

b) *Considering the phenylsulphonylacetonitrile derived compounds*

Lacking a nitrogen acid in this series we cannot split the total chemical shift change [$\Delta(H \rightarrow M)$] into geometry and charge components. However, we can say that the total chemical shift change is similar to that of the malononitrile derived systems.

4.5.2 Comparison of ^{13}C n.m.r. resonances for the potentially carbanionic site

Carbon-13 n.m.r. data relating to the aryldicyanomethane carbon atom (See fig. 4.13) is shown in table 4.8.

a) Considering the malononitrile derived compounds

For this site we see a larger spread of $\Delta(H \rightarrow M)$ values, with the tautomeric compounds (135 and 137) exhibiting large upfield shift changes [no data for compounds (139 and 141)]. Subtracting the previously calculated geometry correction term for this site (27.9ppm, table 4.6) from the carbon acid $\Delta(H \rightarrow M)$ values brings them into line with those of the nitrogen acids. Hence we can say that for this site:

i) the chemical shift change due to the geometry change is *ca* 28ppm downfield (as in table 4.6);

ii) the chemical shift change due to anion formation is *ca* 15 to 23ppm upfield (as for the malononitrile derived compounds in table 4.8).

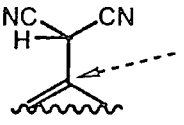
Table 4.8

Parent system	Conjugate acid	-H (ppm)	-M (ppm)	Δ(H → M) (ppm)	Δ(H → M) - 27.9 (ppm)
Malononitrile derived compounds					
F-pyridine	(129)	18.9 *ca*	30	ca 11.1	*ca* -16.8
F-pyridazine	(135)	46.8	28.0	-18.8	
F-*i*-propylpyridazine	(137)	62.6	40.6	-22.0	
F-pyrimidine	(139 & 141)	----	41.8	-----	
F-pyrazine	(144)	26.1	34.7	8.6	-19.3
F-triazine	(---)	----	48.1	-----	
F-*i*-quinoline	(147)	32.6	44.9	12.3	-15.6
F-naphthalene	(153)	18.3	24.0	5.7	-22.2
F-biphenyl (mono)	(149)	18.5	23.9	5.4	-22.5
F-biphenyl (di)	(151)	18.5	23.4	4.9	-23.0
F-4-phenylpyridine (*para*)	(131)	18.5	26.4	7.9	-20.0
Phenylsulphonylacetonitrile Derived Compounds					
F-pyridine	(171)	53.6	58.3	4.7	
F-*i*-propylpyridazine	(173)	55.8	64.1	8.3	
F-biphenyl (mono)	(175)	53.5	51.8	- 1.7	

b) *Considering the phenylsulphonylacetonitrile derived compounds* Again the chemical shift changes [Δ(H → M)] are roughly similar to those of the malononitrile derived compounds.

4.5.3 Comparison of ^{13}C n.m.r. resonances at the rings' substitution site

A similar treatment for the ring carbon atom attached to the substituent (Fig. 4.22) yielded the data shown in table 4.9.



(Fig 4.22)

Table 4.9

Parent system	Conjugate acid	-H (ppm)	-M (ppm)	Δ(H → M) (ppm)	Δ(H → M) - 13.1 (ppm)
Malononitrile derived compounds					
F-pyridine	(129)	121.5	122.3	0.8	-12.3
F-pyridazine	(135)	134.6	125.8	- 8.8	
F-*i*-propylpyridazine	(137)	138.6	136.1	- 2.5	
F-pyrimidine	(139 & 141)	-----	162.5	-----	
F-pyrazine	(144)	123.7	143.9	20.2	7.1
F-triazine	(---)	-----	180.3	-----	
F-*i*-quinoline	(147)	19.8	120.0	0.2	-12.9
F-naphthalene	(153)	113.6	122.5	8.9	- 4.2
F-biphenyl (mono)	(149)	109.8	125.4	15.6	2.5
F-biphenyl (di)	(151)	109.9	124.5	14.6	1.5
F-4-phenylpyridine (*para*)	(131)	109.4	123.0	13.6	0.5
Phenylsulphonylacetonitrile Derived Compounds					
F-pyridine	(171)	120.9	133.4	12.5	
F-*i*-propylpyridazine	(173)	124.7	133.6	8.9	
F-biphenyl (mono)	(75)	109.8	123.2	13.4	

a) Considering the malononitrile derived compounds

Because we are now considering a set of resonances which are greatly influenced by the nature of the individual aromatic rings, and influenced less by tautomerisation, there is a less distinct division between the tautomer (135 and 137) Δ(H → M) values and the carbon acid Δ(H → M) values. However, subtracting the previously calculated geometry correction term (13.1ppm, see table 4.6) moves the carbon acid Δ(H → M) values more into line with those of the tautomers. Hence we can say that:

i) the chemical shift change due to the geometry change is very approximately 13ppm downfield (as in table 4.6);

ii) the chemical shift change due to anion formation is of the order of -3 to 13ppm upfield (as for the malononitrile derived compounds in table 4.9).

b) *Considering the phenylsulphonylacetonitrile derived compounds*

Again the chemical shift changes are roughly similar to those of the malononitrile derived compounds.

4.5.4 Summary of the ^{13}C n.m.r. consequences of tautomerism

In summary we have found that we can split the $\Delta(H \rightarrow M)$ values into a component due to the acquisition of a negative charge and a component due to geometry changes. This model seems to work reasonably well for the resonances arising from the substituent, but works less well for the ring carbon resonances.

4.5.5 Comparison of $^{1}J_{(C-H)}$ values with measured acidities

The one bond ^{13}C to proton couplings for the conjugate acids are listed in table 4.10. It might be expected that a low $^{1}J_{(C-H)}$ coupling constant indicates a relatively weak C-H bond, hence a relatively high carbon acidity. This is indeed what we see if we compare compound (144 or 153) with the more strongly acidic compound (129). Of course the nitrogen acids (135 and 137) do not exhibit $^{1}J_{(C-H)}$ coupling.

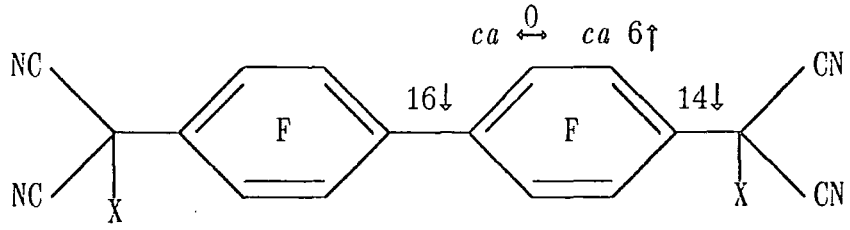
Table 4.10

Parent system	Conjugate acid	^{1}J (C-H) (Hz)	(pK_a) in water
Malononitrile derived compounds			
F-4-phenylpyridine (*para*)	(131)	145.4	
F-pyrazine	(144)	144.7	3.2
F-naphthalene	(153)	144.6	3.0*
F-biphenyl (mono)	(149)	144.3	
F-biphenyl (di)	(151)	142.4	
F-pyridine	(129)	141.8	1.6
F-*i*-quinoline	(147)	*ca* 140	
F-pyridazine	(135)	0	2.9
F-*i*-propylpyridazine	(137)	0	3.2
Phenylsulphonylacetonitrile Derived Compounds			
F-*i*-propylpyridazine	(173)	*ca* 150	
F-pyridine	(171)	149.3	
F-biphenyl (mono)	(175)	148.7	

* measured in aqueous acetone (15%) solution due to low solubility in water

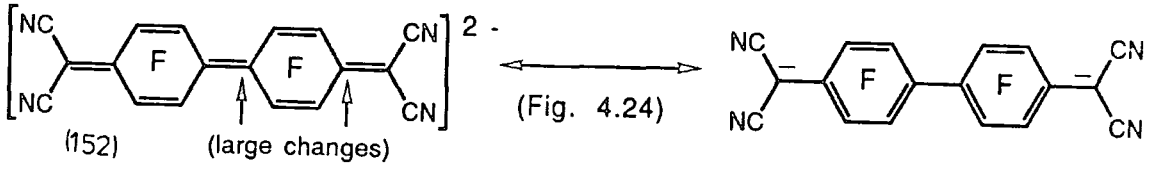
4.5.7 Effects of anion formation upon the ^{13}C n.m.r. spectra of the aromatic rings

The ^{13}C n.m.r. spectra of the aromatic rings are often difficult to assign (often highly coupled and overlapping resonances). This section will discuss some of the systems where assignments have been made. The spectra are presented with an up arrow representing an upfield shift upon anion formation and with 'X' referring to the change from hydrogen to caesium substitution.

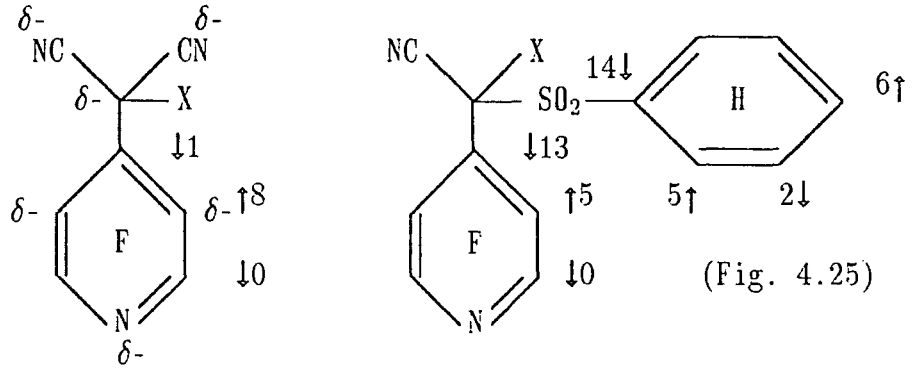


(Fig. 4.23)

In fig. 4.23 we can see considerable chemical shift changes due to changes in the π-bonding structure (Fig. 4.24).



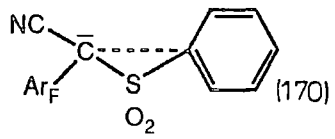
In the systems shown in fig. 4.25 we have upfield shifts occurring



(Fig. 4.25)

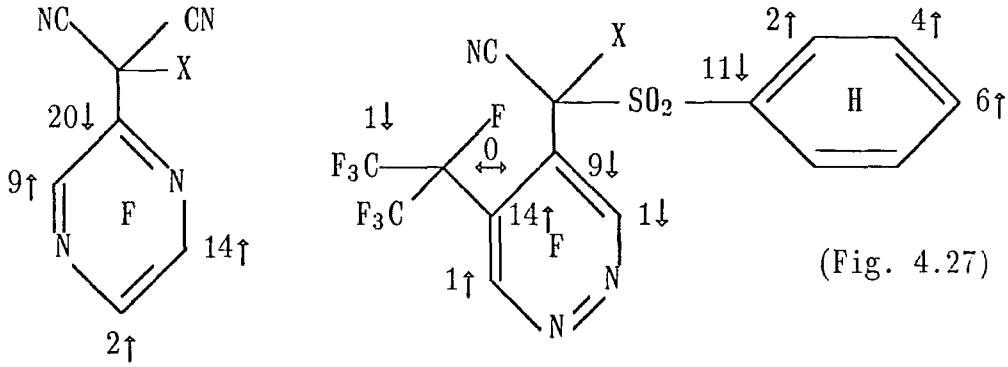
at the ring sites that are expected to carry increased negative charge upon ionisation. Also there is a clear indication of charge transmission into the phenyl ring in the phenylsulphonylacetonitrile derivative. This may be an indication of direct interaction between the carbanionic site and the phenyl ring (Fig. 4.26) (*c.f.* Ramberg-Bäcklund rearrangement[160] where α-halosulphones possessing a γ-hydrogen undergo a 1,3-elimination

on treatment with base followed by sulphur dioxide elimination yielding alkenes).



(170) (Fig. 4.26)

In more complex systems the chemical shift changes are less easy to rationalise (for example fig. 4.27).

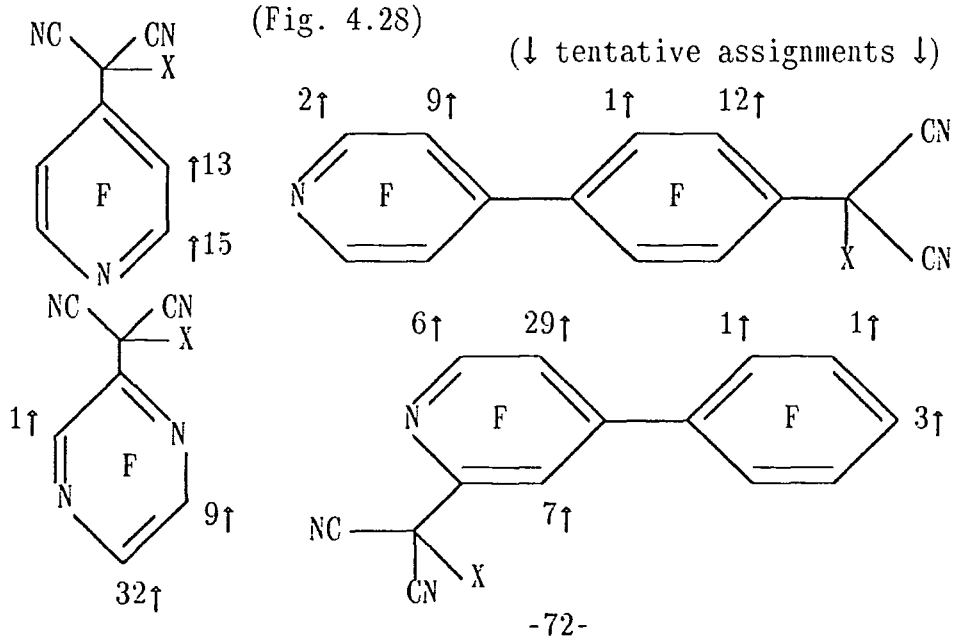


(Fig. 4.27)

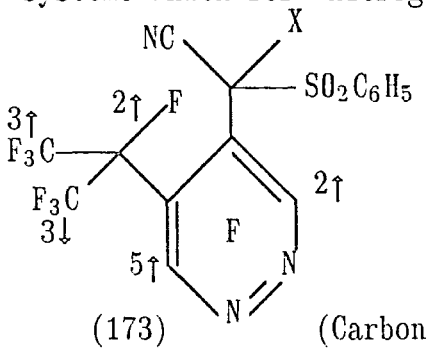
4.5.6 Effects of anion formation upon ^{19}F n.m.r chemical shifts

For the systems that form carbon acids ionisation generally leads to an upfield shift of the aromatic ^{19}F n.m.r. chemical shifts [With perfluorocarbanions successive upfield then downfield shifts are observed[33] (see section 1.3.2.b)]. This is particularly pronounced for fluorine atoms situated *para* to the site of substitution (Fig. 4.28).

(Fig. 4.28)

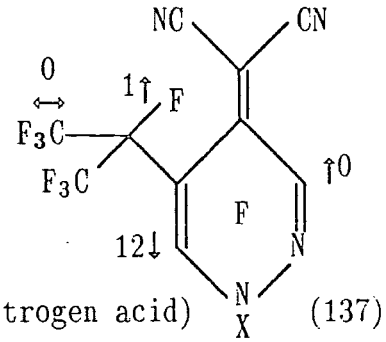


Downfield shifts of aromatic fluorine atoms have been observed in systems which form nitrogen acids (for example see fig. 4.29). By



(173) (Carbon acid)

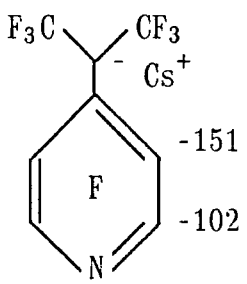
(Fig. 4.29)



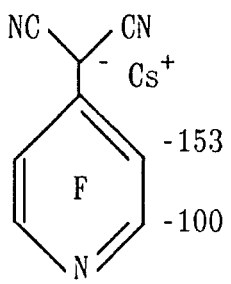
(Nitrogen acid) (137)

a comparison of the systems in fig. 4.29 we can conclude that downfield ^{19}F n.m.r. shifts occur upon anion formation [as for nitrogen acid (137)], but that larger upfield shifts accompany the geometry and π-system changes which occur upon ionisation of carbon acids [see compound (173)]. We find a poor correlation between the trends in the ^{13}C n.m.r. and ^{19}F n.m.r. spectra, often with upfield shifts in the ^{19}F n.m.r. and downfield shifts in the ^{13}C n.m.r at particular sites and *visa-versa*.

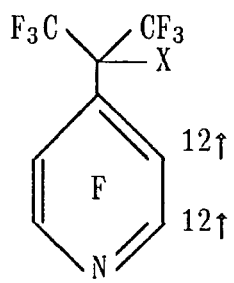
The ^{19}F n.m.r. chemical shifts of pyridyl salts (91 and 130) (Fig. 4.30) are very similar. Upon ionisation of the corresponding conjugate acids similar upfield shifts are observed for the aromatic fluorine atoms in both systems.

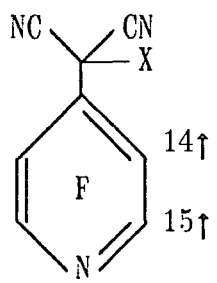


(91)



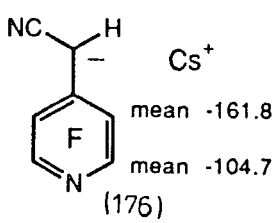
(130)



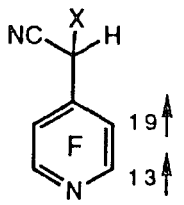


(Fig 4.30)

Similar trends are also observed for the acetonitrile derivative (176) (Fig. 4.31) (Sections 8.6, 9.2.3)



(176)

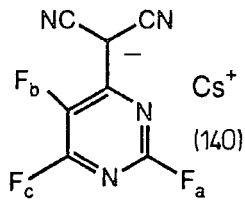


(Fig. 4.31)

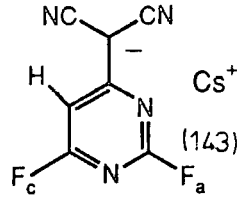
4.6 Concentration Dependence of Nitrile ^{13}C N.m.r Chemical Shifts

4.6.1 Observations

It was observed that at low concentrations the nitrile resonances of salt (140) (Fig. 4.32.a) gave a single sharp ^{13}C n.m.r. peak. However, as the salt concentration was increased this peak split forming a doublet with a progressively increasing line separation (See fig. 4.33 for graph).

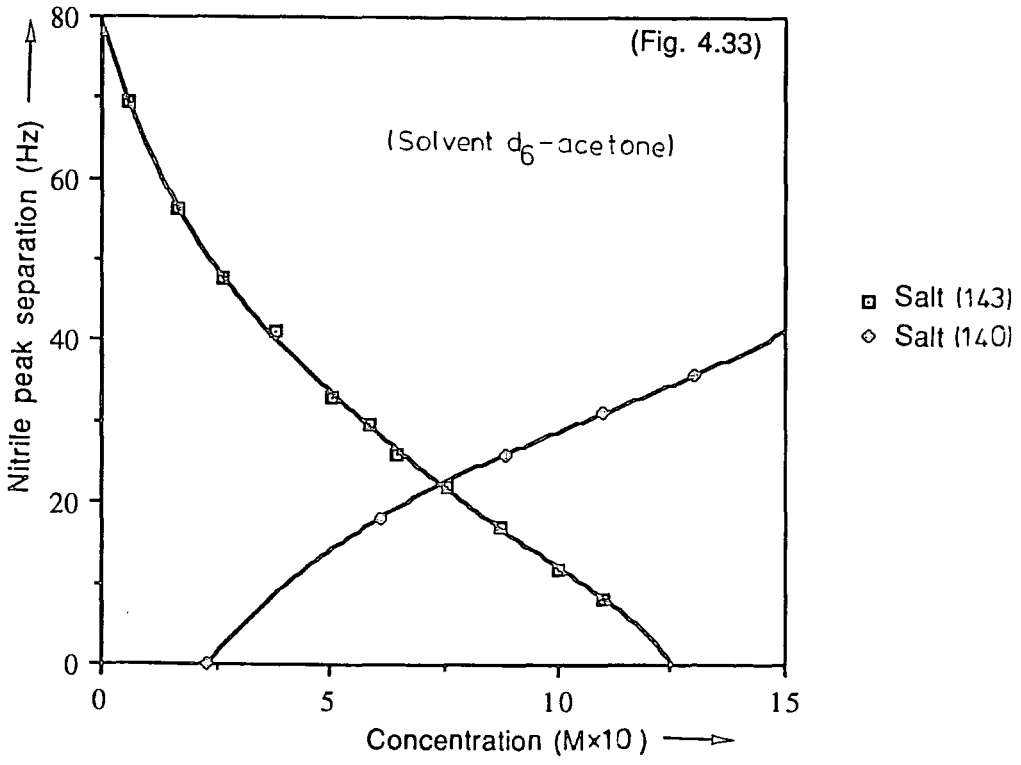


(Fig. 4.32.a)



(Fig. 4.32.b)

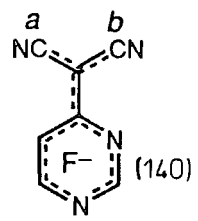
In an attempt to investigate possible coupling between (F_b) (Fig. 4.32.a) and a nitrile group in salt (140) a sample of salt (143) (Fig. 4.32.b), which has a proton replacing (F_b), was prepared. Analysis of salt (143) solutions revealed that the nitrile peak separation now decreased with increasing salt concentration (See Fig. 4.33 for graph).



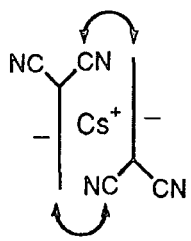
4.6.2 Rationalisation of the concentration dependence

The observation of two lines corresponding to the nitriles' resonance could be attributed to either a coupling of both nitriles equally to a spin I = $^1/_2$ nucleus [*i.e.* fluorine (protons were decoupled)], or to the nitriles occupying magnetically non-equivalent sites with no (or only slow) exchange between them. Unexpectedly for salt (143) increasing the applied magnetic field strength from 62.9 to 90.6MHz (increased by a factor of 1.44) resulted in changes in the both line separation measured in Hz (increased by a factor of 1.30) and measured in ppm (increased by a factor of 0.90). These observations rule out coupling as a cause and can best be explained by there being two non-equivalent nitrile sites (which requires the chemical shift difference to be independent of magnetic field strength). It is unclear why the nitrile peak separation changes in both Hz and ppm when apparently measured at the same temperature.

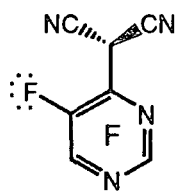
a) *With salt* (140) (Fig. 4.34.a)



(Fig. 4.34.a)



(Fig. 4.34.b)

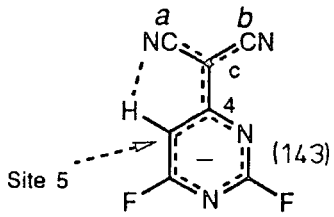


(Fig. 4.34.c)

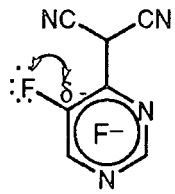
i) At low salt concentration the nitrile groups (*a*) and (*b*) (Fig. 4.34.a) will appear to be magnetically equivalent to each other if the dicyanomethyl group is able to rotate on the n.m.r. timescale. As the salt concentration increases first ion pairing, and then ion stacking may occur. The effect of such aggregation may be an increase in the rotational barrier for the dicyanomethyl rotation (for example as in fig. 4.34.b). This slowed rotation may allow n.m.r. to detect the inequivalence of the nitrile groups. In a dynamic system this would lead to the n.m.r. resonance separation increasing with increasing salt concentration, as observed.

ii) Alternatively, the same result will occur if at low concentration the plane of the nitriles is perpendicular to the plane of the ring (Fig. 4.34.c, possibly due to electron pair repulsions between the indicated fluorine lone pairs and the nitrile π-system when planar), and at higher concentration ion stacking forces the nitriles to move into plane with the ring, hence becoming non-equivalent.

b) *With salt* (143)



(Fig. 4.35.a)



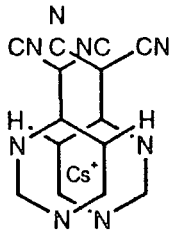
(Fig. 4.35.b)

Inorder for the nitriles (*a*) and (*b*) to be non-equivalent at low salt concentration the dicyanomethyl group must not rotate on the n.m.r. timescale and the anion must be planar. Replacement of fluorine by hydrogen in site five of anion (143) (Fig. 4.35.a) will have two important effects upon dicyanomethyl rotation, these are:

i) possible increase in the strength of the π-bond c-4, slowing rotation [Fluorine will destabilise anion canonical forms which have negative charge at the fluorine substitution site (Fig. 4.35.b) (See section 1.3.1.a)];

ii) possible hydrogen bonding between the hydrogen atom and one of the nitriles may hinder rotation (Fig. 4.35.a)

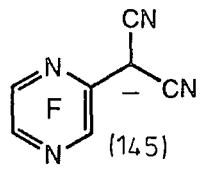
As the salt concentration increases so ion pairing and ion stacking may occur. However, in this salt we have the possibility of hydrogen bonding between anions (Ring nitrogen of one anion to hydrogen in another anion) giving some order to the stacking (Fig. 4.36). In such a structure the dicyanomethyl groups may not be



(Fig. 4.36)

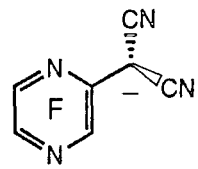
able to rotate, but the nitrile groups may find themselves nearly magnetically equivalent. Hence, in a dynamic system we would expect the nitrile peak separation to decrease with increasing salt concentration, as observed.

c) *With salt* (145)



(145)

(Fig. 4.37.a)



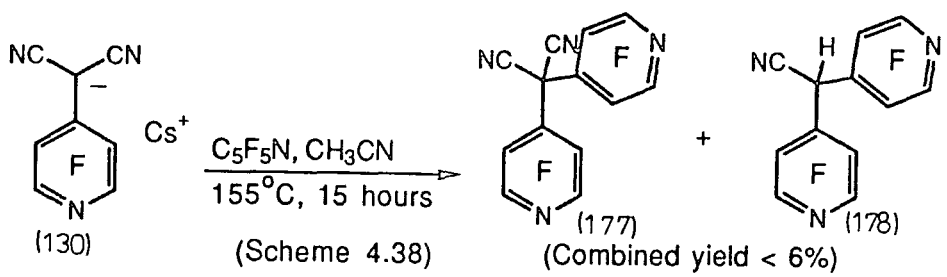
(plane of dicyanomethyl group perpendicular to the ring plane)

(Fig. 4.37.b)

In the case of salt (145) (Fig. 4.37.a) the nitrile resonance was observed as a singlet both at low and moderate salt concentrations. It may be that the anion adopts the conformation indicated in fig.4.37.b in both discrete and stacked anions or that rotation always occurs causing nitrile equivalence. In all of the other anions investigated the nitrile resonances were observed as a single resonance.

4.7 Reactions of the Salts

4.7.1 Salt (130) with pentafluoropyridine



(130)

(Scheme 4.38)

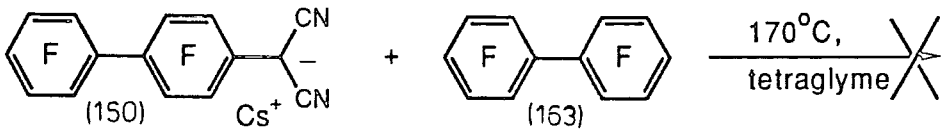
(177)

(178)

(Combined yield < 6%)

Low yields of compounds (177 and 178) (Scheme 4.38) were obtained by the thermal reaction of salt (130) with excess pentafluoropyridine (78). The presence of compound (178) is interesting as it clearly demonstrates the loss of a nitrile group from the dicyanomethane group (important in Chapter 5).

4.7.2 Salt (150) with perfluorobiphenyl

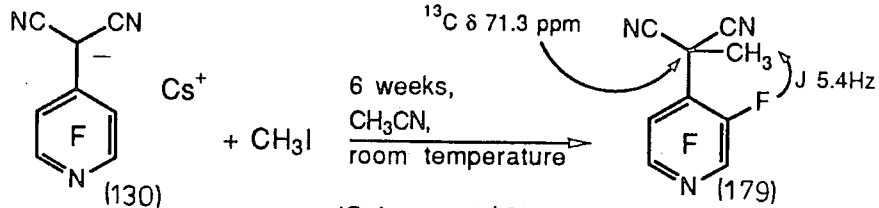


(Scheme 4.39)

An attempt was made to investigate possible oligomerisation reactions using salt (150) (Scheme 4.39) and perfluorobiphenyl (163). However, even under extreme conditions, we could not bring about a coupling reaction [Presumably salt (150) is of low nucleophilicity due to extensive charge delocalisation into the aromatic rings].

4.7.3 Methylation reactions

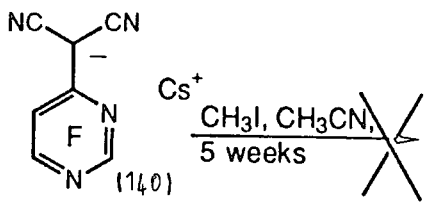
a) *With salt* (130)



(Scheme 4.40)

The reaction between salt (130) and methyl iodide proceeded very slowly (Scheme 4.40) yielding the expected C-methylated product (179) (in 53% isolated yield).

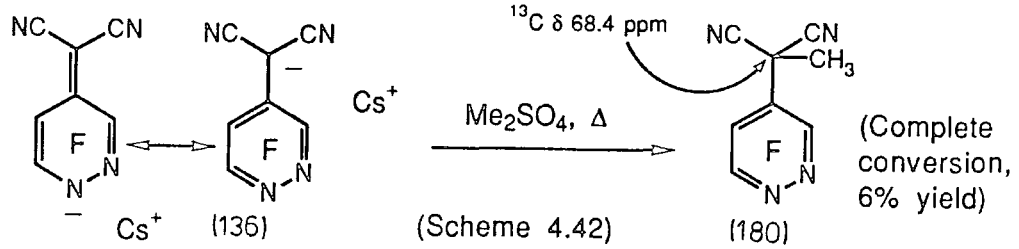
b) *With salt* (140)



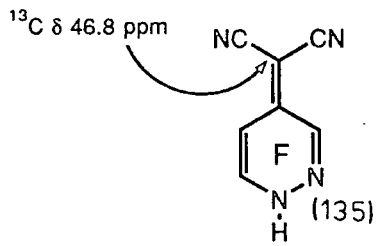
No Reaction (Scheme 4.41)

No reaction was observed between salt (140) and methyl iodide over an extended period indicating the anions relatively high stability (Scheme 4.41).

c) *With salt* (136)



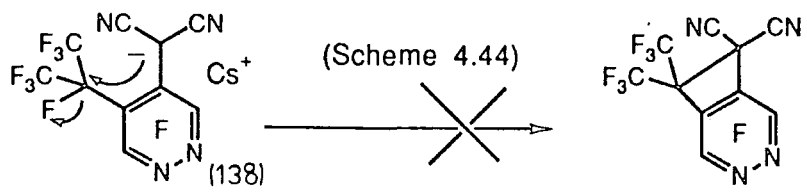
Surprisingly methylation of salt (136) using dimethyl sulphate produced C-methyl derivative (180) rather than an N-methyl derivative [Protonation of anion (136) occurs at nitrogen (see section 4.3.9)]. This assignment was based upon the ^{13}C n.m.r. resonances of compounds (180 and 179) (Scheme 4.42, scheme 4.40) and compound (135) (Fig. 4.43) which clearly show that the indicated carbon atom is sp^3 hybridised [as for compound (179)] rather than sp^2 hybridised [as for compound (135)].



(Fig. 4.43)

4.7.4 Attempted cyclisation of anion (138)

There is no major loss of fluoride ion in the FAB mass spectra of anion (138) (See scheme 4.44), nor is there a significant loss of hydrogen fluoride in the mass spectra of the conjugate acid. Hence the favoured 4-exo-tet (Baldwin terminology[161]) ring closure (Scheme 4.44) does not appear to occur under mass spectrometry conditions. No evidence of cyclisation was observed after heating



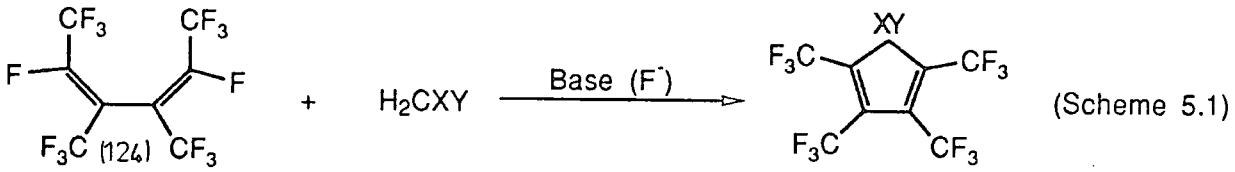
the salt to 160°C in tetrahydrothiophen-1,1-dioxide.
Again we must assume that delocalisation of charge onto the nitriles and into the ring has greatly diminished the nucleophilicity of the carbanion.

Chapter 5

Reactions of Potentially Bifunctional Carbon Nucleophiles With *trans,trans*-Perfluoro-3,4-dimethylhexa-2,4-diene (124)

5.1 Introduction

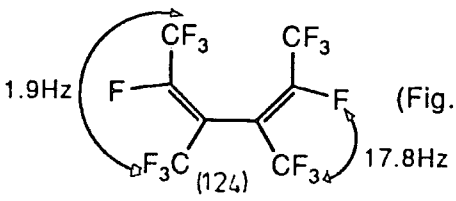
Further to our investigation of the reactions of potentially bifunctional carbon nucleophiles with fluorinated aromatic systems using fluoride ion as a base, we have investigated some of the corresponding chemistry with fluorinated dienes, in particular that with diene (124). This approach had special relevance to our longer term aim of developing a rational route to 5H-polyfluoro-pentakis substituted cyclopentadienes and related systems (Scheme 5.1). FAB mass spectroscopy has proved invaluable in aiding the analysis of often delicate anions.



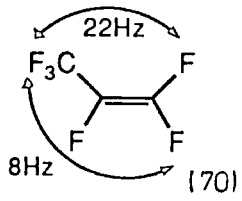
(Scheme 5.1)

5.2 Stereochemistry and Conformation of Diene (124)

The *trans,trans* stereochemistry of diene (124) was confirmed by $^{5}J_{CF_3,CF_3}$ fluorine n.m.r. coupling constant data (*ca* 1.9Hz) (Fig. 5.2). It has been established in related systems that $^{5}J_{(cis\text{-}CF_3,CF_3)}$ is greater than 10Hz and that $^{5}J_{(trans\text{-}CF_3,CF_3)}$ is less than 2Hz,[162,163] and likewise that $^{4}J_{(cis\text{-}CF_3,F)}$ >> $^{4}J_{(trans\text{-}CF_3,F)}$[162] [for example in hexafluoropropene (70)[119] (Fig. 5.3)]. Double bond non-planarity has been reported for some



(Fig. 5.2)



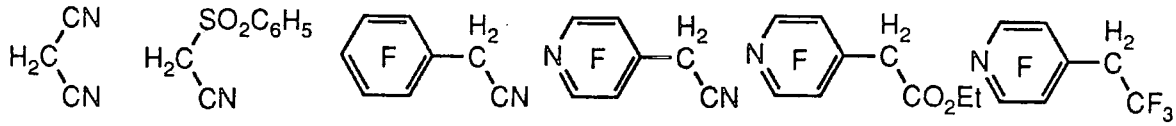
(Fig. 5.3)

fluorinated dienes, including perfluorobuta-1,3-diene[164] which has a reported gas phase C-C-C-C dihedral angle of 47.4 ± 2.4 degrees. It might be expected that the more highly substituted diene (124)

will possess a similar, if not a greater, non-planarity.

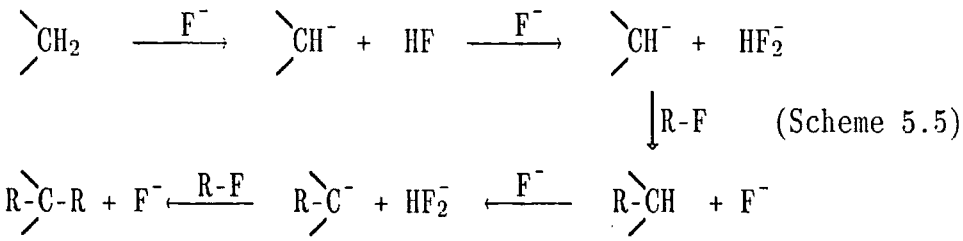
5.3 Potentially Bifunctional Carbon Nucleophiles Investigated

Diene (124) was reacted with the following potential carbon acids: malononitrile (127); phenylsulphonylacetonitrile (128); pentafluorophenylacetonitrile (181); (4'-tetrafluoropyridyl)acetonitrile (182); Ethyl-(4'-tetrafluoropyridyl)acetate (183); 4-(2',2',2'-trifluoroethyl)tetrafluoropyridine (184) (Fig. 5.4).



(127) (128) (181) (182) (183) (Figure 5.4) (184)

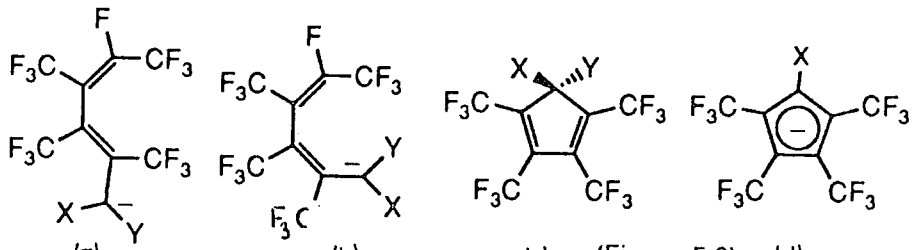
In the reactions of these potential carbon acids, usually at least a triple excess of caesium fluoride was used to remove hydrogen fluoride from the reaction mixtures (Scheme 5.5) and also to ensure that there was always available fluoride ion for the reactions.



(Scheme 5.5)

5.4 Summary of Observed Reaction Sequences

The reactions were usually monitored throughout by fluorine n.m.r. which enabled some of the intermediates to be observed, trapped or isolated. The reaction of diene (124) with carbon acids yielded four types of intermediates or products, and these were: a) *trans,trans*-pentadienyl salts; b) *trans,cis*-pentadienyl salts; c) cyclopentadienes; d) cyclopentadienyl salts (Fig. 5.6).



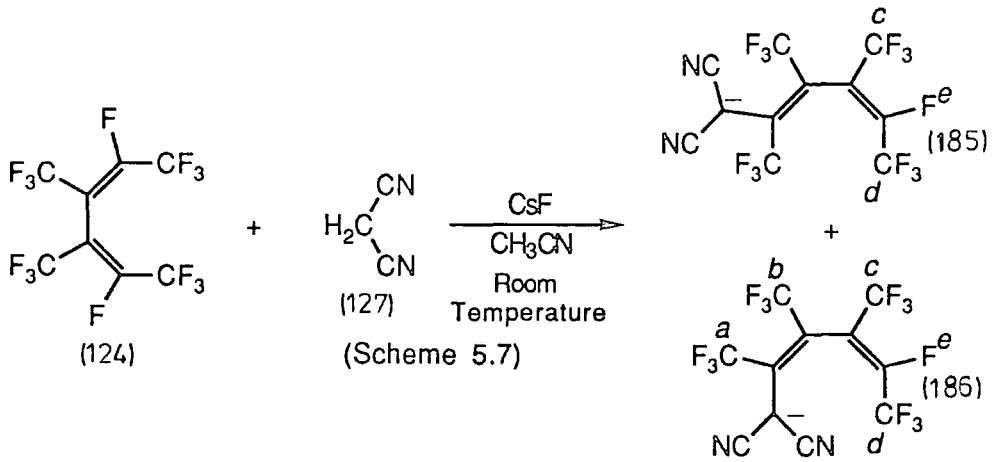
(a) (b) (c) (Figure 5.6) (d)

There were clearly two types of reactions occurring; those in which the first intermediates observed were pentadienyl salts [with acids (127) and (128)] and those in which the first intermediates observed were cyclopentadienes [with acids (181) and (182)].

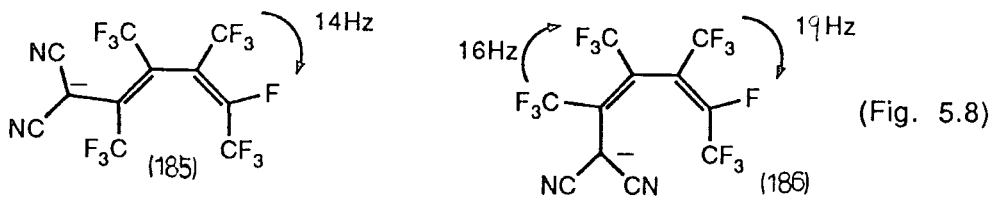
5.5 Diene (124) with Malononitrile (127)

5.5.1 Acyclic anions

The reaction of malononitrile (127) with diene (124) in the presence of caesium fluoride at room temperature, yielded a mixture containing two acyclic salts (185 and 186) (Scheme 5.7) which were not isolated. However, from J_{CF_3,CF_3} fluorine n.m.r. coupling constants the major isomer (*ca* 75%) was assigned as



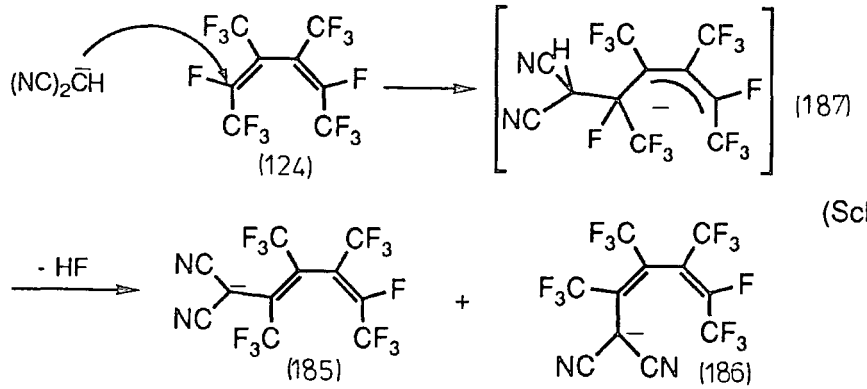
(185), the *trans,trans* isomer (J_{CF_3,CF_3} too small to be resolved) and the minor isomer (*ca* 25%) was assigned as the *cis,trans*



(Fig. 5.8)

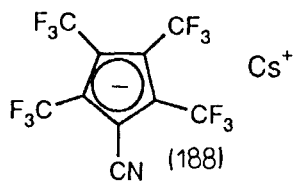
isomer (186) [J_{CF_3,CF_3} *ca* 16Hz for the most downfield CF_3 pair (*a* and *b*), too small to resolve for the most upfield CF_3 pair (*c* and *d*) (Fig. 5.8)]. The assignment of the CF_3 pairs was based upon an observed coupling between fluorine atom (*e*) (Scheme 5.7) and trifluoromethyl group (*c*) [$J_{(cis\text{-}CF_3,F)}$ *ca* 14Hz for anion (185), *ca* 19Hz for anion (186)]. It is noteworthy that trifluoromethyl group (*b*) which might be expected to be the most shielded CF_3

group actually is part of the most downfield pair of resonances rather than the most upfield (similar observations of curious downfield shifts have been recently reported for trifluoromethyl groups adjacent to the site of negative charge in perfluorocarbanions[31]). No evidence was found for the presence of the *cis,cis* or of the *trans,cis* isomers. This nucleophilic substitution reaction would be aided by the stability of the intermediate allyl anion (187) (Scheme 5.9).



(Scheme 5.9)

Fluorine n.m.r. integrations indicated that over a period of five hours, at 35°C, the concentration of salt (186) increased by *ca* 50% while the concentration of salt (185) decreased (Table 9.2, section 9.4.7) (After six hours the ratio of salt (185) to salt (186) was *ca* 3 : 1). Hence, it was inferred that at 35°C salt (185) was slowly isomerising to salt (186). Fluorine n.m.r. observations at 35°C also revealed the gradual increase in the concentration of what was subsequently shown to be a cyclopentadienyl derivative, salt (188) (Fig. 5.10). An experiment

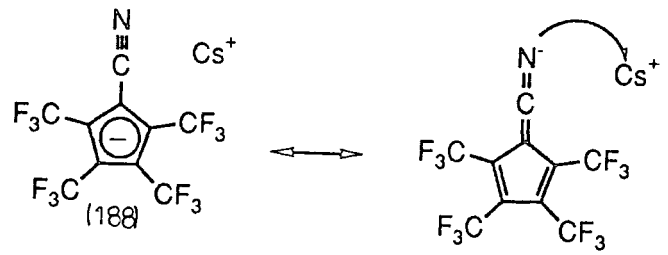


(Fig. 5.10)

using sodium carbonate as the base produced a similar mixture of the three salts (185, 186, and 188). Warming this mixture (55°C for two hours) caused a decrease in the ^{19}F n.m.r. integrals corresponding to salt (185) and an increase in the integrals corresponding to salts (186 and 188). Hence it appears that the reactions are not dependant on the nature of the alkali metal counter ion.

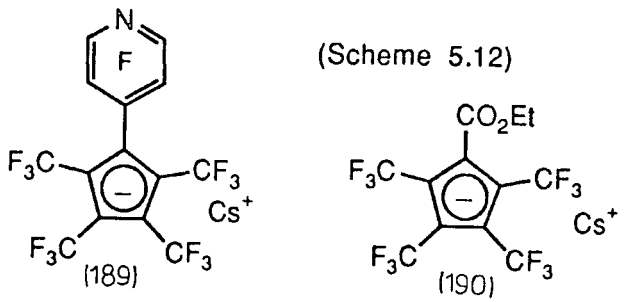
5.5.2 Cyclopentadienyl derivative (188)

Fluorine n.m.r. analysis indicated that salts (185 and 186) were completely transformed into salt (188) by heating at reflux temperature in acetonitrile for between 30 and 60 minutes. Samples of salt (188) were always dark brown in colour. Repeated attempts at purification and repeated elemental analyses proved unsatisfactory. Characterisation was by FAB mass spectroscopy (Strong parent anion peak: M^-, 362) and by carbon and fluorine n.m.r. (see below). As impurities were not apparent in the n.m.r. spectra the origin of the colour was puzzling. We believe that the colour of the salt may be due to an interaction between the caesium and the nitrile (Fig. 5.11) [Colourless solids have been



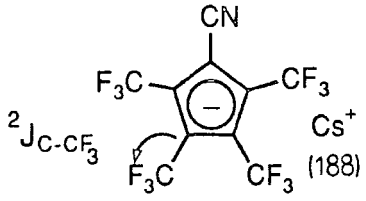
(Figure 5.11)

obtained in the absence of nitrile groups for salt (189) (Scheme 5.12, see section 5.9.2) and for 1-carboxyethyl-2,3,4,5--tetrakis(trifluoromethyl)cyclopentadienyl caesium (190),[168] with the latter being fully characterised.].



(Scheme 5.12)

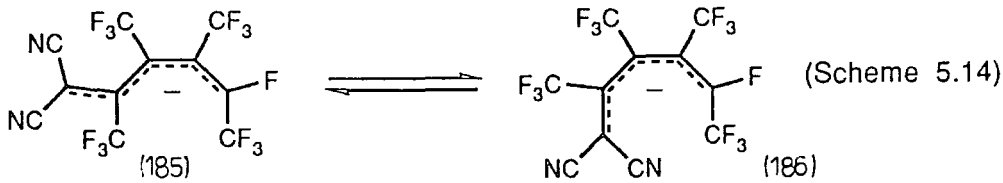
Fluorine n.m.r. shows two close resonances (δ -52.0, -52.6ppm) with some visible but complex fine structure which is presumably due to inter trifluoromethyl couplings. The carbon-13 n.m.r. spectrum clearly shows two trifluoromethyl group environments, a nitrile, and three distinct ring positions [two of which show couplings to a trifluoromethyl group ($^2J_{C\text{-}CF_3}$) (Fig. 5.13)]. The simplicity of the n.m.r. spectra support our assignment containing two planes of symmetry.



(Fig. 5.13)

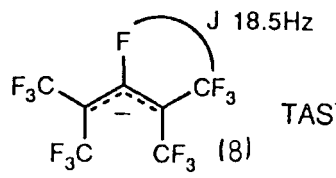
5.5.3 Inter conversion of anions (185 and 186)

In section 5.5.1 reference was made to the isomerisation of salt (185) (*trans,trans*) to salt (186) (*cis,trans*), we have considered a mechanism for this isomerisation.



(Scheme 5.14)

Rotational barriers have been studied in both the allyl[165] and pentadienyl[165,166] systems. Activation barriers of 10.7, 16.7 and 18.0 kcal/mol have been calculated for allyl lithium, allyl potassium and allyl caesium respectively[165] (in tetrahydrofuran). A proton n.m.r. coalescence temperature of 68°C for the exchange of the terminal allyl protons in allyl caesium was reported. In the case of pentadienyl anion it has been reported that the exchange barrier of the terminal methylene protons increases with the radius of the alkali metal counter ion, Li < Na < K < Rb ≃ Cs.[165,166] Farnham and co-workers[32] have reported the synthesis and characterisation of tris(dimethylamino)sulphonium (TAS) salts of allyl anion (8) (Fig. 5.15). At room temperature ^{19}F n.m.r.



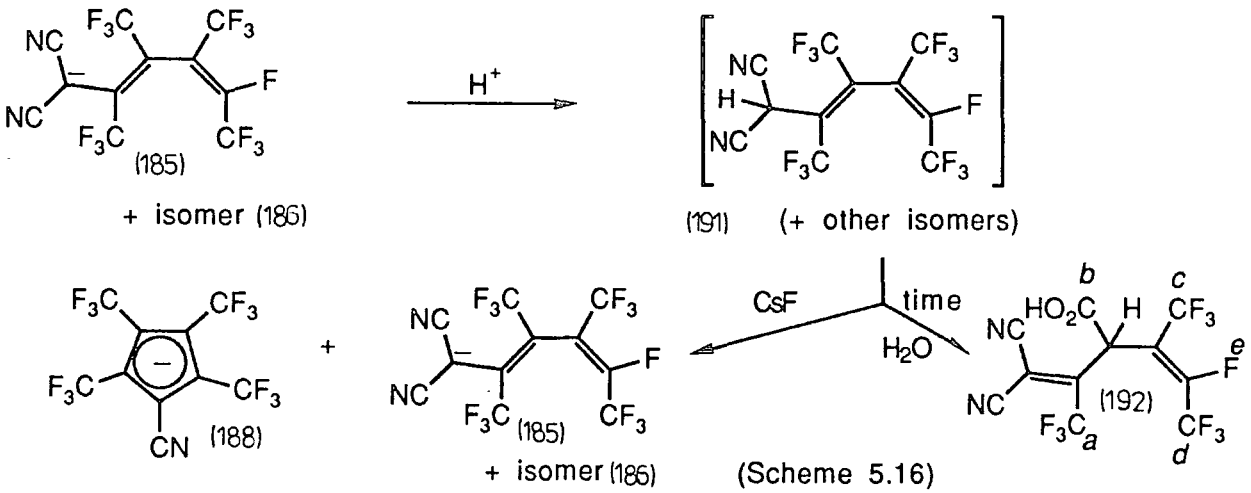
(Fig. 5.15)

reveals two resonances in the ratio 12 : 1 in d_8-THF. Exchange of the trifluoromethyl groups *via* C-F bond dissociation to F^- and $(CF_3)_2C{=}C{=}C(CF_3)_2$ was ruled out because the couplings between CF_3 and CF nuclei were maintained (18.5Hz). Upon cooling the trifluoromethyl resonances broadened and split showing the

formation of two distinct non-interconverting environments (coalescence temperature -10°C). The dynamic behaviour of this and a series of similar anions was attributed to C-C bond rotations. It seems likely that our anions are similarly isomerising, albeit with a very much slower rate of interconversion at our observation temperature (35°C).

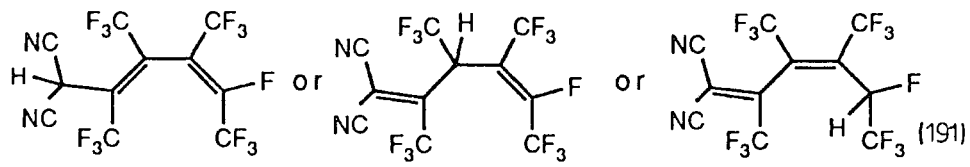
5.5.4 Acidification of salts (185 and 186)

Removal of the solvent from a filtered mixture of salts (185 and 186) yielded a brown solid. It was found (fluorine n.m.r.) that replacing the solvent regenerated the original salt mixture. Acidification (hydrochloric acid) and work-up of this brown solid gave a pale yellow sublimate which has a complex fluorine n.m.r. spectrum. This sublimate is believed to be a mixture of isomers of diene (191) (Scheme 5.16).



(Scheme 5.16)

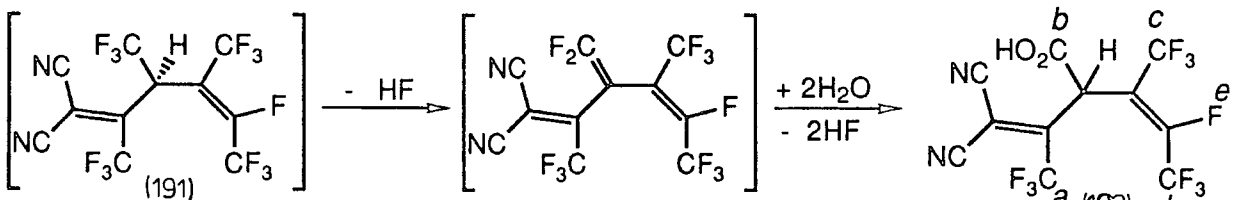
The availability of three distinct protonation sites (Fig. 5.17) in each of the four possible geometrical isomers results in a large number of potential isomers which may account for the complex fluorine n.m.r. spectra. Immediate addition of caesium



(Fig. 5.17)

fluoride and acetonitrile to the sublimate followed by heating at reflux temperature for ten minutes yielded a solution whose fluorine n.m.r. spectrum was consistent with a mixture of acyclic salts (185) (35%) and (186), (25%) and salt (188) (40%) (Scheme 5.16). This transformation coupled with the complex n.m.r. data

strongly suggests that the sublimate is indeed a mixture of isomers of the conjugate acid of anions (185 and 186). The sublimate was observed to be very susceptible to hydrolysis (Scheme 5.16), yielding carboxylic acid (192) (or isomer). For this acid fluorine n.m.r. indicated the presence of only three CF_3 groups and one vinyllic fluorine atom. Couplings with the vinyllic fluorine atom (*e*) (Scheme 5.16) indicate that CF_3 groups *c* and *d* are present. Also $J_{CF_3(c),CF_3(d)}$ of *ca* 1.3Hz indicates that CF_3 groups *c* and *d* are in a *trans*-configuration (see section 5.2). The remaining CF_3 group (δ -61.2ppm) shows some coupling possibly to $CF_3(d)$ (*ca* 2Hz). The presence of a carboxylic acid is clearly demonstrated by an intense infrared absorption from 3600 to 3050cm^{-1} and by a carbonyl resonance in the carbon-13 n.m.r. The molecular formula was confirmed by an accurate mass measurement. From the above data we cannot distinguish the site of protonation nor whether the carboxylic acid function is at site (*a*) or at site (*b*). However, a hydrogen fluoride elimination followed by hydrolysis mechanism can be written yielding the carboxylic acid function at site (*b*) (Scheme 5.18).

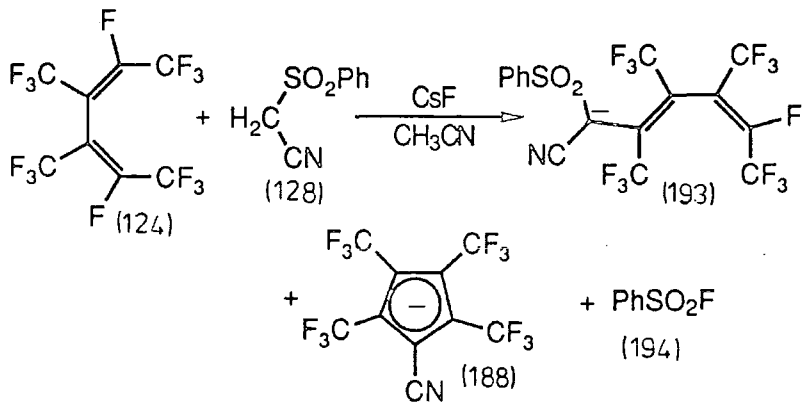


(Scheme 5.18)

5.6 Diene (124) with Phenylsulphonylacetonitrile (128)

In the reaction of phenylsulphonylacetonitrile (128) with diene (124) at room temperature, in the presence of caesium fluoride, a set of resonances consistent with salt (193) were observed by fluorine n.m.r. as a major component of the reaction mixture (*ca* 50% after 30 minutes) (Scheme 5.19). Fluorine n.m.r. coupling constants (J_{CF_3,CF_3} too small to resolve) suggested a *trans,trans* configuration for this anion (See section 5.2 for typical J values). Also detected were resonances consistent with salt (188) (*ca* 50% after 30 minutes) and a resonance consistent with phenylsulphonylfluoride (194) (trace) (δ + 65.8ppm in CH_3CN, Lit.[167] + 65.3ppm in $CDCl_3$) (See section 5.12.1 for discussion). After heating at reflux temperature for 20 minutes fluorine n.m.r.

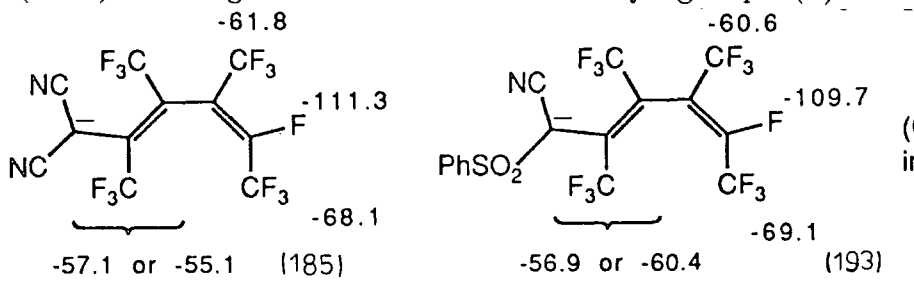
analysis revealed only the resonances attributable to salt (188).



(Scheme 5.19)

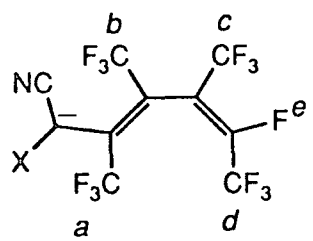
5.6.1 Comparison of anion (185) with anion (193)

From fluorine n.m.r. observation the lifetime of salt (193) (Scheme 5.19) can be seen to be significantly less than that of the bis(dicyano) analogs [salts (185 and 186)]. There is a relatively rapid room temperature conversion of resonances attributable to salt (193) into those of salt (188) (See above), whereas salts (185 and 186) are only very slowly replaced by salt (188) at room temperature (Sections 5.5.1, 5.14). From pK_a values measured in dimethylsulphoxide[159] (pK_a of $PhSO_2CH_2CN \simeq 12.0$ and pK_a of $CH_2(CN)_2 \simeq 11.1$) it can be deduced that the phenylsulphonyl group is a poorer carbanion stabilising group than nitrile. Hence there may be a higher electron density in pentadienyl anion (193) than in anions (185 and 186) which may promote a faster cyclisation of anion (193) (See section 5.10). The fluorine n.m.r. spectra of anions (185 and 193) are outlined in fig. (5.20). Assignments for trifluoromethyl groups (*c*) and (*d*)

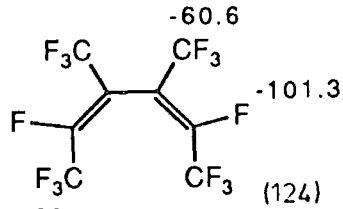


(Chemical shifts in ppm)

(Fig. 5.20)



(key)



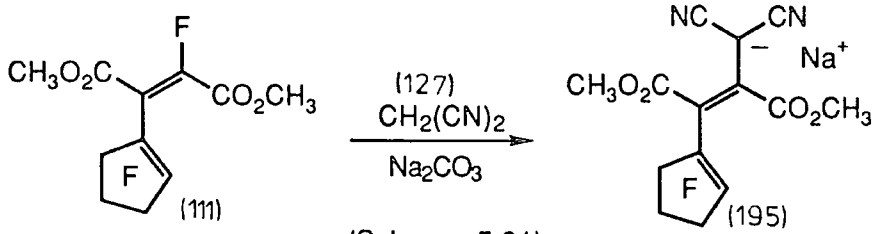
are based upon the coupling constants to the vinyllic fluorine atom (*e*). There is characteristically strong coupling between resonances (*c*) and (*e*) [^4J *ca* 14Hz for anions (185 and 193)], with much weaker coupling between fluorine atoms (*d*) and (*e*) [^3J *ca* 3Hz or non-resolvable for anions (185 and 193)] (See section 5.2). We cannot be certain of the exact assignments for trifluoromethyl groups (*a*) and (*b*).

The substitution of phenylsulphonyl for nitrile clearly does have an effect upon the fluorine n.m.r. chemical shifts of the anions. However, without more precise assignments it proves difficult to rationalise this effect.

5.7 Diene (111) with Malononitrile (127)

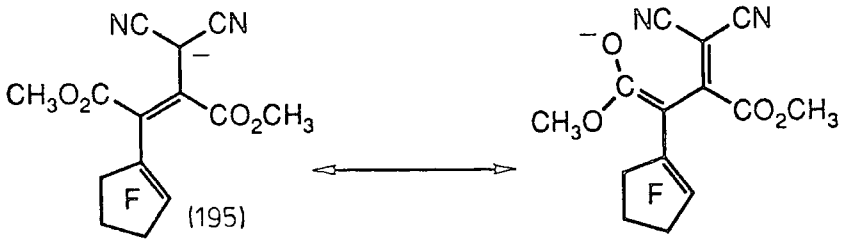
The reaction between diene (111) and malononitrile (127) produced a soluble salt whose fluorine n.m.r. and anionic FAB mass spectra were consistent with salt (195) (unknown configuration) (Scheme 5.21) [FAB anionic mass spectrum shows the parent ion m/e (for further details see section 5.8) and fluorine n.m.r. shows the loss of the exocyclic vinyllic fluorine atom resonance].

Preferential displacement of the exocyclic fluorine atom is more



(Scheme 5.21)

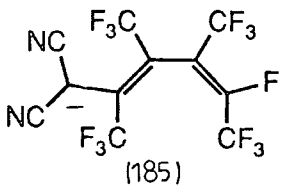
pronounced with this nucleophile than it is with the the harder methoxide ion (Section 3.4.1). Salt (195) seems to be more thermally stable than salts (185 and 193), with heating at 55°C for 23 hours having no observable effect upon the fluorine n.m.r. spectrum of a solution of the salt. Cyclisation may be inhibited by extensive delocalisation of electron density out of the pentadienyl anion and onto a carbonyl oxygen atom (Scheme 5.22).



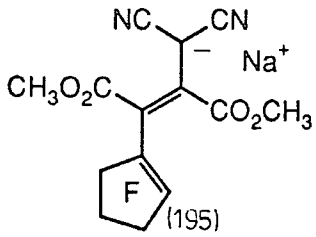
(Scheme 5.22)

5.8 FAB Mass Spectra of the Acyclic Anions

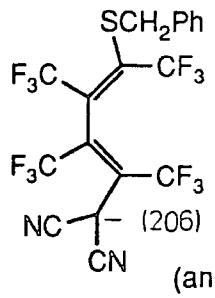
FAB mass spectra have been recorded for most of the acyclic pentadienyl salts (see fig. 5.23) (for details of the salts see sections 5.5.1, 5.7, and 5.11 respectively) (Copies of the FAB mass spectra may be found in the mass spectroscopy appendix.)



(185)
(and isomer)



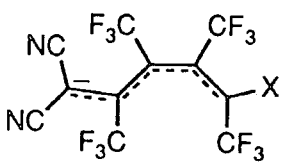
(195)
(or isomer)



(206)
(and isomers)

(Fig. 5.23)

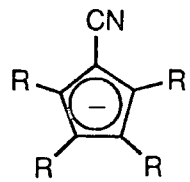
It is interesting to note that for each of the three systems the major fragmentation peak corresponds to a loss of XCN (Fig. 5.24.a) (Table 5.1) yielding a peak with the same m/e as that expected for the corresponding cp anions illustrated in fig. 5.24.b.



(Fig 5.24.a)

R = CF_3 or CO_2Et

X = F or $C_5H_5CH_2S$



(Fig 5.24.b)

Table 5.1 Peak heights in anionic FAB mass spectra

Anion	Parent anion	Parent anion - XCN
(185 and 186)	14	100
(195)	28	100
(206)	100	74

It should be noted that the sample of salts (185 and 186) submitted for FAB analysis was shown by fluorine n.m.r. to contain salt (188) as a minor impurity (< 10%).

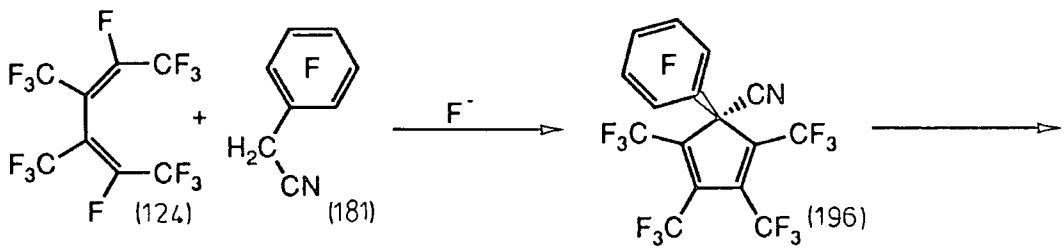
We cannot distinguish between the fragment being a cyclopentadienyl anion or it being an acyclic fragment which has lost the elements of XCN. However, the loss of the elements of $C_6H_5CH_2SCN$ from anion (206) and isomers, where the lost moieties must be 1,5-substituted, tends to suggest a cyclisation rather than just fragmentation.

5.9 Diene (124) with Aryl Substituted Carbon Nucleophiles

In the following sections acyclic pentadienyl anions were not confidently detected, and most likely have a very short lifetime before cyclisation.

5.9.1 With pentafluorophenylacetonitrile (181)

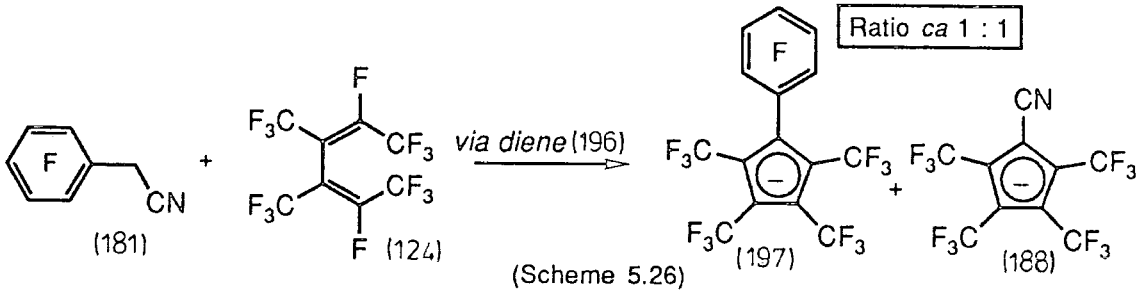
The reaction of diene (124) with pentafluorophenylacetonitrile (181) and caesium fluoride proceeded relatively slowly. The limiting factor seemed to be the formation of a reactive carbanion from the acetonitrile derivative. By following the reaction with fluorine n.m.r., diene (124) could be observed to be converted, seemingly directly, into what was subsequently identified as cp derivative (196) (Scheme 5.25) (such cp derivatives were not observed in the previously discussed reactions involving malononitrile *etc*). This remarkable diene then reacted further under the reaction conditions (See below). After a reaction time of 100 minutes fluorine n.m.r. indicated that all of the diene (124) had reacted. Work-up then enabled the isolation and characterisation of a small quantity of cp derivative (196) (For discussion see section 5.9.4). If the reaction was not worked-up



(Scheme 5.25)

fluorine n.m.r. analysis then revealed that further reaction occurred producing two sets of resonances. One set of resonances was identical to that of salt (188), the other was assigned to salt (197) (For a discussion of n.m.r. spectra see section 5.9.5)

(Scheme 5.26).

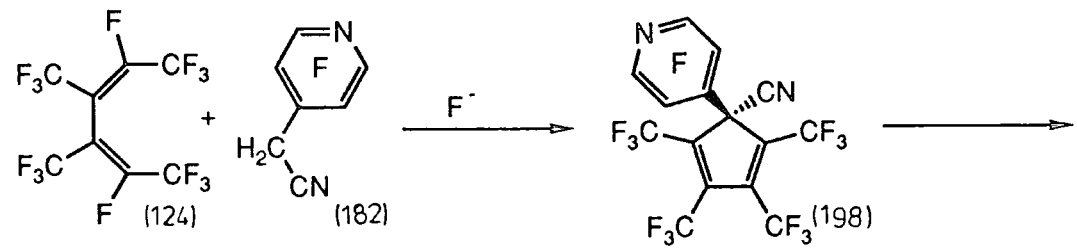


(Scheme 5.26)

Treatment of a stirred solution of isolated cp derivative (196) with caesium fluoride led to an approximately 1:1 mixture of salts (188) and (197). Unfortunately it proved impossible to separate this mixture. Characterisation of salt (197) was by fluorine n.m.r. and FAB mass spectroscopy [strong peak (M^-, 503) corresponding to parent anion] as a mixture with salt (188).

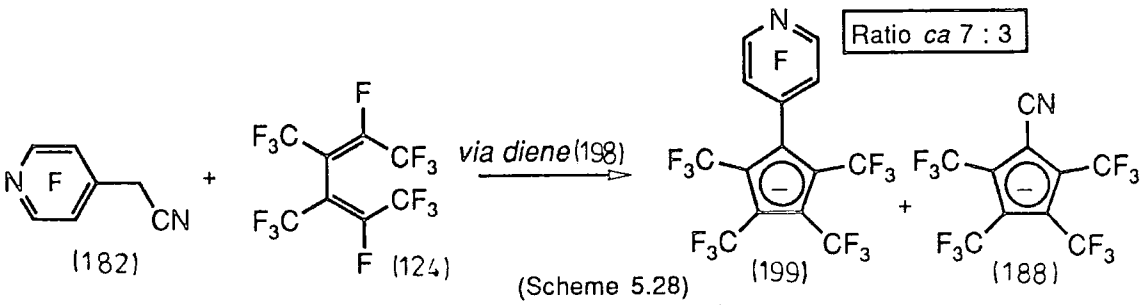
5.9.2 With 4'-tetrafluoropyridylacetonitrile (182)

This reaction proceeded much more rapidly than that of the pentafluorophenyl derivative (181), above. After a reaction time of 10 minutes all of the fluorine n.m.r. resonances attributable to diene (124) had disappeared. Immediate work up of the reaction mixture at this time enabled the isolation and characterisation of another remarkable cyclisation product, cp derivative (198) (Scheme 5.27). Under reaction conditions cp derivative (198)



(Scheme 5.27)

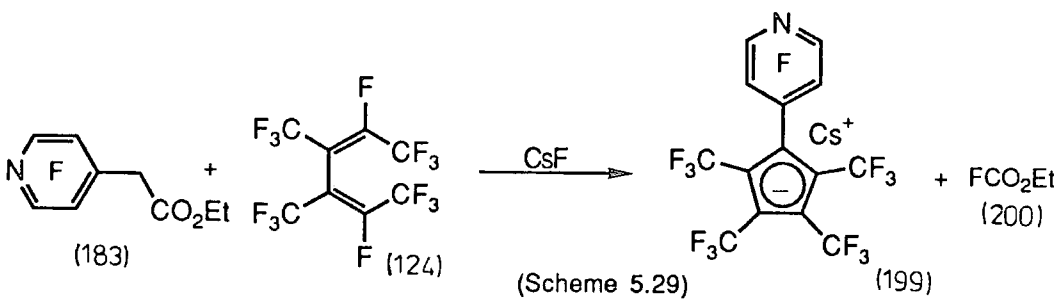
reacted further and fluorine n.m.r. showed two new sets of resonances. Fluorine n.m.r. analysis of the products obtained by further reaction of isolated cp derivative (198) with fluoride ion showed the same two sets of product resonances. One set was identical to that of salt (188) (27%), the other was consistent with salt (199) (73%) (Scheme 5.28). The anionic FAB mass spectra gave the parent m/e peaks for both anions. We were not able to separate this brown mixture. [See section 5.12 for a discussion of the reaction of dienes (196 and 198) with fluoride ion.].



(Scheme 5.28)

5.9.3 With acetate (183)

In order to obviate the purification difficulties of the above synthesis an attempt was made to prepare salt (199) free of similar salts. Simultaneous work using diene (124) and diethylmalonate[168] had shown that under reaction conditions the ethyl ester group was more easily displaced by fluoride ion than was the nitrile group. A sample of ester (183) was prepared and was reacted with diene (124) in the usual manner, ultimately giving a very much purer sample of salt (199) (Scheme 5.29). The white salt obtained, though free of salt (188), could still not



(Scheme 5.29)

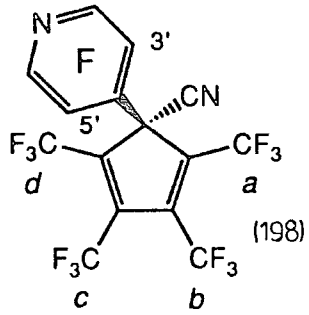
be completely purified to satisfy elemental analysis [This solid showed a very pure parent anion (M^-, 486) in the FAB mass spectrum]. As the impurities did not appear in the n.m.r. spectra we believe them to be inorganic in nature. Interestingly, fluorine n.m.r. of the reaction solution showed a resonance (δ -18.3ppm) very close to the reported resonance (δ -17.5ppm) of ethyl fluoroformate (200)[169] [Similar resonance being observed in the reaction of diene (124) with diethylmalonate[168]].

Small fluorine n.m.r. resonances also suggested the possibility that both an acyclic salt and a cp derivative were present in the reaction solution. However, the assignments were incomplete and were not further substantiated (See section 9.3.7).

5.9.4 Analysis of cp derivatives (196 and 198)

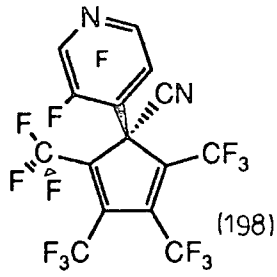
The n.m.r. and mass spectra of cp derivatives (196 and 198) are worthy of comment. The mass spectra will be discussed in section 5.15.4. Clear, well resolved, non-equivalent 3' and 5' fluorine n.m.r. resonances of the phenyl and pyridyl rings indicate that the aromatic groups have very limited rotation relative to the cyclopentadienyl rings (Fig. 5.30). Considering the sharpness of the resonances it seems likely that the rotation of the aromatic substituents is blocked by the two closest trifluoromethyl groups and also possibly by the nitrile. Thus the 3' and 5' fluorines are not appreciably interchanging at room temperature. On average one of the aromatic fluorine atoms resides much closer to a trifluoromethyl group than the other, producing a quartet splitting in one of the 3' or 5' resonances (Fig. 5.30).

The carbon-13 spectra of these two compounds, particularly that of the simpler pyridyl (198) are very well resolved with up to 4 levels of multiplicity observable in the locked pyridyl ring. Interactions with the aromatic ring broaden the carbon-13 n.m.r. resonances of atoms (*a*) and (*d*) in comparison to the resonances of atoms (*b*) and (*c*) (Fig. 5.30) (see n.m.r. appendix for full data).



(198)

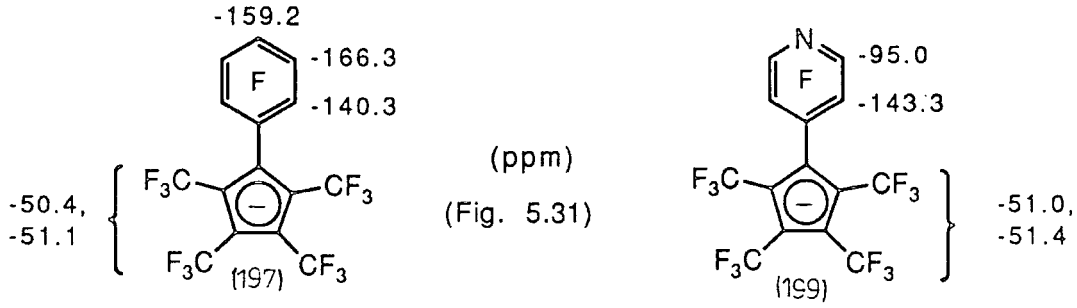
(Figure 5.30)



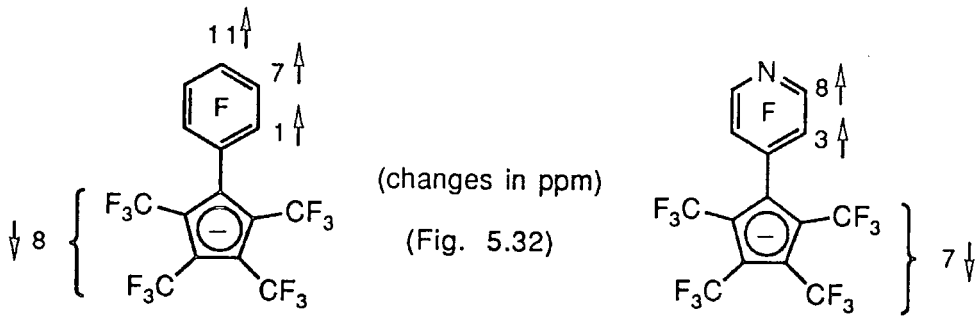
(198)

5.9.5 N.m.r. spectra of anions (197 and 199)

The higher symmetry of cyclopentadienyl anions in comparison to that of cyclopentadienes results in a simplification of the n.m.r. spectra of anions (197 and 199) compared to those of dienes (196 and 198). We now see only three fluorine n.m.r. resonances due to the pentafluorophenyl group in anion (197), and only two resonances due to the tetrafluoropyridyl group in anion (199). Fluorine n.m.r. chemical shifts are illustrated in Fig. 5.31.

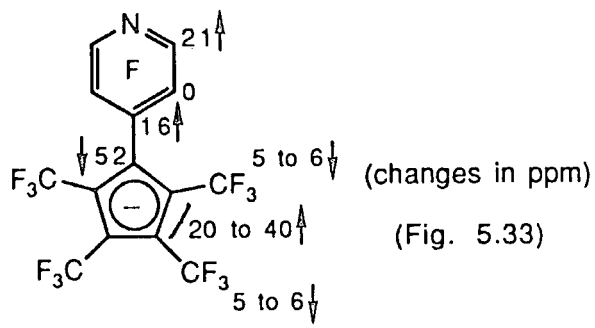


The changes in fluorine n.m.r. chemical shift between the corresponding cyano-substituted cp derivatives (196 or 198) and anion (197 or 199) are illustrated (Fig. 5.32), where an up arrow represents an upfield shift upon anion formation. The trifluoromethyl groups (which are, of course, adjacent to the



sites of negative charge in the ring) move downfield (7 to 8ppm) in a similar manner to those adjacent to charge in perfluorocarbanions (See section 1.3.2.b). The aromatic fluorines move upfield, particularly those *meta* and *para* to the point of substitution. It is peculiar that the fluorine atoms *ortho* to the point of substitution exhibit such small chemical shift changes.

A similar comparison of the carbon-13 n.m.r. spectra for the pyridyl derivatives roughly parallels the fluorine n.m.r. observations (Fig 5.33). The 52ppm downfield shift is almost

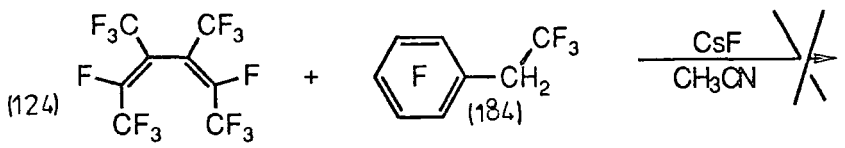


certainly largely due to a change of hybridisation at this site. Again the trifluoromethyl groups move downfield. The large upfield shift change of the pyridyl carbon *meta* to the point of substitution may be evidence of charge transmission into the

pyridyl ring. However, the unchanged *ortho* to the point of substitution resonance is puzzling. It must be noted that in addition to being charged the cyclopentadienyl fragment is also aromatic. The effect of the resulting enhanced ring current in deshielding substituents is difficult to assess.

5.9.6 With Compound (184)

A small scale reaction involving compound (184) (See section 2.3.1) (Scheme 5.34) and diene (124) was investigated. After 45 minutes at room temperature fluorine n.m.r. could not detect any new species in solution. This was probably due to compound (184) failing to ionise with fluoride ion as a base. Heating resulted in a very complex fluorine n.m.r. spectrum. No products could be isolated from this reaction mixture.

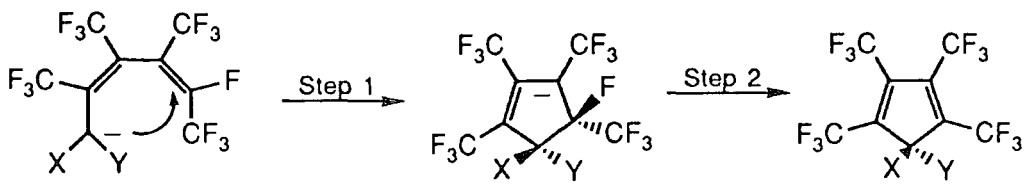


(Scheme 5.34)

5.10 Mechanism of Ring Closure

Two alternative mechanisms for the conversion of pentadienyl anions into cyclopentadienes have been considered and are set out in the following section. Both mechanisms start with the *cis,trans*-pentadienyl anion (for isomerisation from *trans,trans*- see section 5.5.3). Where the *cis,trans*- isomer was not observed we must assume that it was formed but then rapidly cyclises.

5.10.1 Intramolecular nucleophilic displacement



(Scheme 5.35)

Step 1 (Scheme 5.35) is an intramolecular nucleophilic displacement reaction and step 2 is a displacement of fluoride ion from a fluorinated allylic anion. We believe this mechanism to be unlikely for two reasons:

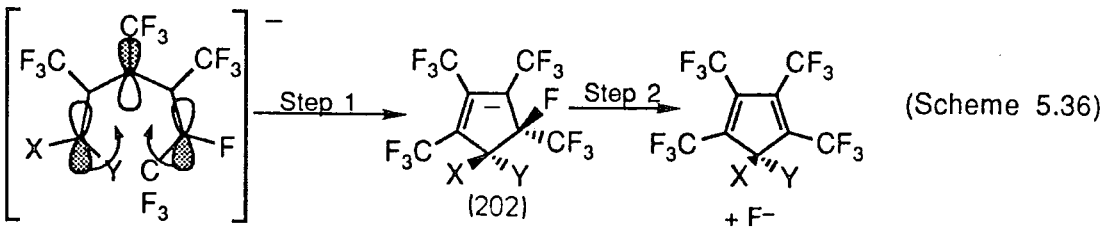
a) the intramolecular nucleophilic attack (step 1) occurs at a site which is deactivated to such attack as a result of being a part of the pentadienyl anion;

b) Baldwins' rules for nucleophilic ring closure[161] classify step 1 as a disfavoured 5-endo-trig ring closure. Disfavoured reactions are described as reactions requiring serious distortion of normal bond angles or distances in order to attain the transition state. Generally such reactions occur with difficulty if at all.

5.10.2 Ring closure *via* 1,5-electrocyclisation

If anion (201) were to undergo a 1,5-electrocyclisation reaction (Scheme 5.36) then cyclopentadienyl anion (202) is formed, which may then lose fluoride ion. We consider a process of this type to be the most likely mechanism. Indeed we believe that such a *pentadienyl-cyclopentenyl* rearrangement to be the first good example for an all carbon open chain pentadienyl anion (See section 1.7).

HOMO of anion (201)

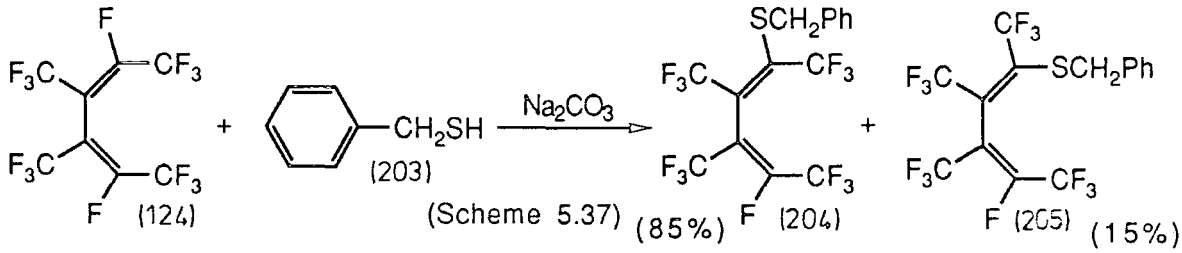


(Scheme 5.36)

5.11 Attempts to Observe a Cyclopentenyl Anion

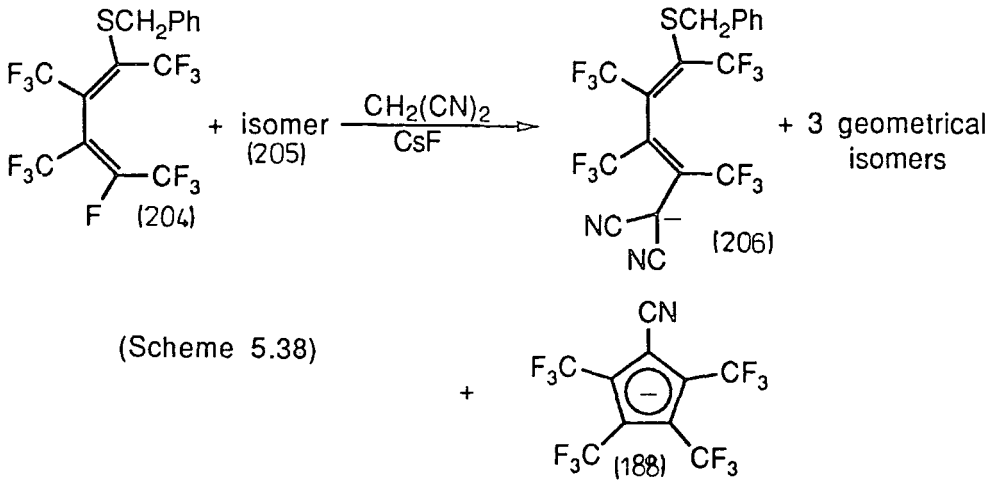
Unfortunately, in the systems already discussed, no direct evidence for any cyclopentenyl anions [such as anion (202), scheme 5.36] has been observed. Instead the products of a rapid loss of fluoride ion (forming cyclopentadienes), or those of a loss of the elements of 'XF' (forming cyclopentadienyl salts, see section 5.12.1) were observed.

We reasoned that in order to observe the intermediate cyclopentenyl anions we had to replace the tertiary fluorine atom in cyclopentenyl anion (202) (X = Y = CN) (Scheme 5.36) with a poorer leaving group. In order to achieve this we first made the mono-thiobenzyl substituted analog of diene (124) (Scheme 5.37). The reaction of benzylthiol (203) with diene (124) in the presence of sodium carbonate produced a mixture (ratio 85:15) of *trans,trans*- and *cis,trans*- mono substituted dienes (204 and 205).



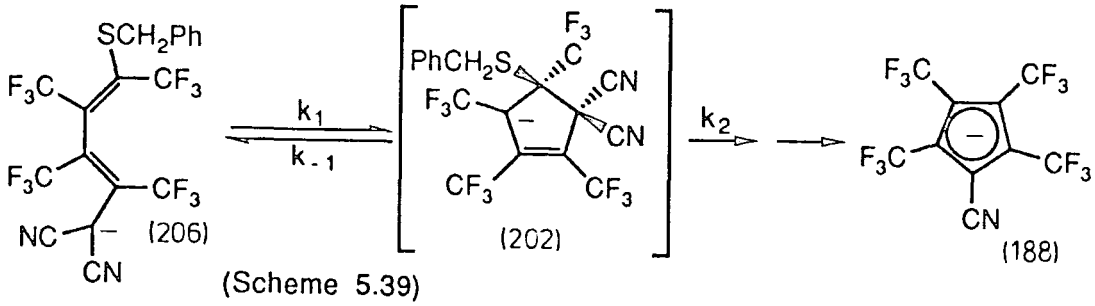
(Scheme 5.37)

Dienes (204 and 205) were then reacted with malononitrile (127) and caesium fluoride in acetonitrile solution at room temperature. Fluorine n.m.r. analysis of the reaction mixture revealed five sets of resonances. From $^{5}J_{CF_3,CF_3}$ coupling constants (See section 5.2 for typical values) it was possible to assign four of the sets of resonances to the four geometric isomers of salt (206) (Scheme 5.38) [$^{5}J_{(trans\text{-}CF_3,CF_3)}$ *ca* 3Hz or unresolved,



(Scheme 5.38)

$^{5}J_{(cis\text{-}CF_3,CF_3)}$ 13.9 to 16.4Hz]. The fifth set of resonances was identical to that of salt (188). Over time the *trans,trans*- and *cis,trans*- isomers seem to equilibrate to a 1:1 ratio, while the *trans,cis* and especially the *cis,cis*-isomers seem to be less stable (See section 9.3.3 for data). Again we failed to observe any direct evidence for an intermediate cyclopentenyl anion (202) (See scheme 5.39).



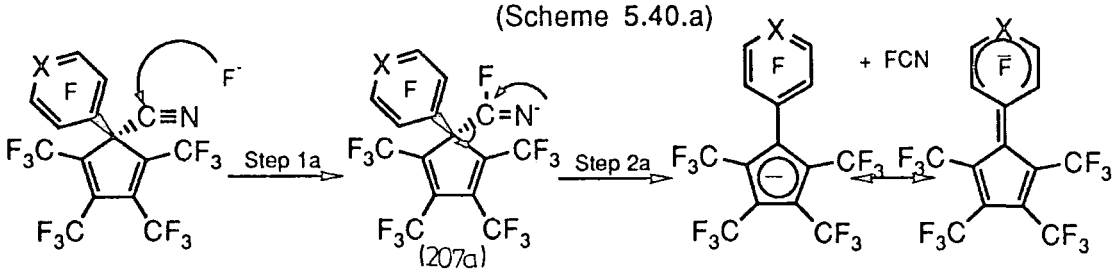
(Scheme 5.39)

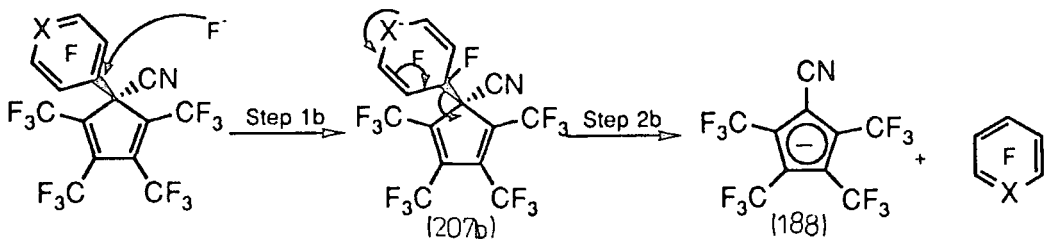
When stored at room temperature the salts were stable in solution (fluorine n.m.r. indicated only 3% cyclisation after eight days). However when the salts were heated at reflux temperature in acetonitrile cyclisation did occur (n.m.r. indicated 37% cyclisation after three hours), the solution having fluorine n.m.r. resonances identical to those of salt (188). This cyclisation is by far the slowest of all those observed which yield salt (188). This could be due to either steric crowding in the cyclisation step (Scheme 5.39) (k_1 small) or to a far more rapid internal return than step 2 ($k_{-1} >> k_2$). We feel the latter to be unlikely as this may lead to skeletal isomerisation of anion (206) *via* ring opening across a different bond to ring closure.

5.12 Conversion of Cp Derivatives to Cyclopentadienyl Anions

The substitution of tetrafluoropyridyl for pentafluorophenyl in diene (196) has a significant effect upon the ratios of the anionic products produced when these dienes are reacted with fluoride ion (Sections 5.9.1, 5.9.2) [for diene (196) salt (197) : salt (188) ≃ 1 : 1, (Scheme 5.26); for diene (198) salt (199) : salt (188) ≃ 7 : 3 (Scheme 5.28)]. The likely mechanisms for the reaction of dienes (196, X = C-F; 198, X = N) with fluoride ion are outlined in Schemes 5.40a and 5.40b.

(Scheme 5.40.a)





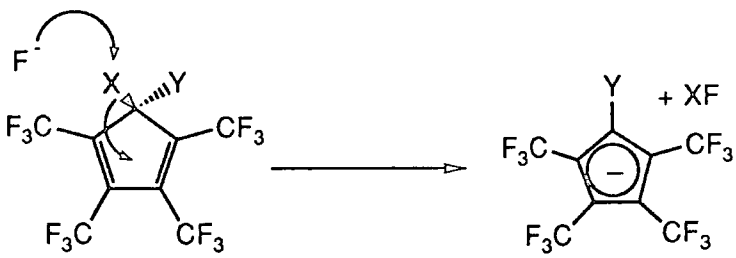
(Scheme 5.40.b)

The nature of 'X' should have little effect upon step 1a, the nitrile being very distant from 'X'. However, step 1b will be enhanced by the greater anionic stabilising power of X = N over X = C-F [para fluorine anion destabilising *via* lone pair repulsions

(section 1.3.1.a)]. Hence, if as we expected, step 1a and 1b were rate limiting we would have observed more salt (188) produced when X = N, which was the reverse of the experimental observation. The nature of the intermediates (207a and 207b) is complicated by the presence of solid caesium fluoride which introduces the possibility of a heterogeneous reaction. Step 2a might be expected to be more favoured for X = N than for X = C-F due to the relative anionic stabilising powers, but the effects of substitution upon intermediate (207b) are less clear cut. Hence we can say only that the observed product ratios are due to step 1 (a and b) not being rate limiting.

5.12.1 Observation of eliminated groups

We may have observed phenylsulphonyl fluoride ($PhSO_2F$) (208) (See section 5.6), and ethylfluoroformate (FCO_2Et) (200) (See section 5.9.3) as elimination products 'XF' (Scheme 5.41) from the conversion of cyclopentadienes to cyclopentadienyl salts.



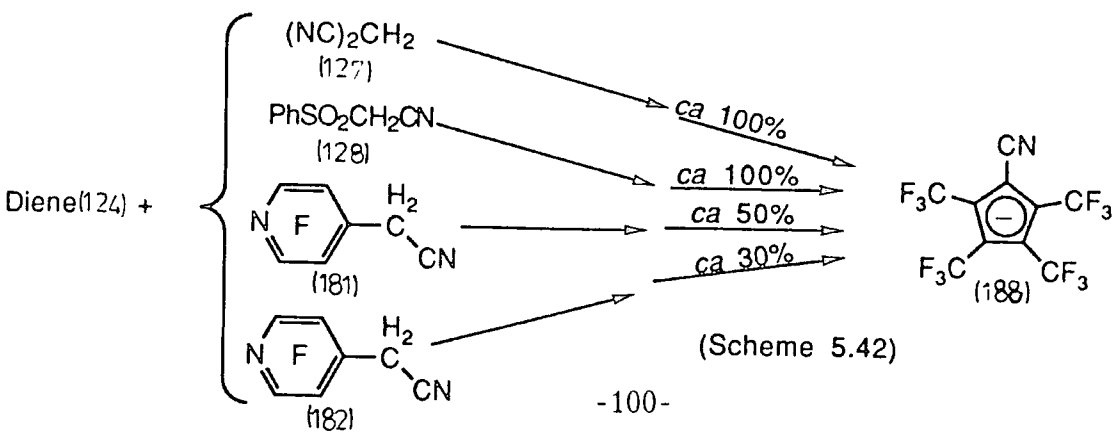
(Scheme 5.41)

X = $PhSO_2$ or C_5F_4N
Y = CN or C_5F_4N

5.13 Nitrile Substituted Anion (188)

5.13.1 Formation

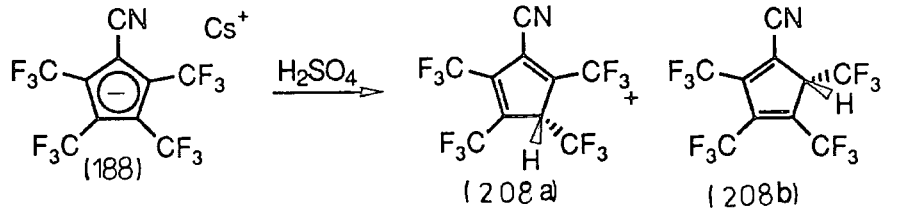
Scheme 5.42 indicates that salt (188) is produced as one of the ultimate products in all four reactions involving substituted acetonitriles and diene (124). Salt (188) is also the final product of the reaction of thiobenzyl substituted dienes (204 and 205) with malononitrile (127) (Section 5.11).



(Scheme 5.42)

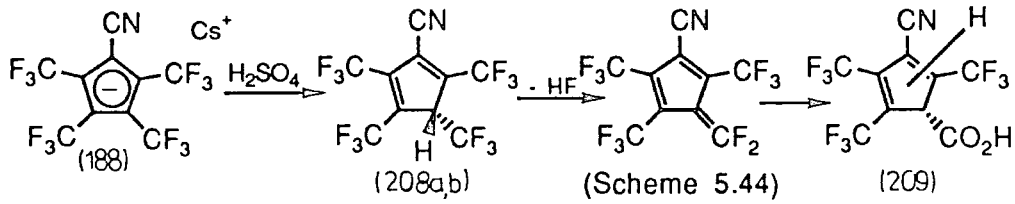
5.13.2 Acidification

The acidity of the conjugate acid of anion (188) should lie between the acidities of the strongest carbon acid with conjugating substituents (pentacyanocyclopentadiene,[68] pk_a < -11) and that of the strongest carbon acid with non-conjugating substituents [pentakis(trifluoromethyl)cyclopentadiene,[69] pk_a < -2] (Sections 1.5.2 and 1.6.4). Dissolving a sample of the caesium salt of anion (188) in concentrated sulphuric acid produced a light brown coloured solution. From the observation of two sets of four fluorine n.m.r. resonances we inferred that the solution contained a mixture of two species (Scheme 5.43) in ratio (56 : 44). Protonation at the nitrile bearing ring position was discounted as this would have led to only two distinct trifluoromethyl group resonances.



(Scheme 5.43)

Upon protonation of salt (188) an approximately 8.5ppm upfield shift of the mean fluorine n.m.r. resonance position is observed (from *ca* -52 to *ca* -60ppm). For pentakis(trifluoromethyl)--cyclopentadienide the corresponding upfield chemical shift change was approximately 10.4ppm[69] (from a mean *ca* -49 to *ca* -59ppm). After several hours sealed tubes of acid (208) developed pressure (presumably oxidation is occurring producing carbon dioxide). After work-up GC/MS [M^-, 338 (-H); 319 (-HF). Parent mass requires M, 339] indicated the possible presence of an isomer of carboxylic acid (209) (Scheme 5.44).

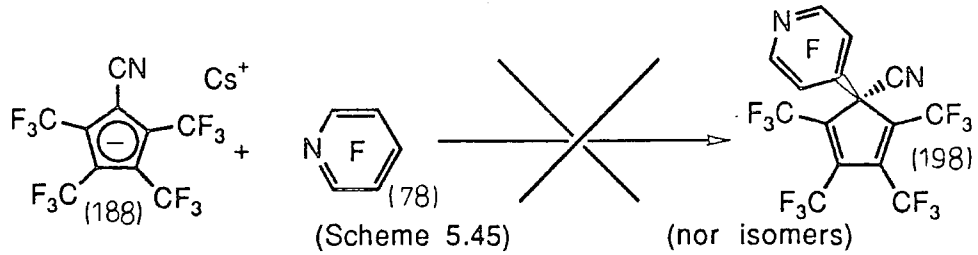


5.13.3 Other attempted reactions of salt (188)

a) *Using pentafluoropyridine* (78)

In order to test the reversibility of the reaction of cp derivative (198) with fluoride ion (Section 5.12), salt (188) and

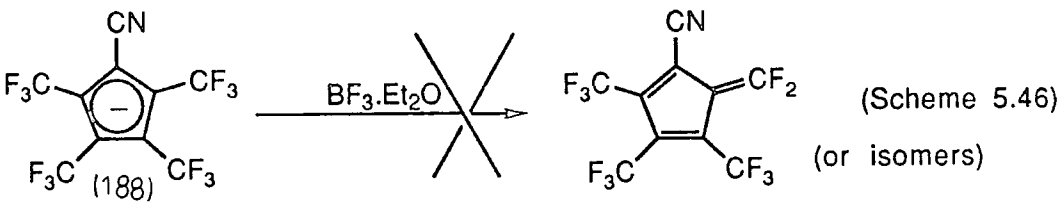
pentafluoropyridine (78) were heated to 140°C in tetraglyme solution and then at 190°C in the absence of solvent in a sealed tube. However no reaction was observed in either case (Scheme 5.45). Hence we can deduce that the reaction is irreversible.



(Scheme 5.45) (nor isomers)

b) *With borontrifluoride etherate*

Following the possible hydrolysis of salt (188) (Section 5.13.2), which may proceed *via* a fulvene type intermediate, an attempt was made to generate a fulvene derivative. However, the addition of



(Scheme 5.46)

(or isomers)

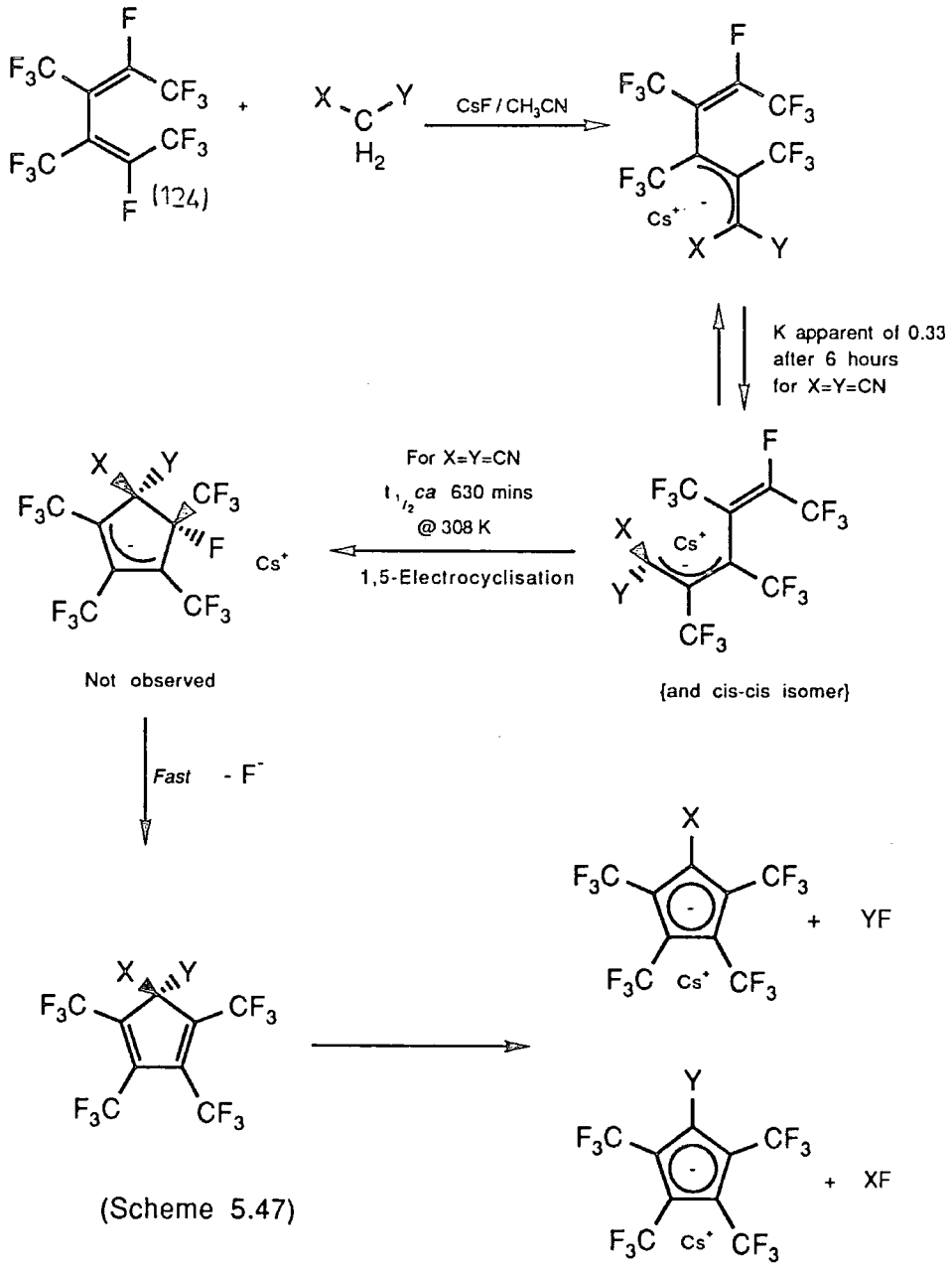
boron trifluoride etherate to a solution of salt (188) (Scheme 5.46) produced no change in the fluorine n.m.r. spectra. This approach was not pursued with stronger Lewis acids due to inevitable complexing of such acids with the nitrile group.

5.14 Overall Reaction Mechanism and Kinetics of Cyclisation

The overall reaction mechanism is detailed in scheme 5.47. We have calculated the half life of the *cis,trans* salt (186) to be *ca* 630 minutes at 35°C (Section 9.4.7), which compares with 80 minutes at 35°C for the cyclo-octadienyllithium anion (65)[105] (Section 1.7.4). Because salt (186) is itself only slowly formed from the *trans,trans* salt (185) the half life of the acyclic anion mixture as a whole will be very much longer than 630 minutes. The comparatively long half life of salt (186) may in part be due to the lower probability of adopting the correct conformation for cyclisation in an acyclic pentadienyl anion as opposed to that in a pentadienyl anion which is constrained within an eight membered

ring.

Proposed Mechanism For Cyclopentadienyl Formation

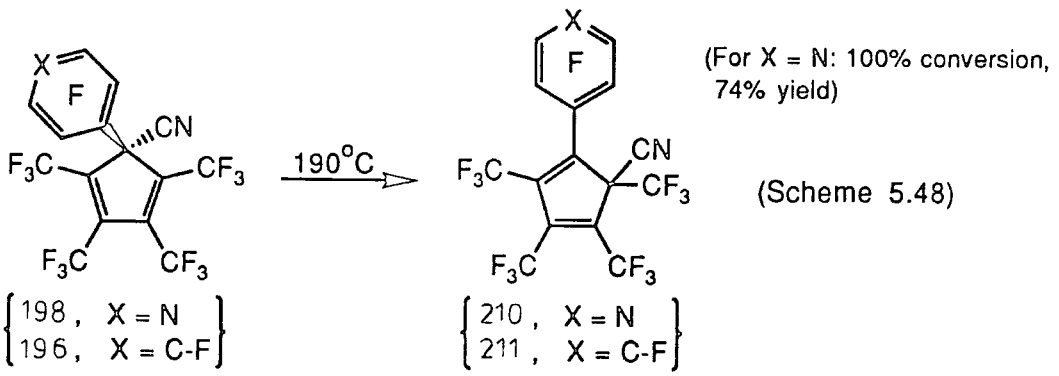


(Scheme 5.47)

5.15 Attempted Diels-Alder Chemistry of Derivatives (196 and 198)

In an attempt to investigate some of the Diels-Alder chemistry of our new dienes we chose to use cyclohexene as a potential dieneophile. In the reaction between cyclohexene and cp derivative (198) a new set of fluorine n.m.r. resonances was observed after the mixture was heated to 150°C in a sealed tube. Subsequent heating at 190°C for several hours led to the complete replacement of the starting material resonances by this new set. Surprisingly elemental analysis and mass spectroscopy indicated

that the product was an isomer of cp derivative (198) and not a Diels-Alder adduct. Repeating the procedure in the absence of cyclohexene gave the same product, although with much more charring. Further analyses, as detailed below, identified the product as cp derivative (210) (Scheme 5.48). A similar compound, product (211), was obtained from cp derivative (196) in the same manner.

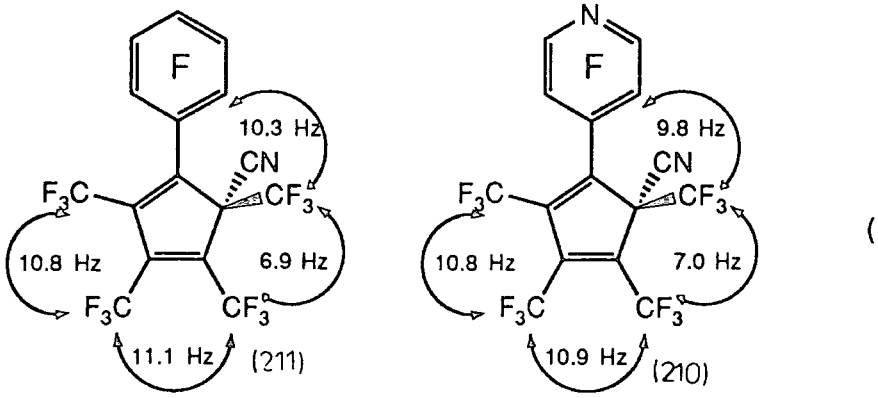


(For X = N: 100% conversion, 74% yield)

(Scheme 5.48)

5.15.1 N.m.r. characterisation of products (210 and 211)

Products (210 and 211) have been studied by high field fluorine n.m.r.. Both compounds show similar spectral features. Coupling constant data (Fig. 5.49) unambiguously assigns the indicated

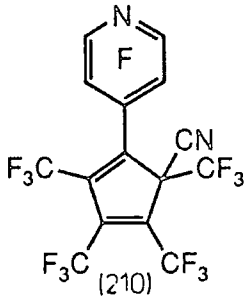


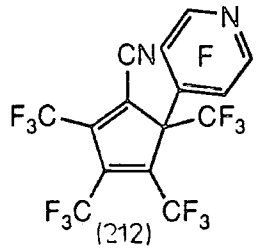
(Fig. 5.49)

trifluoromethyl substitution pattern. As with their isomers (196 and 198) the clear well resolved, non-equivalent aromatic fluorine n.m.r. resonances indicate very restricted rotation of the aromatic substituents. Indeed we again see coupling from one of the aromatic bound fluorine atoms to the sp^3 bound trifluoromethyl group. In the case of pyridyl derivative (210) the existence of this coupling was confirmed by a 2D (C.O.S.Y) n.m.r. experiment.

Although the highly coupled carbon-13 and fluorine n.m.r. spectra of product (210) are consistent with structure (210) they do not completely discount structure (212) (Fig. 5.50) (the orientation

of the pyridyl ring in structure (212) required to produce the observed couplings is, however, difficult to rationalise).





(Fig. 5.50)

5.15.2 Mass spectroscopy

The negative ion mass spectroscopic fragmentation of cp derivatives (196, 198, 211, and 210) (Fig. 5.48) (Table 5.2) is very revealing. In the case of dienes (196 and 198) the aromatic

Table 5.2 Negative Ion Fragmentation for the Cyclopentadienes

Compound	Loss of CF_3	Loss of Aromatic	Loss of CN
(196)	7.0%	100.0%	0.5%
(198)	8.9%	100.0%	5.3%
(211)	100.0%	2.4%	5.9%
(210)	100.0%	1.3%	6.8%

(Percentages refer to proportion of maximum peak height)

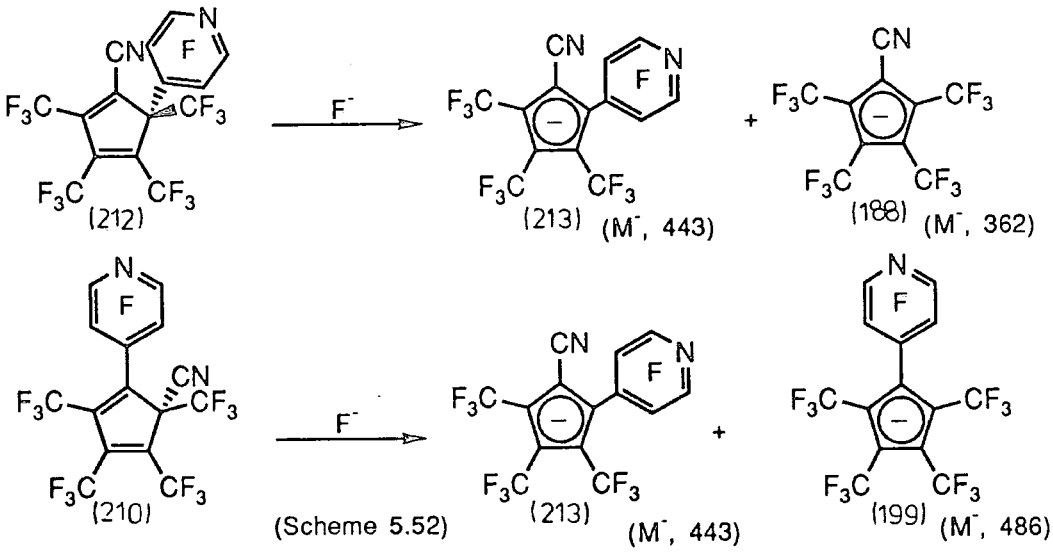
ring is lost relatively easily (Scheme 5.51), converting an sp^3 hybridised ring site into an sp^2 site. However, in the case of dienes (211 and 210) a trifluoromethyl group is almost

(Scheme 5.51)

exclusively lost. As aromatic groups which are attached to the sp^3 carbon (at site 5 in the cyclopentadienyl ring) seem to be readily lost, the almost exclusive loss of a trifluoromethyl group from products (211 and 210) strongly suggests that in these molecules the aromatic groups are not bound at site 5. Hence, the site 5 bound substituents are nitrile and trifluoromethyl, *i.e.* the compounds have structures (211 and 210).

5.15.3 Product (210) with caesium fluoride

This experiment was devised in an attempt to confirm the identity of diene (210). It was reasoned that the reaction of diene (210) with fluoride ion may lead to anion formation *via* the displacement of one of the substituents at site 5 (either the nitrile, the aromatic, or possibly even the trifluoromethyl group). FAB mass spectroscopic / fluorine n.m.r. analysis of such a reaction mixture might then determine which anions are present, hence the correct assignment of product (210). Potential ionic products are shown together with their anionic masses in Scheme 5.52, and



(Scheme 5.52)

some of the measured FAB data is shown in table 5.3. If the FAB data is compared to the ionic masses of the potential products we see evidence for anions (199 and 213) with the detection of only a small peak corresponding to anion (188). Thus we can deduce that diene (210) is the most probable assignment of the starting material. It must be noted that proposed anion (213) must be formed by a fluoride ion induced loss of a trifluoromethyl group, which is a most unusual reaction. The species of m/e 533 may correspond to an ion aggregate of formula $(Cs^+)_2\ [C_5(CF_3)_3]^{3-}$, an artifact of the FAB process {*c.f.* $[Cs\ (Anion)_2]^-$ and $[Cs_2(Anion)]^+$ in FAB spectra in the mass spectroscopy appendix}. Fluorine n.m.r. shows resonances tentatively attributable to a *ca* 3:1 mixture of salts (199) and (213) respectively.

Table 5.3 FAB Mass Spectroscopy Data

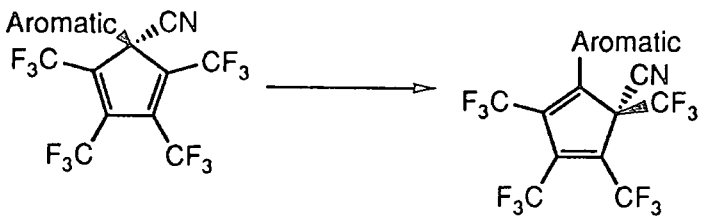
Ion m/e	Percentage Peak height
362	2.9
443	48.6
486	31.9
533	100.0

5.15.4 General points

Although samples of dienes (196, 198, 210, and 211) submitted for mass spectroscopic analysis were of high purity, electron impact ionisation often gave an additional peak 69 mass units (corresponding to an extra CF_3 group) above the expected parent ion mass. The intensity of this peak increased from zero during the acquisition of the spectra {An analysis of the daughter ions derived from the additional peak [using compound (198)] revealed the only fragmentation to be the loss of the elements of CF_4}. As we are convinced that the samples were pure we can only conclude that the extra peaks are due to some form of CF_3 group transfer between molecules (possibly arising from weak dimerisation in the solid state).

5.15.5 Proposed mechanism of formation of products (210) and (211)

It should be noted that isomerically pure products were obtained (Scheme 5.53). As we do not see any evidence for an equilibrium mixture we can deduce that the rearrangement produces an isomer which is much more thermodynamically stable than the starting material. The rearrangement could occur *via* migration of the nitrile group or by a migration of both the aromatic group and a trifluoromethyl group.



(Scheme 5.53)

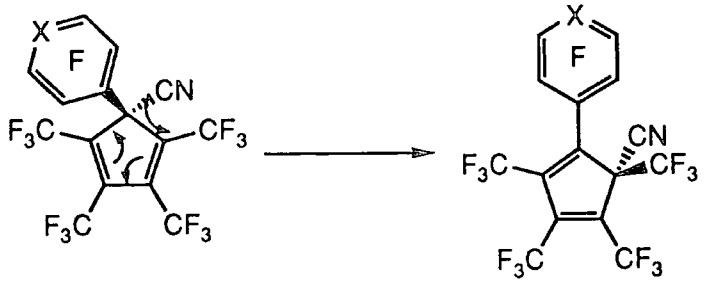
a) *Rearrangement driving force*

The rearrangement results in the bulkiest group, the aromatic, changing from being bound to an sp^3 hybridised carbon atom to being bound to a sp^2 hybridised carbon centre. This will reduce the crowding about the aromatic group especially as the aromatic group is now only adjacent to one bulky trifluoromethyl group. Hence, relief of crowding may be an important driving force for the rearrangement.

A nitrile group bound to an sp^2 site can easily conjugate into a π-system, whereas the bulky aromatic groups may have problems achieving co-planarity with the cyclopentadienyl π-system. As the nitrile is bound to a sp^3 site both before and after rearrangement while the aromatic becomes bound to the sp^2 site, it seems unlikely that the degree of conjugation is an important driving force for the rearrangement.

b) *Migration of nitrile*

A 1,2-nitrile shift could be considered (Scheme 5.54), with transition state stabilisation from the nitrile π-system.

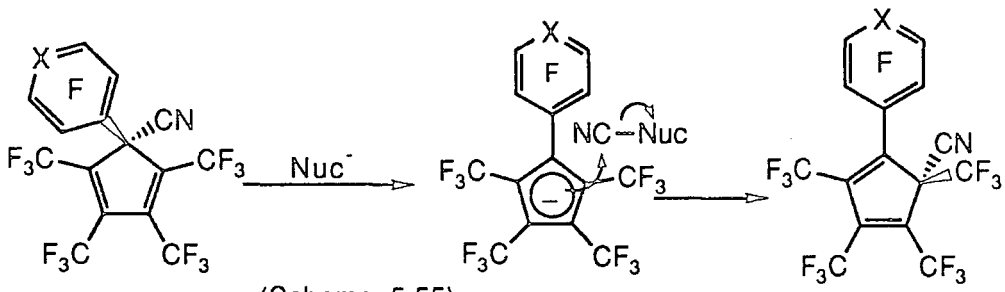


(Scheme 5.54)

This is similar to the rearrangement of organometallic cyclopentadienes first reported by Piper and Wilkinson[170] for π-$C_5H_5Fe(CO)_2\sigma$-C_5H_5 where the sigma-bound cyclopentadienyl group rapidly rotates at room temperature (as observed by proton n.m.r. signal averaging). This effect is observed in a variety of other organometallics including silanes, germanes, and stannanes.[171] It has been demonstrated that the rearrangement proceeds *via* a rapid series of (1,2) shifts.[172] It may be that our systems are following the same mechanism but stopping after the first isomerisation, when much of the steric crowding will have been released.

Alternatively reaction with a nucleophile (for example a trace of fluoride ion from the hydrolysis of, or the thermal decomposition

of, the cp derivative (210 or 211), or interaction of the cp derivative with the quartz vessel) could be considered (Scheme 5.55). However, heating cp derivative (198) with small quantities

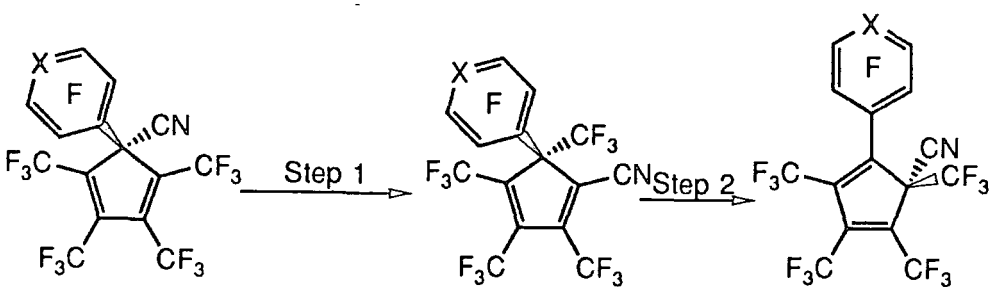


(Scheme 5.55)

of added fluoride did not appear to enhance the isomerisation. Also such a mechanism may be expected to give a mixture of isomeric products.

c) *Migration of the aromatic group*

We believe migration of the aromatic group to be unlikely. If the driving force for the rearrangement is the reduction of crowding, then it is difficult to see how the aromatic group moving from one sp^3 hybridised carbon site to another will be energetically favourable (Step 1, scheme 5.56). There is then the additional problem of subsequently having to migrate a trifluoromethyl group back to the nitrile site (Step 2).



(Scheme 5.56)

Chapter 6 - Experimental to Chapter 2

6.1 Preparation and Purification of Starting Materials

6.1.1 Substrates

a) *Pentafluoronitrobenzene* (71)

Boron trifluoride was bubbled though a mixture of tetrahydrothiophen-1,1-dioxide (40ml) and fuming nitric acid (95%, 15ml) at 0^0C until a saturated solution was formed (*ca* 1 hour). Pentafluorobenzene (31.2g, 186mmol) was added and the mixture was then stirred at 62^0C for 2 hours. During this time a homogeneous yellow solution formed, this was steam distilled. The distillate was extracted with methylene chloride (2 X 30ml) and the combined extracts were dried ($MgSO_4$). Removal of the methylene chloride (Vigreux column) and fractional distillation of the residue gave pentafluoronitrobenzene (71) (31.8g, 150mmol, 80% yield), b.p. 157-160^{0}C (lit.[173] 158-161^{0}C).

b) 2*H-Pentafluoropropene* (69)

i) 2,2,3,4,4,4-*Hexafluorobutan*-1-*ol*

Hexafluoropropene (70) (27.3g, 182mmol), methanol (27.3g, 853mmol) and benzoylperoxide (1.05g, 4.3mmol) were charged into a steel autoclave (*ca* 100ml capacity) and rocked at 100^0C for 270 minutes. After cooling, hexafluoropropene (70) (7.1g, 47.3mmol) was removed leaving a liquid product. This was fractionally distilled yielding 2,2,3,4,4,4-hexafluorobutan-1-ol (72) (15.2g, 115mmol, 85% yield based upon alkene) (b.p. 113-114^{0}C) (lit.[112] 114-115^{0}C).

ii) 2,2,4,4,4-*Hexafluorobutanoic acid* (73)

Alcohol (72) (77.4g, 425mmol) was added dropwise to a stirred solution of potassium dichromate (110g, 374mmol) and concentrated sulphuric acid (150g) in water (100ml), maintained at 80^0C, in a flask (500ml) fitted with a reflux condenser. The solution was stirred for 2 hours at 80^0C, and was then cooled to room temperature overnight. After ether extraction (4 X 100ml) the combined extracts were dried ($MgSO_4$), the ether was removed, with fractional distillation yielding 2,2,3,4,4,4-hexafluorobutanoic acid (57g, 291mmol, 70% yield): b.p. 142-144^{0}C (lit.[112] 143-144^{0}C).

iii) *Sodium*-2,2,3,4,4,4-*hexafluorobutanoate* (73)

2,2,3,4,4,4-Hexafluorobutanoic acid (57.0g, 0.291mmol) was added to a solution of sodium hydroxide (11.0g, 291mmol) in water (10ml). Evaporation of the water and further drying of the ground salt at 80°C under vacuum yielded sodium-2,2,3,4,4,4-
-hexafluorobutanoate (73) (63.4g, 291mmol, 100% yield).

iv) *2H-Pentafluoropropene* (69)

Anhydrous salt (73) (63.4g, 291mmol) was deposited in a horizontal tubular quartz vessel and slowly pyrolysed with a Bunsen flame. Gaseous products were passed through a column charged with *Carbsorb* to remove carbon dioxide. The remaining gas was then collected in a liquid air cooled trap. By comparison of infrared spectra with an authentic sample the gas was identified as 2H-pentafluoropropene (69) (35.2g, 266mmol, 91% yield).

6.1.2 Solvents and Reagents

Tetraglyme was purified by stirring with sodium metal at 95°C for 3 hours followed by fractional distillation under vacuum. The middle fraction was collected over oven dried molecular sieve (Type 4A) and stored under dry nitrogen.

Acetonitrile was dried by heating under reflux over phosphorus pentoxide for 4 hours followed by fractional distillation. The middle fraction was collected over oven dried molecular sieve (type 4A) and stored under dry nitrogen.

Caesium fluoride was ground in a nitrogen filled glove box, then heated to 180°C under vacuum (0.005mmHg) for a period of 16 hours. The salt was then stored and manipulated under an atmosphere of dry nitrogen.

6.2 Fluoride Ion Induced Reactions of 2H-Pentafluoropropene

6.2.1 Standard procedure

The required quantities of dry caesium fluoride, dry tetraglyme, and substrate were rapidly introduced, against a flow of dry nitrogen, into a baked round bottomed flask, fitted with a gas tap and a variable volume gas reservoir. The apparatus was cooled in liquid air, evacuated, and filled with the required mass of 2H-pentafluoropropene. After warming to room temperature the mixture was stirred vigorously for the required time period.

Volatiles were then removed *in vacuo*.

6.2.2 With pentafluoropyridine (78)[111]

A mixture containing pentafluoropyridine (78) (24.5g, 145.2mmol), dry caesium fluoride (36.3g, 238.8mmol), tetraglyme (55ml) and 2H-pentafluoropropene (69) (18.1g, 137.4mmol) was stirred at room temperature for 390 minutes. Recovered volatiles (1.7g) were shown by infrared analysis to mainly consist of 2H-pentafluoropropene (69). The crude product was then added to hydrochloric acid (400ml, 10%). After ether extraction (3 X 80ml) the extracts were combined and dried ($MgSO_4$). Careful removal of the ether (Vigreux column) followed by vacuum transfer of the residue into a cold trap gave a colourless oil. Distillation of which (Fischer-Spaltrohr) gave pentafluoropyridine (78) (b.p. 83-85^{0}C) (4.6g, 30.7mmol, 21% recovery) and a two component mixture [ratio *ca* 4 : 1 (by GC analysis)] (13.6g) (b.p. 120-140^{0}C) and low/none volatiles (*ca* 13g). A portion of the mixture was separated by preparative scale gas chromatography (130^{0}C, 30% SE30 column) yielding perfluoro-4-(2H-hexafluoroisopropyl)pyridine (79)[11] (GC calculated total yield *ca* 10.9g, 36mmol, 32% based upon aromatic): (Found: C, 32.2; H, 0.5; N, 4.7%; M^+, 301. Calc. for $C_8HF_{10}N$: C, 31.9; H, 0.3; N, 4.65%; M, 301); n.m.r spectra (^1H, ^{19}F) number 3a. (n.m.r. data identical to an authentic sample), and tetrafluoro-4-(2.2.2-trifluoroethyl)pyridine[111] (80) (GC calculated total yield *ca* 2.7g, 12mmol, 10% based upon aromatic): (Found: C, 35.9; H, 0.9; N, 5.6%; M^+, 233. $C_7H_2F_7N$ requires: C, 36.1; H, 0.9; N, 6.0%; M, 233); mass spectrum (electron impact) number 1; n.m.r. spectra (^1H, ^{19}F) number 3c; infrared spectrum number 1.

6.2.3 With pentafluorobenzonitrile (82)

A mixture containing pentafluorobenzonitrile (82) (37.2g, 193mmol), caesium fluoride (39.2g, 258mmol), tetraglyme (50ml), and 2H-pentafluoropropene (69) (23.2g, 176mmol) was rapidly stirred at room temperature for a period of 6 hours, during which time the gas reservoir collapsed. Collected volatiles (3.4g), isolated by vacuum transfer, and sealed in an n.m.r. tube, were shown by fluorine n.m.r. analysis to consist mainly of 2H-pentafluoropropene (69). The remaining product was filtered,

washing with dry acetone. Water (50ml) mixed with concentrated hydrochloric acid (15ml) was then added. Ether extraction (3 X 70ml), drying ($MgSO_4$) and the removal of the ether by rotary evaporation yielded a brown oil (*ca* 35g). Distillation (Fischer-Spaltrohr) yielded: fraction (a) (82-85^{0}C, 37mmHg) (15.0g); fraction (b) (107-113^{0}C, 37mmHg) (8.7g); fraction (c) (115-125^{0}C, 37mmHg) (7.3g); fraction (d) (< 150^{0}C, 0.1mmHg) (1.5g). Fraction (a) was shown (by GC) to be pentafluorobenzonitrile (77.7mmol, 44% recovery). By GC / MS the remaining fractions were shown to be three component mixtures in the combined ratio 3.1 : 1.3 : 1. The major two components were separated by preparative scale gas chromatography (carbowax column, 115^{0}C) and were found to be perfluoro-4-(2H-hexafluoroisopropyl)benzonitrile (83) (GC calculated total yield *ca* 10.2g, 31mmol, 27% yield based upon aromatic): (Found: C, 37.0; H, 0.3; N, 4.5%; M^+, 325. $C_{10}HF_{10}N$ requires: C, 36.9; H, 0.3; N, 4.3%; M, 325); mass spectrum (electron impact) number 2; n.m.r. spectra (^1H, ^{19}F) number 6a; infrared spectrum number 2. and tetrafluoro-4-(2',2',2'-trifluoroethyl)benzonitrile (84) (GC calculated total yield *ca* 4.2g, 16mmol, 14% yield based upon alkene): (Found: M^+, 257. C_9HF_7N requires M, 257); mass spectrum (electron impact) number 4; n.m.r. (^1H, ^{19}F) spectra number 7a. The minor isomer crystallised from fraction (d) and was identified as perfluoro-4-[2'-(4'H-4'-methylpent-2-enyl)]benzonitrile (85) [1.5g isolated (3.3g calculated), 3.4mmol, 3.8% based upon initial alkene (6.6% calculated total yield)]: (Found: C, 36.1; H, 0.5; N, 2.9%; M^+, 437. $C_{13}HF_{14}N$ requires: C, 35.7; H, 0.2; N, 3.2%; M, 437); m.p. 141^{0}C; mass spectra (electron impact, chemical ionisation, negative ion) number 5; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 4; infrared spectrum number 3.

6.2.4 With pentafluoronitrobenzene (71)[111]

A mixture containing pentafluoronitrobenzene (71) (12.7g, 59.6mmol), dry caesium fluoride (14.5, 95.7mmol), tetraglyme (20ml) and 2H-pentafluoropropene (69) (7.2g, 54.5mmol) contained in a flask (250ml) was stirred at room temperature for 64 hours. Fluorine n.m.r. identified the recovered volatiles (0.93g) as 1,1,1,3,3,3-hexafluoropropane (6.1mmol, 11% based on alkene). The

reaction mixture was poured into water (100ml), mixed, and ether extracted (3 X 50ml). The combined fractions were dried ($MgSO_4$) and the ether was removed by distillation (Vigreux column). The resulting oil was trap to trap distilled (up to 150°C, 0.01mmHg), leaving a tarry residue (11.1g) which was discarded and a transferred yellow oil (10.2g). Distillation (Fischer Spaltrohr) yielded ether (2.1g); fraction (a) (50-54°C, 10mmHg) (3.2g); fractions (b to g) (54-94°C, 10mmHg) (3.5g) and discarded residue (1.1g). GC indicated fraction (a) to be essentially a two component mixture. The components were separated by GC (75°C, krytox column) yielding pentafluoronitrobenzene (0.2g) (GC calculated total yield *ca* 2.4g, *ca* 11.3mmol, *ca* 19%) and perfluoro-3-methyl-2.1-benzisoxazole (88)[111] (0.4g, 1.5mmol, 3% yield) (GC calculated total yield *ca* 1.1g, *ca* 9% yield): [Found: C, 36.9; N, 5.8%; recorded mass: 258.98236mu. C_8F_7NO requires: C, 37.0; N, 5.4; (calculated mass: 258.98681mu; difference 4.5mmu. C_8F_7NO is the best reasonable match)]; mass spectra (electron impact, chemical ionisation, negative ion) number 7; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 1a; infrared spectra number 4. Fraction (e) was found to have one major component which was isolated by GC (175°C, column SE30 10%) and identified as perfluoro-1-nitro-4-(2'H-hexafluoroisopropyl)benzene (87)[111] (0.2g, 0.6mmol, 1.2% yield) (GC calculated total yield *ca* 0.9g, *ca* 2.7mmol, *ca* 5.6%): (Found: C, 31.0; H, 0.3; N, 4.4%; M^+, 345. $C_9HF_{10}NO_2$ requires: C, 31.3; H, 0.3; N, 4.1%; M, 345); mass spectra (electron impact) number 8; n.m.r. spectra (^1H, ^{19}F) number 2a; infrared spectrum number 5. Fraction (d) (complex mixture) yielded (175°C, SE30 10%) impure perfluoro-1-nitro-4-(2'.2'.2'-trifluoroethyl)benzene (89)[111] (*ca* 0.06g, 0.2mmol, 0.4% based on aromatic) (GC calculated total yield *ca* 0.3g, *ca* 1.1mmol, *ca* 2.2%): (M^+, 277. $C_8H_2F_7NO_2$ requires M^+, 277); mass spectrum (electron impact) number 3. n.m.r. spectrum (^{19}F) number 2c. In addition there were numerous other small components which were not isolated.

6.2.5 Other substrates

a) *Octafluorotoluene*

2H-Pentafluoropropene (69) (0.6g, 4.5mmol) was transferred *in vacuo* into a dry *rotoflo* tube containing tetraglyme (3ml), octafluorotoluene (1.0g, 4.2mmol) and caesium fluoride (0.6g, 3.9mmol). After stirring at room temperature for 3 days no volatiles could be recovered. Following aqueous work up, ether extraction, and vacuum transfer, GC / MS indicated that there had been only negligible reaction involving octafluorotoluene.

b) *Tetrafluoropyrimidine* (156)

2H-Pentafluoropropene (69) (1.25g, 9.5mmol) was transferred *in vacuo* into a dry *rotoflo* tube containing tetraglyme (3ml), tetrafluoropyrimidine (156) (2.0g, 13.0mmol) and caesium fluoride (2.0g, 13.2mmol). After agitation for one hour at room temperature gelation occurred. No unreacted alkene could be transferred and no products were characterised.

6.2.6 Formation of Anions

a) *From 2H-pentafluoropropene* (69)

i) *Using caesium fluoride*

2H-Pentafluoropropene (69) (0.9g, 6.9mmol) was transferred *in vacuo* into a dry *rotoflo* tube containing tetraglyme (3ml) and caesium fluoride (2.3g, 15.3mmol). After stirring overnight at room temperature no volatiles could be recovered. Fluorine n.m.r. analysis of the solution indicated a complex mixture. The reaction was not investigated further.

ii) *Using silver fluoride (in the dark)*

2H-Pentafluoropropene (69) (2.2g, 17.0mmol) was transferred *in vacuo* into a dry *rotoflo* tube containing acetonitrile (10ml) and silver fluoride (2.3g, 18mmol). The tube was agitated for 2 hours. After this time no volatiles could be recovered. Rapid filtering through *celite* and a sinter under dry nitrogen gave a yellow/brown solution (which deposited a silver mirror if exposed to light). From its n.m.r. spectra the solution was believed to contain 2H-hexafluoroisopropyl silver (96): n.m.r. spectra (^{19}F, ^{13}C) number 1b.

b) *From compound* (79) *(See section* 6.3.1*)*

c) *From compound* (83)

Compound (83) (0.1g, 0.3mmol) was added to a mixture of tetraglyme (1ml) and caesium fluoride (0.15g, 1.0mmol) in an n.m.r. tube. After agitation at room temperature for 3 hours n.m.r. analysis was consistent with the solution containing the caesium salt of perfluoro-4-(2H-hexafluoroisopropyl)benzonitrile (94): n.m.r. spectrum (^{19}F) number 6b.

d) *From compound* (85)

Compound (85) (0.15g, 0.3mmol) was added to acetonitrile (2ml) and caesium fluoride (0.3g, 2.2mmol) contained in a flask (5ml). After stirring at room temperature the solution was examined by fluorine n.m.r. and after a further 2 days by carbon and fluorine n.m.r.. The n.m.r. spectra were consistent with the solution containing the caesium salt of perfluoro-4-[4'-(2'H-4-methylpent-2-enyl)]benzonitrile (95): n.m.r. spectra (^{19}F, ^{13}C) number 5.

e) *From compound* (87) (See section 6.4.3)

6.3 Formation of trifluoroethyl derivatives

6.3.1 Pyridine derivative (79) with caesium fluoride

Caesium fluoride (0.7g, 4.9mmol) was added to a solution of compound (79) (0.2g, 0.7mmol) in tetraglyme (3ml) contained in a baked round bottomed flask (10ml). After stirring at room temperature for 3 hours fluorine n.m.r. analysis of a sample of the solution [sample (a)] gave only resonances consistent with the caesium salt of perfluoro-4-(2H-hexafluoroisopropyl)pyridine (91)[111] (n.m.r. spectrum (^{19}F) number 3b). Water (1 drop) was then added and the mixture was stirred for a further 18 hours. Fluorine n.m.r. analysis of a sample of the solution [sample (b)] gave resonances consistent with trifluoroethyl derivative (80). A repeat n.m.r. analysis of sample (a) at this time still gave resonances consistent with salt (91).

6.3.2 Electrochemical reduction of nitrobenzene derivative (87)

(In conjunction with M.W.Briscoe)

Compound (87) (2.0g, 5.9mmol) was dissolved in a solution of tetraethylammoniumtetrafluoroborate (6.2g, 28.4mmol) in dimethylformamide (180ml) contained in an electrochemical cell. A constant potential difference of 1.00V was applied producing a current of 54mA together with a red colouration at the cathode. After 10 hours the current had dropped to 10mA. Fluorine n.m.r. analysis indicated that compound (89) was the principal product. Water was added causing the separation of a lower layer. This layer was collected and trap to trap distilled under reduced pressure. GC / MS analysis confirmed compound (89) to be the major product (M^+, 233)

6.3.3 Nitrobenzene derivative (87) with caesium fluoride

(See section 6.4.3)

6.4 Investigation into the Formation of Compound (88)

6.4.1 'Usual work up' of reaction mixtures

Water (3 drops) was added to the solution, which was then trap to trap distilled *in vacuo*. The resultant oil was then examined by capillary gas chromatography (GC).

6.4.2 Reaction of trifluoroethyl derivative (89) with F^-

Caesium fluoride (0.38g, 2.5mmol) was added to a solution of compound (89) (50μl, *ca* 0.03g, *ca* 0.12mmol), pentafluoronitrobenzene (71) (15μl, *ca* 9.3mg, *ca* 0.04mmol) in tetraglyme (1ml) contained in a small vessel. The vessel was sealed and rotated for a period of 18 hours. Usual work-up followed by capillary GC indicated the presence of pentafluoronitrobenzene (71) and a trace of compound (89) (GC integral ratio 5 : 1).

6.4.3 Reaction of isopropyl derivative (87) with F^-

a) *With pure reagents*

Caesium fluoride (0.20g, 1.3mmol) was added to a very pure sample of compound (87) (30μl, *ca* 0.04g, *ca* 0.12mmol) in tetraglyme (0.5ml) contained in a dry vessel. After agitation for 17 hours usual work up and GC analysis indicated the presence of isoxazole

derivative (88) (trace only), compound (87), and trifluoroethyl derivative (89) (approximately equal quantities of last two). The experiment was repeated under constant fluorine n.m.r. analysis. After 30 minutes all of the resonances attributed to compound (87) had been replaced by resonances attributed to the caesium salt of compound (87) (93): n.m.r. spectrum (^{19}F) number 2b. Over the course of one day anion (83) reacted further (*ca* 50% reaction) yielding resonances attributed to the caesium salt of compound (89) (97): n.m.r. spectrum number 7b. Usual work up and analysis indicated the presence of compound (88) (trace), compound (89), and compound (87) (GC integral ratio ≤1 : 8 : 9).

b) *With pentafluoronitrobenzene* (71) *impurity*

Under identical conditions to (a) caesium fluoride (0.17g, 1.1mmol) was added to compound (82) (10μl, *ca* 6.2mg, *ca* 0.03mmol), pure compound (87) (30μl, *ca* 0.04g, *ca* 0.12mmol) in tetraglyme (0.5ml) contained in a dry vessel. After agitation for 17 hours usual work up and GC analysis indicated the presence of isoxazole derivative (88), compound (71), compound (87), and compound (89) in the ratio *ca* 3 : 2 : 1 : ≤1.

c) *With pentafluorobenzonitrile* (82) *impurity*

Two identical mixtures were prepared consisting of tetraglyme (1.00g), compound (87) (30μl, *ca* 0.04g, *ca* 0.12mmol), and caesium fluoride (0.2g, 1.5mmol). To the first, mixture (a), was added pentafluorobenzonitrile (82) (5μl, *ca* 3mg, *ca* 0.016mmol), to the second, mixture (b), was added pentafluoronitrobenzene (71) (5μl, *ca* 3mg, *ca* 0.015mmol). After agitation for 18 hours at room temperature the solutions were worked up in the usual way. G/C analysis gave the integral ratios shown in table 6.1.

Table 6.1

mixture	ratio of isoxazole derivative (88)	:	ethyl derivative (89)
a (+ NCC_6F_5)	1	:	8.5
b (+ $O_2NC_6F_5$)	1	:	0.6

d) *With varying solution concentrations*

Tetraglyme (0.31g, 0.52g, 0.87g, and 0.97g) was introduced into four dry vessels (a), (b), (c), and (d) respectively. To each of the vessels was added compound (87) (30μl, *ca* 0.04g, *ca* 0.12mmol), pentafluoronitrobenzene (71) (5μl, *ca* 3mg, *ca* 0.015mmol) and caesium fluoride (0.20g, 0.13mmol). The vessels were sealed and rotated for 18 hours after which time the mixtures were worked up in the usual way. The ratios of the normalised (to total 100) GC integrals of the products are presented in table 6.2.

Table 6.2

Reaction	Relative Solvent Mass	Isoxazole Derivative (88)	:	Isopropyl Derivative (87)	:	Ethyl Derivative (89)
a	1.0	51	:	6	:	43
b	1.7	37	:	17	:	45
c	2.8	28	:	20	:	52
d	3.1	6	:	23	:	70

e) *With Pentafluoronitrobenzene* (71) *+ a free radical trap*

i) *Without caesium fluoride*

Compound (87) (30μl, *ca* 0.04g, *ca* 0.12mmol), pentafluoronitrobenzene (71) (10μl) and 2-methyl-2-nitrosopropane dimer (0.0157g, 0.09mmol) were dissolved in tetraglyme (0.5ml). After rotating at room temperature for 20 hours followed by usual work up GC analysis detected only starting materials.

ii) *With caesium fluoride*

Mixtures (a and b) were prepared containing compound (87) (30μl, *ca* 0.04g, 0.12mmol), pentafluoronitrobenzene (71) (10μl, *ca* 6.2mg, *ca* 0.03mmol), tetraglyme (0.5ml) and caesium fluoride (0.10g, 0.7mmol) contained in small dry vessels. To mixture (b) was added 2-methyl-2-nitrosopropane dimer (0.0140g, 0.08mmol). Both vessels were sealed and rotated for a period of 20 hours followed by usual work up and GC analysis. The ratios of the normalised (to total 100) GC integrals of the products are presented in table 6.3.

Table 6.3

Reaction	Isoxazole Derivative (88)	:	Isopropyl Derivative (87)	:	Ethyl Derivative (89)
a (control)	69	:	24	:	7
b	32	:	32	:	36

f) *Attempt to form a substituted isoxazole derivative*

Caesium fluoride (0.36g, 2.4mmol) was added to a mixture of pentafluoronitrobenzene (71) (10μl, *ca* 6.2mg, *ca* 0.03mmol), benzonitrile derivative (83) (40μl, *ca* 0.05g, *ca* 0.15mmol), and tetraglyme (0.6ml) contained in a small dry vessel. After rotating for 19 hours, followed by usual work up, GC analysis revealed roughly equal proportions of compounds (83), trifluoroethyl derivative (84), and pentafluoronitrobenzene (71), with no significant peaks unaccounted for.

Chapter 7 - Experimental to Chapter 3

7.1 Fluoride Ion Induced Reaction of Pentafluoropyridine (78) With Dimethylacetylenedicarboxylate (DMAD) (105)

Pentafluoropyridine (78) (2.65g, 15.7mmol), caesium fluoride (4.0g, 26.3mmol), and tetrahydrothiophen-1,1-dioxide (45ml) were introduced into a dry round bottomed flask under an atmosphere of dry nitrogen. The mixture was maintained at a temperature of 80 to 90^{0}C while DMAD (105) (2.3g, 15.1mmol) was added dropwise over a period of 160 minutes. After a further three hours at this temperature the mixture was cooled and poured onto water (200ml). Ether extraction (3 X 40ml) with drying ($MgSO_4$) and combining of fractions followed by trap to trap distillation *in vacuo* yielded an orange oil and a tarry none-volatile. GC / MS analysis of the oil indicated the presence of DMAD (105), tetrahydrothiophen-1,1-dioxide and two species in the ratio 3 : 2 which were identified as *trans* and *cis* isomers of 2-fluoro-3-(4'-tetrafluoropyridyl)dimethylbut-2-en-1.4-dioate (106 and 107): (Found: M^+, 311. $C_{11}H_6FO_4N$ requires M, 311); mass spectrum (electron impact) number 9; n.m.r. spectra (^1H, ^{19}F) numbers 8a and 8b. Despite repeated aqueous washings pure samples of compounds (106 and 107) could not be obtained

7.2 Fluoride Ion Induced Reactions of Perfluorinated Cyclic Alkenes With Dimethylacetylenedicarboxylate (DMAD) (105)

7.2.1 With perfluorocyclobutene (108)

Caesium fluoride (3.6g, 24.7mmol) was introduced against a flow of dry nitrogen into a *rotoflo* tube containing dry tetraglyme (20ml). After cooling DMAD (105) (3.45g, 243mmol) was introduced and the mixture was immediately frozen in a liquid air bath and evacuated. Perfluorocyclobutene (108) (10.3g, 63.3mmol) was then condensed onto the frozen mixture *in vacuo*. The mixture was allowed to thaw behind a safety screen situated in a fumes cupboard. After stirring at room temperature for a period of 315 minutes volatiles (1.9g) were recovered. Proton n.m.r analysis of the volatiles did not show methyl group resonances (the volatiles were believed to be perfluorocyclobutene and its oligomers). The reaction mixture was poured onto cold water (150ml) forming three layers. The lower layer (2.6g) was trap to trap distilled *in*

vacuo (2.1g transferred). Analysis by GC/MS indicated that the layer was largely (> 80%) perfluorocyclobutene (108), and its dimers and trimers.[174] After trap to trap distillation (1.8g transferred) of the middle layer GC/MS indicated the presence of a complex mixture of products including a component with the correct molecular mass to be *cis* or *trans*-2-fluoro-3-(1'-pentafluorocyclobutyl)dimethylbut-2-en--1.4-dioate (109) (*ca* 13% of GC integral): (Found: M^+, 304. $C_{10}H_6F_6O_4$ requires: M, 304.); mass spectrum (electron impact) number 10.

7.2.2 With perfluorocyclopentene (110)

This reaction was performed many times, a typical experiment is detailed below. Perfluorocyclopentene (110) (bpt 27°C) was manipulated in a vacuum system or fumes cupboard due to its volatility at room temperature.

Caesium fluoride (11.9g, 78mmol) and tetraglyme (40ml) were mixed in a dry *rotoflo* tube. The tube and contents were frozen in liquid air and perfluorocyclopentene (110) (47.6g, 224mmol) was introduced *in vacuo*. The mixture was thawed and equilibrated in a water bath to a temperature of 14°C. After opening the tube to an atmosphere of dry nitrogen, a septum was fitted replacing the tap. DMAD (105) (10.2g, 71.9mmol) was added dropwise through the septum into the rapidly stirred solution over the course of 255 minutes. The tube was then resealed and warmed to room temperature overnight. Volatiles (37.7g, 178mmol) were recovered and identified as perfluorocyclopentene (110) by the comparison of infrared spectra with an authentic sample. The mixture was then combined with the reaction mixture from a similar reaction (11.7g, 55.4mmol of octafluorocyclopentene (110) consumed), and then poured onto ice water (1 litre). After mixing and standing, a lower layer was collected. The aqueous layer was extracted with ether (3 X 50ml), combining the ethereal fractions with the lower layer. After drying ($MgSO_4$) with the removal of the ether by rotary evaporation, trap to trap distillation followed by distillation (Fischer Spaltrohr) afforded a mixture of *cis* and *trans* isomers of 2-fluoro-3-(1'-heptafluorocyclopentyl)dimethylbut-2-en-1.4-dioate (111 and 112) (*cis*:*trans* ratio *ca* 3:2) (b.p. 58-63°C, 0.04mmHg)

(14.4g, 40.7mmol, 40% based upon perfluorocyclopentene consumed). Upon standing the *trans*-isomer crystallised: (Found: C, 37.6; H, 1.9; F, 42.45%; M^+, 354. $C_{11}H_6F_8O_4$ requires: C, 37.3; H, 1.7; F, 42.9%; M, 354.); m.p. 48°C; mass spectrum (electron impact, chemical ionisation, negative ion) number 11; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 9; infrared spectrum number 6. The *cis* isomer was not isolated: (Found: M^+, 354. $C_{10}H_6F_8O_4$ requires: M, 354); mass spectra (electron impact, chemical ionisation, negative ion) identical to number 11; n.m.r. spectra (^1H, ^{19}F) number 10.

7.2.3 With perfluorocyclohexene (113)

Caesium fluoride (9.6g, 63.1mmol) was added to a mixture of perfluorocyclohexene 113) (11.3g, 43.2mmol) and tetraglyme (40ml) contained in a dry *rotoflo* tube under an atmosphere of dry nitrogen. DMAD (105) (6.3g, 44.4mmol) was slowly added to the mixture over the course of 100 minutes at room temperature. The mixture was stirred at this temperature for a further 160 minutes, and was then poured into distilled water (1500ml). After mixing and standing the two lower layers which formed were collected. Distillation yielded fraction (a) (b.p. 80 °C, atmospheric pressure) (3.7g), fraction (b) (80°C, 0.05mmHg) (0.65g) and non-volatile residue (3.9g). Fraction (a) was subsequently identified as perfluorocyclohexene (113) by the comparison of GC retention times with an authentic sample. GC and GC/MS indicated that fraction (b) was a mixture of DMAD (105) (*ca* 20% of GC integration) and two principal products (*ca* 20% and 45% of GC integration). Upon standing crystallisation of the major product occurred, this product was identified as *trans*-2-fluoro-(1'-nonafluorocyclohexyl)dimethylbut-2-en--1,4-dioate (114): (0.25g, 0.6mmol, 1.4% yield based upon alkene): (Found: C, 35.9; H, 1.4; F, 46.6%; M^+, 404. $C_{12}H_6F_{10}O_4$ requires: C, 35.6; H, 1.5; F, 47.0%; M, 404); m.p. 66°C; mass spectrum (electron impact) number 12; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 11; infrared spectrum number 7. The other product was assigned as the *cis*- isomer (115): (Found: M^+, 404. $C_{12}H_6F_{10}O_4$ requires: M, 404); n.m.r. spectra (^1H, ^{19}F) number 12a; mass spectrum (electron impact) number 12.

7.3 Reactions of Dienes (111 and 112)

7.3.1 With neutral methanol

Methanol (0.24g, 7.5mmol) was added to a solution of dienes (111 and 112) (2.65g, 7.5mmol) in acetonitrile (10ml) contained in a round bottomed flask. The solution was stirred at room temperature for a period of 3 days. Fluorine n.m.r. analysis of a portion of the mixture indicated that no reaction had occurred.

7.3.2 With methanol in the presence of sodium hydrogen carbonate

Sodium hydrogen carbonate (3.0g, 35.5mmol) was added to a solution of a dienes (111 and 112) (2.1g, 6.0mmol), methanol (1.5g, 48.1mmol), and acetonitrile (10ml) contained in a round bottomed flask. After stirring at room temperature for 3 days the mixture was filtered, collecting a solution and a white solid (2.8g) which was discarded. Volatiles were removed from the solution by rotary evaporation, and the resultant oil was trap to trap distilled *in vacuo* yielding a colourless oil (2.0g). GC / MS indicated the presence of two principal components in the ratio 6 : 5. The major component partially crystallised and was identified as 2-fluoro-3-[1'-(2'-methoxy-hexafluorocyclopentyl)]dimethylbut-2-en-1.4-dioate (117) (0.3g, 0.8mmol, 14% yield): (Found: C, 39.3; H, 2.3%; M^+, 366. $C_{12}H_9F_7O_5$ requires: C, 39.3; H, 2.5%; M, 366); m.p. 48^{0}C; mass spectra (electron impact, chemical ionisation, negative ion) number 13; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 13; infrared spectrum number 8. The other component was not isolated but was identified as 2-methoxy-3-(1'-heptafluorocyclopentyl)dimethylbut-2-en-1.4-dioate (116): (Found: M^+, 366. $C_{12}H_9F_7O_5$ requires: M, 366); mass spectrum (electron impact) number 14; n.m.r. spectra (^{1}H, ^{19}F) number 12b. Combined crude yield: 2.0g, 5.4mmoles, *ca* 90%.

7.3.3 With potassium sulphide

To a solution of dienes (111 and 112) (6.2g, 17.5mmol) in an acetonitrile solution (10ml) was added freshly ground dry potassium sulphide (2.6g, 23.5mmol) contained in a dry flask (50ml). After an initial exotherm the solution was stirred at room temperature for a period of 20 hours. The solvent was

removed by rotary evaporation and was replaced with chloroform. A solid (1.5g) was collected by filtration and discarded. The solvent was again removed by rotary evaporation and the residue was trap to trap distilled yielding a colourless oil (2.6g). On standing the oil started to crystallise and also precipitated a small quantity of a white powder. In an earlier experiment this powder had been identified as sulphur (the powder did not dissolve in common solvents nor give infrared absorptions). The oil was again trap to trap distilled yielding a colourless oil which again crystallised and was identified as
2,3-biscarbomethoxy-4,5-hexafluoropropylbicyclo[3.3.0]thiophene (118) (1.8g, 5.1mmol, 29% yield) (Found: C, 37.7; H, 1.6; F, 33.3%; M^+, 348. $C_{11}H_6F_6O_4S$ requires: C, 37.9; H, 1.7; F, 32.8%; M, 348); m.p. 40°C; mass spectra (electron impact, chemical ionisation, negative ion) number 15; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 14; infrared spectrum number 9.

7.3.4 With catechol (120) in the presence of sodium hydrogen carbonate

To a solution of dienes (111 and 112) (isomeric mixture) (1.15g, 3.3mmol) in acetonitrile (40ml) was added sodium hydrogen carbonate (1.5g, 17.5mmol) and catechol (120) (0.8g, 6.9mmol). The mixture was stirred at room temperature for a period of 15 days. Filtration yielded a white powder (1.0g) and a pale green solution. Removal of the solvent under reduced pressure yielded a yellow solid (1.3g). Washing with a little cold ether left a white solid (1.05g). A small sample of this material was sublimed (0.05mmHg, 70°C) for analysis, and was identified as
1,6-benzodioxocin derivative (121) (see scheme 3.16) (2.1mmol, 64% yield): (Found : C, 55.9; H, 2.7; F, 15.9%; M^+,494. $C_{23}H_{14}O_8F_4$ requires: C, 55.9; H, 2.8; F, 15.4%; M, 494); m.p. 152°C; mass spectra (electron impact, chemical ionisation) number 16; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 15; infrared spectrum number 10.

7.3.5 With 1.2-benzenedithiol (122) in the presence of sodium carbonate

Sodium hydrogen carbonate (1.4g, 17.0mmol) and 1,2-benzenedithiol (122) (1.1g, 7.75mmol) were added to dienes (111 and 112) (isomeric mixture) (1.2g, 3.4mmol) dissolved in acetonitrile (10ml) contained in a round bottomed flask. After stirring at room temperature for a period of three days volatiles were removed under reduced pressure, and then chloroform (50ml) was added. Filtration yielded a yellow solution and a white powder (1.2g), which was discarded. Removal of the solvent from the solution yielded a yellow solid (1.4g). A sample of this solid was washed with acetonitrile and then recrystallised from ethanol, and was identified as 1.6-benzodithiocin derivative (123) (See fig. 3.18) [2.5mmol crude, 73% yield based upon dienes (111 and 112)]: (Found: C, 48.0; H, 2.9%; M^+, 578; recorded mass 577.9465mu. $C_{23}H_{15}F_5S_4O_4$ requires: C, 47.8; H, 2.6%; M, 578; accurate mass 577.9773mu, difference 30.8mmu, $C_{23}H_{15}F_5S_4O_4$ is the best reasonable match); m.p. 138^{0}C; mass spectra (electron impact, chemical ionisation) number 17; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 16; infrared spectrum number 11.

7.3.6 Attempted reaction with potassium hydroxide

Potassium hydroxide (0.2g, 4.1mmol) was added to a solution of dienes (111 and 112) (1.3g, 3.5mmol) in dimethylformamide (dry, 10ml) contained in a round bottomed flask. The mixture was stirred at room temperature for a period of 25 hours. Addition of water (30ml) and chloroform extraction (3 X 30ml) followed by drying and removal of volatiles by rotary evaporation yielded a red oil (0.8g). GC / MS analysis indicated a complex mixture a small component of which had a correct m/e for the desired furan derivative (126): (Found: M^+, 332. $C_{11}H_6F_6O_5$ requires: M, 332); mass spectrum (electron impact) number 6.

Chapter 8 - Experimental to Chapter 4

8.1 Procedural note

The following two sections define phrases that are used throughout this chapter.

8.1.1 "Calibrated fluorine n.m.r."

To assess the extent of reaction a small known mass of hexafluorobenzene was added to the reaction mixture as an internal ^{19}F n.m.r. standard. The mass of substrate remaining was then easily calculable from its ^{19}F n.m.r. integrals.

8.1.2 "Ether extraction and usual work-up"

Multiple ether extractions were performed upon aqueous solutions/mixtures. The fractions were then combined and dried ($MgSO_4$). Ether was then removed by rotary evaporation yielding a solid residue.

8.1.3 Measurement of pK_a values

A standard solution of the substrate in distilled water was prepared. The pH of a known volume of this solution was recorded. The solution was then progressively diluted with its pH being recorded after each dilution.

Using: $HA \rightleftharpoons H^+ + A^-$ and $K_a = \dfrac{[H^+]}{[HA]_o - [H^+]}$ (lit.[175])

we can calculate a value for the pK_a from each acidity measurement. For example for the pyridazine derivative (135) (Section 8.3.3):

Molarity of standard solution (50ml) = $[HA]_o = 1.030 \times 10^{-3}M$

Volume of water added (ml)	Measured pH	Calculated pKa
0	3.186	2.95
10	3.232	2.90
20	3.285	2.91
30	3.332	2.91
40	3.372	2.91
50	3.408	2.91
60	3.438	2.89
80	3.498	2.89
100	3.549	2.88
	mean pK_a =	2.91

8.2 Preparation of starting materials

8.2.1 2,4,6-Trifluoropyrimidine (155)

Caesium fluoride (75.1g, 494mmol) was added to a solution of tetrahydrothiophen-1,1-dioxide (40ml) and 2,4,6-trichloropyrimidine (24.7g, 134.7mmol), contained in a flask (1 litre) fitted with a reflux condenser. The solution was heated to a temperature of 125°C for a period of 3 hours. Volatiles were removed under reduced pressure and were identified as pure 2,4,6-trifluoropyrimidine (155) (13.0g, 96.8mmol, 72% yield): b.p. 97-99°C (lit.[176] 98-100°C); (^{1}H n.m.r.: δ 6.7ppm, singlet. ^{19}F n.m.r.: δ -41.0, singlet, integral 1; δ -52.5, singlet, integral 2.).

8.2.2 Perfluoro-4-isopropylpyridazine (157)[177]

a) *Perfluoro-4,5-bis-isopropylpyridazine*[177]

Caesium fluoride (1.0g, 6.7mmol), tetrahydrothiophen-1,1-dioxide (40ml), hexafluoropropene (70) (19.3g, 128.7mmol), and tetrafluoropyridazine (158) (8.15g, 53.6mmol) were introduced into a dry flask (200ml) equipped with an expandable gas reservoir. After stirring for two days at room temperature a partial vacuum had formed in the apparatus. A white solid was collected by reduced pressure distillation of the reaction mixture. This solid was identified as crude perfluoro-4,5-bis-isopropylpyridazine (19.7g, 43.5mmol, 81% yield) by comparison of its fluorine n.m.r. spectrum with that of an authentic sample.[177]

b) *Perfluoro-4-isopropylpyridazine*[177]

A mixture of perfluoro-4,5-bis-isopropylpyridazine (19.5g, 43.1mmol), tetrafluoropyridazine (158) (9.5g, 62.5mmol), and caesium fluoride (6.3g, 41.5mmol) in tetrahydrothiophen-1,1-dioxide (95ml) was stirred for 8 hours while maintained at a temperature of 120°C. The volatile product (14.0g) was collected by distillation yielding perfluoro-4-isopropylpyridazine (157) (10.1g, 33.5mmol, 63% yield based upon initial tetrafluoropyridazine) (b.p. 81-83°C, 7mmHg) (fluorine n.m.r. in agreement with literature[177])

8.2.3 Perfluoro-(4-phenyl)pyridine (159)

n-Butyllithium (11.0ml of a 2.5M solution in hexane, 27.5mmol) was added to a stirred solution of pentafluorobenzene (5.0g, 30.0mmol) dissolved in dry ether (70ml) maintained at a temperature of -78°C, under a dry nitrogen atmosphere. After 15 minutes pentafluoropyridine (78) (6.0g, 35.7mmol) was added dropwise. After stirring for a further 15 minutes the solution was allowed to warm to room temperature. Volatiles were then removed by rotary evaporation. Sublimation of the residue (100°C, 0.01mmHg) yielded compound (159) (7.7g, 24.3mmol, 88% yield based upon n-butyllithium). Fluorine n.m.r. was in agreement with the literature[178]

8.3 Reactions of malononitrile (127) with fluorinated aromatics

8.3.1 With pentafluoropyridine (78)

Malononitrile (127) (5.1g, 77.3mmol) was added to a stirred mixture of acetonitrile (50ml), pentafluoropyridine (78) (18.7g, 110.9mmol), and potassium fluoride (27.5g, 474mmol), contained in a dry round bottomed flask (200ml). The mixture was stirred at room temperature for 1 hour and then at reflux temperature for 3 hours. Volatiles, which were removed under reduced pressure, were shown, by calibrated fluorine n.m.r. (see section 8.1.1), to contain pentafluoropyridine (78) (*ca* 6.0g, *ca* 35.5mmol, *ca* 32% crude recovery) as the only fluorocarbon component. To the residue was added concentrated hydrochloric acid (30g, 296mmol) dissolved in distilled water (350ml), producing a green solution containing a white precipitate. Ether extraction (4 X 50ml) and usual work-up of this mixture (see section 8.1.2), followed by sublimation of the residue (80°C, 0.01mmHg) yielded a white solid, subsequently identified as 4'-tetrafluoropyridylmalononitrile (129) (14.7g, 68.5mmol, 88.6% yield based upon malononitrile); (Found: C, 44.4; H, 0.5; N, 19.2; F, 35.5%; M^+, 215; M^-, 214. $C_8HF_4N_3$ requires: C, 44.7; H, 0.4; N, 19.5; F, 35.3%; M, 215); m.p. 125°C; mass spectra (electron impact, chemical ionisation, negative ion) number 18; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 17; infrared spectrum number 12; pK_a 1.6 ± 0.1.

Caesium fluoride (20.1g, 131.9mmol) was added to a stirred solution of pyridine derivative (129) (14.7g, 68.5mmol) dissolved in acetonitrile. After 30 minutes at room temperature the

solution was filtered, the solvent was then removed by rotary evaporation leaving a yellow powder. Recrystallisation of this powder from hot distilled water (25ml) gave a pale yellow solid which was subsequently identified as the caesium salt of 4'-tetrafluoropyridylmalononitrile (130) (21.6g, 62.2mmol, 80% yield based upon malononitrile). An analytical sample was prepared by recrystallisation from ethanol: [Found: C, 27.6; N, 12.3; F, 21.9%; M^-, 214 (FAB). $C_8F_4N_3Cs$ requires: C, 27.7; N, 12.1; F, 21.9%; M^-, 214]; m.p. 255-260^{0}C (decomposition); mass spectra (FAB ±) number 19; n.m.r. spectra (^{19}F, ^{13}C) number 18; infrared spectrum number 13.

8.3.2 With perfluoro-(4-phenyl)pyridine (159)

Caesium fluoride (6.7g, 44.1mmol) was added to a stirred solution of compound (159) (4.7g, 14.9mmol) and malononitrile (127) (0.9g, 14.1mmol) in acetonitrile (20ml), contained in a flask (100ml). After 16 hours at room temperature fluorine n.m.r. indicated a *ca* 50% consumption of compound (159). Heating at reflux temper ature for a further 30 minutes had no observable effect upon the degree of reaction. Volatiles were then removed under reduced pressure. Dry acetone was added to the residue, the mixture was filtered and then the acetone was removed under reduced pressure. Recrystallisation of the residue from distilled water yielded a yellow solid (5.4g) and concentration of the recrystallisation liquor yielded another yellow solid (0.5g). Recrystallisation of the first solid from distilled water and then from acetonitrile yielded the impure caesium salt of {1'-[4'-(4''-tetrafluoropyridyl)--tetrafluorophenyl]}malononitrile (132) (3.9g, 7.9mmol, 56% yield): n.m.r. spectrum (^{19}F, ^{13}C) number 27. Concentrated hydrochloric acid (6.0g, 59.2mmol) was added to a solution of salt (132) (1.62g, 3.3mmol) dissolved in distilled water (30ml). Ether extraction (3 X 20ml) and usual work-up, followed by sublimation (80^{0}C, 0.01mmHg) yielded a pale yellow solid which was subsequently identified as {1'-[4'-(4''-tetrafluoropyridyl)tetrafluorophenyl]}--malononitrile (131) [0.9g, 2.5mmol, 76% yield based upon salt (132)]: Recorded mass: 362.96867mu: ($C_{14}HN_3F_8$ requires: 363.00427mu; difference 35.6mmu; $C_{14}HN_3F_8$ is the best reasonable

match); mass spectra (electron impact, chemical ionisation, negative ion) number 21; n.m.r. (^{1}H, ^{19}F, ^{13}C) number 26. Recrystallisation of the second solid from acetonitrile yielded an impure solid identified by fluorine n.m.r. (spectrum number 23b) as the caesium salt of {2'-[4'-(pentafluorophenyl)-3',5',6'-trifluoropyridyl]}malononitrile (134) (0.95mmol crude, *ca* 7% yield). Concentrated hydrochloric acid (5 drops) was added to an aqueous solution of salt (134) (30mg, *ca* 0.06mmol) producing a white precipitate. Ether extraction and usual work-up yielded an off-white solid which was subsequently identified as {2'-[4'-(pentafluorophenyl)-3',5',6'-trifluoropyridyl]}-malononitrile (133) [*ca* 10mg, 0.03mmol, *ca* 45% yield based upon salt (134)]: (Recorded mass: 362.99764mu. $C_{14}HN_3F_8$ requires: 363.00427mu; difference 6.6mmu. $C_{14}HN_3F_8$ is the best reasonable match); m.p. 122°C; mass spectra (electron impact, chemical ionisation, negative ion) number 20; n.m.r. (^{1}H, ^{19}F) number 23a; infrared spectrum number 14.

8.3.3 With tetrafluoropyridazine (158)

Malononitrile (127) (8.5g, 128mmol) produced a red colouration when added to a stirred mixture of tetrafluoropyridazine (158) (20.9g, 138mmol), caesium fluoride (48.9g, 322mmol), and acetonitrile (50ml), contained in a flask (500ml). The solution was heated at reflux temperature for 4 hours, after which time calibrated fluorine n.m.r. indicated tetrafluoropyridazine (158) (1.8g, 12mmol) to be a component of the solution. The solvent was removed under reduced pressure. The residue was recrystallised twice, initially from distilled water, and then from acetonitrile, yielding pale yellow crystals subsequently identified as the caesium salt of (4'-trifluoropyridazyl)malononitrile (136) (33.8g, 103mmol, 80.1% yield based upon malononitrile): (Found: C, 25.3; N, 16.8; F, 17.4. $C_7F_3N_4Cs$ requires: C, 25.5; N, 17.0; F, 17.3%.); m.p. 216°C (decomposition); n.m.r. spectra (^{19}F, ^{13}C) number 29; infrared spectrum number 15.

To salt (136) (5.8g, 17.5mmol) dissolved in distilled water (100ml, 50°C) was added concentrated hydrochloric acid (10g, 98mmol) producing an instant off-white coloured precipitate. Ether extraction (4 X 40ml) and usual work-up yielded a yellow solid. Recrystallisation of which from ethylacetate, yielded a

pale yellow solid subsequently identified as 3',5',6'-trifluoropyridazyl-4'-ylidenemalononitrile (135) [2.1g, 10.7mmol, 61% yield based upon salt (136)]: (Found: C, 42.1; H, 0.4; F, 29.2; N, 28.7%; M^+, 198. $C_7HF_3N_4$ requires: C, 42.4; H, 0.5; F, 28.8; N, 28.3%; M, 198); decomposes at 150°C; mass spectra (electron impact, chemical ionisation, negative ion) number 22; n.m.r spectra (^1H, ^{19}F, ^{13}C) number 28; infrared spectrum number 16; pK_a 2.9. Purification via sublimation (70°C, 0.01mmHg) led to extensive decomposition [yield *ca* 30% based upon salt (136)].

8.3.4 With perfluoro-4-isopropylpyridazine (157)

Caesium fluoride (7.8g, 51.3mmol) was added to a solution of compound (157) (2.9g, 9.6mmol) and malononitrile (127) (0.5g, 8.2mmol), in acetonitrile (20ml). The mixture was stirred at room temperature for 150 minutes. The reaction mixture was then filtered, washing the residue with dry acetone. The removal of volatiles, under reduced pressure, yielded a tarry yellow hydroscopic solid which was identified as the crude caesium salt of 4'-(perfluoro-5'-isopropylpyridazyl)malononitrile (138) (3.7g, 7.8mmol, 95% yield based upon malononitrile): [Found: M^-, 347 (FAB). $C_{10}N_4F_9Cs$ requires: M, 347]; mass spectra (FAB ±) number 23; n.m.r. (^1H, ^{19}F, ^{13}C) number 31.

Concentrated hydrochloric acid (5.1g, 50mmol) was added to a solution of crude (138) (1.1g, 2.3mmol) in distilled water (30ml), at room temperature, producing a yellow precipitate. Ether extraction and usual work-up yielded a yellow solid. Sublimation of this solid (100°C, 0.01mmol) yielded a pale yellow solid subsequently identified as 3',5'-difluoro-(4'-heptafluoroisopropyl)pyridazyl-4'--ylidenemalononitrile (137) [0.6g, 1.8mmol, 78% yield based upon salt (138)]: (Found: C, 34.7; H, 0.4; N, 16.5%; M^+, 348. $C_{10}HF_9N_4$ requires: C, 34.5; H, 0.3; N, 16.1%; M, 348); m.p. 81°C; mass spectra (electron impact, chemical ionisation, negative ion) number 24; n.m.r. spectra (^{19}F, ^{13}C) number 30; infrared spectrum number 17; pk_a *ca* 3.2.

8.3.5 With tetrafluoropyrimidine (156)

Caesium fluoride (25.0g, 164mmol) was added to a solution of acetonitrile (20ml), tetrafluoropyrimidine (156) (9.2g, 60.5mmol), and malononitrile (127) (3.4g, 51.4mmol), contained in a flask (100ml). The stirred mixture was maintained at a temperature of 45°C for 4 hours, after which time calibrated fluorine n.m.r. indicated the presence of tetrafluoropyrimidine (156) (1.6g, 10.5mmol). The volatiles were removed under reduced pressure leaving an off-white residue. This residue was recrystallised from hot distilled water yielding a white solid which was subsequently identified as the caesium salt of (4'-trifluoropyrimidyl)malononitrile (140) (12.2g, 37.0mmol, 72% yield based upon malononitrile): [Found: C, 25.8; N, 17.35%; M^-, 197 (FAB). $C_7F_3N_4Cs$ requires: C, 25.5; N, 17.0%; M^-, 197]; m.p. 206°C (decomposition); mass spectra (FAB ±) number 25; n.m.r. spectra (^{19}F, ^{13}C) number 36; infrared spectrum number 18.

To a stirred solution of crude salt (140) (2.9g, 8.1mmol) in acetonitrile (15ml), under an atmosphere of dry nitrogen, was added trimethylsilylbromide (2.0g, 13.2mmol) through a septum. An instant white precipitate was produced. After 5 minutes stirring, analysis (fluorine n.m.r.) indicated 3 species in solution (ratio 8 : 3 : 1). The solution was filtered under dry nitrogen and the solvent was removed under reduced pressure leaving a brown solid (1.5g). Sublimation of this solid (80°C, 0.05mmHg) yielded a white solid subsequently identified as a mixture of two isomers of 2',6'-difluoro-1H-pyrimidyl-4'-ylidenemalononitrile (139,141) [0.13g, 0.7mmol, 9% based upon salt (140)]: (Found: C, 42.5; H, 0.6; N, 28.2%; M^+, 198. $C_7HF_3N_4$ requires: C, 42.45; H, 0.5; N, 28.3%; M, 198); m.p. 125-130°C (decomposes); mass spectra (electron impact, chemical ionisation, negative ion) number 26; n.m.r. spectra (^{19}F, ^{13}C) number 35; infrared spectrum number 19. The minor component of the reaction mixture was thought to be a silyl derivative but was not investigated further.

8.3.6 With 2,4,6-trifluoropyrimidine (155)

Caesium fluoride (14.5g, 95.5mmol) was added to a solution of malononitrile (3.0g, 45.3mmol), and compound (155) (6.6g, 49.3mmol), in acetonitrile (20ml). The mixture was maintained at reflux temperature for 2 hours, and was then cooled to room

temperature. Calibrated fluorine n.m.r. indicated the presence of compound (155) (*ca* 0.5g, 3.7mmol) in solution. Volatiles were removed under reduced pressure. The residual solid was recrystallised from distilled water, yielding a solid which was identified as the

caesium salt of 2'-(4',6'-difluoropyrimidyl)malononitrile (142) (6.0g, 19.2mmol, 42% yield based upon malononitrile): [Found: C, 27.2; H, 0.2; N, 18.3%; M^-, 179 (FAB). $C_7HF_2N_4Cs$ requires C, 26.9; H, 0.3; N, 17.9%; M^-, 179]; decomposes *ca* 250^{0}C; mass spectra (FAB ±) number 27; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 38; infrared spectrum number 20. Concentration of the recrystallisation liquor, followed by cooling yields a yellow solid (7.6g). Recrystallisation of which from acetonitrile and then from ethylacetate yielded a white solid which was identified as the caesium salt of 4'-(2',6'-difluoropyrimidyl)malononitrile (143) (5.0g, 16.0mmol, 35% yield based upon malononitrile): [Found: C, 27.0; H, 0.55; F, 11.9; N, 17.6%; M^-, 179 (FAB). $C_7HF_2N_4Cs$ requires C, 26.9; H, 0.3; F, 12.2; N, 17.9%; M^-, 179]; m.p. 202^{0}C; mass spectra (FAB ±) number 28; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 37; infrared spectrum number 21.

8.3.7 With tetrafluoropyrazine (160)

Caesium fluoride (13.4g, 8.8mmol) was added to a solution of acetonitrile (10ml), tetrafluoropyrazine (160) (6.15g, 40.5mmol), and malononitrile (127) (2.65g, 40.2mmol). After two days stirring at room temperature calibrated fluorine n.m.r. indicated only a small degree of reaction. The mixture was then heated to 80^{0}C for four hours. Volatiles were removed under reduced pressure, calibrated fluorine n.m.r. indicating that tetrafluoropyrazine (2.5g, 16.4mmol) was present in the solution. The residue was recrystallised from distilled water, yielding a purple solid. Concentrated hydrochloric acid (40g, 395mmol) was added to an aqueous solution of this solid. Ether extraction (3 X 10ml) and usual work-up yielded a white powder subsequently identified as (3',5',6'-trifluoropyrazyl)malononitrile (144) (3.3g, 16.4mmol, 68% based upon tetrafluoropyrazine consumed): (Found: C, 42.7; H, 0.5; N, 28.7%; M^+, 198. $C_7HF_3N_4$ requires: C, 42.45; H, 0.5; N, 28.3%; M, 198); m.p. 81^{0}C; mass spectra (electron impact, chemical ionisation, negative ion) number 29;

n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 39a; infrared spectrum number 22; pK_a 3.2.

Caesium fluoride (1.9g, 12.4mmol) was added to a solution of pyrazine derivative (144) (0.5g, 2.5mmol) in aqueous ethanol (50%, 10ml). After stirring at room temperature for 5 minutes, the mixture was filtered, washing the residue with dry acetone. Volatiles were then removed under reduced pressure. Recrystallisation twice from ethanol yielded a pale yellow solid which was subsequently identified as the caesium salt of (3',5',6'-trifluoropyrazyl)malononitrile (145) (0.36g, 1.1mmol, 44% yield): [Found: C, 25.8; N, 17.4. $C_7F_3N_4Cs$ requires C, 25.5; N, 17.0%.]; decomposition *ca* 172°C; n.m.r. spectra (^{19}F, ^{13}C) number 39b; infrared spectrum number 23.

8.3.8 With trifluoro-1,3,5-triazine (161)

Potassium fluoride (3.65g, 62.9mmol) was added to a solution of trifluoro-1,3,5-triazine (161) (4.1g, 30.0mmol) and malononitrile (127)(1.8g, 27.6mmol), in acetonitrile (30ml), under a dry nitrogen atmosphere. The mixture was stirred at room temperature for 15 hours, after which time calibrated fluorine n.m.r. indicated complete reaction. Volatiles were removed under reduced pressure. Dry acetone was then added to the residue and the solution was filtered. Removal of the acetone by rotary evaporation yielded a white solid subsequently identified as the potassium salt of 2'-(4',6'-difluoro-1,3,5-triazyl)malononitrile (146) (5.5g, 25.1mmol, 91% yield based upon malononitrile). An analytical sample was recrystallised from ethanol: (Found: C, 32.9; N, 32.2%; M^-, 180 (FAB). $C_6F_2N_5K$ requires C, 32.9; N, 32.0%; M, 180); m.p. decomposes *ca* 230°C; mass spectra (FAB ±) number 30; n.m.r. spectra (^{19}F, ^{13}C) number 40; infrared spectrum number 24.

Caesium fluoride (1.8g, 11.8mmol) and salt (146) (0.3g, 1.2mmol) were dissolved in an acetone/distilled water mixture. Volatiles were then removed under reduced pressure. Dry acetone was added to the residue, the mixture was then filtered to remove excess caesium and potassium fluorides, washing with more dry acetone. This was repeated and volatiles were removed under reduced pressure. The resultant white powder was identified as the caesium salt of 2'-(4',6'-difluoro-1,3,5-triazyl)malononitrile

(0.2g, 0.7mmol, 59% yield) : (Found: C, 23.3; N, 22.4%. $C_6F_2N_5Cs$ requires: C, 23.0; N, 22.4%); n.m.r. spectra (^{19}F, ^{13}C) number 40.

8.3.9 With perfluoroisoquinoline (162)

Potassium fluoride (15.0g, 258mmol) was added to a stirred solution of perfluoroisoquinoline (162) (9.5g, 37.3mmol), malononitrile (127) (2.5g, 37.4mmol), in acetonitrile (50ml), contained in a flask (200ml) fitted with a reflux condenser. The mixture was maintained at reflux temperature for a period of 4 hours. The solution was then cooled and the volatiles were removed under reduced pressure. The residue was recrystallised from hot water, and then from acetonitrile, yielding a pale green solid (8.7g) subsequently identified as the impure potassium salt of [1'-(hexafluoroisoquinyl)]malononitrile (148) (*ca* 25.5mmol, *ca* 68% yield): n.m.r. spectra (^{19}F, ^{13}C) number 51.

Concentrated hydrochloric acid (3.3g, 32.5mmol) was added to impure salt (148) (0.9g, 2.6mmol) in distilled water (20ml), producing a yellow precipitate. Ether extraction and usual work-up gave a pale brown solid (0.7g). Recrystallisation of this solid twice from ethylacetate gave a pale brown solid subsequently identified as [1'-(hexafluoroisoquinyl)]malononitrile (147) (0.5g, 1.7 mmol, 64%): (Found: C, 48.1; H, 0.3; F, 37.45; N, 14.1%; M^+, 301. $C_{12}HF_6N_3$ requires: C, 47.8; H, 0.3; F, 37.9; N, 13.95%; M, 301); m.p. 110^{0}C; mass spectra (electron impact, chemical ionisation, negative ion) number 31; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 50; infrared spectrum number 25.

8.3.10 One equivalent of malononitrile (127) with perfluorobiphenyl (163)

Caesium fluoride (9.2g, 60.5mmol) was added to a stirred solution of acetonitrile (40ml), malononitrile (0.5g, 7.4mmol), and perfluorobiphenyl (2.7g, 8.2mmol), contained in a flask (100ml) fitted with a reflux condenser. After 2 hours at reflux temperature calibrated fluorine n.m.r. indicated the total consumption of perfluorobiphenyl. Volatiles were then removed under reduced pressure. The residue was recrystallised twice, initially from distilled water and then from acetonitrile yielding a pale yellow powder which was subsequently identified as the impure caesium salt of 1'-(nonafluorobiphenyl)malononitrile (150)

(3.4g, *ca* 6.6mmol, *ca* 89% yield based upon malononitrile): N.m.r. spectra (^{19}F, ^{13}C) number 43.

Concentrated hydrochloric acid (3.3g, 32.4mmol) was added to a solution of salt (150) (0.6g, 1.1mmol) in hot distilled water (10ml) producing an instant white precipitate. Ether extraction and usual work-up, followed by recrystallisation from ethylacetate afforded a white solid which was subsequently identified as 1'-(nonafluorobiphenyl)malononitrile (149) [0.25g, 0.66mmol, 60% yield based upon salt (150)]: (Found: C, 47.5; H, 0.4; N, 7.4%; M^+, 380. $C_{15}HF_9N_2$ requires: C, 47.4; H, 0.3; N, 7.4%; M, 380); m.p. 171°C; mass spectra (electron impact, chemical ionisation, negative ion) number 32; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 42; infrared spectra number 26.

8.3.11 Two equivalents of malononitrile (127) with perfluorobiphenyl (163)

Caesium fluoride (19.3g, 127mmol) was added to a stirred mixture of acetonitrile (50ml), malononitrile (127) (2.0g, 30.3mmol), and perfluorobiphenyl (163) (5.05g, 15.1mmol) contained in a flask (100ml) equipped with a reflux condenser. The mixture was heated at reflux temperature for a period of 18 hours. Volatiles were then removed under reduced pressure, dry acetone was added, and the mixture was filtered. The acetone was then removed by rotary evaporation leaving a pale yellow solid which was identified as slightly impure dicaesium salt of 1,4'-(octafluorobiphenyl)bismalononitrile (152) [$(n\text{-}Bu_4N^+)_2$ salt ref.[149]] (10.0g, *ca* 14.5mmol, *ca* 96% crude yield): N.m.r. spectra (^{19}F, ^{13}C) number 47.

Concentrated hydrochloric acid (2.9g, 29mmol) was added to crude salt (152) (3.1g, *ca* 4.5mmol) in distilled water (20ml) which produced a white precipitate. Ether extraction and usual work-up yielded a white solid 1,4'-(octafluorobiphenyl)bismalononitrile (151) [0.9g, 2.1mmol, *ca* 47% yield based upon impure salt (152)]: (Found: C, 50.8; H, 0.5; N, 13.2%; M^+, 426. $C_{18}F_8N_4H_2$ requires: C, 50.7; H, 0.5; N, 13.2%; M, 426); m.p. 236°C; mass spectra (electron impact, chemical ionisation, negative ion) number 33; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 46; infrared spectrum number 27.

8.3.12 With perfluoronaphthalene (164)

Caesium fluoride (11.2g, 73.4mmol) was added to a solution of perfluoronaphthalene (164) (4.9g, 17.9mmol), malononitrile (127) (1.15g, 17.4mmol) and acetonitrile (50ml), contained in a flask (100ml). After stirring for 42 hours at room temperature, analysis (fluorine n.m.r.) indicated that all of the perfluoronaphthalene had reacted. Volatiles were removed under reduced pressure yielding a yellow solid (7.3g). A small analytical sample was recrystallised from ethanol and was identified as the

caesium salt of β-heptafluoronapthylmalononitrile (154) (sodium salt[150]) (16.3mmol, 94% based upon malononitrile): (Found: C, 34.4; N, 6.6. $C_{13}F_7N_2Cs$ requires C, 34.7; N, 6.2%); m.p. *ca* 200°C (decomposed); n.m.r. spectra (^{19}F, ^{13}C) number 49.

Concentrated hydrochloric acid (4.2g, 41mmol) was added to salt (154) (1.25g, 2.8mmol) in distilled water (15ml). Ether extraction and usual work-up yielded an off-white solid (0.75g). Recrystallisation from ethylacetate produced a white solid identified as β-heptafluoronapthylmalononitrile (153) (0.6g, 1.9mmol, 67% yield): (Found: C, 49.0; H, 0.4; N, 8.9%; M^+, 318. Calc. for $C_{13}HF_7N_2$: C, 49.1; H, 0.3; N, 8.8%; M, 318); m.p. 128°C (Lit.[150] 127.5-129°C); n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 48; infrared spectrum: C-H stretch at 2910cm^{-1}; no visible nitrile stretch; pK_a *ca* 3.0 [measured in aqueous acetone (15% by volume) due to low solubility of substrate].

8.3.13 Attempted multiple substitution reactions

a) *With triazine derivative* (146) (see section 8.3.8)

Caesium fluoride (3.4g, 22.4mmol) was added to a stirred mixture of potassium salt (146) (1.1g, 4.9mmol), malononitrile (127) (0.6g, 8.8mmol), and acetonitrile (20ml), contained in a flask (100ml) fitted with a reflux condenser. The mixture was heated at reflux temperature for 270 minutes. Analysis (fluorine n.m.r.) indicated that no reaction had occurred. This reaction was not pursued further.

b) *With naphthalene derivative* (154) (See section 8.3.12)

Caesium fluoride (6.0g, 39.7mmol) was added to a stirred mixture of salt (154) (1.8g, 4.0mmol), malononitrile (127) (0.3g, 3.9mmol), and acetonitrile (15ml), contained in a flask (100ml) fitted with a reflux condenser. The mixture was heated at reflux temperature for 300 minutes. Analysis (fluorine n.m.r.) indicated that no reaction had occurred. This reaction was not pursued further.

c) *With biphenyl derivative* (150) See section 8.3.11

8.4 Derivatives of malononitrile derived compounds

8.4.1 From pyridine derivative (130) (See section 8.3.1)

a) *With methyl iodide*

Methyl iodide (4.6g, 35.2mmol) was added to a solution of salt (130) (1.8g, 5.1mmol) dissolved in acetonitrile (20ml), at room temperature, in a darkened flask. Over several days a small quantity of white precipitate was formed. The reaction mixture was analysed periodically using fluorine n.m.r.. After 6 weeks stirring at room temperature, the mixture was filtered. The volatiles were removed under reduced pressure, leaving an orange solid (1.15g). Sublimation (50^0C, 0.01mmHg) of this solid yielded a white solid identified as methyl-(4'-tetrafluoropyridyl)malononitrile (179) [0.6g, 2.7mmol, 53% yield based upon salt (130)]: (Found: C, 47.2; H, 1.25; N, 18.2%; M^+, 229. $C_9H_3F_4N_3$ requires: C, 47.2; H, 1.3; N, 18.3%; M, 229); m.p. 82^0C; mass spectra (electron impact, chemical ionisation, negative ion) number 34; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 21; infrared spectrum number 28.

b) *With pentafluoropyridine* (78)

Pentafluoropyridine (78) (5.3g, 31.6mmol) was added to a mixture of acetonitrile (4.2g) and salt (130) (3.5g, 10.0mmol), contained in a nickel tube (150ml capacity). The tube was sealed, and was then rocked at a temperature of 109^0C for a period of 7 hours. The tube was then cooled and opened. Removal of volatiles yielded a brown powder (*ca* 3.6g). Fluorine n.m.r. analysis identified this powder as salt (130).

Pentafluoropyridine (78) (6.0g, 3.6mmol), acetonitrile (5g), and salt (130) (2.6g, 7.5mmol) were introduced into the nickel tube. The tube was sealed and rocked at a temperature of 155^{0}C for a period of 15 hours. The tube was then cooled and opened. Removal of volatiles under reduced pressure afforded a brown solid residue (3.5g). Sublimation of which yielded a white solid (0.2g) which was subsequently identified as a mixture of decafluoro(bis-4'-pyridyl)malononitrile (177) (major): [(Found: C, 42.9; N, 15.2%; M^+, 364. $C_{13}F_8N_4$ requires: C, 42.9; N, 15.4%; M, 364); sublimes at *ca* 180^{0}C; mass spectra (electron impact, negative ion) number 35; n.m.r. spectra (^{19}F, ^{13}C) number 22a; infrared spectrum number 29], and decafluoro(bis-4'-pyridyl)acetonitrile (178)[179] (minor): (Found: M^+, 339. Calc. for $C_{12}HF_8N_3$: M, 339); n.m.r. spectra (^{19}F, ^{13}C) number 22b. A pure sample of the major isomer (177) was obtained by recrystallisation of the mixture from ethanol.

8.4.2 From pyridazine derivative (136) with dimethylsulphate

Pyridazine derivative (136) (4.4g, 13.3mmol) (section 8.3.3) was dissolved in dimethylsulphate (26.8g, 213mmol) contained in a flask (100ml) fitted with a reflux condenser, sealed by a stream of dry nitrogen. The solution was heated at 100^{0}C for 60 minutes, and was then cooled to room temperature. Distilled water (150ml) was added followed by ether extraction and usual work-up. Sublimation (80^{0}C, 0.01mmHg) of the resultant residue afforded a yellow solid subsequently identified as methyl-(4'-trifluoropyridazyl)malononitrile (180) (0.16g, 0.75mmol, 6% yield): (Found: C, 45.5; H, 1.45; N, 26.1%; M^+, 212. $C_8H_3F_3N_4$ requires C, 45.3; H, 1.4; N, 26.4%; M, 212); m.p. 180^{0}C; mass spectra (electron impact, chemical ionisation, negative ion) number 36; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 32; infrared spectrum number 30. Fluorine n.m.r. analysis of the crude reaction solution revealed only resonances attributable to compound (135).

8.4.3 From alkylpridazine salt (138) with heating

Salt (138) (1.3g, 2.7mmol) was dissolved in tetrahydrothiophen-1,1-dioxide (20ml), contained in a flask (50ml) fitted with a distillation head, water cooled condenser and

receiver. The stirred solution was maintained at a temperature of 160°C for a period of 6 hours. During this time no volatiles transferred. Analysis (fluorine n.m.r.) of the cooled solution indicated salt (138) as the only fluorine containing constituent. This experiment was not pursued further.

8.4.4 From salt (150) with perfluorobiphenyl (163)

Perfluorobiphenyl (163) (0.2g, 0.6mmol) was added to a solution of salt (150) (0.3g, 0.6mmol) in tetraglyme (10ml) contained in a round bottomed flask (50ml) fitted with a reflux condenser. The mixture was heated to 170°C for a period of 7 hours, Analysis (fluorine n.m.r.) of a portion of the solution indicated that no reaction had occurred.

8.4.5 Hydrolysis of triazine derivative (145)

Salt (145) (*ca* 9.6g, *ca* 44.1mmol) (See section 8.3.8) was added to distilled water (50ml) in a flask (100ml). The mixture was heated, the last solid was seen to dissolve at a temperature of 50-55°C. At *ca* 60°C the rapid precipitation of a white solid (*ca* 9.0g) occurred. This solid proved to be insoluble in most common solvents. Multiple recrystallisation of this solid from 50% aqueous acetic acid yielded 1',3',5'-triazyl-4',6'-dione-2'-ylidenemalononitrile (169) (*ca* 1.5g): [Found: H, 1.4; N, 39.8%; M^+, 177; recorded mass: 177.02658mu. $C_6H_3N_5O_2$ requires: H, 1.7; N, 39.6%; M, 177; (calculated mass: 177.02867mu; difference 2.1mmu; $C_6H_3N_5O_2$ is the best reasonable match); m.p. (mild discolouration 300-320°C); mass spectra (electron impact, chemical ionisation, negative ion) number 37; n.m.r. spectra (^1H, ^{13}C) number 41; infrared spectrum number 31.

8.4.6 Concentration dependence of ^{13}C n.m.r. nitrile resonances for the pyrimidine and pyrazine derivatives (140, 143, and 145)

a) *For salt* (140)

A series of solutions of varying concentrations of salt (140) dissolved in d_6-acetone were analysed using carbon-13 n.m.r., running at 62.9MHz. The peak separation of the nitrile resonances (measured in Hertz) was noted. The data is shown in table 8.1.

Table 8.1

Concentration of Salt (140) (M)	Nitrile Peak separation (Hz)
0.229	0.000
0.608	18.240
0.882	26.102
1.136	31.134
1.342	35.851

b) *For salt* (143)

A series of solutions of varying concentrations of salt (143) dissolved in d_6-acetone were analysed using broad band proton decoupled carbon-13 n.m.r., running at 62.9MHz. The peak separation of the nitrile resonances (measured in Hertz) was noted. The data is shown in table 8.2.

Table 8.2

Concentration of Salt (143) (M)	Nitrile Peak separation (Hz)
0.061	69.355
0.165	56.166
0.266	47.738
0.378	41.008
0.502	33.083
0.588	29.624
0.646	25.850
0.756	22.139
0.872	17.234
1.004	11.699
1.104	8.365
saturated	0.0

A sealed sample of a solution of concentration 0.467M, with a peak separation of 34.40Hz (0.547ppm) at 62.9MHz was analysed at Edinburgh University, running at 90.6MHz at the same operating temperature. In this the peak separation was seen to be 44.77Hz (0.494ppm).

c) *For salt* (145)

A solution (0.06M) of salt (145) in perdeuteroacetone was analysed by ^{13}C n.m.r., and the nitrile resonance was observed as a singlet. With a much higher concentration solution (unmeasured) the resonance was again observed as a singlet.

8.5 Reactions of phenylsulphonylacetonitrile (128) with fluorinated aromatics

8.5.1 With pentafluoropyridine (78)

Caesium fluoride (29.5g, 194mmol) was added to a solution of pentafluoropyridine (78) (13.7g, 81.1mmol) and phenylsulphonylacetonitrile (128) (11.9g, 65.6mmol), in acetonitrile (30ml). While stirring for 2 hours at room temperature a yellow colour developed. After this time analysis (fluorine n.m.r.) indicated that the reaction was complete. Volatiles were removed under reduced pressure. Dry acetone (excess) was added, the resulting mixture was filtered, washing the residue with more acetone. The acetone was then removed by rotary evaporation, leaving a pale yellow solid.
Recrystallisation of which from dry ethanol yielded a white solid subsequently shown to be the caesium salt of phenylsulphonyl-(4'-tetrafluoropyridyl)acetonitrile (170) (20.3g, 43.9mmol, 67% yield): (Found: C, 33.6; H, 0.85; N, 5.7. $C_{13}H_5F_4N_2SO_2Cs$ requires: C, 33.8; H, 1.1; N, 6.1%); m.p. 204°C (decomposition); n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 20; infrared spectrum number 32.

Concentrated hydrochloric acid (10.0g, 98.6mmol) was added to a solution of salt (170) (11.0g, 23.8mmol) in distilled water (50ml) producing a white precipitate. Ether extraction and usual work-up followed by recrystallisation from ethylacetate produced a white solid which was subsequently identified as phenylsulphonyl-(4'-tetrafluoropyridyl)acetonitrile (171) (4.2g, 12.7mmol, 53% yield): (Found: C, 47.25; H, 1.6; N, 8.4. $C_{13}H_6F_4N_2SO_2$ requires: C, 47.3; H, 1.8; N, 8.45%); m.p. 130°C; mass spectra (electron impact, chemical ionisation, negative ion) number 38; n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 19; infrared spectrum number 33.

8.5.2 With perfluoro-4-isopropylpyridazine (157)

Caesium fluoride (8.4g, 55.5mmol) was added to a solution of perfluoro-4-isopropylpyridazine (157) (4.7g, 15.4mmol) and phenylsulphonylacetonitrile (128) (2.6g, 14.1mmol), dissolved in acetonitrile (20ml), producing an instant red colouration. After stirring at room temperature for 4 hours, analysis (fluorine n.m.r.) indicated nearly complete reaction. Removal of volatiles under reduced pressure, followed by addition of dry acetone, filtering, and finally removal of the acetone by rotary evaporation, afforded the slightly impure caesium salt of phenylsulphonyl-[4'-(3'-heptafluoroisopropylpyridazyl)]--acetonitrile (172) (*ca* 7.5g, *ca* 12.6mmol, *ca* 89% yield): Mass spectra (FAB±) number 39; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 34.

Concentrated hydrochloric acid (2.2g, 21.3mmol) was added to salt (173) (1.25g, *ca* 2.2mmol) dissolved in hot distilled water (20ml), producing an instant white precipitate. Ether extraction and usual work-up afforded a white solid identified as phenylsulphonyl-[4'-(3'-heptafluoroisopropylpyridazyl)]--acetonitrile (173) (0.75g, 1.7mmol, *ca* 77% yield): (Found: C, 38.9; H, 1.25; N, 8.7. $C_{15}H_6F_9N_3SO_2$ requires: C, 38.9; H, 1.3; N, 9.1%); m.p. 184^{0}C; mass spectra (electron impact, chemical ionisation, negative ion) number 40; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 33; infrared spectrum number 34.

8.5.3 With perfluorobiphenyl (163)

Caesium fluoride (3.2g, 21.3mmol) was added to a solution of perfluorobiphenyl (163) (1.8g, 5.5mmol) and phenylsulphonylacetonitrile (128) (0.9g, 4.8mmol), in acetonitrile (20ml). After stirring at room temperature for a period of 20 hours, the flask contained a yellow solution with a white precipitate. Calibrated fluorine n.m.r. analysis indicated that perfluorobiphenyl (0.6g, 1.8mmol) was a component of the solution. Volatiles were removed under reduced pressure. Dry acetone was added to the residue, the mixture was then filtered, and the acetone was removed by rotary evaporation. The residue was then recrystallised initially from water and then from methanol, affording a pale yellow solid, which was identified as the impure

caesium salt of phenylsulphonyl-(1'-nonafluorobiphenyl)acetonitrile (174) (1.4g, 2.2mmol, 46% yield): n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 45.

Concentrated hydrochloric acid (1.0g, 9.9mmol) was added to a solution of salt (174) (0.35g, *ca* 0.56mmol) dissolved in hot distilled water (30ml) producing an instant white precipitate. Ether extraction and usual work-up yielded a white solid, which was identified as phenylsulphonyl-(1'-nonafluorobiphenyl)acetonitrile (175) (0.19g, 0.38mmol, *ca* 68% yield): (Found: C, 48.8; H, 1.5; N, 2.8. $C_{20}H_6F_9NSO_2$ requires: C, 48.5; H, 1.2; N, 2.8%); m.p. 145^{0}C; mass spectra (electron impact, chemical ionisation, negative ion) number 41; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 44; infrared spectrum number 35.

8.6 4'-Tetrafluoropyridylacetonitrile (182) with Fluoride Ion

Caesium fluoride (4.5g, 29.9mmol) was added to a solution of compound (182) (for preparation and characterisation see section 9.2.3) (2.3g, 12.0mmol) in acetonitrile (20ml) contained in a flask (50ml). After stirring at room temperature for a period of 2 hours fluorine n.m.r. analysis indicated the presence of the caesium salt of 4'-tetrafluoropyridylacetonitrile (176): n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 25a.

Chapter 9 - Experimental to Chapter 5

9.1 Procedural note

9.1.1 Fast atom bombardment (FAB) mass spectroscopy

Samples were prepared for FAB analysis in the following manner:

a) solvents were removed under reduced pressure followed by drying under vacuum;

b) a sample of the residue was dissolved in the FAB matrix medium (usually glycerol);

c) FAB spectra were obtained as soon as practicable thereafter

d) finally, in order to confirm the survival of the salt through the drying process, a sample of the residue was analysed by fluorine n.m.r. after dissolving in an appropriate solvent.

9.2 Preparation of starting materials

9.2.1 Perfluoro-*trans,trans*-3,4-dimethylhexa-2,4-diene (124)

This diene was prepared by S.J.Mullins (these laboratories) in *ca* 90% purity from available perfluorodimethylhex-3-ene (tetrafluoroethylene tetramer) using a sodium amalgam route.

9.2.2 Pentafluorophenylacetonitrile (181)

a) *Ethylcyanopentafluorophenylacetate*[180]

Over the course of 15 minutes ethylcyanoacetate (28.2g, 250mmol) was added to a stirred mixture of dimethylformamide (170ml) and anhydrous sodium carbonate (28.2g, 266mmol), contained in a round bottomed flask (1 litre), heated by means of an isomantle to 150°C. The mixture was then maintained at a temperature of 110-120°C, while hexafluorobenzene (47.2g, 254mmol) was added dropwise over a period of 25 minutes. After another 45 minutes at this temperature the solution was cooled to room temperature. The reaction mixture was then poured into ice water (1 litre) and acidified to blue litmus with sulphuric acid (20%). A lower fluorocarbon layer was separated. The aqueous layer was extracted with ether (2 X 50ml). Fractions were then combined, dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure, leaving a dark oil. This oil crystallised upon standing, yielding crude ethylcyano(pentafluorophenyl)acetate (fluorine n.m.r. spectrum in agreement with literature[180]) (38.9g crude, *ca* 139mmol, *ca* 56% yield based upon ethylcyanoacetate).

b) *Pentafluorophenylacetonitrile* (181)[180]

Aqueous acetic acid (50%, 100ml) and concentrated sulphuric acid (4ml) were added to crude ethylcyano(pentafluorophenyl)acetate (38.9g), contained in a flask (1 litre). The mixture was heated, at reflux temperature, until the evolution of carbon dioxide had ceased (21 hours). Water (100ml) was then added and the mixture was cooled in an ice bath. The lower fluorocarbon layer was removed and combined with ether (100ml), which was then washed with a little aqueous sodium hydrogen carbonate (10%). The ethereal layer was separated, and the solvent was then removed under reduced pressure. Distillation (Fischer Spaltrohr) afforded pentafluorophenylacetonitrile (181) (15.2g, 80mmol, 32% based on ethylcyanoacetate): (bp 137^{0}C, 50 mmHg) (Found: C, 46.2; H, 0.7; N, 6.4%; M^+, 207. Calc. for $C_8H_2F_5N$: C, 46.4; H, 1.0; N, 6.7%; M, 207); n.m.r. spectra (^{1}H, ^{19}F) in agreement with lit.[180]

9.2.3 (4'-Tetrafluoropyridyl)acetonitrile (182)

a) *Ethylcyano(4'-Tetrafluoropyridyl)acetate*[181]

Over the course of 10 minutes ethylcyanoacetate (20.9g, 184.4mmol) was added to a stirred mixture of dimethylformamide (160ml) and anhydrous sodium carbonate (22.0g, 208mmol), contained in a round bottomed flask (1 litre), heated by means of an isomantle to 150^{0}C. The mixture was then maintained at a temperature of 120^{0}C while pentafluoropyridine (78) (31.5g, 186.4mmol) was added dropwise over a period of 20 minutes. After an additional 3 hours at this temperature the solution was cooled to room temperature. After addition of ice water (500ml) the solution was acidified with sulphuric acid (20%). A lower fluorocarbon layer was collected, which crystallised upon standing. The aqueous layer was extracted with ether (2 X 50ml). Fractions were then combined and dried ($MgSO_4$). Volatiles were then removed under reduced pressure, leaving a dark oil identified as crude ethylcyano(4'-tetrafluoropyridyl)acetate (47.7g) [n.m.r. spectra (^{1}H, ^{19}F) number 24a].

b) *4'-(Tetrafluoropyridyl)acetonitrile* (182)

Aqueous acetic acid (50%, 100ml) and concentrated sulphuric acid (4ml) were added to crude ethylcyano(4'-tetrafluoropyridyl)acetate (44.2g), contained in a flask (1 litre). The mixture was heated at reflux temperature until the evolution of carbon dioxide had ceased (14 hours). Water (100ml) was added and the mixture was then cooled in an ice bath. A lower fluorocarbon layer was separated and the aqueous fraction was extracted with ether (1 X 50ml). Fractions were then combined, dried ($MgSO_4$), filtered, and volatiles were then removed under reduced pressure. Distillation (Fischer Spaltrohr) afforded (4'-tetrafluoropyridyl)acetonitrile (182) : (14.2g, 74.7mmol, 44% overall based upon ethylcyanoacetate) (112^{0}C, 7 mmHg): (Found: C, 44.0; H, 1.0; N, 14.7%; M^+, 190; M^-, 189. Calc for $C_7H_2F_4N_2$: C, 44.2; H, 1.1; N, 14.7%; M, 190); n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 24b.

9.2.4 Ethyl-(4'-tetrafluoropyridyl)acetate (183)

a) *Bisethyl-2-(4'-tetrafluoropyridyl)propandioate*[182]

Over the course of 10 minutes diethylmalonate (31.9g, 199mmol) was added dropwise to a stirred mixture of dimethylformamide (200ml) and anhydrous sodium carbonate (23.5g, 222mmol), contained in a round bottomed flask (1 litre), heated by means of an isomantle to 130^{0}C. Over a period of 5 minutes pentafluoropyridine (78) (34.8g, 205.9mmol) was added to the mixture which was maintained at a temperature of 130^{0}C. After 5 more hours at 130^{0}C the solution was cooled to room temperature and aqueous hydrochloric acid (10%, 300ml) was added. The mixture (brown oil with a green upper layer) was extracted with ether (3 X 100ml). Fractions were combined and dried ($MgSO_4$). Ether was removed by rotary evaporation yielding a brown oil consistent with crude bisethyl-2-(4'-tetrafluoropyridylpropandioate) (fluorine n.m.r. δ -92, int 2; δ -142, int 1; δ -146, int 1).

b) *(4'-tetrafluoropyridyl)acetic acid*

Aqueous acetic acid (50%, 300ml) and concentrated sulphuric acid (7ml) were added to the crude bisethyl-2-
-(4'-tetrafluoropyridylpropandioate), contained in a round bottomed flask (1 litre). This mixture was heated at reflux temperature for 20 hours and then the solution was cooled to room

temperature. Non-fluorinated volatiles were removed by rotary evaporation, yielding crude (4'-tetrafluoropyridyl)acetic acid.

c) *Ethyl-(4'-tetrafluoropyridyl)acetate* (183)

Absolute ethanol (400ml) and concentrated sulphuric acid (15ml) were added to the crude (4'-tetrafluorophenyl)acetic acid (as prepared above), contained in a round bottomed flask (1 litre). The solution was heated at reflux temperature for a period of 18 hours, and was then cooled to room temperature and neutralised ($NaHCO_3$). Non-fluorinated volatiles were removed by rotary evaporation. The residue was dissolved in ether (100ml), washed with water (40ml), the layers were separated, the aqueous layer was extracted with ether (1 X 20ml), and then the ethereal layers were combined, dried ($MgSO_4$) and filtered. Ether was removed by rotary evaporation. Distillation (Fischer Spaltrohr) yielded ethyl-(4'-tetrafluoropyridyl)acetate (183) (110-114^{0}C, 18mmHg) (*ca* 14g, *ca* 30% yield based upon diethylmalonate). Recorded mass 237.03908mu; ($C_9H_7F_4O_2N$ requires 237.04129mu; difference 2.2mmu; $C_9H_7F_4NO_2$ is the best reasonable match.); mass spectrum (electron impact) number 55; n.m.r. spectra (^1H, ^{19}F) number 25b; infrared spectrum number 36.

9.2.5 Perfluoro-*trans,trans*-3,4-dimethylhexa-2,4-diene (124) with benzylthiol (203)

Anhydrous sodium carbonate (2.0g, 18.7mmol) was added to a mixture of diene (124) (6.7g, 18.6mmol), benzylthiol (203) (2.3g, 18.6mmol) and acetonitrile (20ml), contained in a flask (100ml). The mixture was stirred at room temperature for 6 days. After filtration and then washing the residue with more acetonitrile, hydrocarbon volatiles were removed under reduced pressure leaving a yellow oil. This oil was transferred *in vacuo* to a cold trap. The now colourless oil was identified as an 85:15 mixture of 2-thiobenzyl-1,1,1,5,6,6,6-heptafluoro-3,4-bis(trifluoromethyl)-*trans,trans*-hexa-2,4-diene (204) (5.6g, 11.9mmol, 64% yield): n.m.r. spectra (^1H, ^{19}F, ^{13}C) number 53; and 2-thiobenzyl-1,1,1,5,6,6,6-heptafluoro-3,4-bis(trifluoromethyl)-*cis,trans*-hexa-2,4-diene (205): n.m.r. spectra (^1H, ^{19}F) number 54. For mixture: (Found: C, 38.3; H, 1.5%; M^+, 91; M^-, 375 (fragmentation). $C_{15}H_7F_{13}S$ requires: C, 38.6, H, 1.5%; M, 466);

mass spectra (electron impact, chemical ionisation, negative ion) number 42; infrared spectrum number 37.

9.3 Reactions of Dienes With Carbon Acids

9.3.1 Diene (124) with malononitrile (127)

a) *At room temperature with caesium fluoride*

Caesium fluoride (7.0g, 46.1mmol) was added to a mixture of perfluoro-*trans,trans*-3,4-dimethylhexa-2,4-diene (124) (4.5g, 12.5mmol), malononitrile (0.8g, 12.3mmol), and acetonitrile (10ml), contained in a dry round bottomed flask (250ml). An instant orange/brown colouration was produced. Analysis (fluorine n.m.r.) indicated that after 30 minutes stirring at room temperature all of the diene had reacted. Filtration and removal of volatiles under reduced pressure yielded a brown solid suitable for FAB analysis. The products were subsequently identified as a mixture of caesium (perfluoro-2-cyano-3.4.5-trimethyl-*trans.trans*-hepta-3.5-dienenitrile anion) (185) (*ca* 75%) and caesium (perfluoro-2-cyano-3.4.5-trimethyl-*cis.trans*-hepta-3.5--dienenitrile anion) (186) (*ca* 25%): [Found for mixture: M^+, 133; M^-, 407 (FAB). Cs^+ $(C_{11}F_{13}N_2)^-$ requires: M^+, 133; M^-, 407.]; Mixture mass spectra (FAB ±) number 43; n.m.r. spectra (^1H, ^{19}F, ^{13}C) numbers 56 and 57a. By following the system (fluorine n.m.r.) at room temperature over many hours, the slow appearance of a new product was observed.

b) *At reflux temperature with caesium fluoride*

Heating this mixture for one hour at reflux temperature effected the total conversion of salts (185 and 186) to the above new product. Filtration, washing the residue with dry acetone, followed by the removal of solvents under reduced pressure and recrystallisation from dry acetone, yielded a brown solid subsequently identified as 1-cyano-tetrakis-(2.3.4.5-trifluoromethyl)cyclopentadienylcaesium (188) (4.4g, 8.9mmol) (73%): (Found: M^+, 133; M^-, 362 (FAB). Cs^+ $[C_{10}F_{12}N]^-$ requires: M^+, 133; M^-, 362.); mass spectra (FAB ±) number 44; n.m.r. spectra (^{19}F, ^{13}C) number 58a; infrared spectrum number 38. Repeated elemental analyses were unsatisfactory (*e.g.* Found: C, 25.1; N, 4.2; Cs, 25.5. $C_{10}F_{12}NCs$ requires: C, 24.2; N, 2.8; Cs, 26.9%).

c) *With anhydrous sodium carbonate as base*

A mixture containing diene (124) (5.6g, 15.4mmol), malononitrile 127) (1.01g, 15.3mmol), acetonitrile (20ml), and anhydrous sodium carbonate (7.7g, 72.8mmol) was stirred at room temperature for a period of 21 hours in a round bottomed flask (100ml). Analysis (fluorine n.m.r.) indicated three species in solution, namely: salt (185) (81%); salt (186) (15%); and salt (188) (4%). The solution was then heated at 55^0C for a period of 2 hours, analysis (fluorine n.m.r.) then indicated salt (185) (67%); salt (186) (24%); salt (188) (9%).

9.3.2 Diene (124) with phenylsulphonylacetonitrile (128)

Caesium fluoride (3.2g, 21.1mmol) was added to a mixture consisting of diene (124) (0.9g, 2.5mmol), phenylsulphonylacetonitrile (128) (0.4g, 2.4mmol), and acetonitrile (10ml), contained in a round bottomed flask (50ml). After stirring at room temperature for 30 minutes, analysis (fluorine n.m.r.) revealed in solution: caesium [2-phenylsulphonyl-6,7,7,7-tetrafluoro-3,4,5-tris(trifluoromethyl)hepta-2,5-dienenitrile anion] (193) (*ca* 50%) [n.m.r. spectrum (^{19}F) number 57b.]; salt (188) (*ca* 50%); and phenylsulphonyl fluoride (194) (trace) (fluorine n.m.r. chemical shift + 65.8 ppm in CH_3CN. Lit.[167] + 65.3 ppm in $CDCl_3$). After 20 minutes at reflux temperature, analysis (fluorine n.m.r.) indicated that salt (188) was the only fluorocarbon species in solution.

9.3.3 Dienes (204 and 205) with malononitrile (127)

Caesium fluoride (0.6g, 4.1mmol) was added to a mixture of dienes (204 and 205) (85:15 ratio) (0.4g, 0.88mmol), malononitrile (127) (0.05g, 0.88mmol), and acetonitrile (10ml), contained in a flask (50ml), causing an instant yellow colouration. Fluorine n.m.r. analyses were performed after 4 hours stirring at room temperature; after a further 15 minutes at reflux temperature; then after another 15 minutes under reflux; finally after another 150 minutes under reflux. Five species were observed and identified: these were (*trans,trans*), (*cis,trans*), (*cis,cis*), and (*trans,cis*) isomers of

caesium [2-cyano-6-thiobenzyl-7,7,7-trifluoro-3,4,5-tris(trifluoro methyl)-hepta-3,5-dienenitrile anion] (206): n.m.r. spectra (^{19}F) numbers 55a, 55b, 55c, and 55d. For mixture: (Found: M^+, 133; M^-, 511 (FAB). $C_{18}H_7N_2F_{12}SCs$ requires: M^+, 133; M^-, 511); mixture mass spectra (FAB ±) number 45. The fifth component had a fluorine n.m.r. spectrum identical to that of salt (188).

Table 9.1 Variation of solution composition

	Isomers of Anion (206)				
	trans,trans	*cis,trans*	*cis,cis*	*trans,cis*	Salt (188)
4 hours 20°C	53%	34%	9%	5%	0%
8 days 20°C	38%	38%	15%	8%	3%
15 min reflux	44%	37%	17%	5%	3%
30 min reflux	30%	37%	19%	5%	8%
180 min reflux	23%	24%	10%	6%	37%

9.3.4 2-Fluoro-3-(1'-(heptafluorocyclopentyl))dimethyl but-2-en-dioate (111) with malononitrile (127)

Anhydrous sodium carbonate (2.6g, 24.5mmol) was added to a mixture of diene (111) (2.65g, 7.5mmol), malononitrile (127) (0.5g, 7.6mmol), and acetonitrile (20ml). While stirring at room temperature, for one hour, a deep red colouration developed. The mixture was filtered, the filtrate was then heated to a temperature of 55°C for a period of 3 hours; followed by maintenance at a temperature of 55°C for a further 20 hours. After each stage the solution was examined by fluorine n.m.r., with the spectra found to be similar in all cases. Filtration and removal of volatiles from a portion of the solution yielded a brown solid suitable for FAB analysis. The solution was subsequently shown to contain sodium [3-carbomethoxy-4-cyano-3-(1'-heptafluorocyclopentyl)methylpent-2-enoatenitrile anion] (195) (90% of fluorine n.m.r. integration): [Found: M^-, 399 (FAB). Na^+ $(C_{14}H_6F_7N_2O_4)^-$ requires: M^-, 399]; n.m.r. spectrum (^{19}F) number 63b; mass spectra (FAB ±) number 46.

9.3.5 Diene (124) with pentafluorophenylacetonitrile (181)

This reaction was first performed using fluorine n.m.r. to monitor the composition of the reaction solution, with respect to time, in order to optimise the yield of any transient

intermediates.

Caesium fluoride (15.7g, 103.2mmol) was added to a stirred mixture of diene (124) (7.05g, 19.5mmol), compound (181) (4.0g, 19.4mmol) and acetonitrile (15ml). A deep green colouration was produced. After 100 minutes stirring at room temperature, analysis (fluorine n.m.r.) indicated the nearly total consumption of diene (124). Filtration, washing with dry acetone (10ml), then removal solvents under reduced pressure, followed by sublimation (95^0C, 0.1mmHg) yielded a white solid (0.5g), which was subsequently identified as 5-cyano-5-pentafluorophenyl-1,2,3,4-tetrakis(trifluoromethyl)--cyclopentadiene (196) (0.95mmol, 4.8%): (Found: C, 36.0; N, 2.3%; M^+, 529, 598; M^- 460. $C_{16}F_{17}N$ requires: C, 36.3; N, 2.6%; M, 529); m.p. 66^0C; mass spectra (electron impact, chemical ionisation, negative ion) number 47; n.m.r. spectra (^{19}F, ^{13}C) number 62; infrared spectrum number 39. Analysis (fluorine n.m.r.) also indicated the further reaction of diene (196) yielding salt (188) and 1-(pentafluoro-phenyl)-2,3,4,5-tetrakis(trifluoromethyl)--cyclopentadienyl caesium (197) (see section 9.4.3) in solution.

9.3.6 Diene (124) with (4'-tetrafluoropyridyl)acetonitrile (182)

This reaction was first performed using fluorine n.m.r. to monitor the composition of the reaction solution with respect to time, in order to optimise the yield of any transient intermediate(s).

Caesium fluoride (8.5g, 55.9mmol) was added to a stirred mixture of diene (124) (4.1g, 11.4mmol), compound (182) (2.2g, 11.4mmol), and acetonitrile (10ml), contained in a round bottomed flask (100ml). An instant orange colouration was produced. After stirring at room temperature for 10 minutes the solution was filtered, washing the residue with dry acetone (50ml). The majority of the solvents were removed by careful distillation. Distilled water (20ml) was added causing crystallisation. A brown solid (2.9g) was collected. Sublimation (90^0C, 0.05 mmHg) yielded 5-cyano-5-(2',3',5',6'-tetrafluoropyridyl) -1,2,3,4-tetrakis(trifluoromethyl)cyclopentadiene (198) (2.6g, 5.1mmol, 45%); (Found: C, 35.4; F, 59.3; N, 5.8%; M^+, 512, 581. $C_{15}F_{16}N_2$ requires: C, 35.2; F, 59.4; N, 5.5%; M, 512); m.p. 73^0C; mass spectra (electron impact, chemical ionisation, negative ion)

number 48; n.m.r. spectra (^{19}F, ^{13}C) number 60; infrared spectrum number 40. In reaction mixtures that were not worked-up immediately analysis (fluorine n.m.r.) revealed the presence of, what was subsequently identified as a mixture of salt (188) and salt (199) (Section 9.3.7).

9.3.7 Diene (124) with ethyl-(4'-tetrafluoropyridyl)acetate (183)

This reaction was first performed using fluorine n.m.r. to monitor the composition of the reaction solution with respect to time.

Caesium fluoride (5.0g, 32.9mmol) was added to a stirred mixture of diene (124) (5.0g, 13.8mmol), acetate (183) (3.2g, 13.5mmol), and acetonitrile (25ml), contained in a flask (250ml). The mixture was stirred for 2 days at room temperature. After filtration volatiles were removed under reduced pressure. The remaining light brown oil was allowed to crystallise for three weeks. Washing the partially crystalline oil with chloroform yielded a white powder [3.2g, 5.2mmol, 38% based upon acetate (183)], after recrystallisation from ethanol this solid was identified as 1-(2',3',5',6'-tetrafluoropyridyl)-2,3,4,5-tetrakis(trifluoromethyl)cyclopentadienyl caesium (199): (Found: M^+, 133; M^-, 362 (FAB). $C_{14}F_{16}NCs$ requires M^+, 133; M^-, 362); n.m.r. spectra (^{19}F, ^{13}C) number 64a; mass spectra (FAB ±) number 49. Repeated elemental analyses were unsatisfactory (*e.g.* Found: C, 25.2; N, 1.7. $C_{14}F_{16}NCs$ requires: C, 27.1; N, 2.3%). Analysis (fluorine n.m.r.) after a reaction time of 45 minutes indicated the presence of ethylfluoroformate [fluorine n.m.r. δ -18.3 ppm; lit.[169] -17.5 ppm (5% solution in benzene)]. After a reaction time of one day the fluorine n.m.r. spectrum of the reaction mixture had greatly simplified. Analysis of the n.m.r. spectra tentatively indicated the presence of an acyclic intermediate [fluorine n.m.r. (weak resonances) δ -54.3 (s, int 3); -63.0 (d, int 3, J *ca* 18 Hz); -66.9 (s, int 3); -69.6 (s, int 3); -111.1 (s, int 1); -92.8 (s, int 2); -143.7 (s, int 2)], and a possible cyclopentadiene derivative [fluorine n.m.r. δ -56.8 (s, int 1); -61.8 (s, int 1); pyridyl resonances too weak for assignment]

9.3.8 Diene (124) with 4-(2',2',2'-trifluoroethyl)-
-tetrafluoropyridine (184)

Caesium fluoride (2.8g, 18.6mmol) was added to a stirred mixture of diene (124) (1.1g, 3.0mmol), compound (184) (0.7g, 3.0mmol), and acetonitrile (5ml), contained in a dry round bottomed flask (10ml) at room temperature. The solution became orange in colour and was monitored by fluorine n.m.r. over the following 45 minutes, during which time no significant change was observed. Analysis after heating to reflux temperature for 15 minutes resulted in very complex fluorine n.m.r. spectra. No products could be isolated and the reaction was not investigated further.

9.4 Other Reactions

9.4.1 Salts (185 and 186) with hydrogen chloride

a) *With aqueous hydrogen chloride*

Concentrated hydrochloric acid (2.9g) was added to a solution of anions (185 and 186) (1.6g, 3.2mmol) in acetonitrile (20ml). The resultant brown solution was extracted with ether (2 X 10ml). Volatiles were removed under reduced pressure from the ethereal solution, yielding a brown solid. Sublimation (110^0C, 0.005 mmHg) yielded a white solid which was identified as an isomer of 4-carboxy-2-cyano-6,7,7,7-tetrafluoro-3,5-bis(trifluoromethyl) hepta-2,5-dienenitrile (192)): (0.2g, 0.5mmol, 16% yield) (Recorded mass 383.98192mu; $C_{11}H_2F_{10}N_2O_2$ requires 383.99577mu; difference 13.7 mmu; $C_{11}H_2F_{10}N_2O_2$ is the best reasonable match); m.p. *ca* 160^0C (decomposition); mass spectra (electron impact, chemical ionisation, negative ion) number 50; n.m.r. spectra (^{1}H, ^{19}F, ^{13}C) number 52b; infrared spectrum number 41.

b) *With anhydrous hydrogen chloride*

Anhydrous hydrogen chloride gas was bubbled into a solution (brown) of salts (185 and 186). After saturation, the solution (red) was filtered to remove a white precipitate. Volatiles were removed under reduced pressure yielding a brown solid which on sublimation (50^0C, 0.05 mmHg) yielded a light yellow solid believed to be a mixture of isomers of 2-cyano-6,7,7,7-tetrafluoro-3,4,5-tris(trifluoromethyl)hepta-2,5--dienenitrile (191) (Complex fluorine n.m.r.). After standing for

7 days, analysis [Mass spectra (electron impact, chemical ionisation, negative ion); n.m.r. (^{19}F); and infrared] indicated that the solid had hydrolysed to carboxyl ic acid (192).

9.4.2 Sublimate (191) with fluoride ion

Caesium fluoride (1.9g, 12.4mmol) was added to a solution of freshly prepared sublimate (191) (0.19g, 0.5mmol) in dry acetonitrile (10ml), contained in a round bottomed flask (100ml) equipped with a reflux condenser. After stirring for 10 minutes at reflux temperature analysis (fluorine n.m.r.) indicated that the solution contained: salt (185) (35%); salt (186) (25%); and salt (188) (40%). After further refluxing (total of 4 hours) analysis (fluorine n.m.r.) indicated that salt (188) was the only fluorocarbon species in solution.

9.4.3 Dienes (196) and (198) with caesium fluoride

Two mixtures were prepared simultaneously

Experiment a) *Diene* (196)

Caesium fluoride (0.7g, 4.9mmol) was added to a solution of diene (196) (0.0489g, 0.092mmol) in acetonitrile (3ml), contained in a dry vessel. The initially colourless solution became green.

Experiment b) *Diene* (198)

Caesium fluoride (0.85g, 5.6mmol) was added to a solution of diene (198) (0.0562g, 0.110mmol) in acetonitrile (3ml), contained in a dry vessel. The initially colourless solution became orange.

Both vessels were stirred for a period of 630 minutes at room temperature. The solutions were then filtered and volatiles were removed under reduced pressure. After adding fresh solvent the solutions (now both orange in colour) were then examined by fluorine n.m.r. and mass spectroscopy (FAB ±).

By comparison of spectra with authentic samples solution (a) was shown to contain principally a mixture of salt (188) (52%) and salt (197) (48%) (proportions based upon n.m.r. integrals): (Found: M^+, 133; M^-, 503. $C_{15}F_{17}Cs$ requires: M^+, 133; M^-, 503);

mass spectrum (FAB ±) number 51; n.m.r. spectrum (^{19}F) number 58b. Solution (b) was shown to contain principally a mixture of salt (188) (27%) and salt (199) (73%).

9.4.4 Salt (188) with sulphuric acid

Crude salt (188) (2.3g, 4.6mmol) was mixed with concentrated sulphuric acid (26.9g), contained in a flask (50ml), yielding a light brown solution. Analysis (fluorine n.m.r.) indicated that the solution contained a mixture of two isomers of 2-cyano-tetrakis-(1.2.3.5-trifluoromethyl)cyclopentadiene (208): n.m.r. spectrum (^{19}F) number 59. The solution was diluted with water and extracted with ether. Much of the ether was then removed by rotary evaporation, yielded a solution which was examined by GC/MS. The possible presence of an isomer of 2-cyano-5-carboxy-tris(2.3.4-trifluoromethyl)cyclopentadiene (209) was indicated: Mass spectrum: Negative ion M^-, 338 fragmentation: 19 (F). $C_{10}H_2F_9NO_2$ requires: M, 339).

9.4.5 Anion (188) with boron trifluoride etherate

Boron trifluoride etherate (0.5ml) was added to a mixture of salts (188) and (199) (0.1g). Analysis (fluorine n.m.r.) of the solution indicated no change in the anionic spectra.

9.4.6 Attempted reaction between salt (188) and pentafluoropyridine (78)

a) *At* 140 *degrees centigrade*

Pentafluoropyridine (78) (5.1g, 30,2mmol) was added to a solution of salt (188) (1.4g, 2.8mmol) dissolved in dry tetraglyme (20ml), contained in a round bottomed flask (100ml), maintained at a temperature of 140°C. After 4 hours at 140°C analysis (fluorine n.m.r.) indicated the presence of unchanged starting materials only.

b) *At* 190 *degrees centigrade*

Salt (188) (0.09g, 0.2mmol) and pentafluoropyridine (78) (0.24g, 1.4mmol) were sealed in a quartz tube (4mm external diameter). The tube was then heated in an oil bath to 190°C for 140 minutes. Analysis (fluorine n.m.r.) indicated the presence of unchanged starting materials only.

9.4.7 Kinetics of reaction of diene (124) with malononitrile (127)

Caesium fluoride (7.5g, 49mmol) was added to a mixture of diene (124) (2.1g, 5.7mmol), malononitrile (127) (0.4g, 5.8mmol) and acetonitrile (5ml), contained in a round bottomed flask (100ml). After 10 minutes stirring at room temperature, a sample of the mixture (including a little solid caesium fluoride) was transferred into an n.m.r. tube (5mm). The solution was then monitored by high field fluorine n.m.r. operating in the variable temperature mode at 35°C. The first spectrum recorded indicated that all of the added diene (124) had already reacted. Subsequent spectra were automatically acquired at preset time intervals. Salts (185), (186), and (188) were observed in the solution. Table 9.2 shows the variation of the fluorine n.m.r. resonance integrations during the observation period.

Table 9.2 Fluorine n.m.r. integrations changing with time

Time (mins)	Salt (185)	Salt (186)	Salt (188)
0	160	28	8
30	158	32	10
50	156	35	12
80	156	35	16
100	152	35	16
140	152	38	18
180	147	39	21
210	144	40	21
240	139	39	22
270	143	42	23
300	141	43	25
330	138	42	27
360	133	43	27

Please note in tables 9.2 and 9.3 arbitrary fluorine n.m.r. integrals are measured in mm. The time is measured in minutes from the first n.m.r. observation.

In the following table the following abbreviations are used:

t_1	the time at the start of an arbitrary *ca* 150 minute period;
t_2	the time at the end of an arbitrary *ca* 150 minute period;
Δt	the time interval between t_1 and t_2 in minutes;
Δ[Salt (188)]	the increase in the n.m.r. integration due to salt (188) during this period;
$\overline{[\text{Salt}_{(186)}]}$	the average n.m.r. integration of salt (186) during this period;
k	the approximate 1st order rate constant calculated for this period;
K	the apparent equilibrium constant between salt (185) and salt (186) during this period.

Now from the first order rate equation:

$$\text{Rate} = k \times \overline{[\text{Salt}_{(186)}]} \times {}^{12}/_{13}$$

Where multiplying by a factor of ${}^{12}/_{13}$ corrects for the different number of fluorine atoms in salt (186) compared with salt (188), allowing the use of integration data to represent concentrations. Expressing rate as a change in concentration with respect to time:

$$\frac{d[\text{Salt (188)}]}{dt} \approx \frac{\Delta[\text{Salt (188)}]}{\Delta t} = k \times \overline{[\text{Salt}_{(186)}]} \times {}^{12}/_{13}$$

Assuming that Δt and Δ[Salt (188)] are small.
Rearranging allows the calculation of k in table 9.3.

Table 9.3 Analysis of data

t_1	t_2	Δt	Δ[Salt (188)]	$\overline{[\text{Salt}_{(186)}]}$	k ($\times 10^3 s^{-1}$)	$\overline{[\text{Salt}_{(185)}]}$	K
0	140	140	10	34	2.28	156	0.22
30	180	150	11	36	2.21	154	0.23
50	210	160	9	37	1.65	151	0.25
80	240	160	6	38	1.07	148	0.26
100	270	170	7	39	1.14	146	0.27
140	300	160	7	40	1.18	144	0.28
180	330	150	6	41	1.06	142	0.29
210	360	150	6	42	1.03	140	0.30

Discounting the results with $t_{\frac{1}{2}}$ less than 80 minutes, due to inaccuracies caused by the small [salt (188)] values, enables the calculation of a mean k value of *ca* 1.1 X 10^{-3} min^{-1}.

Given[175] $t_{\frac{1}{2}} = (1/k) \ln 2$

Hence, the half life of the reaction can be calculated to be *ca* 630 minutes.

9.4.8 Attempted Diels-Alder reaction of diene (198) with cyclohexene

Diene (198) (0.5g, 1.0mmol) and cyclohexene (0.2g, 2.4mmol) were introduced into a dry quartz tube (5mm external diameter), which was then sealed. The tube was heated enclosed in a metal jacket, within an oil bath, to a temperature of 190°C, in the dark, for a period of 6 hours. After this time the tube was cooled and opened, yielding a brown solution. Removal of cyclohexene by distillation, followed by recrystallisation of the residue, from ether, yielded a white solid subsequently identified as 1-cyano-2-(2',3',5',6'-tetrafluoropyridyl)-1,3,4,5-tetrakis(trifluoromethyl)cyclopentadiene (210) (0.6g, 74%) : (Found: C, 35.1; N, 5.5%; M^+, 512; $C_{15}F_{16}N_2$ requires C, 35.2; N, 5.5%; M, 512; m.p. 73°C; mass spectra (electron impact, chemical ionisation, negative ion) number 52; n.m.r. spectra (^{19}F, ^{13}C) number 61; infrared spectrum 42.

9.4.9 Diene (198) heated with added caesium fluoride (solvent free)

Diene (198) (0.17g, 0.33mmol) and caesium fluoride (0.04g, 0.26mmol) were introduced into a quartz tube (5mm external diameter). This tube was heated to 110°C for 1 hour, in the dark. Analysis (fluorine n.m.r.) showed that no change had occurred. The tube was then heated to 150°C for 6 hours, after cooling analysis (fluorine n.m.r.) of the resulting black solid indicated that very little isomerisation had occurred (at least 95% of the fluorine n.m.r. integration related to starting material).

9.4.10 Diene (198) with caesium fluoride in acetonitrile

Diene (198) (0.08g, 0.16mmol), acetonitrile (0.5ml), and caesium fluoride (0.5g, 3.2mmol) were introduced into a dry round bottomed flask (5ml). The flask was sealed, and the contents were stirred at room temperature for a period of 18 hours. Subsequent analysis (fluorine n.m.r.) indicated a *ca* 3:1 mixture of salt (199) and an ion tentatively identified as 5-cyano-1-(tetrafluoropyridyl)-2,3,4-tris(trifluoromethyl)cyclopentadienyl caesium (213): n.m.r. spectrum (^{19}F) number 64b. FAB (±) spectra number 53 was recorded of the mixture indicating the presence of salt (199) (M^-, 486); salt (213) (M^-, 443) and various other species, possibly including ion aggregates.

9.4.11 Thermal isomerisation of diene (196)

Diene (196) (0.0399g, 0.075mmol) and cyclohexene (0.05g, 0.71mmol) were introduced into a dry quartz tube (4mm external diameter). After sealing the tube was heated to a temperature of 190^{0}C in an oil bath for a period of 3 hours, in the dark. The tube was then cooled, and opened yielding a brown solution. Removal of cyclohexene under reduced pressure followed by recrystallisation, from freon-11, yielded a white solid subsequently identified as 5-cyano-1-(pentafluorophenyl)-2,3,4,5-tetrakis(trifluoromethyl)cyclopentadiene (211) (0.0275g, 0.052mmol, 69%):(Recorded mass 528.93881 mu; $C_{16}F_{17}N$ requires 528.97593 mu; difference 37.1 mmu; $C_{16}F_{17}N$ is the best reasonable match); mass spectra (electron impact, chemical ionisation, negative ion) number 54; n.m.r. spectra (^{19}F, ^{13}C) number 63a.

Appendix I - N.M.R. Spectra

1a. Perfluoro-3-methyl-2,1-benzisoxazole (88)
1b. 2H-hexafluoroisopropyl silver (96)
2a. Perfluoro-1-nitro-4-(2'H-hexafluoroisopropyl)benzene (87)
2b. Caesium salt (93)
2c. Perfluoro-1-nitro-4-(2',2',2'-trifluoroethyl)benzene (89)
3a. Perfluoro-4-(2H-hexafluoroisopropyl)pyridine (79)
3b. Caesium salt (91)
3c. Tetrafluoro-4-(2,2,2-trifluoroethyl)pyridine (80)
4. Benzonitrile derivative (85)
5. Caesium salt (94)
6a. Perfluoro-4-(2H-hexafluoroisopropyl)benzonitrile (83)
6b. Caesium salt (94)
7a. 4-(2',2',2'-trifluoroethyl)benzonitrile (84)
7b. Caesium salt (97)
8a. Pyridyl-but-2-en-1,4-dioate derivative (106)
8b. Pyridyl-but-2-en-1,4-dioate derivative (107)
9. *trans*- compound (112)
10. *cis*- compound (111)
11. *trans*- compound (114)
12a. *cis*- compound (115)
12b. Compound (116)
13. Compound (117)
14. Thiophene derivative (118)
15. 1,6-Benzodioxocin derivative (121)
16. 1,6-Benzodithiocin derivative (123)
17. 4'-Tetrafluoropyridylmalononitrile (129)
18. Caesium salt (130)
19. Phenylsulphonylacetonitrile pyridine derivative (171)
20. Caesium salt (170)
21. Methyl-(4'-tetrafluoropyridyl)malononitrile (179)
22a. Decafluoro(bis-4'-pyridyl)malononitrile (177)
22b. Decafluoro(bis-4'-pyridyl)acetonitrile (178)
23a. Malononitrile derivative (133)
23b. Caesium salt (134)
24a. Ethylcyano-(4'-tetrafluoropyridyl)acetate
24b. 4'-Tetrafluoropyridylacetonitrile (182)
25. Ethyl-(4'-tetrafluoropyridyl)acetate (183)

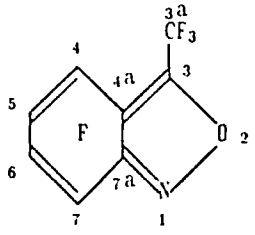
26. Malononitrile derivative (131)
27. Caesium salt (132)
28. Pyridazyl-ylidene-malononitrile derivative (135)
29. Caesium salt (136)
30. Isopropyl-pyridazyl-ylidene-malononitrile derivative (137)
31. caesium salt (138)
32. Methyl-(4'-trifluoropyridazyl)malononitrile (135)
33. Acetonitrile derivative (171)
34. caesium salt (170)
35. Pyrimidyl-ylidene-malononitrile derivatives (139 & 141)
36. Caesium salt (140)
37. Caesium salt (143)
38. Caesium salt (142)
39. (3',5',6'-trifluoropyazyl)malononitrile (144)
40. Potassium triazyl malononitrile derivative (146)
41. Hydrolysate (169)
42. 1'-(Nonafluorobiphenyl)malononitrile (149)
43. Caesium salt (150)
44. Phenylsulphonylacetonitrile derivative (175)
45. Caesium salt (174)
46. 1,4'-(octafluorobiphenyl)bismalononitrile (151)
47. Dicaesium salt (152)
48. β-Heptafluoronapthylmalononitrile (153)
49. Caesium salt (154)
50. 1'-(hexafluoroisoquinyl)malononitrile (147)
51. Potassium salt (148)
52a. Perfluoro-*trans*,*trans*-3,4-dimethylhexa-2,4-diene (124)
52b. Carboxylic acid (192)
53. Thiobenzyl sustituted *trans*,*trans*- diene (204)
54. Thiobenzyl sustituted *cis*,*trans*- diene (205)
55. Four isomers of caesium salt (206)
56. *trans*,*trans*-Pentadienyl caesium salt (185)
57a. *cis*,*trans*-Pentadienyl caesium salt (186)
57b. *trans*,*trans*-Pentadienyl caesium salt (193)
58a. Caesium cyclopentadienide derivative (188)
58b. Caesium cyclopentadienide derivative (197)
59. Isomers of cyclopentadiene derivative (208)
60. Cyclopentadiene derivative (198)
61. Cyclopentadiene derivative (210)

62. Cyclopentadiene derivative (196)
63a. Cyclopentadiene derivative (211)
63b. Sodium pentadienyl anion (195)
64a. Caesium cyclopentadienide derivative (199)
64b. Caesium cyclopentadienide derivative (213)

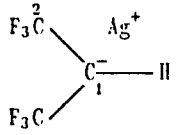
N.m.r. spectra of salts and of their conjugate acids were recorded in d_6-acetone solution, other spectra were recorded in *d*-chloroform solution. All spectra were recorded using a Brücker AC 250 spectrometer. Reference compounds (^{19}F - $CFCl_3$, ^{13}C & ^{1}H - Me_4Si) were used internally.

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a) (in $CDCl_3$)				
^{19}F n.m.r.				
- 63.3	d	*ca* 9.2	3	3a
-138.7	m		1	4
-157.0	m (overlapping)		2	5 & 6
-146.8	m		1	7
^{13}C n.m.r.				
148.7	q	41.4		3
118.8	q	272.4		3a
138.3	ddd	271.3, 13.4, 3.7		4
104.8	d	19.3		4a
143.6	dt	261.9, 14.3		5
138.7	dt	253.8, 14.6		6
132.6	ddd	258.8, 14.0, 4.9		7
148.9	m			7a
Compound (b) (in $CDCl_3$)				
^{19}F n.m.r.				
- 52.0	d	13.2		2
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
32.9	d hept.	126.3, 40.3		1
130.9	q	270		2

Spectra #1a

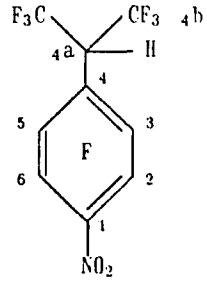


Spectra #1b

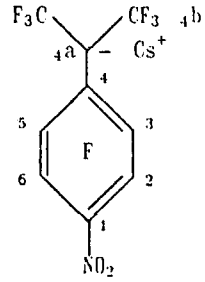


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a) (in $CDCl_3$)				
^{1}H n.m.r.				
4.8	heptet	*ca* 8 Hz		4a
^{19}F n.m.r.				
- 64.0	s		6	4b
-145.0	s		1	2 or 6
-145.2	s		1	2 or 6
-133.8	s		1	3 or 5
-135.2	s		1	3 or 5
Salt (b) (in tetraglyme)				
^{19}F n.m.r.				
- 49.1	s		6	4b
-147.1	s		2	Aromatic-F
-150.2	s		2	Aromatic-F
Compound (c) (in $CDCl_3$)				
^{19}F n.m.r.				
- 65.0	s		3	4b
-147.2	s		2	2 & 6
-138.4	s		2	3 & 5

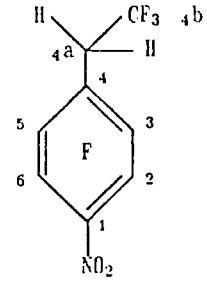
Spectra #2a



Spectra #2b

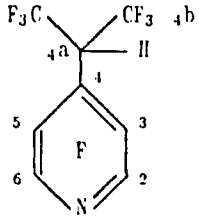


Spectra #2c

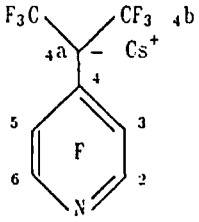


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a) (in $CDCl_3$)				
^{19}F n.m.r.				
- 64.5	s		6	4b
- 90.0	s		2	2 & 6
-138.5	s		1	3 or 5
-140.3	s		1	3 or 5
Salt (b) (in tetraglyme)				
^{19}F n.m.r.				
- 47.8	s		6	4b
-102.3	s		2	2 & 6
-151.1	s		2	3 & 5
Compound (c) (in $CDCl_3$)				
^{1}H n.m.r.				
3.6	q	9.6		4a
^{19}F n.m.r.				
- 65.8	s		3	4b
- 91.8	s		2	2 & 6
-142.9	s		2	3 & 5

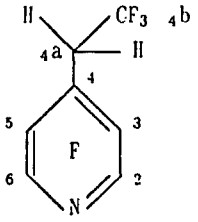
Spectra #3a



Spectra #3b

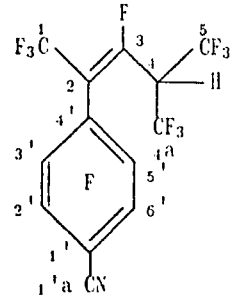


Spectra #3c



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
5.1	d heptet	(F3) 28.4, 7.3 (F4a,F5)		4
^{19}F n.m.r.				
- 60.0	d	(F3) 20.2	3	1
- 91.6	s (broad)		1	3
- 63.9	s		6	4a & 5
-131.6	m (4 lines)		2	2' & 6'
-135.7	s (broad)		2	3' & 5'
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
121.3	q	275.3		1
110.5	dm	(F3) *ca* 38, *ca* 16 (F1, F3',F5')		2
156.8	d	288.0		3
50.0	dm	135.8, (8+ lines in m)		4
122.0	q (broad)	285.2		4a & 5
98.5	t (sharp)	*ca* 19 (F2')		1'
107.7	t	*ca* 3.5 (F2')		1'a
146.1	ddt	253.5, 14.7, 3.2		Aromatic C-F
150.0	ddt	260.6, 16.4, 4.7		Aromatic C-F
112.7	t (broad)	*ca* 38 (F3')		4'

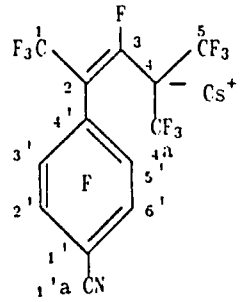
Spectra #4



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
(in CH_3CN)				
^{19}F n.m.r.				
- 50.9	m (broad)		3	1
- 77.3	decet	18.8 (8+ lines visible)	1	3
- 51.1	dd	18.7	6	4a & 5
-137.1	m	(8+ lines)	2	2' & 6'
-136.9	m (broad)		2	3' & 5'
^{13}C n.m.r.				
126.3	q	267.9		1
108.7 (partially obscured)		108.7		2
168.9	d	264.4		3
ca 69.4	m (7+ lines)	*ca* 35		4
127.6	q	265.1		4a & 5
89.7	t	19.4		1'
109.2	s			1'a
146.3	d	245.6		Aromatic C-F
147.7	dd	253.3, *ca* 15.3		Aromatic C-F

4' not observed nor assigned

Spectra #5

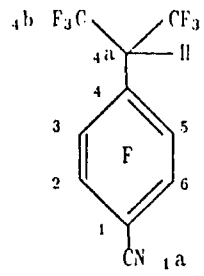


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a) (in $CDCl_3$)				
^1H n.m.r.				
4.8	heptet	7.7		4a
^{19}F n.m.r.				
- 64.3	m		6	4b
-129.9	s		1	2 or 6
-130.6	s		1	2 or 6
-132.0	m		1	3 or 5
-137.6	s		1	3 or 5
^{13}C n.m.r. (Broad band proton decoupled)				
97.3	m			1
106.3	s			1a
145.6	d	261.0		2
147.2	dm	264.0		3 or 5
147.6	dm	260.1		3 or 5
112.3	t	*ca* 14		4
46.2	heptet	33.1		4a
121.5	q	283.5		4b

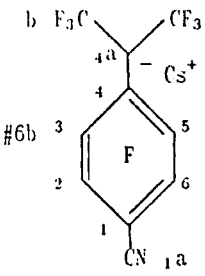
Compound (b) (in $CDCl_3$)

^{19}F n.m.r.				
- 48.1	s		6	4b
-142.1	s		2	Aromatic-F
-145.3	s		1	Aromatic-F

Spectra #6a

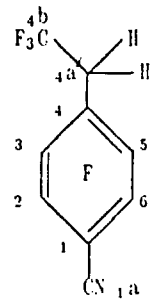


Spectra #6b

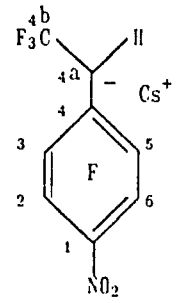


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a)				
^{1}H n.m.r.				
3.7	q	9.1		4a
^{19}F n.m.r.				
- 65.8	s		3	4b
-132.2	m		2	
-138.2	m		2	
Compound (b) (tentative)				
^{19}F n.m.r.				
-147.0	s (obscured)		2	2 & 6
-134.9	s		1	3 or 5
-135.3	s		1	3 or 5
- 56.7	d	134	3	4b

Spectra #7a

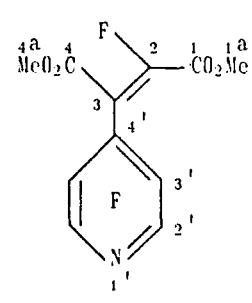


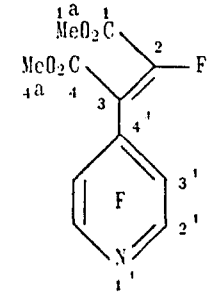
Spectra #7b



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
(Observed as an impure mixture in $CDCl_3$)				
^{1}H n.m.r. (mixture)				
3.6 to 4.0	m			O-CH_3
Trans Isomer (58%) (a)				
^{19}F n.m.r.				
- 97.0	s		1	2
- 91.7	m		2	2'
-140.5	m		2	3'
Cis Isomer (42%) (b)				
^{19}F n.m.r.				
- 98.6	m		1	2
- 90.7	m		2	2'
-138.7	m		2	3'

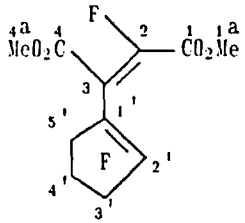
Spectra #8a, Spectra #8b





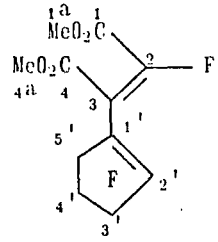
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
(in $CDCl_3$)				
^{1}H n.m.r.				
4.0	s		1	1a or 4a
4.1	s (broad)		1	1a or 4a
^{19}F n.m.r.				
- 93.1	s		1	2
-122.8	m		1	2'
-119.8	d	*ca* 14 (^{3}J F2')	2	3'
-129.8	s		2	4'
-109.1	d	*ca* 10 (F2')	2	5'
^{13}C n.m.r. (Broad band proton decoupled)				
158.6	d	34.1 (^{2}J F2)		1
53.8	s			1a & 4a
153.8	d	297.6		2
160.6	s			4
106.1	tdd (^{2}J F5'),(F2' 48.5, 24.7, 4.2 (F2)			1'
157.5	dtm	*ca* 310, *ca* 45 (^{2}J F3')		2'
ca 114	tm	*ca* 257 (overlapping)		3',4', & 5'

Spectra #9



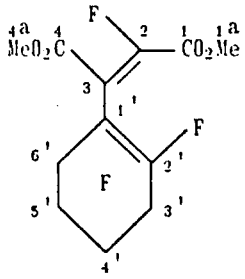
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
(in $CDCl_3$, as a mixture with *trans*-isomer)				
^{1}H n.m.r.				
4.0	s		1	1a or 4a
4.1	s (broad)		1	1a or 4a
^{19}F n.m.r.				
-101.8	m	*ca* 17	1	2
-115.6	m		1	2'
-119.0	d	*ca* 15 (^{3}J F2')	2	3'
-130.3	s		2	4'
-108.0	t	12.6 (F2')	2	5'

Spectra #10



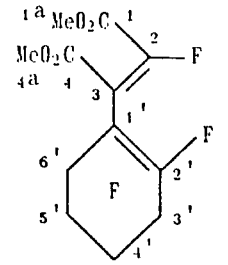
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
(Recorded in $CDCl_3$, at 298K)				
^{1}H n.m.r.				
3.9	s			1a & 4a
^{19}F n.m.r.				
- 93.3	s (very sharp)		1	2
-118.8	s (sharp)		1	2'
-120.3	s (very broad)		2	3'
-134.4	s (very broad)		4	4' & 5'
-110.1	s (very broad)		2	6'
^{13}C n.m.r. (Broad band proton decoupled)				
158.3	d	*ca* 21 (^{2}J F1)		1
53.5	s			1a & 4a
153.7	d (sharp)	297		2
160.4	s			4
150.1	d (broad)	255.4		2'
100 to 115	t (broad, overlapping)			3',4', 5',6'

Spectra #11

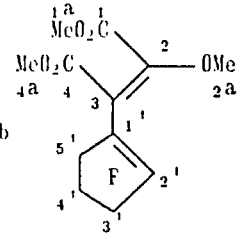


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a) (2:7 mixture with *trans*-isomer in $CDCl_3$)				
^{1}H n.m.r.				
3.9				1a & 4a
^{19}F n.m.r.				
- 98.8	s (very sharp)		1	2
-115.0	s		1	2'
-119.8	s		2	3'
-134.4	s		2	4' or 5'
-134.6	s		2	4' or 5'
-109.5	s		2	6'
Compound (b) (In $CDCl_3$ as a mixture with 2'-methoxy isomer)				
^{1}H n.m.r.				
3.9	s		1	1a or 4a
4.0	s		1	1a or 4a
4.2	s		1	2a
^{19}F n.m.r.				
-123.5	m		1	2'
-120.2	d	14.1 (^{3}J F2')	2	3'
-131.4	s		2	4'
-109.8	d	10.1 (^{4}J F2')	2	5'

Spectra #12a

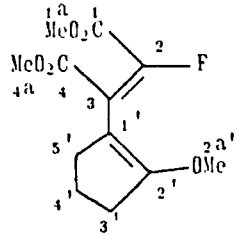


Spectra #12b



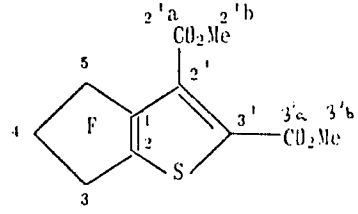
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
	(in $CDCl_3$)			
^{1}H n.m.r.				
3.9	s		1	1a or 4a
4.0	s		1	1a or 4a
4.2	s		1	2'a
^{19}F n.m.r.				
-106.4	s		3	2 & 5'
-114.9	s		2	3'
-130.3	s		2	4'
^{13}C n.m.r.	(Broad band proton decoupled)			
159.1	d	30.8 (^{2}J F2)		1
53.6	s			1a & 4a
151.0	d	286		2
111.5	d	*ca* 35 (^{2}J F2)		3
163.1	d	10.0 (^{3}J F2)		4
ca 106.0	m			1'
154.2	t	*ca* 19 (^{2}J F3')		2'
59.6	s			2'a
112.3	tt	261, 25.6 (^{2}J F4')		3' or 5'
115.3	tt	257, 24.2 (^{2}J F4')		3' or 5'
110.1	tp	273, 24.6 (^{2}J F3', ^{2}J F5')		4'

Spectra #13



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
4.1	s (broader)		1	2'b
4.0	s (sharp)		1	3'
^{19}F n.m.r.				
-102.7	s		1	3 or 5
-106.8	s		1	3 or 5
-124.8	s		1	4
^{13}C n.m.r.	(Broad band proton decoupled)			
140.0	m			1 or 2
141.4	m			1 or 2
109 to 118	t (overlapping)			3,4 & 5
144.4	s			2'
159.6	s			2'a or 3'a
160.7	s			2'a or 3'a
53.4	s			2'b or 3'b
53.7	s			2'b or 3'b
131.1	s			3'

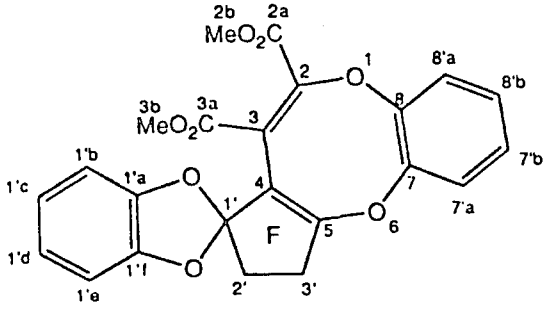
Spectra #14



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
3.4	s		3	2b or 3b
3.8	s		3	2b or 3b
6.9	s		4	Ar-H
7.1	m		1	Ar-H
7.2	m		2	Ar-H
7.4	d		1	Ar-H
^{19}F n.m.r.				
-130.0	s		2	2'
-118.4	s		1	3'
^{13}C n.m.r. (Broad band proton decoupled)				
161.4	s			2 or 3
163.1	s			2 or 3
52.9	s			2a or 3a
53.2	s			2a or 3a
111.3	tt	270.6, 22.2		2' or 3'
112.7	tt	259.4, 25.5		2' or 3'

Aromatic C-H resonances at 109.1, 121.9, 122.9, 124.7, 126.0, 127.6 ppm
Others at 114.6, 143.6, 145.0, 146.5, 149.0, 149.3 ppm

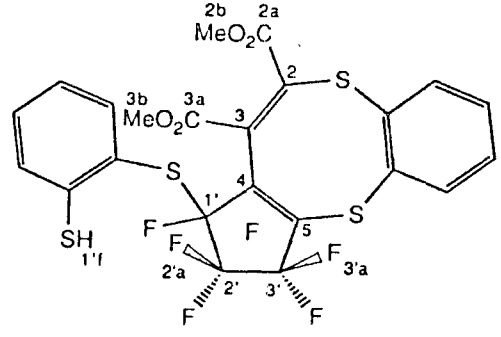
Spectra #15



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
3.8	s		3	2b or 3b
3.9	s		3	2b or 3b
5.5	s		1	1'f
7.1	m	(overlapping)	7	aromatic C-H
7.2	m		1	aromatic C-H
^{19}F n.m.r. (Some second order character)				
-121.1	s (broad)		1	1'
-111.3	dt	258.4, 16.0	1	2'
-125.4	dt	258.2, 12.7	1	2'
-114.7	dd	221.2, 12.0	1	3'above
-128.6	ddd	223.1, 13.9, 5.2	1	3'below
^{13}C n.m.r. (Broad band proton decoupled)				
169.0	s			2a or 3a
167.4	s			2a or 3a
53.8	s			2b or 3b
54.9	s			2b or 3b
134.6	d	*ca* 26		4
121.9	s			Aromatic C-H
126.7	s			Aromatic C-H
150.6	d	*ca* 290		1'
112.2	t	*ca* 260		2' or 3'
114.2	t	*ca* 270		2' or 3'

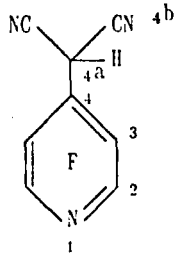
Unassigned others at 136.9, 118.3, 70.3 ppm + some obscured

Spectra #16



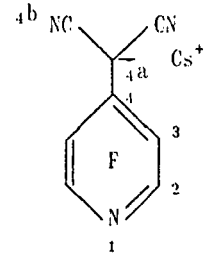
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
5.4	s			4a
^{19}F n.m.r.				
- 84.8	s		1	2
-139.9	s		1	3
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
144.5	dt	248.3, 15.0 (^{2}J F3)		2
141.6	dd	252.1, 36.8 (^{2}J F2)		3
121.5	m			4
18.9	d	141.8		4a
110.4	s			4b

Spectra #17



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
-100.1	s		1	2
-152.7	m		1	3
^{13}C n.m.r.				
144.6	dt	234, 15.9 (^{2}J F3)		2
133.9	dm	263		3
122.3	(couplings obscured)			4
(not observed)[1]				4a
122.2	s			4b

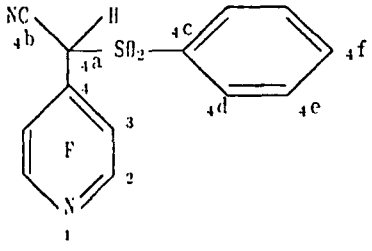
Spectra #18



[1] Presumably under acetone CD_3 peak at *ca* 30ppm

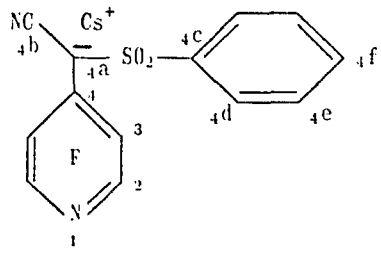
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
6.6	s		1	4a
7.8	t	7.7	2	4e
7.9	(obscured)		3	4d & 4f
^{19}F n.m.r.				
- 90.2	m		1	2
-139.7	m		1	3
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
144.4	dtm	244.7, 15.6 (^{2}J F3)		2
141.5	dd	265.5, 36.0 (^{2}J F2)		3
120.9	t	12.9 (^{2}J F3)		4
53.6	d	149.3		4a
111.2	d	10.6 (^{2}J H4a)		4b
135.4	t	small (^{2}J H4d)		4c
130.8	dm	*ca* 168		4d & 4e
137.3	dt	164.0, 7.3 (^{2}J H4e)		4f

Spectra #19



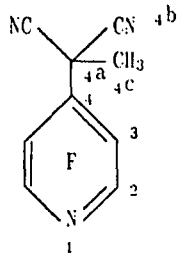
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
7.5	s		3	4d & 4f
8.0	s		2	4e
^{19}F n.m.r.				
- 98.2	m		1	2
-143.1	m		1	3
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
144.6	dt	237.1, 17.8 (^{2}J F3)		2
136.6	dd	248.6, 31.0 (^{2}J F2)		3
133.4	m			4
58.3	s			4a
123.5	s			4b
149.1	s			4c
126.2	d	163.7		4d
129.1	dd	162.6, small		4e
131.6	d	168.6		4f

Spectra #20



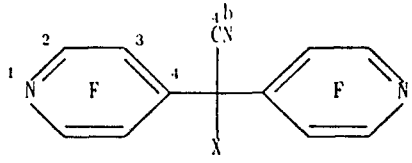
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
2.5	d	5.4 (J F3)		4c
^{19}F n.m.r.				
- 89.6	m (6+ lines)		1	2
-139.4	m (6+ lines)		1	3
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
145.1 (overlapping)	dt	244.2, 16.2 (^{2}J F3)		2
140.7 (overlapping)	dd	263.1, 37.2 (^{2}J F2)		3
126.1	s			4
71.3	s			4a
113.8	s			4b
26.6	d	136.9		4c

Spectra #21



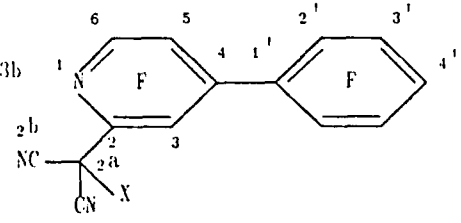
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound a (X = CN)				
^{19}F n.m.r.				
- 88.4	d	(^{3}J F3) 7.8	1	2
-137.8	d	(^{3}J F2) 7.8	1	3
^{13}C n.m.r.				
145.0	d	240.9		2
140.7	dd	266.1, *ca* 37 (^{2}J F2)		3
122.6	s			4
(not observed in this weak spectrum)				4a
109.0	s			4b
Compound b (X = H) (as a mixture with last compound)				
^{19}F n.m.r.				
- 86.3	s		1	2
-140.6	s		1	2
^{13}C n.m.r. (Broad band proton decoupled)				
ca 145	d	*ca* 240		2
ca 140.7	dd	*ca* 260, 36 (^{2}J F2)		3
125.2	s			4
23.3	s			4a
113.1	s			4b

Spectra #22a, Spectra #22b



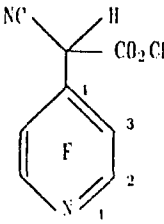
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
Compound a (X = H)				
^{1}H n.m.r.				
6.5	s			2a
^{19}F n.m.r.				
-121.1	m		1	3
-130.0	m		1	5
- 86.2	t	7.1 (F3,F5)	1	6
-137.4	s		2	2'
-161.2	t	5.0 (F2',F4')	2	3'
-149.5	t	5.5 (F3')	2	4'
Compound b (X = Cs)				
^{19}F n.m.r. (Some second order character in phenyl ring)				
-128.3	dq	(F6) 31.5, 8.0 (F5,F2')	1	3
-158.6	dq	(F6) 26.9, 7.4 (F3,F2')	1	5
- 92.3	dd	(F3) 31.5, 27.0 (F5)	1	6
-138.5	dm	14.3 (F3')	2	2'
-162.4	dd	(F4') 20.4, 14.4 (F2')	2	3'
-152.5	tt	(F3') 20.5, 2.8 (F2')	1	4'

Spectra #23a, Spectra #23b

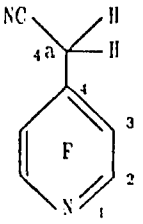


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
Compound a (crude, neat)				
^{1}H n.m.r.				
1.4	t	7.1 (^{3}J CH_2)	3	CH_3
4.4	q	7.1 (^{3}J CH_3)	2	CH_2
^{19}F n.m.r.				
- 90.3	s		1	2 or 6
- 90.7	s		1	2 or 6
-141.3	s		1	3 or 5
-142.2	s		1	3 or 5
Compound b				
^{1}H n.m.r.				
4.2	t	*ca* 1.1 (F3)	1	4a
^{19}F n.m.r.				
- 91.5	(complex second order)		1	2
-143.1	(complex second order)		1	3
^{13}C n.m.r. (Proton coupled)				
144.1	dt	242.9, 13.6 (^{2}J F3)		2
141.6	ddt	259.3, 35.3, 4.5 (^{2}J F2), (H4a)		3
125.9	m			4
12.9	t	140.5		4a
115.0	t	10.9 (^{2}J H4a)		4b

Spectra #24a

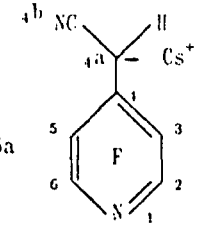


Spectra #24b

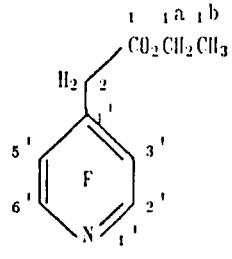


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound a				
^{1}H n.m.r.				
3.1 (?)	s	(broad)	1	4a
^{19}F n.m.r.				
-104.4	m		1	2 or 6
-104.9	m		1	2 or 6
-160.2	m	*ca* 18.8	1	3 or 5
-163.4	m	*ca* 19 (complex)	1	3 or 5
^{13}C n.m.r. (Proton coupled)				
37.0	d	169.7		4a
128.6	s			4b
130-146	(Aromatic carbons, highly coupled, overlapping)			
Compound b				
^{1}H n.m.r.				
4.2	q	6.9	2	1a
1.3	t	6.9	3	1b
4.0	s		2	2
^{19}F n.m.r.				
- 93.0	s		1	2' & 6'
-144.0	s		1	3' & 5'

Spectra #25a

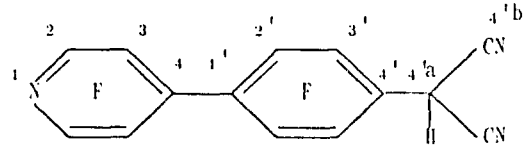


Spectra #25b



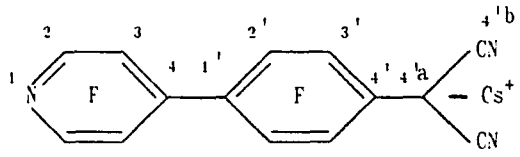
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
6.6	s			4'a
^{19}F n.m.r. (Complex second order spectrum)				
- 90.2	m (6+ lines)		1	2
tentatively				
-138.5	m (8+ lines)		1	3
-139.1	m (16+ lines)		1	2'
-131.7	m (10+ lines)		1	3'
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
141.0	dd	255.2, 35.5 (^{2}J F2)		3
120.2	t	16.6 (^{2}J F3)		4
111.5	t	16.6 (^{2}J F2')		1'
109.4	t	18.8 (^{2}J F3')		4'
18.5	d	145.4		4'a
111.0	d	13.1 (^{2}J H4a')		4'b
tentatively				
144.6	dt	240.6, 15.7		2
145.1	dd	259.4, 9.3		2'
146.0	dd	253.7, 15.3		3'

Spectra #26



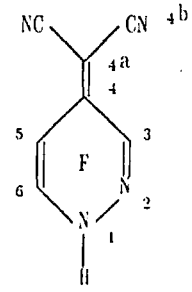
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r. (Complex second order spectrum)				
- 92.2	m (6+ lines)		1	2
tentatively				
-147.5	d	11.9	1	3
-140.3	m (14+ lines)	*ca* 12.9	1	2'
-143.5	q	12.4	1	3'
^{13}C n.m.r.				
141.1	dd	258.7, 34.7 (^{2}J F2)		3
26.4	s			4'a
123.3	s			4'b
tentatively				
139.8	dm	241.2		2 or 2' or 3'
147.7	dm	*ca* 245		2 or 2' or 3'
127.9	t	*ca* 19 (^{2}J F3)		4
90.4	t	*ca* 20 (^{2}J F2')		1'
ca 123	(weak, overlapping)			4'

Spectra #27



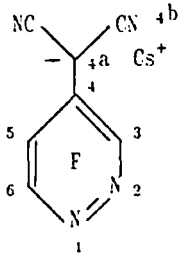
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
12.2	s (very broad)			1
^{19}F n.m.r.				
-118.6	s (broad)		1	3
-149.5	s (broad)		1	5
- 74.5	s (broad)		1	6
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
150.7	d	271.5		3
134.6	(overlapping)			4
46.8	s			4a
116.0	s			4b
155.7	d	234.8		5
136.7	d	253.6		6

Spectra #28



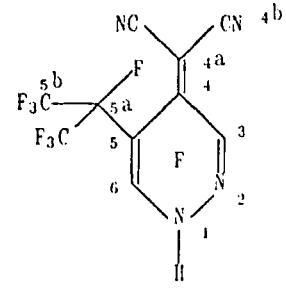
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
-108.1	t	26.0 (F5,F6)	1	3
-143.9	t	28.5 (F3,F6)	1	5
- 79.7	t	30.5 (F3,F5)	1	6
^{13}C n.m.r.				
156.1	dd	230.3,	10.9 (F6)	3
125.8	d	27.4		4
28.0	s			4a
121.2	s			4b
158.7	dd	237.6, 5.4		5
138.1	ddd	262.1, 29.0,	10.8 (F5)(F3)	6

Spectra #29



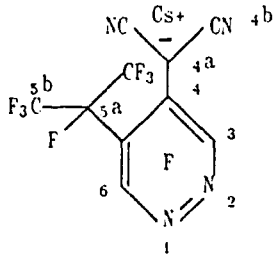
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
11.6	s (broad)			1
^{19}F n.m.r.				
- 74.6	d	17.4 (F6)	1	3
-170.8	heptet of d	(F5b),(F6) 6.1, 2.7	1	5a
- 73.0	dd	(F6) 26.2, 6.1 (F5a)	6	5b
- 91.0	m	*ca* 26 (F5b)	1	6
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
155.5	d	253.5		3
138.6	dd	(^{2}J F3) 20.3, 7.2 (F5a?)		4
62.6	s			4a
115.8	s			4b
91.2	m (obscured)			5
93.3	d heptet	211.1, 36.0 (^{2}J F5b)		5a
121.1	qd	289.5, 28.0 (^{2}J F5a)		5b
157.4	dd	272.9, 10.2 (F3)		6

Spectra #30



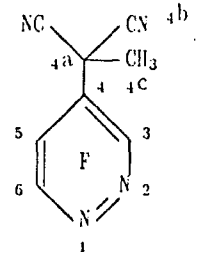
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
- 74.5	d	30.2 (F6)	1	3
-172.0	m (6 lines)	*ca* 4 (F5b)	1	5a
- 73.0	dd (F6)	26.8, 5.2 (F5a)	6	5b
- 79.5	m (6 lines)	*ca* 28 (F3),(F5a)	1	6
^{13}C n.m.r.				
159.5	d	242.3		3
136.1	dd	(^{2}J F3) 23.5, 6.7 (F6)		4
40.6	d		6.5	4a
120.8	d		2.8	4b
96.3	m	(obscured)		5
94.5	d heptet	209.7, 35.5 (^{2}J F5b)		5a
121.6	qd	288.8, 28.1 (^{2}J F5a)		5b
162.0	dd	232.3, 7.9 (F5a)		6

Spectra #31



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
4.0	d	3.6 (F3)		4c
^{19}F n.m.r.				
-111.8	t (broad)	*ca* 12 (F5,6,H4c)	1	3
-148.0	dd	38.8, 11.1 (F6,F3)	1	5
- 77.2	dd	38.8, 14.2 (F5,F3)	1	6
^{13}C n.m.r. (Broad band proton decoupled)				
150.2	dd	274.5, 21.5		3
133.7	d	*ca* 24.9		4
68.4	s			4a
119.9	d	16.4 [2]		4b
41.9	s			4c
154.1	dd	246.4, 20.6		5
137.6	dd	251.6, 14.5		6

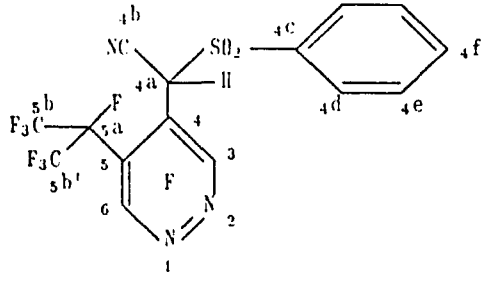
Spectra #32



[2] Coupling or inequivalence?

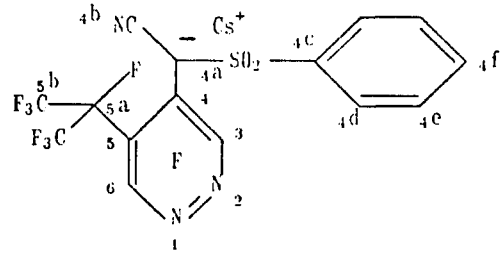
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
6.9	dd	10.1, 2.7 (F3)	1	4a
8.1	d	5.6	2	4d
7.8	t	7.8 (H 4f)	2	4e
8.0	t	7.5 (H 4e)	1	4f
^{19}F n.m.r.				
- 72.9	d (broad)	31.1 (F6)	1	3
-170.4	q	8.0 (F5b')	1	5a
- 69.7	dq (F6?)	33.9, 7.7 (F5b')	3	5b
- 75.5	dq (F5a)	7.9, 7.9 (F5b)	3	5b'
- 74.5	m (10+ lines)	*ca* 16	1	6
^{13}C n.m.r.				
161.0	d	232.4		3
124.7	d	26.5 (F3)		4
55.8	d (d)	*ca* 150 (H/D exchange)		4a
111.2	s			4b
136.9				4c
131.0	d	*ca* 168		4d & 4e
137.5	d	164.0		4f
121.2	dd	(F5a) 31.4, 22.2 (F6)		5
94.5	d hept.et	256.4, 36.5 (F5b, F5b')		5a
120.4	qd	287.9, 27.6 (F5a)		5b & 5b'
164.8	d	247.0		6

Spectra #33



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
7.5	(obscured)		3	4d & 4f
7.8	d	7.4	2	4e
^{19}F n.m.r.				
- 74.4	d	30.2 (F6)	1	3
-172.5	s (unresolved)		1	5a
- 72.9	dd (F6)	25.1, 4.1 (^{2}J F5a)	6	5b
- 79.0	m (6+ lines)	*ca* 27 (F3)	1	6
^{13}C n.m.r.				
161.6	dd	236.7, 4.5 (F6)		3
133.6	dd	30.5, 5.6 (^{2}J F3)		4
64.1	s			4a
123.0	d	4.5		4b
147.4	s			4c
129.3	d	163.2		4d
126.7	d	165.9		4e
132.0	d	167.7		4f
106.9	t	22.3 (^{2}J F5a, ^{2}J F6)		5
94.3	d hept.et	218.2, 33.1 (^{2}J F5b)		5a
121.5	qd	289.6, 28.8 (^{2}J F5a)		5b
163.4	d	242.0		6

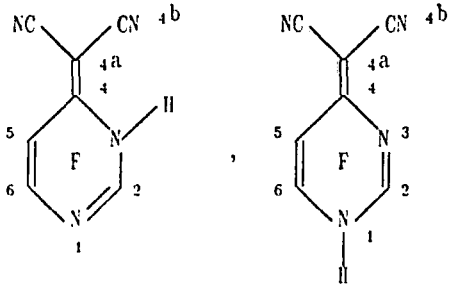
Spectra #34



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.	Tautomer a			
- 48.4	(broad)		1	2
-154.6	(broad)		1	5
- 74.0	(broad)		1	6
^{19}F n.m.r.	Tautomer b			
- 57.8	(broad)		1	2
-165.9	(broad)		1	5
- 90.2	(broad)		1	6
^{13}C n.m.r.	Only partial assignment possible (Broad band proton decoupled)			
114.1	(broad)			4b

Other resonances notably at 69.4, 114.1, 132.5, 136.0, 155.7 ppm

Spectra #35a, Spectra #35b



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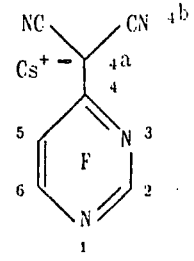
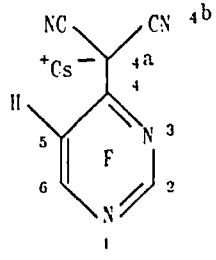
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
- 50.8	d	25.7 (F5)	1	2
-169.3	dd	(F5) 25.8, 17.3 (F6)	1	5
- 92.4	m		1	6
^{13}C n.m.r.				
133.0	ddd	250.2, 22.7, 7.9 (F6),(F5)		2
162.5	m (8 lines)			4
41.8	d	7.4		4a
120.6	(2 singlets)			4b
157.2	ddd	242.2, 20.2, 14.7 (F6),(F2)		5
155.9	ddd	209.1, 22.2, 3.3 (F5),(F2)		6

Spectra #36



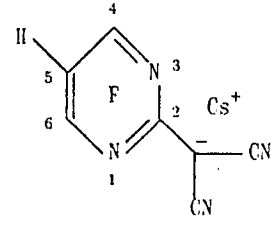
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
6.0	s			5
^{19}F n.m.r.				
- 47.3	(broad)		1	2
- 69.8	(broad)		1	6
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
163.1	dd	209.2, 22.9		2
175.2	dd	16.7, 9.2		4
43.8	d	7.4		4a
120.9	(2 singlets)			4b
88.6	ddd	170.8, 32.1, 4.9		5
171.8	ddd	243.2, 18.6, small		6

Spectra #37



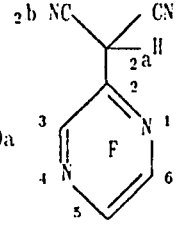
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
5.6	t	2.7		5
^{19}F n.m.r.				
- 60.7	s			2 & 6
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
172.6	(weak, broad)			2
43.7	(weak)			2a
121.9	s			2b
172.5	dd	248.2, 10.8 (F4 or F6)		4 & 6
77.4	dd	178.6, 39.4		5

Spectra #38

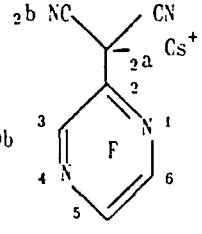


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a)				
^{1}H n.m.r.				
6.3	s			2a
^{19}F n.m.r.				
- 82.6	dd	(F6) 42.6, (F5) 7.7	1	3
- 85.1	dd	(F6) 19.2, 7.5 (F3)	1	5
- 92.2	dd	(F3) 42.6, 19.7 (F5)	1	6
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
123.7	dd	(^{3}J F3) 31.3,*ca* 8 (F5)		2
26.1	d	144.7		2a
110.9	d		12.8 (^{2}J H2a)	2b
152.2	d	258.2		3
145.7	dd	252.3, 29.5 (^{2}J F6)		5
146.8	ddd	265.3, 34.2, 8.8 (F5), (F3)		6
Compound (b)				
^{19}F n.m.r.				
- 83.4	dd	(F6) 46.7, 12.1 (F5)	1	3
-116.8	dd	(F6) 19.1, 12.2 (F3)	1	5
-101.2	dd	46.7, 19.2 (F5)	1	6
^{13}C n.m.r.				
143.9	m			2
34.7	s			2a
122.3	s			2b
143.7	d	256.8		3
143.5	ddd	233.4, 27.9, 3.8 (F6),(F3)		5
133.1	ddd	240.6, 38.4, 6.1 (F5),(F3)		6

Spectra #39a

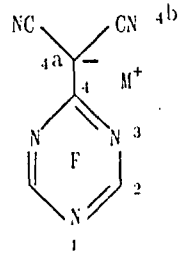


Spectra #39b



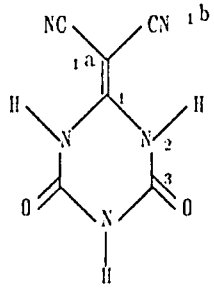
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
- 43.5	s			5
^{13}C n.m.r. for potassium salt				
170.8	dd	220.5, 21.0 (J F6)		2
180.3	t	15.9 (J F2)		4
48.1	s			4a
119.0	s			4b
^{13}C n.m.r. for caesium salt				
170.9	dd	220.1, 21.3 (J F6)		2
180.3	t	15.7 (J F2)		4
48.4	s			4a
119.0	s			4b

Spectra #40



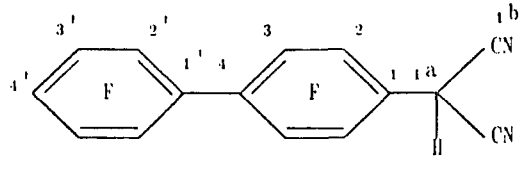
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
				In d_6-DMSO
^{1}H n.m.r.				
11.7	s (broad)		2	
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
152.3	s			1 or 3
162.3	s			1 or 3
44.3	s			1a
118.5	s			1b

Spectra #41



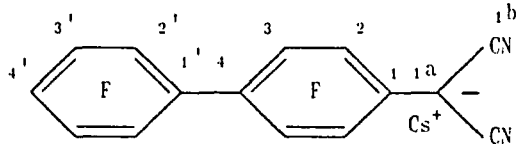
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
4.9				1a
^{19}F n.m.r.				
-138.1	dd	(^{3}J) 17.5, 8.8	2	2 (or 3)
-139.1	dd	(^{3}J) 17.1, 8.6	2	3 (or 2)
-136.7	m		2	2'
-161.6	dd	(F4') 20.2, 14.1 (F2')	2	3'
-150.6	tt	(F3') 20.4, 3.2 (F2')	1	4'
^{13}C n.m.r.				
109.8	(overlapping)			1
18.5	s			1a
111.1	d	144.3		1b
102.3	m			4
109.8	(overlapping)			1'
146.0	d	254.9		4'
139.1	dm	254.9		Ar-F2
144.0	dm	276.8		Ar-F
145.6	d	*ca* 250 (overlapping)		2 X Ar-F

Spectra #42



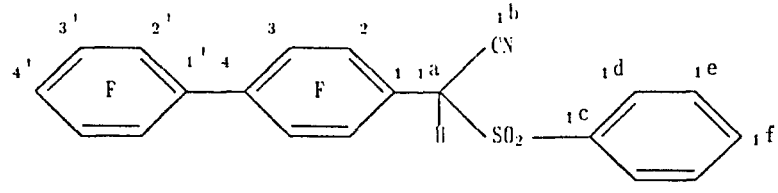
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
-144.5	d	11.7	2	2
-141.6	d	11.3	2	3
-139.0	ddd	24.2, 8.9, *ca* 2.1	2	2'
-157.5	dd	20.6, 14.9	2	3'
-154.3	t	20.5	1	4'
^{13}C n.m.r. (Broad band proton decoupled)				
125.4	t	(broad)		1
23.9	s			1a
123.2	s			1b
90.2	t	18.3		4
103.9	t	18.7		1'
141.5	dm	248.6		4'
137.9	dt	251.4, 13.6		Ar-F
139.1	dm	242.4		Ar-F
144.1	dt	237.1, *ca* 10		Ar-F
144.7	dd	247.3, *ca* 10		Ar-F

Spectra #43



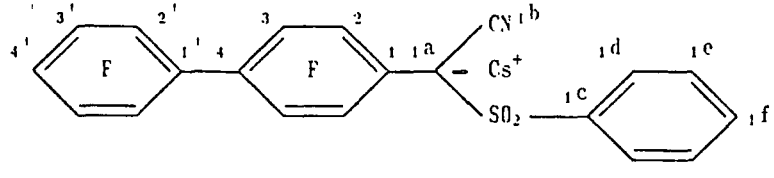
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
6.6	s		1	1a
7.8	(overlapping)		3	1d & 1f
8.1	t	7.1	2	1e
^{19}F n.m.r.				
-137.4	(no visible coupling)		4	2,3,2'
-138.0	(no visible coupling)		2	2,3,2'
-161.6	m		2	3'
-150.6	tt	(F3') 20.5, 3.5 (F2')	1	4'
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
109.8	(overlapping)			1
53.5	d	148.7		1a
111.8	d	*ca* 7 (^{2}J H1a)		1b
135.9	s			1c
135.9	d	167.6		1d & 1e
137.2	dt	163.8. 7.1		1f
139.0	dt	253.5, *ca* 14		Ar-F
145.3	d	*ca* 250 (2 overlapping)		2 X Ar-F
146.4	dd	259.9, 15.2		Ar-F
102.3	t	*ca* 18		4
109.8	(overlapping)			1'
143.8	dm	255.5		4'

Spectra #44



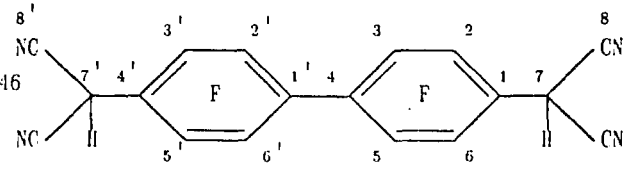
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
7.4	(overlapping)		3	1d & 1f
7.9	s		2	1e
^{19}F n.m.r. (Approximate multiplicities due to 2nd order nature)				
-143.3	dd	21.6, 9.9	2	2
-138.3	dd	21.2, *ca* 8	2	3
-138.8	m		2	2'
-162.8	dd (F4')	20.5, 14.4 (F2')	2	3'
-153.6	t (F3')	20.5	1	4'
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
123.2	t	16.0		1
51.8	s			1a
124.7	s			1b
150.4	t	small		1c
128.8	d	165		1d
126.1	d	171		1e
130.9	dt	161.1, 7.4		1f
96.9	t	20.5 (^{2}J F3)		4
104.3	t	20.0 (^{2}J F2')		1'
142.8	d	253		4'
138.8	dm	248.8		Ar-F
143.4	d	243		Ar-F
144.7	d	237.3		Ar-F
145.5	d	252.2		Ar-F

Spectra #45



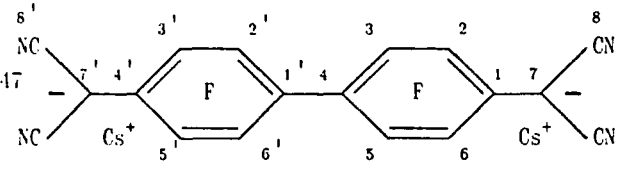
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
4.9				1a
^{19}F n.m.r.				
-136.3	dd	16.5, 8.0	1	2,6,3' & 5'
-138.8	dd	(broad, overlapping)	1	3,5,2' & 6'
^{13}C n.m.r. (Broad band proton decoupled and proton coupled)				
109.9	t	*ca* 13		1(') or 4(')
ca 110.5	(obscured)			1(') or 4(')
145.3	dd	254.6, 13.9		Ar-F
146.2	dd	255.0, 13.9		Ar-F
18.5	d	142.4		7 or 7'
111.1	d	*ca* 9 (^{2}J H1a)		8 or 8'

Spectra #46



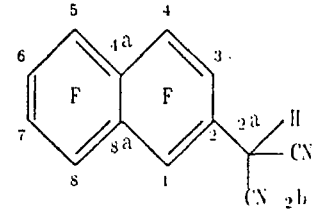
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
-144.4	dm	12.0	1	Aromatic F
-147.7	dm	16.7	1	Aromatic F
^{13}C n.m.r.				
124.5	(obscured)			1 & 4'
140.0	dm	234.9, 11.7 (3+ lines)		2,6,3' & 5'
145.3	dd	246.5, 10.9		3,5,2' & 6'
94.1	t	17.5 (^{2}J F3)		4 & 1'
23.4	s			7 & 7'
124.5	s			8 & 8'

Spectra #47



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r.				
6.6				2a
^{19}F n.m.r.[3]				
-116.8	dd	(F8) 68.8, 18.2	1	1
-138.4	ddd	15.9, 7.9, *ca* 3.8	1	3
-146.1	ABtt	(F5) 58.8, 16.1, *ca* 2.3	1	4
-147.3	ABtt	(F4) 58.8, 17.2, *ca* 4.2	1	5
-151.5	tt	17.9, *ca* 3.8	1	6
-154.8	m		1	7
-143.8	dtt	(F1) 68.9, 16.5, *ca* 4.2	1	8
^{13}C n.m.r. Only a partial assignment was possible				
113.6	t	(broad)		2
18.3	d	144.6		2a
111.2	d	7.9		2b

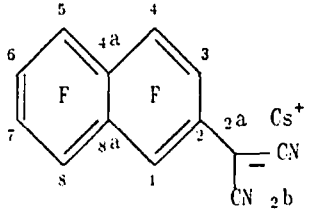
Spectra #48



[3]Most probable assignments for 1 and 5.

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.[4]				
-127.7 (-128.2)	dt	(F8) 66.9, 13.2	1	1
-137.2 (-136.1)	m		1	3
-153.1 (-154.0)	dt	(F5) 55.2, 14.5	1	4
-149.6 (-150.6)	dt	(F4) 55.5, 16.4	1	5
-164.9 (-166.2)	t	18.4	1	6
-160.1 (-160.5)	m		1	7
-150.2 (-150.6)	dt	(F1) 66.8, 15.9	1	8
^{13}C n.m.r. Only a partial assignment was possible				
122.5	s			2
24.0	s			2a
124.8	s			2b
103.0				4a or 8a
108.4				4a or 8a

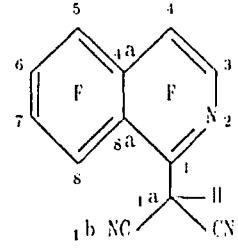
Spectra #49



[4]Shifts in brackets for sodium salt in HMPA
See ref. number 150

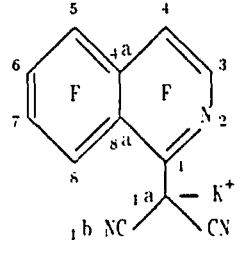
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{1}H n.m.r. Spectrum run in $CDCl_3$ as solvent				
6.2	s (broad)			1a
^{19}F n.m.r.				
- 96.4	d	18.9	1	3
-147.7	ddd	53.1, 19.5, *ca* 4	1	4
-144.9	dtt	53.4, 16.6, *ca* 5	1	5
-147.2	m		1	6
-152.6	t (broad)	18.5	1	7
-139.4	d	18.1	1	8
^{13}C n.m.r. Only a partial assignment possible (Broad band proton decoupled)				
119.8	t	*ca* 10		1
32.6	s (broad)			1a
111.8	s			1b
137.9	s (broad)			4a
114.9	d	14.6		8a
Unassigned peaks				
148.3	dd	237.2, 15.5		
139.5	d	258.8		
141.1	dt	256.8, 16.2		6 or 7
142.3	d	261.2		
143.42	d	*ca* 260 (overlap of 2 resonances)		

Spectra #50



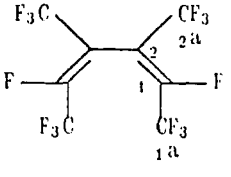
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
- 97.5	d	25.3	1	3
-173.6	dddd	49.6, 25.3, 3.5, 2.2	1	4
-151.5	dm	49.6 (20+ lines)	1	5
-154.6	m	(19+ lines)	1	6
-164.7	tq	20.1, 4.0	1	7
-127.2	m	(15+ lines)	1	8
^{13}C n.m.r.				
120.0	s (broad)			1
44.9	s			1a
123.3	s			1b
154.2	dm	16.3		4a or 8a
108.2	d	14.5		4a or 8a
148.4	dd	225.8, 13.5		Ar-F
128.1	dd	246.6, 33.6		Ar-F
144.9	d	*ca* 260		Ar-F
142.2	dt	253.8, 15.0		Ar-F
138.0	dt	247.6, 17.0		Ar-F
140.6	d	*ca* 250		Ar-F

Spectra #51

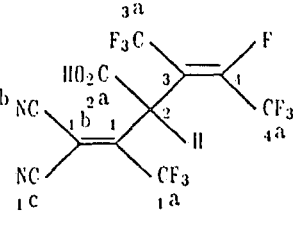


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a)				
^{19}F n.m.r.				
-101.3	m		1	1
- 68.5	dq (^{2}J F1)	4.0, *ca* 1.9 (F2a)	3	1a
- 60.6	dq (F1)	17.8, *ca* 1.8 (F1a)	3	2a
^{13}C n.m.r.				
154.7	dq	290.1, 41.8 (^{2}J F1a)		1
118.9	qd	275.0, 38.4 (^{3}J F1)		1a
109.5	m			2
121.9	q	275.8		2a
Compound (b)				
^{1}H n.m.r.				
4.1	s (broad)			2a
^{19}F n.m.r.				
- 61.2	q	*ca* 2.1 (F4a?)	3	1a
- 61.0	dm (^{4}J F4)	17.4, *ca* 1.3 (F4a)	3	3a
-110.9	m (8+ lines)	*ca* 7.5	1	4
- 68.8	ddd (^{3}J F4)	8.0, 2.0, *ca* 1.3 (F3a)	3	4a
^{13}C n.m.r. (Spectrum weak, notable features only) (Broad band ^{1}H decoupled)				
113.0	s			1c
67.2	s			1b
121.8	q	*ca* 280		CF_3's
95.1	s			2
169.7	s			2a

Spectra #52a

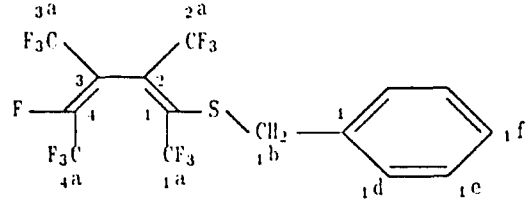


Spectra #52b



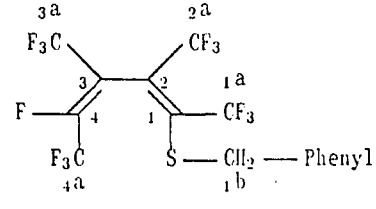
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
	(Recorded in 15% *cis,trans* : 85% *trans,trans* mixture)			
^{1}H n.m.r.	(Coincident with Z,E-isomer)			
7.3	m		5	Aromatic H
4.4	m		2	1b
^{19}F n.m.r.				
- 57.7	s		3	1a or 2a
- 58.4	s (Overlapping)		3	1a or 2a
- 60.4	d	15.8 (F4)	3	3a
-108.0	m	*ca* 7 (F4a,F3)	1	4
- 69.2	s		3	4a
^{13}C n.m.r.	(Broad band proton decoupled and proton coupled)			
145.4	q	33.3 (^{2}J F1a)		1
121.0	q	277.2		1a or 2a
122.4	q	277.8		1a or 2a
40.5	t	146.4		1b
135.9	s			1c
129.9	d	159.3		1d
130.3	dt	158.6, small		1e
129.3	dt	161.5, small		1f
126.3	q	*ca* 35 (^{2}J F2a)		2
144.0 (V.Weak)	qd	(^{2}J F3a) *ca* 35, *ca* 13 (^{2}J F4)		3
121.7	qd	277.1, 4.8 (^{3}J F4)		3a
151.3	dq	286.7, 39.8 (^{2}J F4a)		4
117.9	qd	275.6, 38.8 (^{2}J F4)		4a

Spectra #53

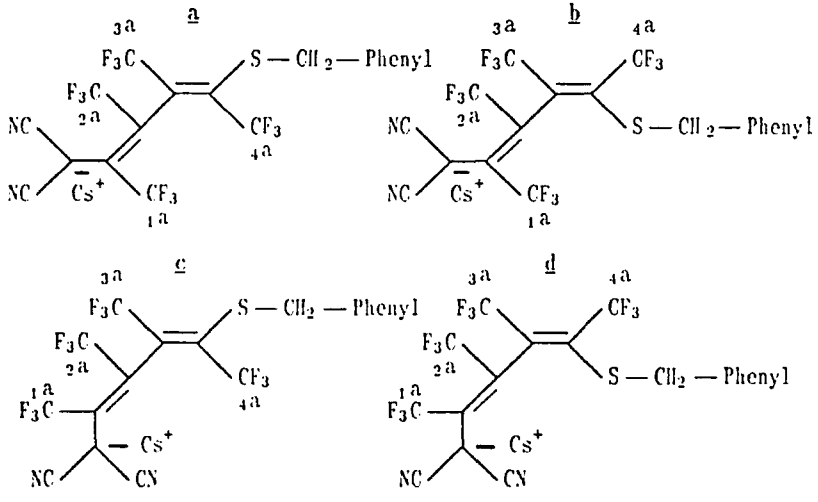


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
	(Recorded in 15% *cis,trans* E : 85% *trans,trans* mixture)			
^{1}H n.m.r.	(Coincident with E,E-isomer)			
7.3	m		5	Aromatic H
4.4	m		2	1b
^{19}F n.m.r.				
- 57.3	m (Broad)		3	1a or 2a
- 58.4	(Obscured)		3	1a or 2a
- 59.4	d	15.5 (F4)	3	3a
-109.2	qq	16.0, 7.8 (F3a,F4a)	1	4
- 69.7	d	7.6 (^{3}J F4)	3	4a

Spectra #54

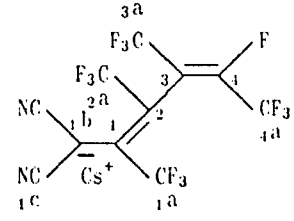


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
	(Recorded as a mixture in CH_3CN)			
^{19}F n.m.r.	*trans, trans* - Isomer (Spectra #55a)			
- 54.0	heptet	*ca* 3.4	1	CF_3
- 57.5	heptet	*ca* 3.1	1	CF_3
- 57.7	s		1	CF_3
- 58.6	m		1	CF_3
^{19}F n.m.r.	*trans, cis* - Isomer (Spectra #55b)			
- 58.2	m	*ca* 3 (F1a or F2a)	1	1a or 2a
- 53.6	q	*ca* 3 (F1a or F2a)	1	1a or 2a
- 57.2	q	14.3 (F3a or F4a)	1	3a or 4a
ca- 57.9 (obscured)	(q)	*ca* 15 (F3a or F4a)	*ca* 1	3a or 4a
^{19}F n.m.r.	*cis, trans* - Isomer (Spectra #55c)			
- 58.8	q	16.4 (F1a or F2a)	1	1a or 2a
- 51.5	qm	*ca* 16 (F1a or F2a)	1	2a or 2a
- 58.0	s		1	3a or 4a
- 61.0	s		1	3a or 4a
^{19}F n.m.r.	*cis, cis* - Isomer (Spectra #55d)			
- 58.4	q	16.0 (F2a)	1	1a
- 50.7	qm	*ca* 15.9 (F1a)	1	2a
- 57.6	qm	*ca* 13.9 (F4a)	1	3a
- 56.2	q	14.3 (F3a)	1	4a



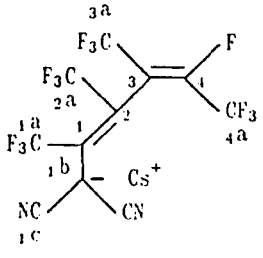
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
	(Reaction solution at 298K)			
			(CH_3CN solvent)	
^{19}F n.m.r.				
- 57.1	s		3	1a or 2a
- 55.1	s		3	2a or 1a
- 61.8	d	13.8 (F4)	3	3a
-111.3	q	8.0 (^{3}J F4a)	1	4
- 68.1	m (4+ lines)	*ca* 3	3	4a
^{13}C n.m.r.	(Incomplete assignment)			
ca 117.3	(weak, obscured)			CF_3
120.7	q	278.2		CF_3
122.4	q	279.8		CF_3
123.2	q	270.8		CF_3
84.9	d	(weak)		1,2, or 3
ca 142	m	(weak)		1,2, or 3
36.9	s			1b
119.8	s			1c
149.5	dq	284.8, 37.9 (^{2}J F4a)		4

Spectra #56

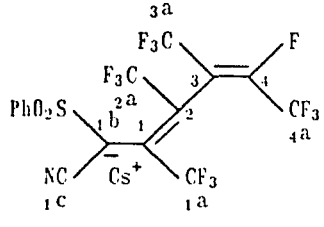


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a)				
^{19}F n.m.r.				
- 52.8	q	16.3 (F1a or 2a)	3	1a or 2a
- 59.9	q	16.0 (F1a or 2a)	3	1a or 2a
- 62.2	d	19.3 (F4)	3	3a
-110.7	m	*ca* 9	1	4
- 71.2	s		3	4a
Compound (b) (CH_3CN solvent)				
^{19}F n.m.r.				
- 60.4	s		3	1a or 2a
- 56.9	s		3	2a or 1a
- 60.6	d	14.4 (F4)	3	3a
-109.7	m		1	4
- 69.1	s		3	4a

Spectra #57a

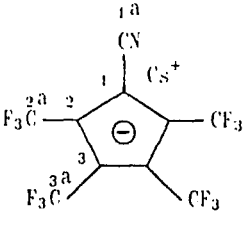


Spectra #57b

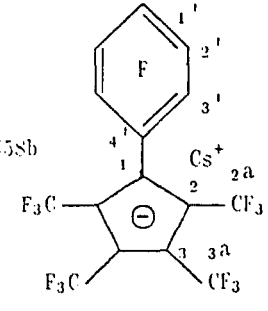


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a)				
^{19}F n.m.r.				
- 52.0	m	> 5	1	2a or 3a
- 52.6	m		1	2a or 3a
^{13}C n.m.r.				
90.2	s			1
116.4	s			1a
111.3	q	43.5 (^{2}J F2a or F3a)		2 or 3
115.6	q	36.4 (^{2}J F2a or F3a)		2 or 3
124.0	q	271.2		2a or 3a
124.4	q	266.2		2a or 3a
Compound (b) (As a *ca* 50:50 mixture with the above compound)				
^{19}F n.m.r.				
- 50.4	s		6	2a or 3a
- 51.1	s		6	2a or 3a
-159.2	t	20.5	1	1'
-166.3	td	21.4, *ca* 6.6	2	2'
-140.3	dd	23.1, 6.6	2	3'

Spectra #58a



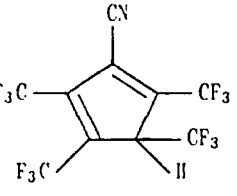
Spectra #58b



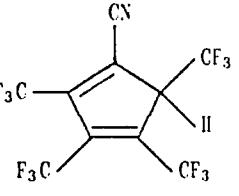
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.	(Major isomer 56%)	(Solvent conc H_2SO_4)		
- 58.3	q	*ca* 9.2	1	
- 60.7	pentet	10.3	1	
- 60.9	q	9.7	1	
- 62.9	q	8.0 (coincident)	1	
^{19}F n.m.r.	(Minor isomer 44%)	(Solvent conc H_2SO_4)		
- 58.5	pentet	8.7	1	
- 61.0	q	7.1	1	
- 62.0	q	7.4	1	
- 62.9	q	8.0 (coincident)	1	
^{13}C n.m.r.	(Complex)			

Tentative structures of isomers :-

Spectra #59a, #59b



and

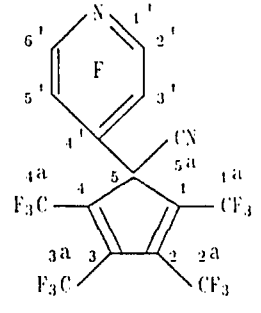


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
- 56.1	m	(fine)	6	2 X CF_3
- 60.3	m	(fine)	6	2 X CF_3
- 85.7	ddd	28.7, 20.1, 13.0	1	2' or 6'
- 87.7	ddd	28.7, 21.7, 13.6	1	2' or 6'
-139.3	tdq ($^{ortho*}_{para}$)	24.8, 6.4, 3.2 (F1a)	1	3' or 5'
-141.5	ddd	28.2, 21.7, 6.7	1	3' or 5'

In above J *ca* 28 Hz are para, *ca* 20 Hz are ortho, *ca* 13 or 6 Hz are meta.

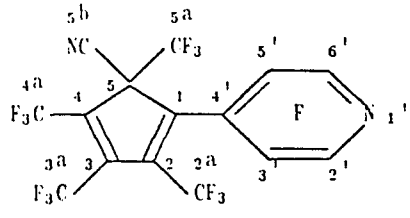
^{13}C n.m.r.			
139.7	q	(^{2}J CF_3) 39.3 (broad)	1 & 2
120.0	q	274.0 (2 close resonances)	1a & 4a
119.4	q	274.5	2a & 3a
52.1	s		5
107.0	s		5a
	[*For below C-F couplings* (*ortho*) (*para*) (*meta*)]		
145.0	dddd	244.9, 16.9, 12.5, 3.9	2' or 6'
146.5	dddd	245.8, 17.6, 12.3, 3.3	2' or 6'
139.8	dddd	263.0, 31.0, 6.8, *ca* 2.0	3' or 5'
142.6	ddd	268.4, 31.0, 6.9	3' or 5'
118.6	tt	9.5, *ca* 2.5	4'

Spectra #60



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
- 61.0	q (F3a)	10.9	3	2a
- 59.9	heptet	10.9 (F2a, F4a)	3	3a
- 55.9	qq (F3a)	10.8, 7.0 (F5a)	3	4a
- 65.6	dq (F5')	9.8, 7.0 (F4a)	3	5a
		{*para, ortho, meta for below*}		
- 88.0	ddd	29.7, 20.6, 13.3	1	2' or 6'
- 88.9	ddd	29.7, 20.5, 13.3	1	2' or 6'
-134.5	ddd	29.7, 20.7, 4.0	1	3'
-139.4 (>> 8+ lines)	m	(F5a) *ca* 10	1	5'
^{13}C n.m.r.				
133.4	s (broad)			1
136.3	qq	(F2a) 39.3, 3.7 (F3a)		2
120.0	q	273.5		2a or 3a
119.6	q	273.4		2a or 3a
141.7	q	(F3a/F4a) 37.2 (broad)		3 & 4
119.2	q	273.2 (broader than 5a,3a,2a)		4a
61.1	q	32.6 (F5a)		5
121.4	q	289.4		5a
106.9	s			5b
145.2	dm	244.2 (2nd order resonance)		2' & 6'
140.0	ddd	268.9, 29.4, 6.7 (^2J),(*para*)		3' or 5'
141.4	ddd	265.9, 30.4, 6.7 (^2J),(*para*)		3' or 5'
121.6	m (partially obscured)			4'

Spectra #61

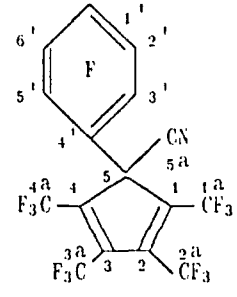


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
^{19}F n.m.r.				
- 56.9	m	(fine)	6	1a or 2a
- 60.8	m	(fine)	6	1a or 2a
-148.6	tt (ortho)	21.0, 5.7 (meta)	1	1'
-158.1	td (ortho)	20.7, 5.9 (meta)	1	2' or 6'
-159.8	td (ortho)	21.2, 7.1 (meta)	1	2' or 6'
-139.4	dm	*ca* 16 *ca* 3.5	1	3' or 5'
-142.5	dq	21.2, *ca* 7 (F1a)	1	3' or 5'

In above J *ca* 21 Hz are ortho and / or para, J *ca* 6 Hz are meta.

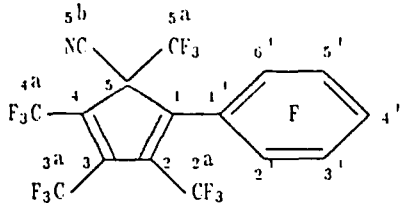
^{13}C n.m.r.				
140.2	q	(^{2}J F1a or F2a) 37.8 (broad)		1,2,3 & 4
119.4	q	274.5 (2 close resonances)		1a & 4a
120.0	q	274.2		2a & 3a
51.8	s			5
107.4	s			5a
144.6	dtt	253.3, 13.3, 5.5		1'
139.4	dtm	252.7, *ca* 15		2' or 6'
140.7	dtm	*ca* 248, *ca* 15		2' or 6'
144.9	dm	*ca* 242		3' or 5'
146.0	dm	*ca* 260		3' or 5'
100.4	td	11.3, 5.1		4'

Spectra #62

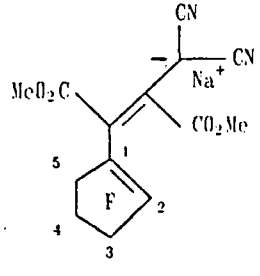


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a)				
^{19}F n.m.r.				
- 61.0	q (F3a)	11.1	3	2a
- 59.8	heptet	10.7 (F2a, F4a)	3	3a
- 55.8	qq (F3a)	10.8, 6.9 (F5a)	3	4a
- 65.7	dq (F6')	10.3, 6.9 (F4a)	3	5a
-133.6	dtd	19.3, 7.1, 4.4	1	2'
-159.9	td	21.3, 7.6	1	3' or 5'
-160.3	td	21.3, 7.6	1	3' or 5'
-147.1	tt (*ortho*)	20.7, 8.6 (*meta*)	1	4'
-138.4	m		1	6'
Compound (b)				
^{19}F n.m.r.				
-126.4	s		1	2
-115.7 & -118.3	AB	255.8	2	3
-127.6 & -128.8	AB	231.6	2	4
-107.3 & -109.5	AB	250.4	2	5

Spectra #63a

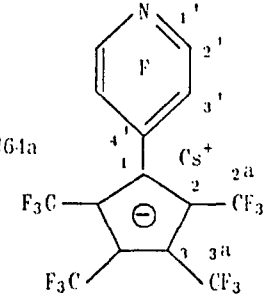


Spectra #63b

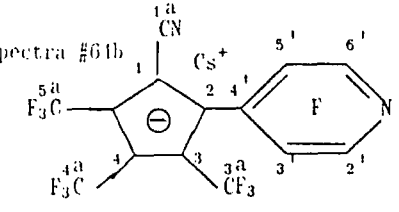


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
Compound (a)				
^{19}F n.m.r.				
- 51.0	m (fine)		6	2a or 3a
- 51.4	m (fine)		6	2a or 3a
- 95.0	m (2nd order, 6+ lines)	*ca* 15	2	2'
-143.3	m (2nd order, 5+ lines)	ca 14	2	3'
^{13}C n.m.r.				
104.5	s			1
110.1	m			2 or 3
118.0	m			2 or 3
125.4	q	270.4		2a or 3a
124.9	q	269.9		2a or 3a
124.9	dt	244.1, 16.2 (^{2}J F3')		2' & 6'
141.5	dd	252.3, 32.9 (^{2}J F2')		3' & 5'
134.7	t	18.5 (^{2}J F3')		4'
Compound (b) (tentative)				
^{19}F n.m.r. (of impure ion)				
- 52.0	s		3	CF_3
- 52.7	(2 close resonances)		6	2 X CF_3
- 93.2	m		2	2' & 6'
-141.6	m		2	3' & 5'

Spectra #64a



Spectra #61b

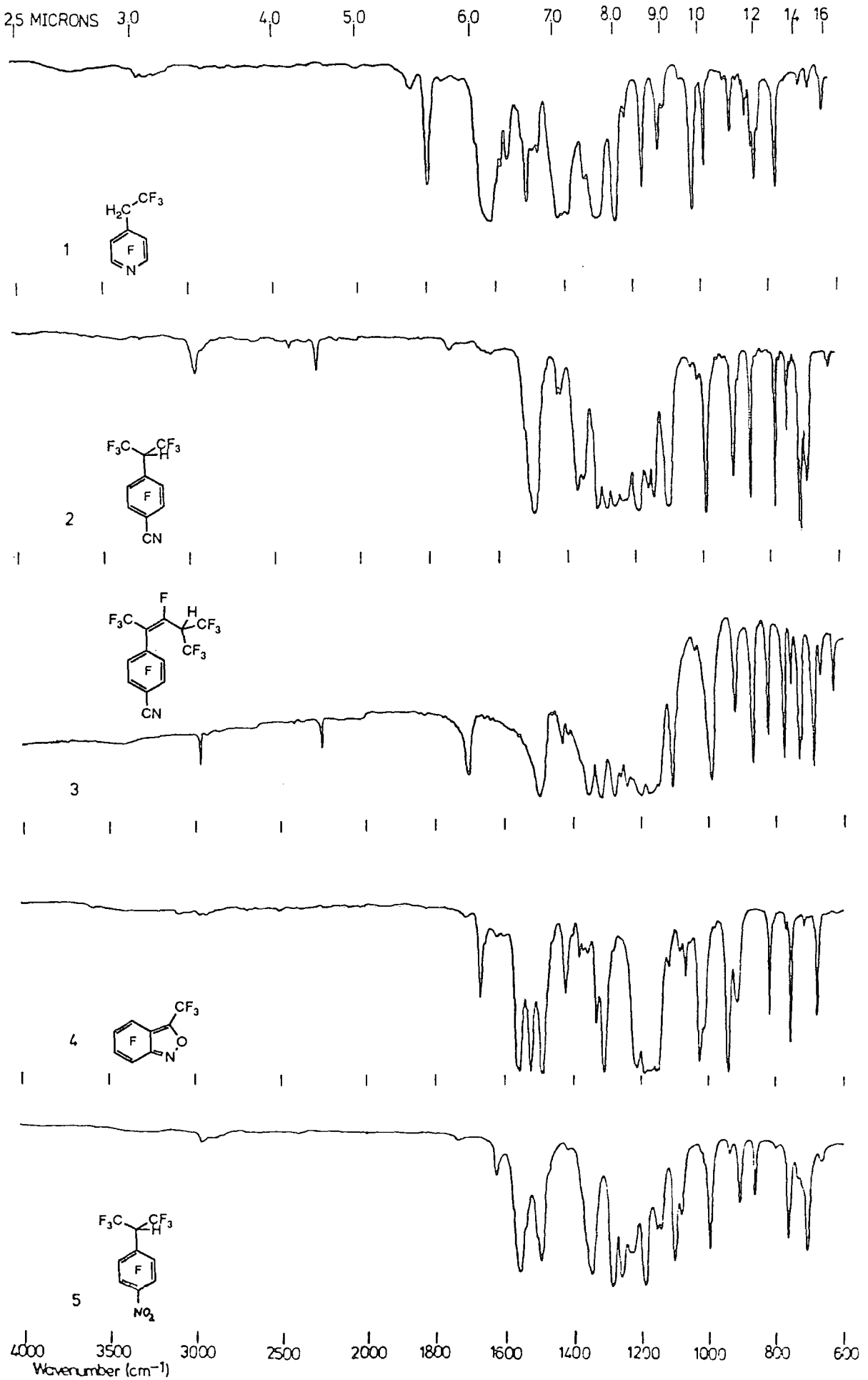


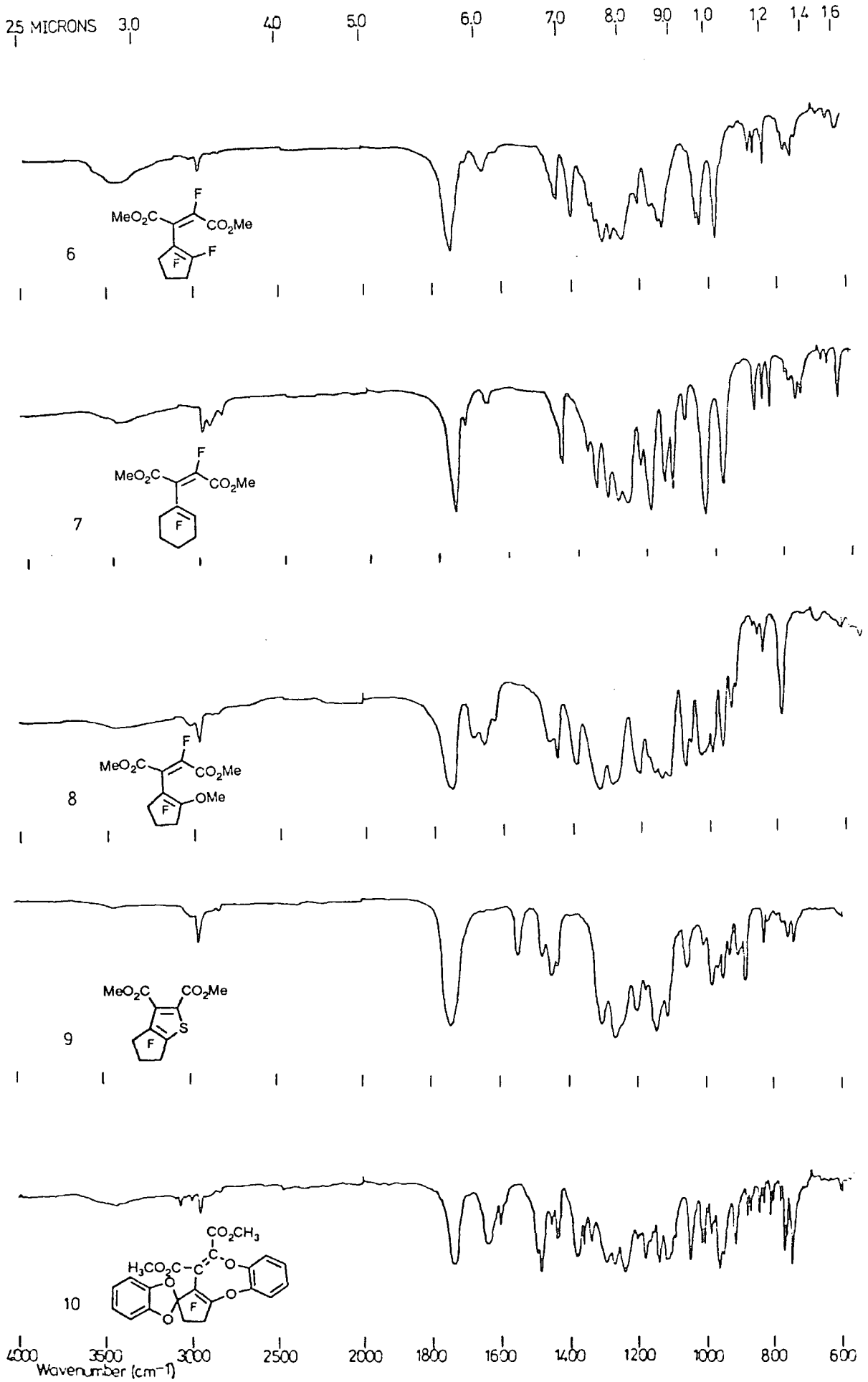
Appendix II - Infrared Spectra

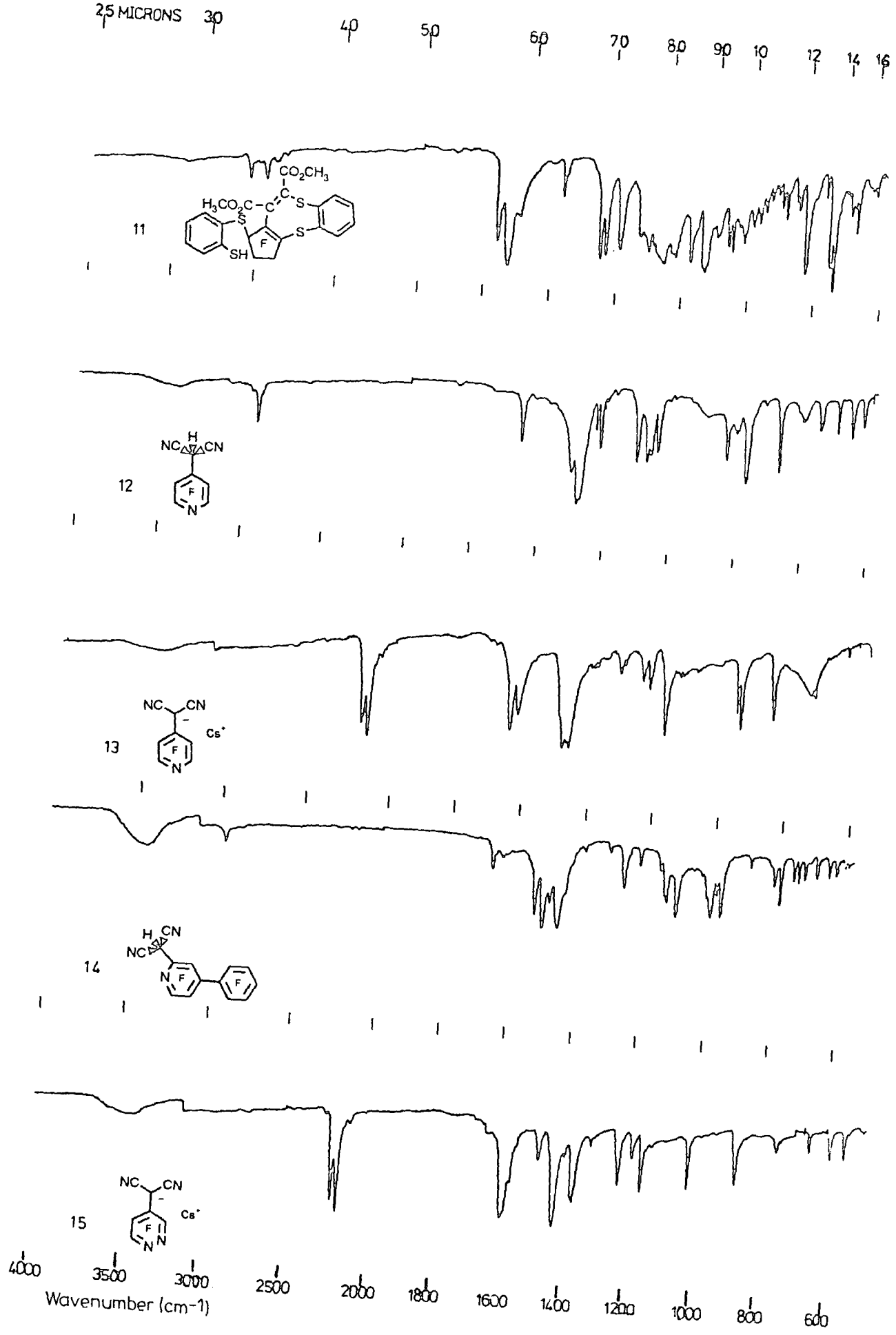
All solids were recorded in KBr disk form, liquids were recorded as thin films between KBr plates.

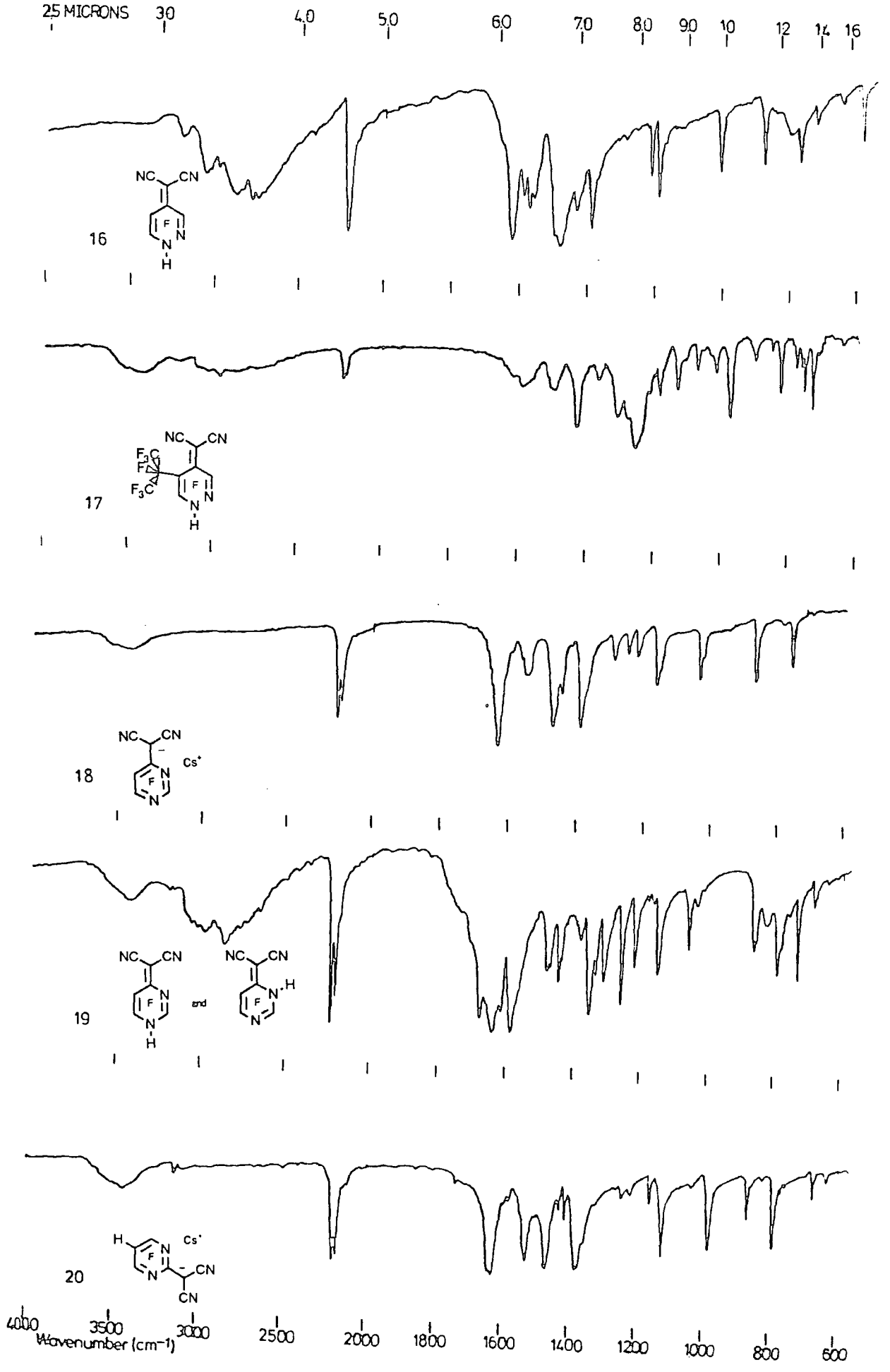
1. Tetrafluoro-4-(2,2,2-trifluoroethyl)pyridine (80)
2. Perfluoro-4-(2H-hexafluoroisopropyl)benzonitrile (83)
3. Benzonitrile derivative (85)
4. Perfluoro-3-methyl-2,1-benzisoxazole (88)
5. Perfluoro-1-nitro-4-(2'H-hexafluoroisopropyl)benzene (87)
6. Cyclopentyl derivative (112)
7. Cyclohexyl derivative (114)
8. Compound (117)
9. Thiophene derivative (118)
10. 1,6-Benzodioxocin derivative (121)
11. 1,6-Benzodithiocin derivative (123)
12. 4'-Tetrafluoropyridylmalononitrile (129)
13. Caesium salt (130)
14. Malononitrile derivative (133)
15. Caesium salt (136)
16. Pryidazyl-ylidene-malononitrile derivative (135)
17. Isopropyl-pryidazyl-ylidene-malononitrile derivative (137)
18. Caesium salt (140)
19. Pyrimidyl-ylidene-malononitrile derivatives (139 and 141)
20. Caesium salt (142)
21. Caesium salt (143)
22. (3',5',6'-trifluoropyrazyl)malononitrile (144)
23. Caesium salt (145)
24. Potassium salt (146)
25. 1'-(hexafluoroisoquinyl)malononitrile (147)
26. 1'-(nonafluorobiphenyl)malononitrile (149)
27. 1,4'-(octafluorobiphenyl)bismalononitrile (151)
28. Methyl-(4'-tetrafluoropyridyl)malononitrile (179)
29. Decafluoro(bis-4'-pyridyl)malononitrile (177)
30. Methyl-(4'-trifluoropyridazyl)malononitrile (135)
31. Hydrolysate (169)
32. Caesium salt (170)
33. Acetonitrile derivative (171)
34. Isopropyl-pyridazyl-acetonitrile derivative (172)

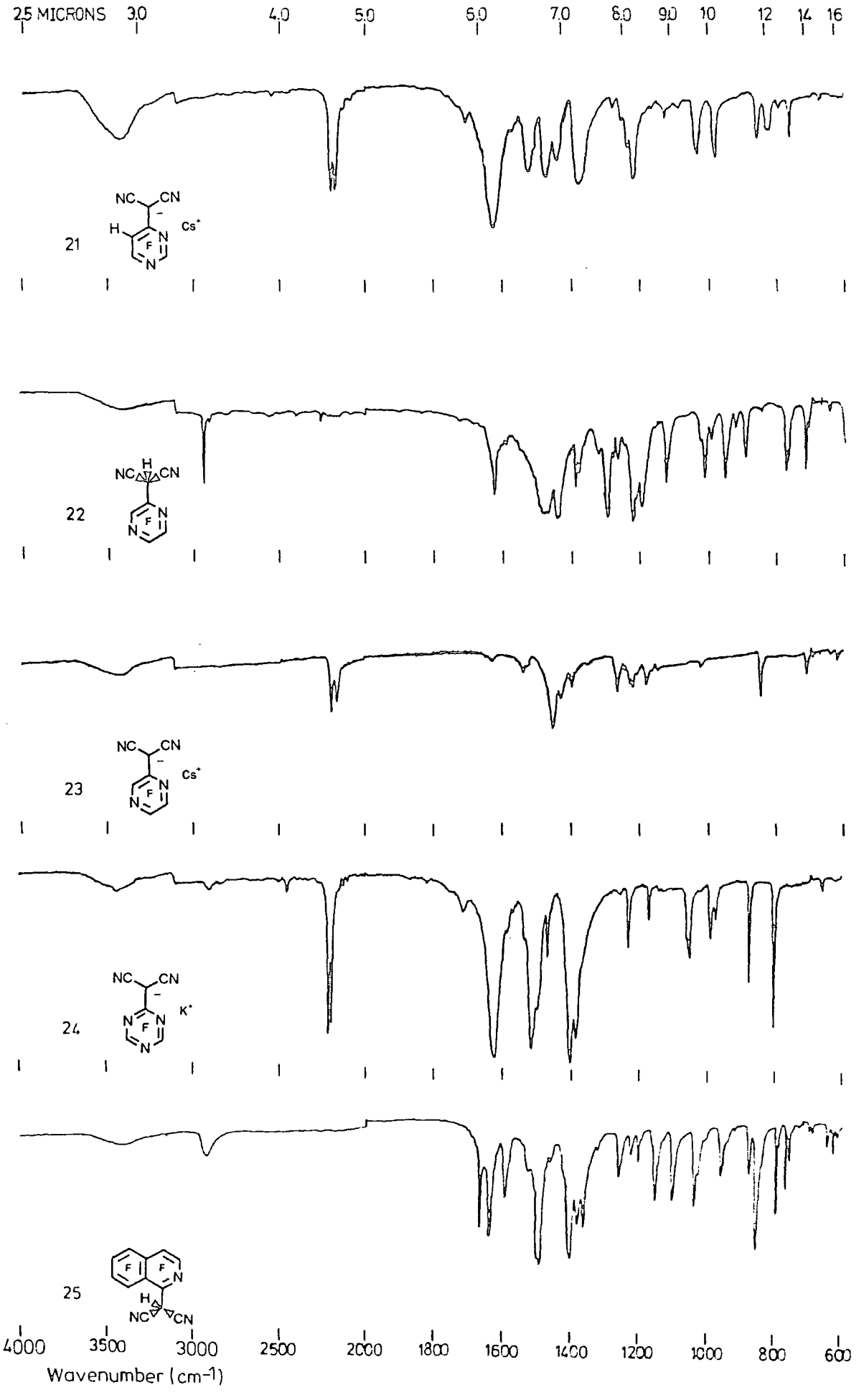
35. Acetonitrile derivative (175)
36. Ethyl-(4'-tetrafluoropyridyl)acetate (183)
37. Thiobenzyl substituted dienes (204 and 205)
38. Caesium salt (188)
39. Cyclopentadiene derivative (196)
40. Cyclopentadiene derivative (198)
41. Carboxylic acid (192)
42. Cyclopentadiene derivative (211)

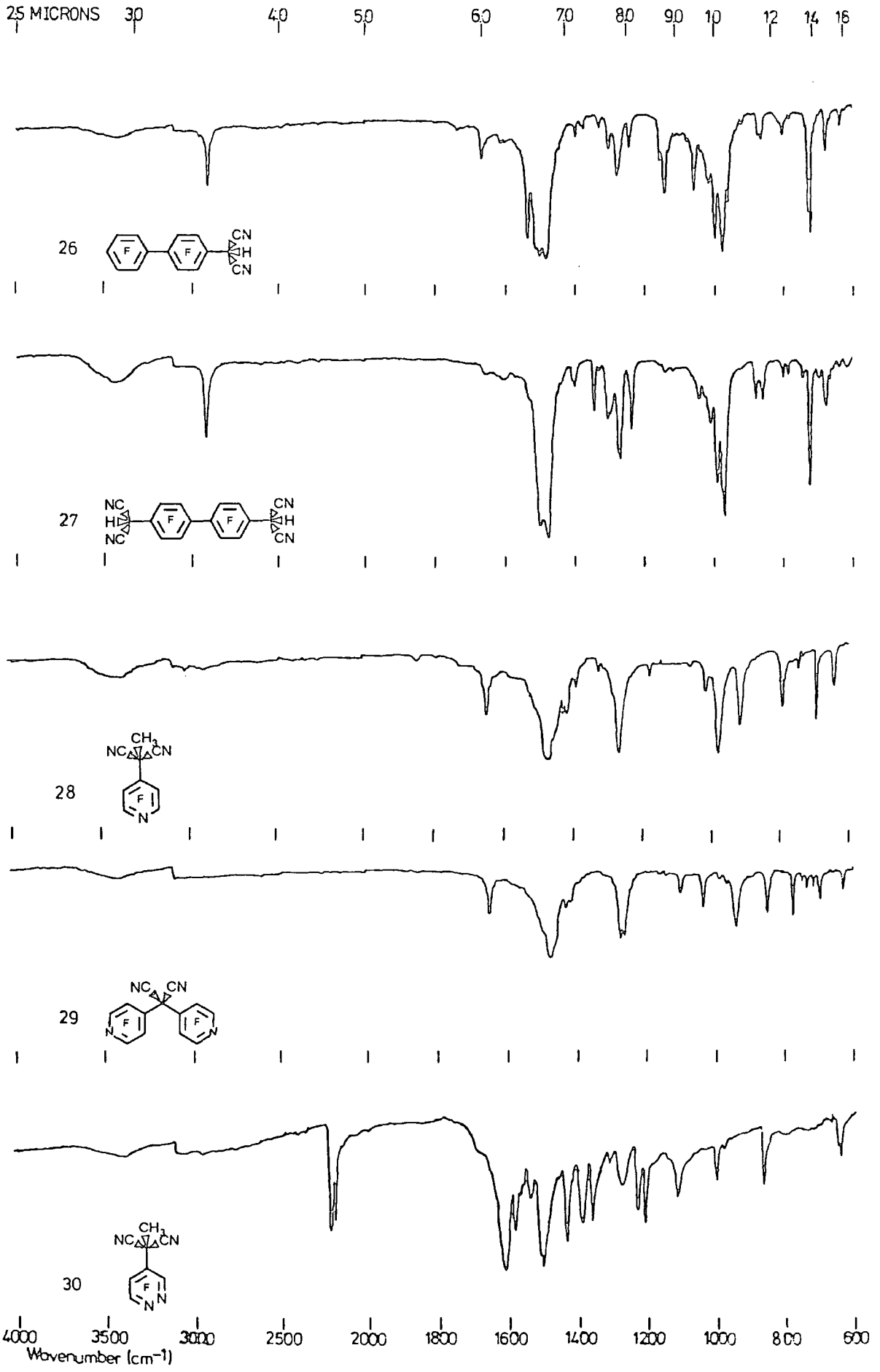

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16
1
2
3
4
5
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600
Wavenumber (cm⁻¹)

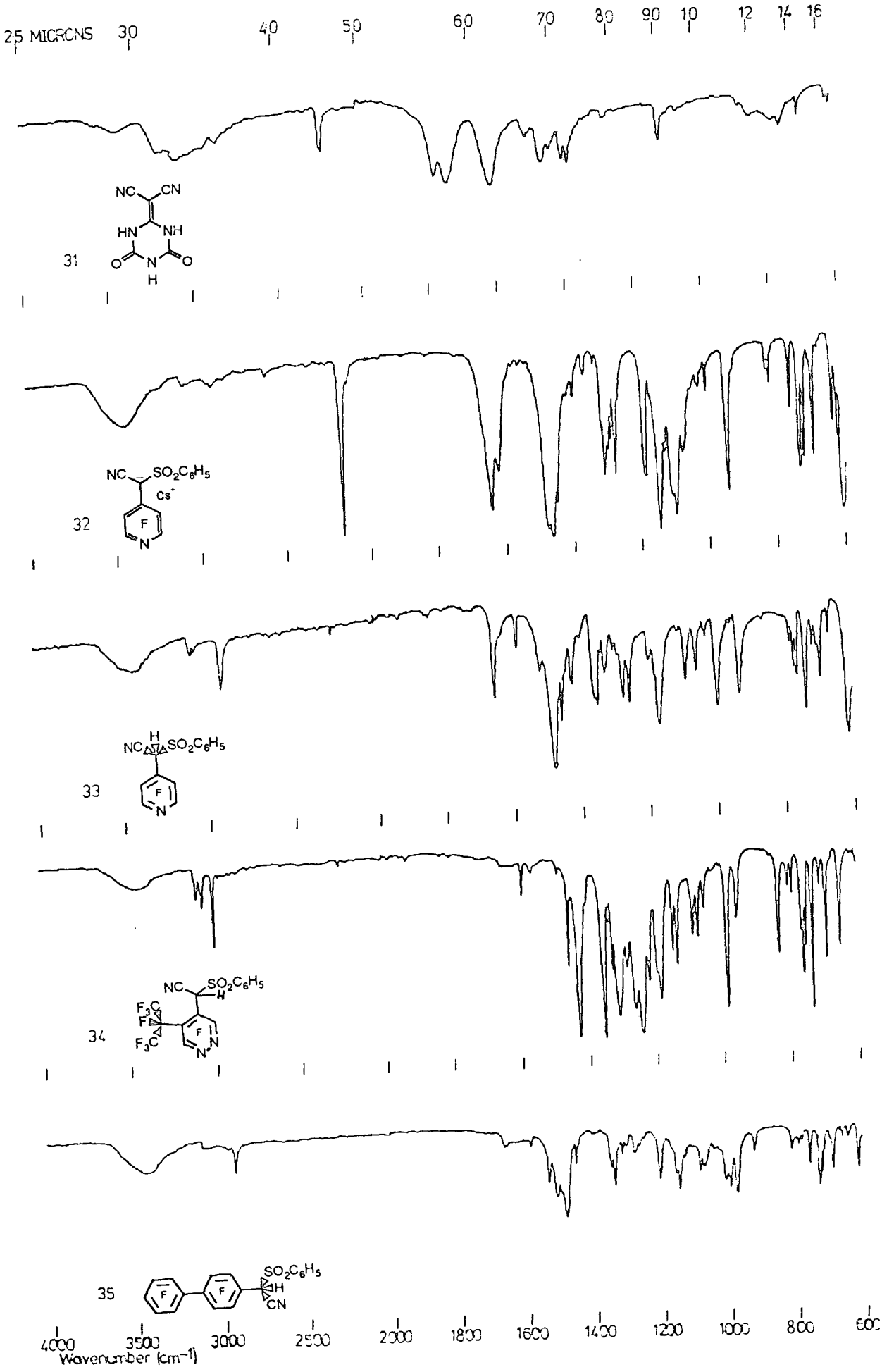

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 1.0 1.2 1.4 1.6
6
7
8
9
10
Wavenumber (cm⁻¹)
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600

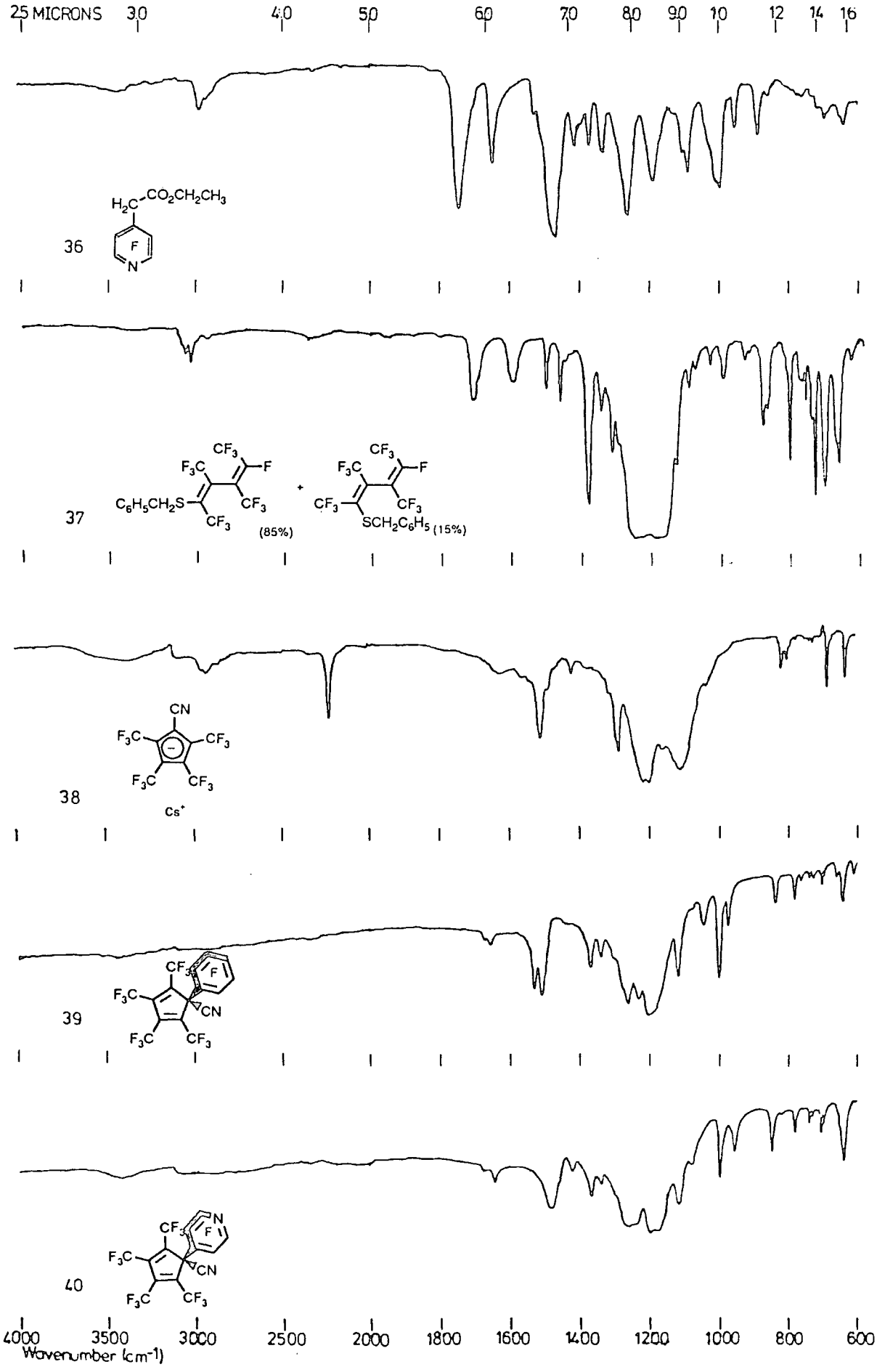

2.5 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
11
12
13
14
15
Cs+
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)

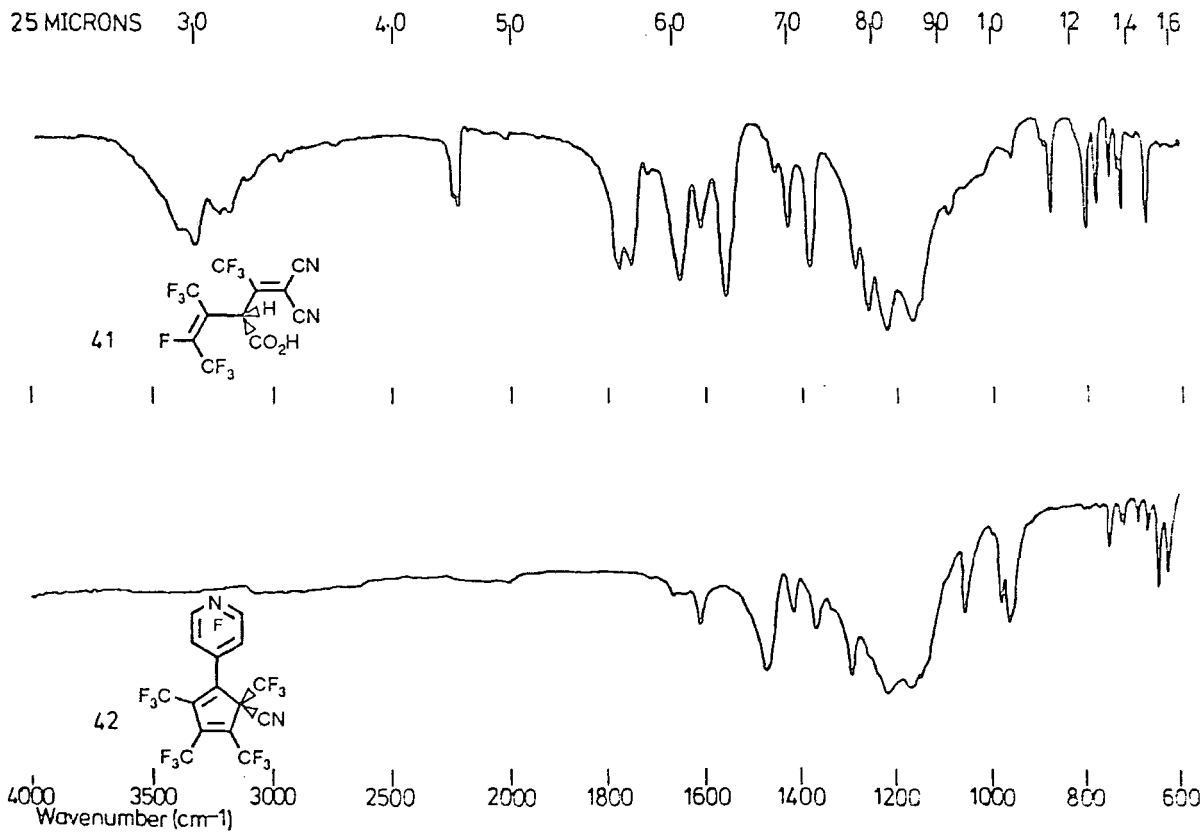

25 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
16
17
18
19
and
20
Cs+
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)


2.5 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
21
22
23
24
25
Cs+
K+
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)


2.5 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
26
27
28
29
30
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber (cm⁻¹)


2.5 MICRONS 30 40 50 60 70 80 90 10 12 14 16
31
32
33
34
35
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600
Wavenumber (cm⁻¹)


25 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16
36
37
(85%)
(15%)
38
Cs+
39
40
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600
Wavenumber (cm-1)


25 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
1.0
1.2
1.4
1.6
41
42
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)

Appendix III - Mass Spectra

The ionisation mode(s) used are stated on the individual spectra, the following abbreviations have been used:

EI - Electron impact ionisation
CI - Chemical ionisation (Ammonia reagent gas)
Cl- - Negative ion
FAB - Fast atom bombardment with positive and negative modes

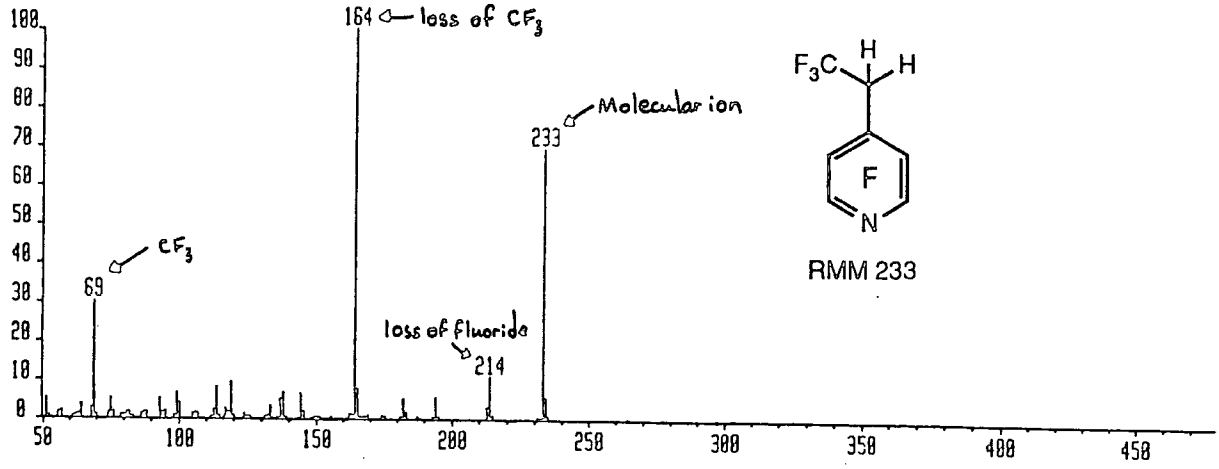
1. Tetrafluoro-4-(2,2,2-trifluoroethyl)pyridine (80)
2 Perfluoro-4-(2H-hexafluoroisopropyl)benzonitrile (83)
3. Tetrafluoro-1-nitro-(2',2',2'-trifluoroethyl)benzene (89)
4. Tetrafluoro-4-(2',2',2'-trifluoroethyl)benzonitrile (84)
5. Benzonitrile derivative (85)
6. Furan derivative (126)
7. Perfluoro-3-methyl-2,1-benzisoxazole (88)
8. Perfluoro-1-nitro-4-(2'H-hexafluoroisopropyl)benzene (87)
9. Pyridyl-but-2-en-1,4-dioate derivatives (106 and 107)
10. Cyclobutyl-but-2-en-1,4-dioate derivative (109)
11. Cyclopentyl-but-2-en-1,4-dioate derivatives (111 and 112)
12. Cyclohexyl-but-2-en-1,4-dioate derivatives (113 and 114)
13. Cyclopentyl derivative (117)
14. Cyclopentyl derivative (116)
15. Thiophene derivative (118)
16. 1,6-Benzodioxocin derivative (121)
17. 1,6-Benzodithiocin derivative (123)
18. 4'-Tetrafluoropyrimidylmalononitrile (129)
19. Caesium salt of 4'-Tetrafluoropyrimidylmalononitrile (130)
20. Malononitrile derivative (133)
21. Malononitrile derivative (131)
22. Pyridazyl-ylidene-malononitrile derivative (135)
23. Caesium salt (138)
24. Isopropyl-pyridazyl-ylidene-malononitrile derivative (137)
25. Caesium salt of (4'-trifluoropyrimidyl)malononitrile (140)
26. Pyrimidyl-ylidene-malononitrile derivatives (139 and 141)
27. Pyrimidyl caesium salt (142)
28. Pyrimidyl caesium salt (143)
29. (3',5',6'-trifluoropyrazyl)malononitrile (144)
30. Potassium triazylmalononitrile derivative (146)
31. [1'-(hexafluoroisoquinyl)]malononitrile (147)

32. 1'-(Nonafluorobiphenyl)malononitrile (149)
33. 1,4'-(octafluorobiphenyl)bismalononitrile (152)
34. Methyl-(4'-tetrafluoropyridyl)malononitrile (179)
35. Decafluoro(bis-4'-pyridyl)malononitrile (177)
36. Methyl-(4'-trifluoropyridazyl)malononitrile (135)
37. Triazyl-ylidene-malononitrile derivative (169)
38. Phenylsulphonyl-(4'-tetrafluoropyridyl)acetonitrile (170)
39. Caesium salt (172)
40. Acetonotrile derivative (172)
41. Biphenyl-malononitrile derivative (175)
42. Thiobenzyl substituted dienes (204 and 205)
43. Pentadienyl caesium salts (185 and 186)
44. Cyclopentadienyl caesium salt (188)
45. Thiobenzyl substituted pentadienyl salts (206a to 206d)
46. Pentadienyl sodium salt (195)
47. Cyclopentadiene derivative (196)
48. Cyclopentadiene derivative (198)
49. Pyridyl substituted cyclopentadienyl salt derivative (199)
50. Carboxylic acid (192)
51. Phenyl substituted cyclopentadienyl salt derivative (197)
52. Cyclopentadiene derivative (210)
53. Caesium salt (130) (very impure)
54. Cyclopentadiene derivative (211)
55. Ethyl-(4'-tetrafluoropryidylacetate (183)

HPGR5B

Mass Spec. Number 1

EI+



RMM 233

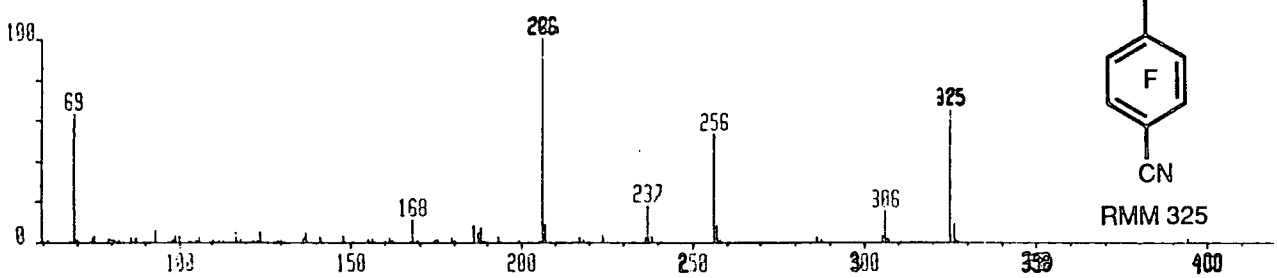
EI+ Data

Mass	% Base						
51.00	4.86	81.01	1.27	105.01	1.24	144.03	6.49
55.00	1.20	82.01	1.56	106.01	1.45	164.03	100.00
56.01	1.58	86.00	1.18	113.02	2.28	165.04	7.65
57.02	1.93	87.01	1.55	114.02	7.89	182.03	4.96
64.03	3.48	88.02	1.45	117.01	2.63	183.04	1.53
68.02	2.41	93.00	4.96	118.02	1.80	194.04	5.50
69.01	30.03	94.01	1.36	119.02	9.33	213.04	2.69
74.01	1.44	95.02	1.66	133.03	3.31	214.04	10.72
75.01	4.83	99.01	6.51	137.02	5.02	233.05	69.64
76.02	1.55	100.01	4.07	138.02	6.69	234.06	5.53

HPGT5A

Mass Spec. Number 2

EI+



RMM 325

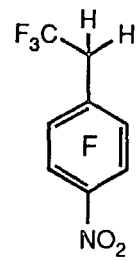
EI+ Data

Mass	% Base			Mass	% Base
61.08	0.53	130.15	0.77	217.22	2.02
68.09	0.79	136.14	1.18	219.22	0.85
69.08	62.61	137.15	3.72	224.23	3.39
70.08	0.63	141.14	1.82	236.24	2.15
74.08	1.21	148.16	2.48	237.25	17.62
74.16	1.09	155.16	1.13	238.26	2.43
75.10	2.77	156.17	1.09	256.26	52.60
79.09	1.58	160.16	0.53	257.27	8.11
80.10	0.70	161.17	2.21	258.26	0.61
81.09	0.71	162.17	0.79	286.28	2.15
82.10	0.56	167.18	0.99	287.28	0.64
86.10	1.64	168.19	10.50	305.31	3.05
87.11	1.55	169.19	1.00	306.31	14.88
92.11	0.71	174.18	0.58	307.31	1.59
93.10	5.26	175.19	1.26	325.33	64.92
98.11	1.47	179.18	1.74	326.34	8.95
99.12	3.11	180.19	0.60	327.32	0.54
100.12	2.51	186.20	7.93	394.42	1.43
103.12	0.67	187.20	5.00		
105.12	1.80	188.22	6.97		
106.13	2.43	189.21	0.57		
110.12	0.87	193.20	1.92		
112.12	0.51	199.20	0.66		
113.12	0.81	205.20	0.95		
117.13	4.74	206.22	100.00		
118.14	1.38	207.22	9.10		
122.13	0.53				
123.14	1.01				
124.14	4.82				
129.14	0.65				

Mass Spec. Number 3

EI + Data

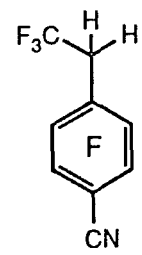
MASS	% BASE
27.52	12.11
28.53	6.69
28.57	2.02
29.53	56.65
30.55	15.70
31.55	2.99
36.63	3.26
44.77	17.19
45.74	4.71
50.82	5.41
55.88	2.99
57.94	4.10
58.96	7.84
60.94	3.31
60.95	2.04
68.03	16.46
69.04	28.15
71.09	2.15
74.18	4.88
75.22	11.58
79.33	3.64
80.37	3.20
81.39	3.40
83.35	4.32
87.31	6.08
88.30	4.05
90.32	2.58
92.24	3.15
93.22	11.66
98.16	3.94
99.16	41.24
100.15	4.10
111.09	2.48
112.09	4.41
117.06	8.23
118.06	68.31
119.07	9.54
123.07	3.07
130.06	2.05
131.07	2.78
137.07	18.33
142.07	2.17
143.08	7.65
144.08	5.37
148.07	2.00
149.07	2.23
150.08	5.18
161.08	20.88
162.08	8.39
163.08	3.48
164.08	6.11
166.08	100.00
167.08	8.17
169.08	3.01
177.08	4.94
180.08	2.71
181.09	58.27
182.09	10.51
191.09	14.33
192.09	4.06
199.09	6.26
200.07	0.48
204.67	0.09
205.07	0.66
207.13	0.28
208.09	2.25 ← CF_3
209.09	0.20
210.09	0.93
211.09	1.57
212.08	2.83
213.10	2.04
214.10	0.20
217.06	0.20
218.12	0.10
219.07	0.25
222.07	0.15
224.12	0.11
224.14	0.09
224.18	0.08
226.08	0.18
227.09	1.89
228.07	0.33
229.05	0.20
230.09	1.91
231.10	0.33
232.11	0.61
233.15	0.15
240.08	1.59
241.10	0.85
243.27	0.25
243.37	0.20
243.61	0.28
243.70	0.26
244.27	0.69
244.81	0.20
245.04	0.20
245.16	0.17
245.22	0.15
246.21	0.14
247.10	0.34
258.09	0.85
259.07	0.24
259.15	0.13
259.58	0.09
259.82	0.59
260.09	59.49
261.10	6.11
262.09	0.44
276.84	0.26
277.11	17.88 ← M^+
277.39	0.20
277.45	0.20
278.12	1.88
279.13	0.36
281.13	0.20



RMM 277

EI + Data

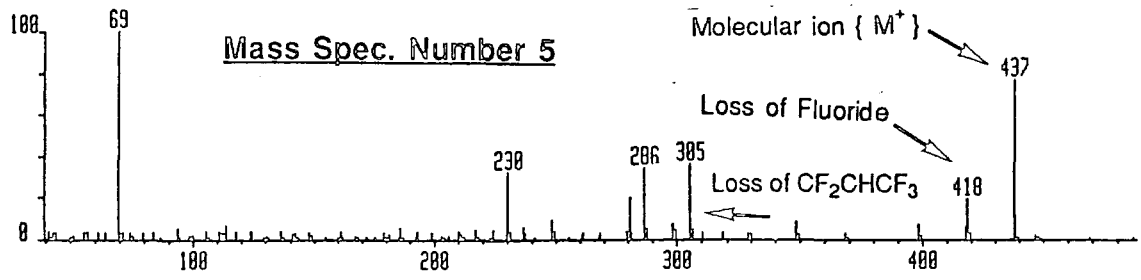
Mass	% Base
27.02	0.73
28.00	28.73
29.00	0.17
29.03	0.27
30.99	8.19
31.98	6.35
33.00	0.30
37.00	0.14
38.00	0.30
39.01	0.70
39.95	4.17
41.03	1.80
42.03	1.12
43.04	4.07
43.97	0.40
49.99	0.31
50.98	2.12
54.98	0.13
55.99	0.53
56.99	0.63
57.05	0.28
60.98	0.45
61.99	0.27
62.99	0.16
63.99	0.47
67.98	0.53
68.97	8.91
73.96	0.73
74.97	2.69
75.97	0.17
78.96	0.56
79.96	0.52
80.96	0.41
81.97	0.34
83.96	0.09
85.96	0.82
86.97	0.92
87.97	1.22
91.01	0.54
91.96	0.84
92.02	0.27
92.95	3.05
93.96	0.85
97.95	0.50
98.96	1.54
99.95	2.21
102.95	0.29
103.95	0.19
104.94	0.98
105.95	1.06
109.94	0.15
110.94	0.41
111.94	0.57
112.93	0.31
116.93	1.22
117.94	0.72
118.95	1.48
119.95	0.13
122.94	0.69
123.93	1.86
124.93	0.12
129.94	0.42
130.92	0.18
135.92	0.08
136.93	1.46
137.48	0.06
137.93	1.49
140.92	0.69
142.92	0.68
143.92	0.83
147.91	0.53
148.91	0.11
149.93	0.47
154.91	0.35
155.92	0.14
156.92	0.87
160.90	4.90
161.90	5.14
162.91	0.37
166.89	0.12
167.90	5.62
168.91	0.70
173.89	0.27
174.90	0.22
178.89	0.28
180.89	0.45
185.88	1.19
186.89	0.74
187.89	100.00 ← $-CF_3$
188.90	8.75
189.90	0.37
192.88	0.35
204.86	0.41
205.87	4.08
206.88	0.32
217.87	0.34
236.85	0.99
237.85	5.15 ← $-F^-$
238.85	0.44
254.82	0.37
256.83	34.44 ← M^+
257.83	3.15
258.83	0.11



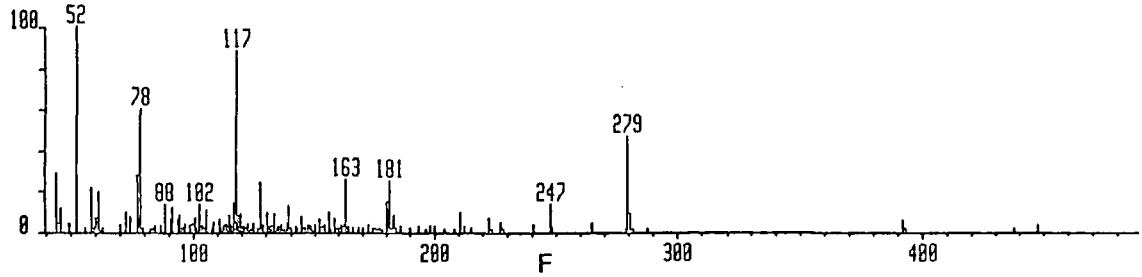
RMM 257

Mass Spec. Number 4

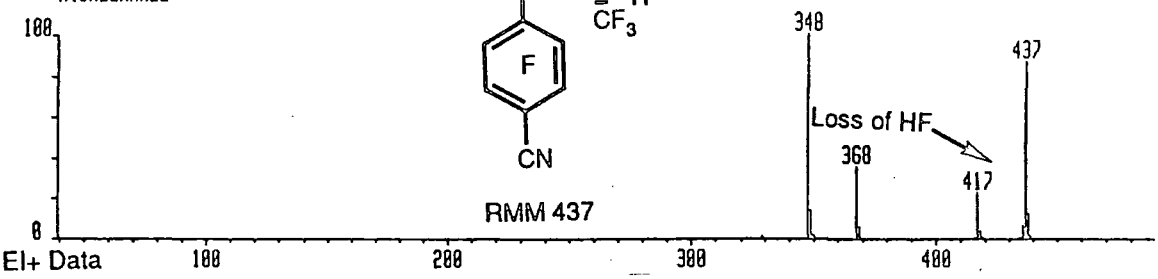
HPGF02o x1 Bgd=1 EI+
BpH=0 I=2.8v Ha=507
H.GREENHALL



HPGF07o x1 Bgd=6 CI+
BpH=0 I=18v Ha=447
H.GREENHALL



HPGF014o x1 Bgd=11 CI-
BpH=0 I=3.2v Ha=581
H.GREENHALL

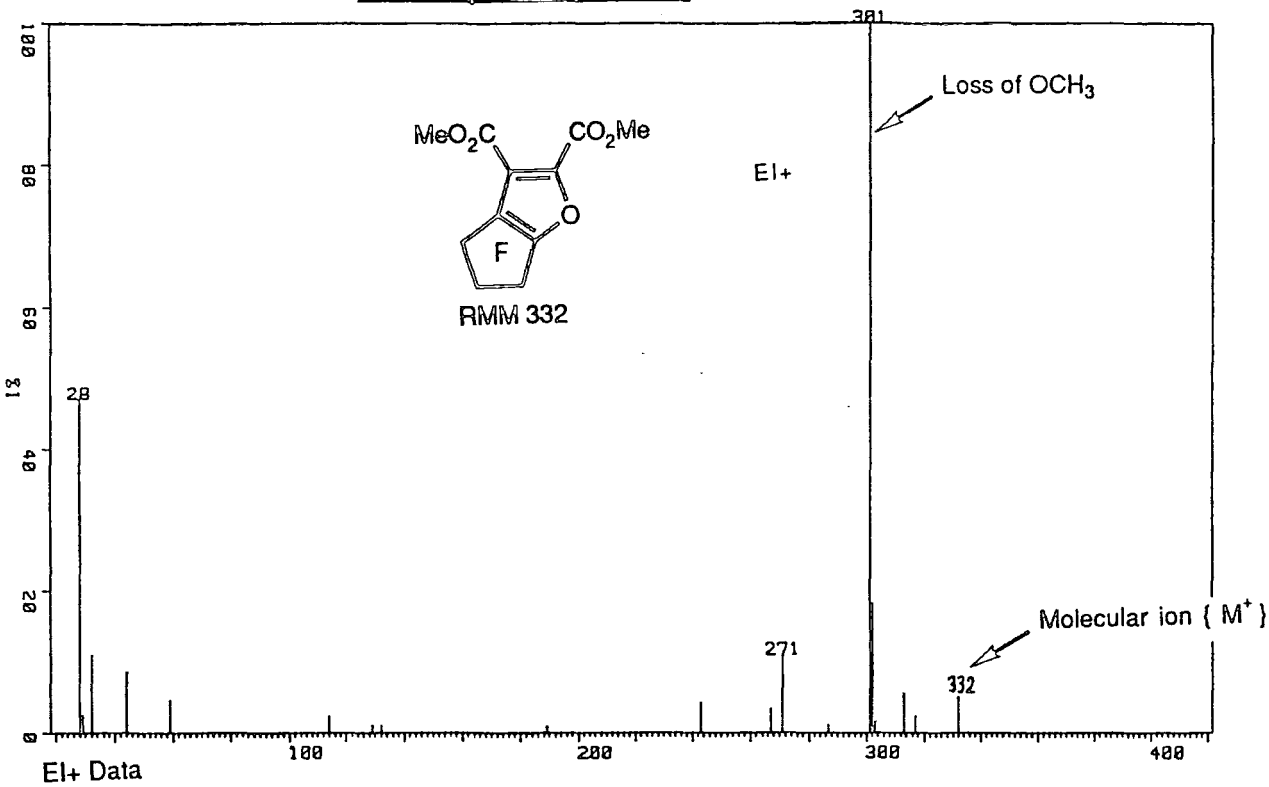


RMM 437

EI+ Data

Mass	% Base						
41.08	3.12	181.17	1.86	255.24	0.67	349.34	2.07
43.06	2.49	186.17	4.70	256.23	0.23	350.31	0.23
43.10	2.65	192.18	1.46	256.32	0.18	350.41	0.16
44.04	2.61	193.18	3.04	260.25	1.41	368.37	2.66
51.06	1.51	199.19	2.52	261.26	2.96	369.38	0.59
55.05	2.44	200.17	0.18	262.26	0.36	398.38	6.81
55.11	2.81	200.20	0.26	267.25	0.56	399.39	1.22
56.12	2.58	200.24	0.14	268.26	2.97	417.40	5.07
57.12	3.15	203.18	1.13	269.28	0.31	418.41	18.79
61.07	2.48	204.19	0.54	272.27	0.27	419.42	2.84
64.11	2.46	205.18	0.45	273.25	0.36	436.23	0.21
69.06	100.00	206.20	1.35	279.27	3.71	437.42	76.39
70.07	2.73	207.23	0.19	280.27	19.41	437.91	0.17
71.16	2.62	210.19	3.29	281.28	2.76	438.43	10.88
74.08	2.51	211.20	2.36	285.28	0.27	439.43	0.74
75.08	1.46	212.21	0.55	285.33	0.14	446.61	1.53
79.09	2.66	213.21	0.14	285.93	0.27	447.62	0.43
83.17	2.65	216.20	0.15	285.98	0.17	448.54	0.18
93.08	4.57	217.20	4.14	286.02	0.09		
98.09	1.03	218.21	0.69	286.27	33.62		
99.10	1.45	222.17	0.20	287.28	4.44		
100.10	1.32	222.27	0.14	288.28	0.14		
105.10	3.22	223.22	1.01	291.29	0.09		
106.11	1.01	224.21	3.99	292.29	0.24		
110.12	3.04	225.21	0.34	298.29	7.03		
111.11	2.73	229.21	2.14	299.30	4.16		
112.10	2.88	230.22	31.95	300.30	0.44		
113.11	6.20	231.23	3.17	304.91	0.11		
117.11	3.22	232.23	0.31	304.98	0.10		
123.13	3.05	236.22	5.72	305.30	35.72		
124.12	3.36	237.23	2.70	306.30	4.17		
130.13	1.30	241.23	0.98	307.31	0.27		
136.13	3.08	242.20	0.19	310.31	2.37		
141.13	2.17	242.25	0.19	311.31	0.44		
142.14	2.80	242.29	0.16	317.29	0.33		
148.14	2.69	248.24	8.95	318.32	2.51		
149.16	1.60	249.24	3.40	319.33	0.43		
161.16	3.30	250.19	0.17	323.34	0.12		
167.16	1.37	250.27	0.45	329.31	2.40		
179.17	2.53	253.29	0.15	330.33	1.77		
		254.19	0.26	331.32	0.23		
		254.27	0.29	348.34	8.02		

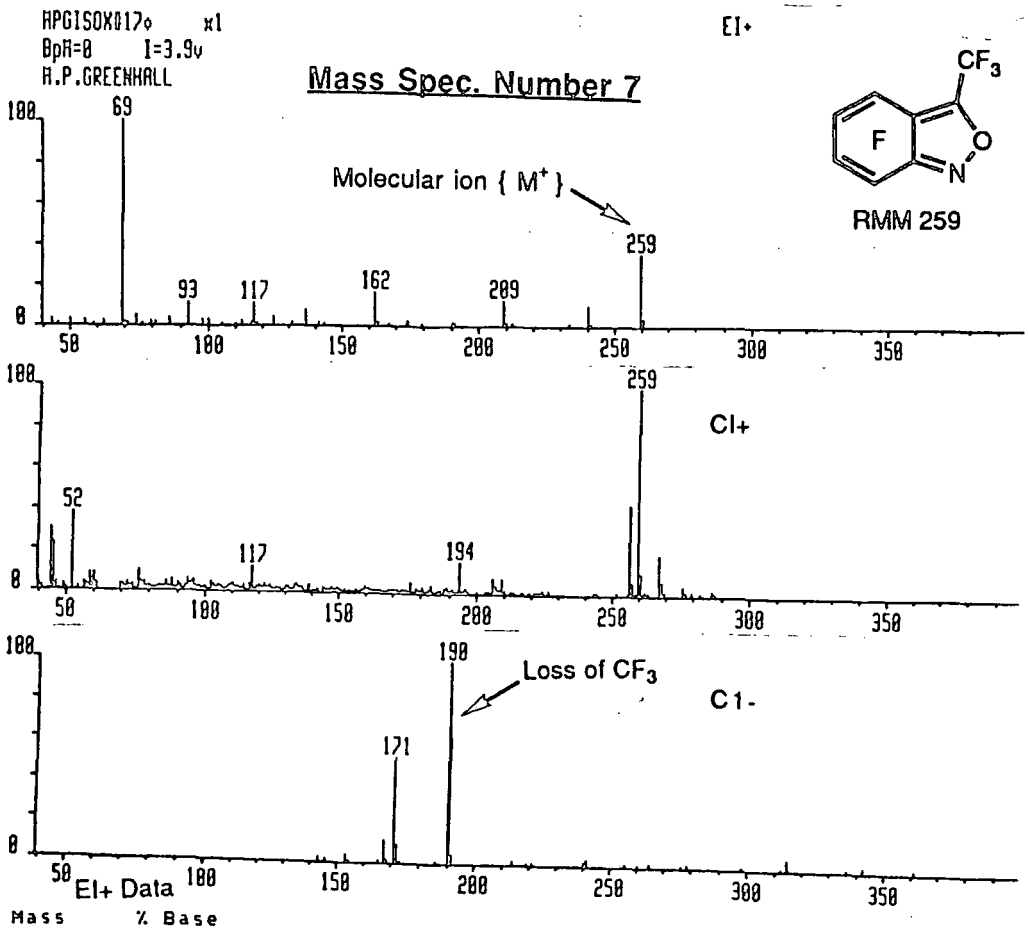
Mass Spec. Number 6



EI+ Data

Mass	% Base				
28.00	47.25	131.90	1.08	301.00	100.00
29.00	2.45	189.04	1.03	302.01	18.24
31.99	10.96	195.00	0.60	303.01	1.68
43.99	8.73	243.00	4.40	313.02	5.66
59.02	4.68	243.99	0.45	316.99	2.53
114.00	2.38	266.99	3.55	332.02	5.21
128.91	1.13	270.98	11.06		
		286.98	1.20		

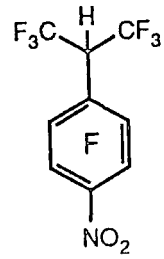
Mass Spec. Number 7



EI+ Data

Mass	% Base				
69.05	25.64	136.11	1.92	259.21	9.05
74.06	1.16	162.14	4.19		
93.08	2.76	209.16	3.20		
117.10	2.72	240.19	2.40		

Mass Spec. Number 8

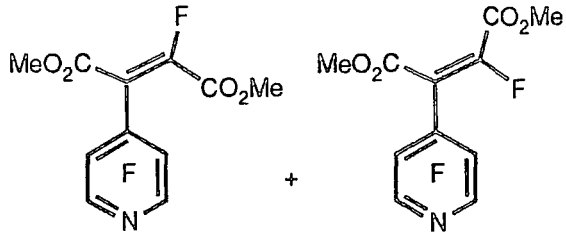


RMM 354

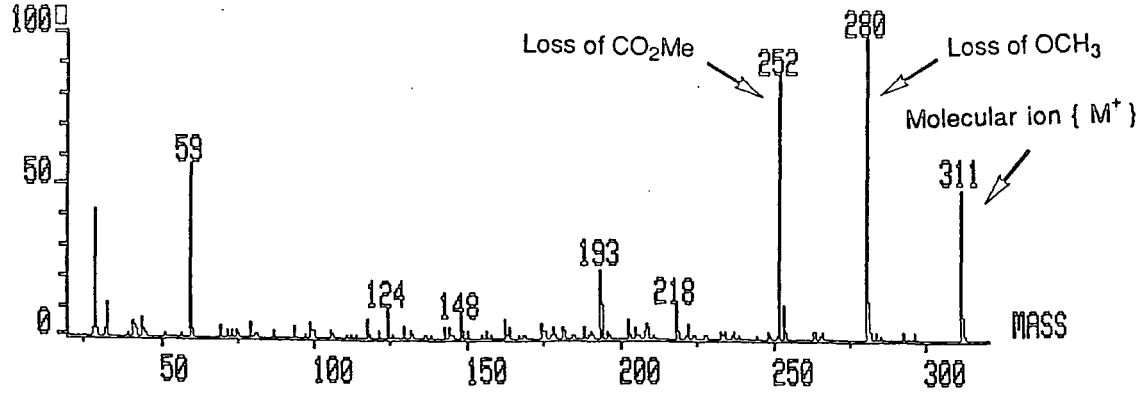
EI+ Data

MASS	X BASE
280.11	0.54
281.12	0.11
284.66	0.05
286.61	0.09
286.71	0.06
287.13	1.09
289.02	0.11
289.21	0.08
289.33	0.06
289.36	0.05
289.98	0.08
290.53	0.06
290.75	0.08
290.99	0.08
291.25	0.04
291.77	0.09
292.32	0.06
292.91	0.08
294.02	0.05
294.09	0.04
295.10	0.54
295.68	0.04
295.73	0.04
296.11	0.12
297.11	0.09
297.21	0.08
297.84	0.06
298.10	1.15
298.79	0.08
299.10	2.34
300.10	0.42
306.09	0.33
307.12	0.07
309.06	0.07
310.11	0.22
311.53	0.05
312.90	0.05
313.07	0.10
313.18	0.04
313.37	0.08
313.65	0.06
314.16	0.06
314.43	0.05
314.56	0.06
314.76	0.14
315.11	12.90
315.49	0.06
315.63	0.06
316.12	1.39
316.77	0.06
317.12	1.70
317.71	0.05
318.17	0.14
322.12	0.24
325.10	0.24
325.77	0.09
326.10	8.80
327.11	0.81
328.13	0.07
329.10	1.56
330.09	0.19
337.30	0.06
341.16	0.08
341.22	0.06
341.93	0.04
341.98	0.04
342.25	0.06
342.80	0.05
343.14	0.06
343.41	0.08
343.65	0.08
343.76	0.06
344.54	0.51
345.11	96.65
345.78	0.09
346.11	4.34
346.40	0.08
346.84	0.06
347.13	0.54
366.06	0.04
367.14	0.05
372.14	0.06
391.12	0.25
415.12	0.16

Mass Spec. Number 9



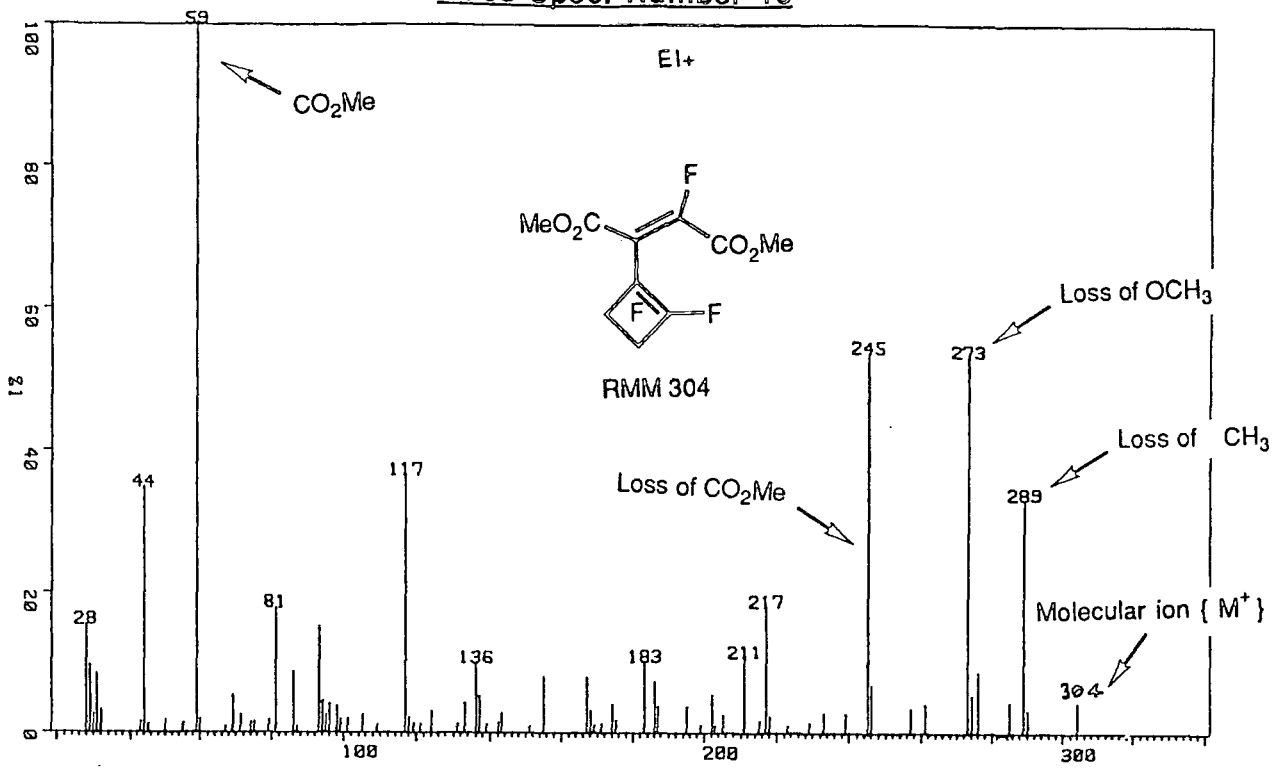
RMM 311 RMM 311



EI+ Data

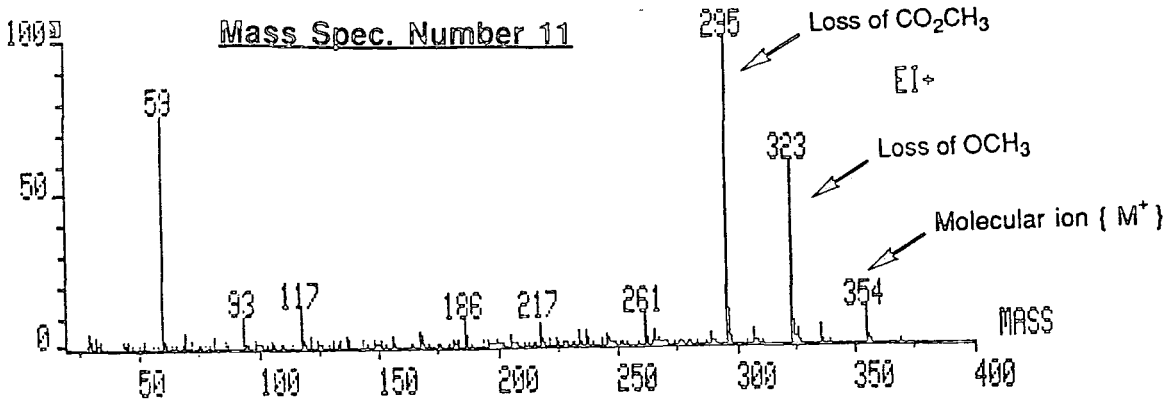
Mass	% Base		
28.21	27.70	220.85	0.32
32.17	6.20	221.86	5.16
40.09	2.30	222.86	0.66
41.16	1.35	223.86	0.32
43.16	3.34	224.89	0.12
59.03	17.44	226.23	0.15
78.92	2.39	226.72	0.30
92.93	2.57	227.26	0.13
97.91	3.55	230.86	0.11
116.90	6.58	231.86	1.64
123.91	9.88	232.87	0.51
128.90	1.87	233.87	0.62
130.90	1.11	234.86	0.20
142.88	2.65	235.86	0.39
143.89	2.97	236.84	0.78
147.90	6.73	237.85	0.33
148.90	1.55	239.85	0.25
149.89	1.16	243.88	0.82
161.89	5.36	245.82	0.15
163.90	2.15	247.84	1.10
173.89	4.23	248.85	0.45
174.88	1.31	249.83	0.15
175.89	2.17	250.84	0.52
177.88	2.83	251.84	100.00
180.88	2.86	252.85	10.61
181.89	1.65	253.85	0.93
187.89	2.54	261.83	0.26
189.91	1.10	262.86	1.01
192.88	23.40	263.87	1.06
193.90	11.62	264.84	0.28
194.89	1.19	265.85	0.40
201.85	6.05	267.86	0.14
202.87	0.70	276.82	0.15
203.60	0.14	279.55	0.09
203.95	3.75	279.83	84.38
204.62	0.14	280.83	9.91
204.86	0.78	281.82	1.05
205.84	0.50	282.84	0.81
206.88	1.23	284.85	0.27
207.88	5.28	291.86	1.68
208.86	2.27	292.86	0.22
209.85	0.46	295.82	1.28
210.85	0.22	310.84	63.90
211.87	0.26	311.27	0.11
215.87	0.18	311.85	8.15
217.85	11.21	312.84	0.99
218.84	0.99		
219.83	0.14		

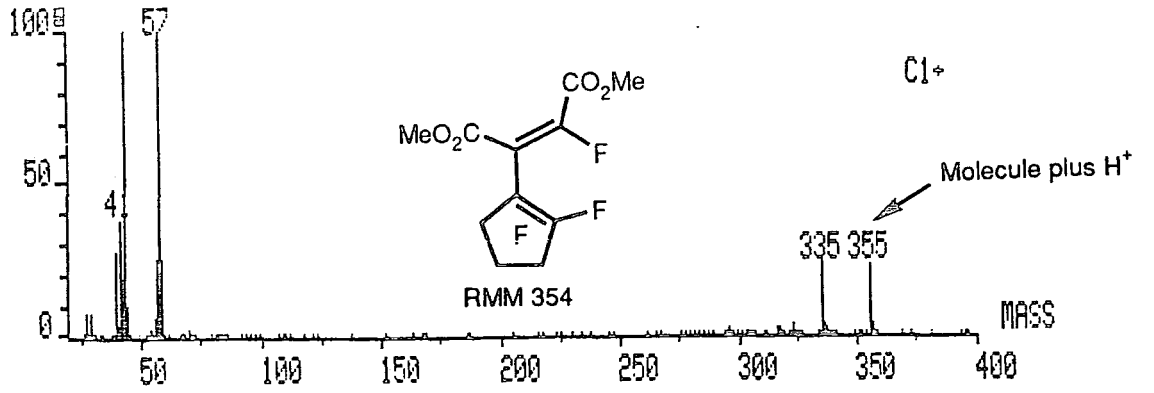
Mass Spec. Number 10

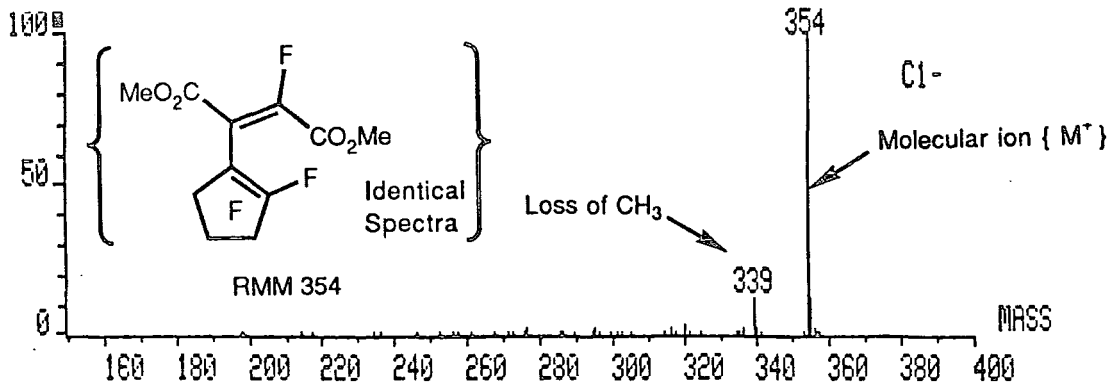


EI+ Data

Mass	% Base				
28.01	15.54	131.01	1.42	209.02	0.27
29.01	9.74	131.91	0.32	210.03	0.14
30.02	2.70	132.03	0.61	210.98	10.84
31.00	8.85	133.00	4.34	211.99	0.88
31.03	3.98	134.00	0.14	214.00	0.45
32.00	3.30	136.00	10.09	215.00	1.83
32.03	1.64	137.01	5.28	217.01	18.08
43.03	1.59	138.02	0.30	218.02	2.40
44.00	34.82	139.03	1.27	223.01	1.13
45.02	1.31	141.94	1.56	226.02	0.54
50.01	1.89	143.01	2.92	226.99	0.83
55.01	1.53	145.01	0.53	229.04	1.64
59.03	100.00	148.00	0.62	230.00	0.66
60.03	1.98	149.01	0.30	231.00	0.67
67.01	1.05	150.02	0.46	233.01	2.93
69.01	5.37	151.03	1.01	238.03	0.32
71.00	2.66	152.01	0.37	239.00	2.90
74.01	1.64	155.00	8.12	240.01	0.15
75.02	1.67	156.00	0.66	245.01	53.73
79.01	1.91	157.01	0.32	246.02	6.87
81.02	17.86	158.99	0.25	247.02	0.52
86.01	8.79	160.99	0.23	254.97	0.18
87.01	1.01	163.02	0.17	257.03	3.60
93.03	15.14	164.00	0.54	258.02	0.39
93.95	4.55	165.00	0.39	261.01	4.22
95.00	2.59	166.99	7.97	262.00	0.23
95.95	4.20	167.99	3.15	270.02	0.16
98.01	3.83	169.00	1.11	273.01	53.26
99.01	1.97	170.01	0.21	274.01	5.42
100.01	0.72	170.98	1.53	275.02	0.66
101.03	2.15	173.99	4.09	276.03	8.68
102.00	0.23	175.01	1.91	277.03	0.69
102.02	0.23	176.02	0.21	285.03	4.47
105.01	2.68	179.03	0.37	286.04	0.37
106.01	0.41	181.02	0.65	289.00	33.07
109.00	1.20	183.00	10.24	290.01	3.31
112.02	0.25	184.00	0.83	291.02	0.37
113.01	0.54	186.00	7.32	304.02	4.40
114.00	0.14	187.01	3.87	305.03	0.67
117.01	36.46	188.01	0.30		
118.01	2.26	189.00	0.45		
119.02	1.45	190.01	0.14		
120.03	0.32	193.00	0.20		
121.03	1.42	195.01	3.81		
124.00	3.16	196.02	0.56		
125.01	0.76	197.01	0.37		
126.01	0.32	198.02	0.39		
126.92	0.47	199.00	1.23		
127.03	0.10	202.00	5.50		
128.92	0.45	203.01	1.07		
130.91	0.32	205.02	2.64		
		207.02	0.23		



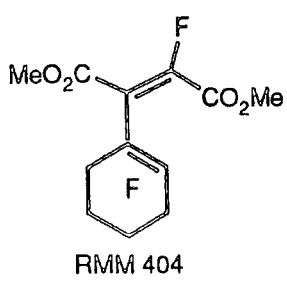




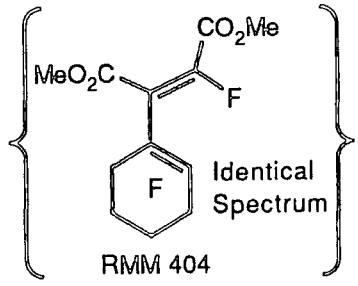
EI+ Data

Mass	% Base	Mass	% Base
28.98	3.05	323.90	4.15
30.99	1.65	324.91	0.50
58.98	71.11	325.91	3.26
59.98	1.58	326.92	0.40
68.96	3.74	334.91	5.04
80.96	2.01	335.92	0.69
85.95	1.58	338.88	0.38
92.97	8.31	353.91	9.79
97.94	1.37	354.92	1.25
116.93	11.22	355.91	0.16
120.97	2.31	368.90	0.38
130.93	1.74		
135.93	2.32		
147.92	1.80		
154.92	1.99		
166.92	3.58		
167.92	2.48		
185.90	7.09		
186.90	2.18		
204.90	3.00		
216.91	3.62		
217.91	1.27		
232.89	3.98		
235.90	4.55		
236.91	1.62		
244.90	2.34		
260.88	7.67		
264.90	3.59		
288.88	1.57		
294.90	100.00		
295.90	10.00		
303.89	0.11		
306.91	2.78		
307.92	0.38		
310.89	0.20		
322.89	40.05		

Mass Spec. Number 12



RMM 404

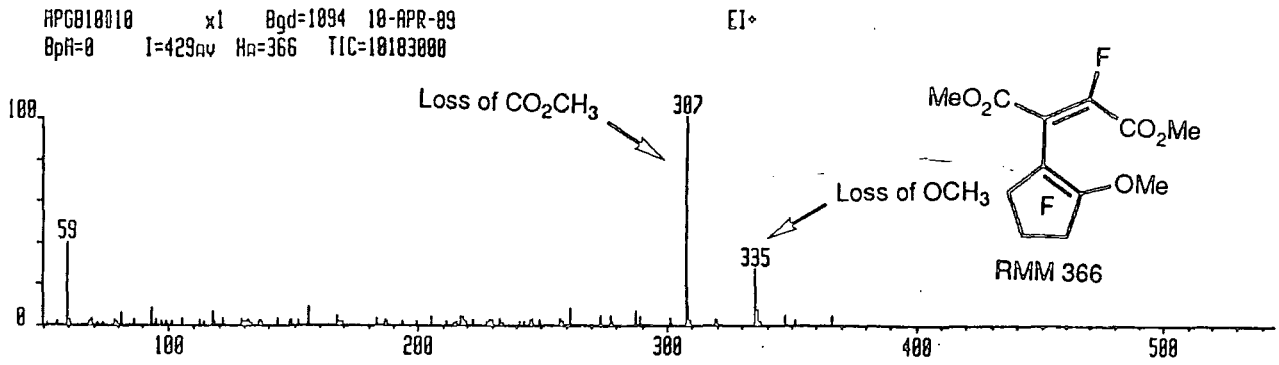


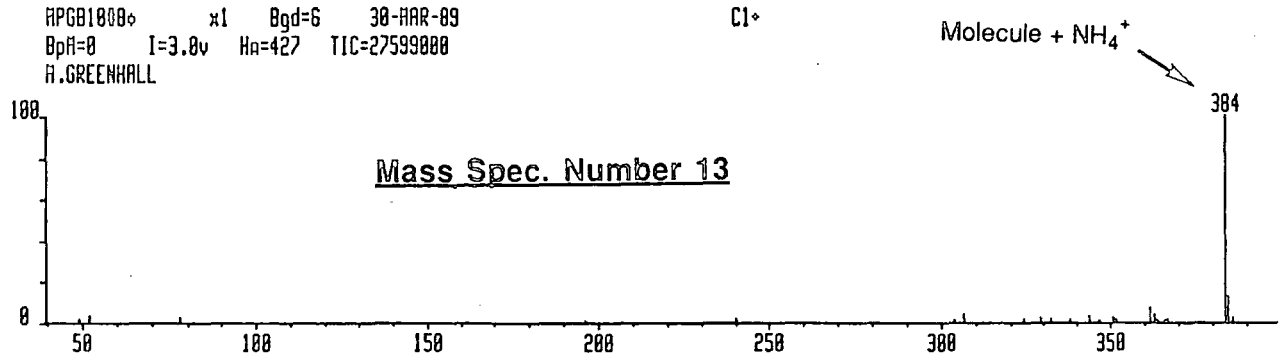
RMM 404

EI+

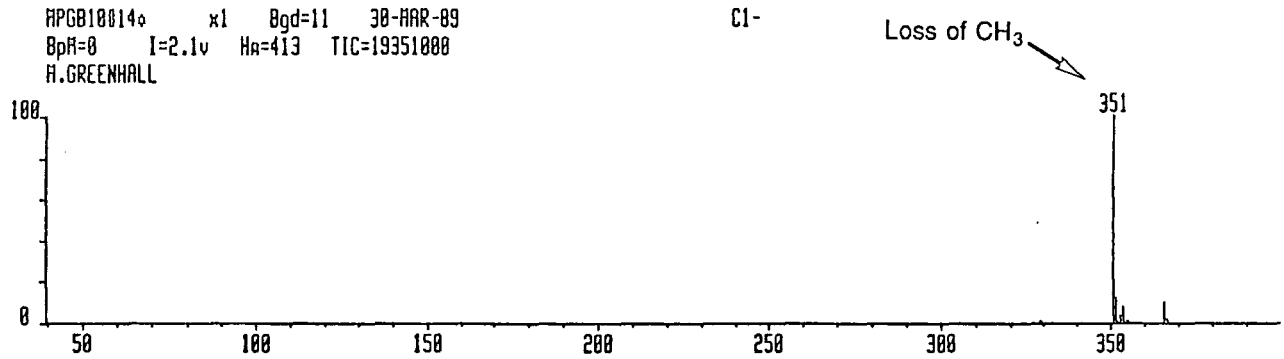
EI+ Data

Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
27.75	3.35	136.10	1.98	210.14	2.94	276.19	0.25	336.22	0.20
27.77	4.22	137.10	0.61	211.14	1.77	277.19	0.09	338.23	0.04
28.77	11.29	138.11	0.07	212.15	0.21	278.20	0.07	339.19	0.60
29.78	2.96	141.09	2.69	213.16	0.39	279.19	0.53	341.23	0.16
30.77	3.59	142.06	0.43	214.15	0.15	280.21	0.11	344.27	0.08
30.79	4.75	143.10	0.57	216.16	0.09	281.17	0.10	345.21	33.35
31.77	1.21	145.09	0.18	217.13	5.33	281.23	0.13	346.22	4.07
31.81	1.68	148.09	2.19	218.14	1.28	283.17	0.58	347.23	0.43
42.87	1.28	149.10	0.37	219.14	1.08	284.22	0.10	351.22	0.41
43.85	4.47	150.11	0.20	220.16	0.14	286.18	1.93	354.20	0.11
44.90	1.68	151.12	0.25	221.14	0.27	287.19	0.28	355.23	0.43
50.91	1.34	155.12	2.13	223.13	0.10	289.17	0.20	357.24	2.47
58.96	100.00	156.14	0.23	224.15	0.07	291.18	0.29	358.25	0.31
59.97	2.53	157.13	0.04	225.16	0.20	292.20	0.07	361.24	0.16
69.01	8.07	160.12	1.66	226.15	0.09	293.20	0.23	366.26	1.78
71.01	1.56	161.13	1.23	227.16	0.07	294.20	0.08	367.25	0.40
81.06	2.92	162.13	0.15	229.15	0.61	294.51	0.11	373.24	34.03
86.05	1.51	163.14	0.73	230.16	0.16	294.74	0.13	374.25	3.89
93.06	3.77	164.12	0.10	231.17	0.30	294.83	0.09	375.25	0.46
93.10	5.62	167.12	2.81	232.16	0.06	294.91	0.09	376.27	0.23
98.06	1.76	168.12	1.23	233.15	0.45	295.19	1.59	385.27	2.82
99.07	1.13	169.12	0.14	235.15	0.16	295.36	0.09	386.27	0.50
100.06	1.41	174.12	0.30	236.15	1.87	295.54	0.07	389.24	0.32
101.09	0.37	175.14	0.23	237.16	0.84	296.18	0.39	404.23	8.37
102.07	0.12	176.11	0.07	238.18	0.06	297.19	4.73	405.23	1.01
103.07	0.34	179.12	3.08	239.16	0.73	298.20	0.50	406.22	0.13
104.09	0.10	180.13	0.47	243.15	0.61	299.19	0.13		
105.07	1.01	181.14	1.09	245.15	1.04	300.21	0.32		
106.08	0.30	182.15	0.29	246.17	0.18	302.17	0.16		
109.07	0.18	183.12	0.29	247.17	0.32	306.21	0.71		
110.07	0.80	186.12	4.91	248.16	0.47	307.20	1.22		
111.08	0.64	187.13	1.02	249.16	0.46	308.22	0.22		
112.08	0.28	188.10	0.08	250.18	0.15	309.23	0.09		
113.08	0.56	188.14	0.09	251.18	0.50	310.23	0.46		
114.08	0.08	189.13	0.11	254.16	0.10	311.17	2.81		
117.09	10.89	191.13	0.14	255.16	2.20	312.17	0.22		
118.09	0.85	192.13	0.96	256.17	0.15	313.20	0.17		
119.10	0.27	193.12	0.70	257.18	0.19	314.20	0.10		
121.13	3.44	194.15	0.10	258.18	0.14	315.19	1.63		
122.10	0.50	195.12	0.66	261.15	0.22	316.21	0.23		
123.10	0.36	198.12	1.77	262.19	0.10	317.22	0.11		
124.10	0.93	199.13	2.68	264.15	0.19	319.23	0.17		
125.12	0.23	200.14	0.35	265.16	0.34	320.26	0.08		
126.10	0.10	201.15	0.17	267.16	2.32	323.21	0.63		
127.01	0.13	202.12	0.19	268.17	0.61	324.23	0.10		
129.10	1.01	203.12	0.07	269.18	9.04	325.19	0.03		
130.11	0.27	205.13	1.89	270.18	1.31	326.21	0.34		
131.10	2.52	206.14	0.23	271.17	0.45	327.21	0.50		
132.12	0.28	207.13	0.18	273.18	0.22	328.23	1.38		
133.10	0.45	208.14	0.18	274.18	0.06	329.23	0.54		
		209.16	0.07	275.18	1.52	335.21	1.48		





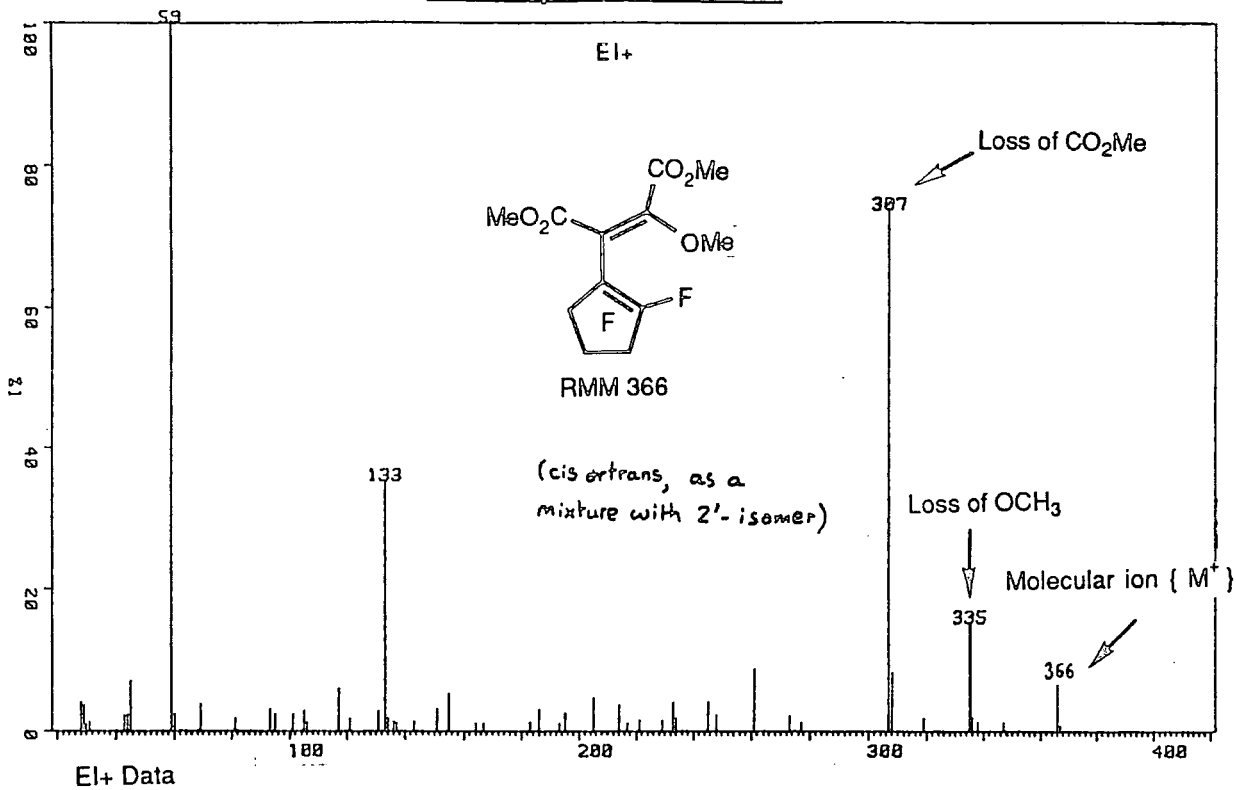
Mass Spec. Number 13



EI+ Data

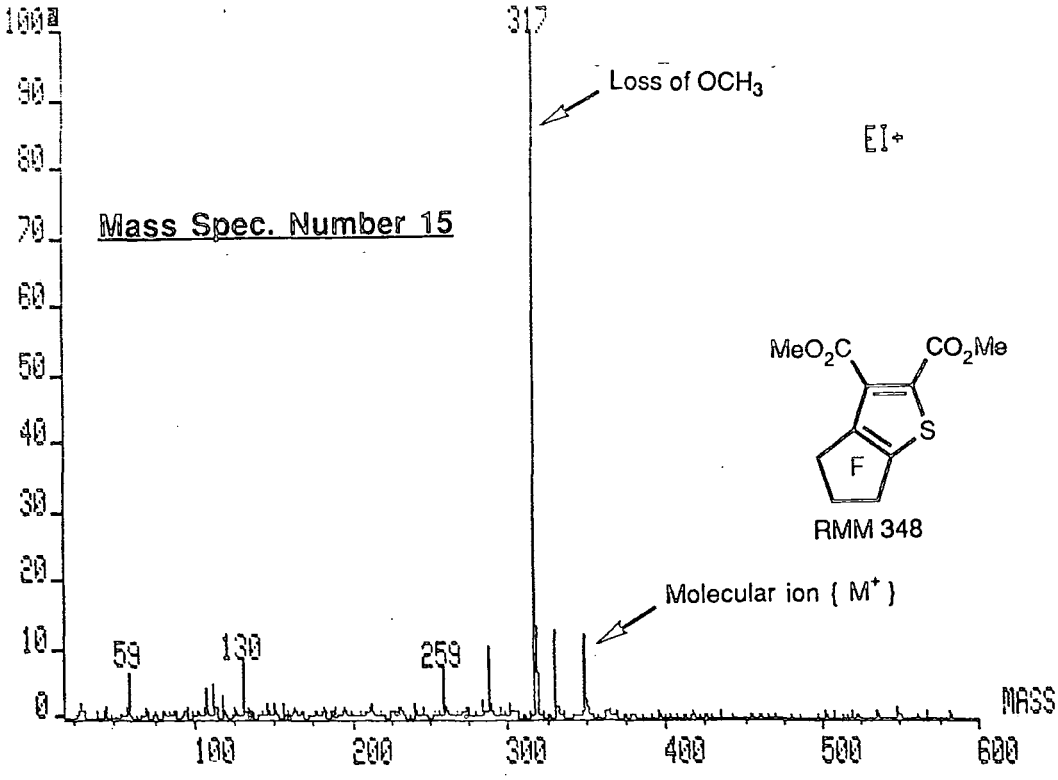
Mass	% Base				
55.14	1.07	183.20	2.84	336.26	6.47
59.10	39.01	186.22	1.92	337.29	1.35
60.11	1.78	187.20	1.35	347.26	4.33
68.04	1.07	193.29	1.07	351.26	1.78
69.10	2.49	199.16	1.35	366.30	4.05
69.17	1.21	205.17	3.62		
78.11	1.92	211.17	1.35		
79.12	1.39	214.13	0.82		
81.11	5.33	215.13	1.35		
86.11	1.78	217.17	3.06		
93.15	7.50	218.15	3.48		
95.10	1.92	219.26	1.21		
97.20	1.21	222.39	1.71		
99.15	1.07	228.19	1.35		
101.15	1.14	229.21	1.95		
105.13	2.77	230.18	1.78		
112.14	1.71	233.20	2.91		
114.16	1.63	234.20	0.64		
117.13	5.90	241.25	1.35		
118.15	1.39	243.18	1.21		
121.16	2.52	245.20	1.92		
121.21	0.82	246.20	2.49		
129.05	2.52	249.24	1.78		
130.01	1.35	257.28	2.84		
131.06	2.13	258.23	0.92		
132.06	2.34	258.30	1.35		
133.15	0.78	261.19	7.60		
136.05	0.78	273.21	4.19		
136.08	1.49	277.25	4.05		
136.15	1.78	278.31	1.35		
137.14	1.21	287.24	5.75		
143.15	2.49	289.28	3.06		
148.10	1.35	301.27	2.52		
148.16	1.07	307.27	100.00		
148.22	1.78	308.27	8.74		
151.24	1.78	309.32	2.20		
155.14	7.89	319.23	1.71		
167.17	3.98	319.34	1.78		
168.19	1.07	335.28	26.36		
169.19	1.07				

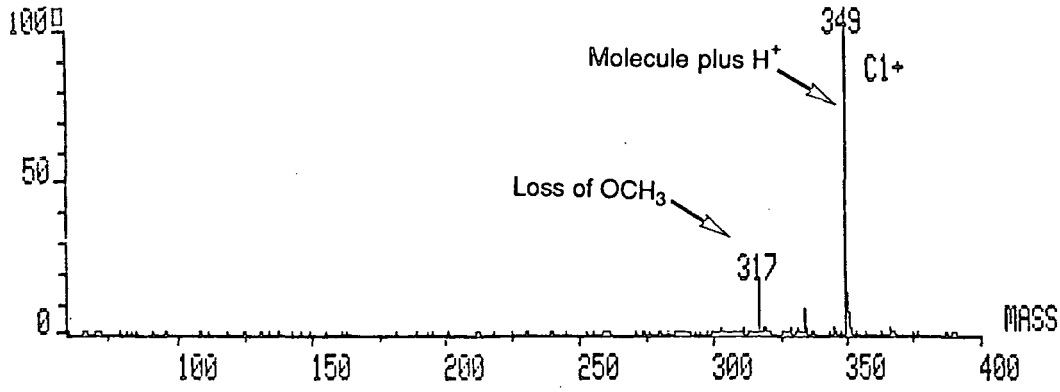
Mass Spec. Number 14

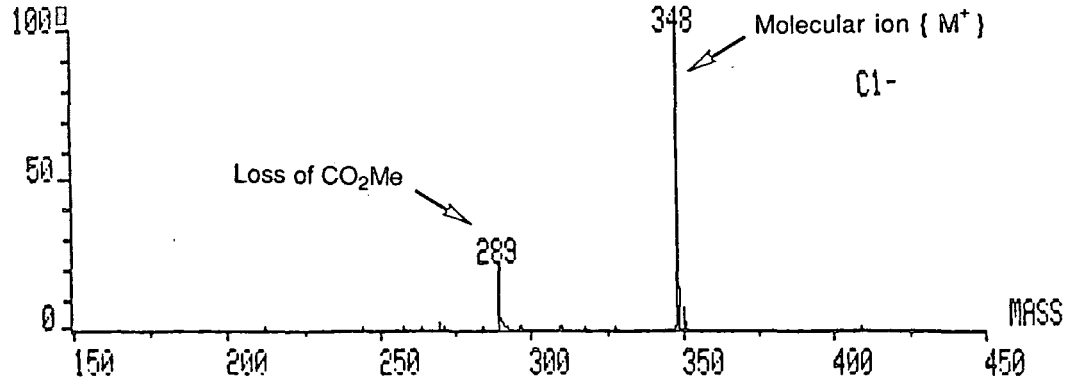


EI+ Data

Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
28.00	4.14	185.04	0.39	237.03	0.41	315.02	0.11
29.01	3.73	186.00	3.09	238.99	0.67	319.04	1.87
30.01	1.02	187.01	0.65	241.04	0.05	320.05	0.18
31.01	1.27	188.03	0.05	242.01	0.06	321.01	0.07
43.02	2.29	189.03	0.21	242.06	0.04	323.03	0.17
43.99	2.35	193.00	1.17	243.01	0.12	328.05	0.15
45.03	7.05	194.01	0.05	245.00	4.11	331.01	0.09
59.02	100.00	195.00	2.57	246.01	0.63	334.01	0.39
60.03	2.46	196.00	0.40	247.01	0.87	335.02	15.31
69.00	3.83	197.01	0.38	248.02	2.33	336.03	1.95
81.02	1.89	198.01	0.17	249.02	0.55	337.03	0.20
93.02	3.16	199.01	0.76	251.03	0.30	338.05	1.38
95.00	2.45	200.01	0.32	257.02	0.29	339.05	0.11
101.03	2.45	201.02	0.39	258.01	0.13	347.05	1.28
105.00	3.01	202.00	0.22	259.02	0.08	348.05	0.11
106.01	1.30	203.01	0.04	260.98	8.81	351.01	0.78
117.01	6.12	204.99	4.70	261.98	0.79	352.03	0.05
121.03	1.82	206.00	0.64	263.00	0.15	366.04	6.56
131.01	3.01	207.02	0.67	267.03	0.18	367.04	0.81
133.05	35.34	208.02	0.11	269.03	0.05	368.04	0.10
134.05	1.99	209.01	0.05	273.00	2.16		
136.00	1.50	210.02	0.07	273.99	0.27		
137.01	1.18	211.00	0.58	274.99	0.82		
143.00	1.54	212.01	0.08	276.01	0.17		
150.02	0.82	213.03	0.09	277.02	1.27		
151.03	3.14	213.99	3.68	278.02	0.23		
152.02	0.23	215.00	0.64	279.03	0.25		
155.00	5.28	217.01	1.17	280.04	0.09		
156.01	0.61	218.01	0.34	281.10	0.09		
157.01	0.37	219.01	0.56	281.37	0.08		
161.01	0.10	220.02	0.63	281.62	0.08		
162.01	0.11	220.99	1.62	281.87	0.07		
163.03	0.39	221.40	0.02	281.99	0.06		
164.01	1.21	221.54	0.06	282.05	0.04		
165.02	0.14	221.76	0.07	285.03	0.22		
167.01	1.12	221.87	0.05	286.02	0.05		
168.02	0.51	222.01	0.16	287.02	0.32		
169.02	0.74	222.15	0.04	291.04	0.22		
170.03	0.93	222.21	0.04	292.00	0.65		
171.00	0.57	223.01	0.10	293.01	0.72		
174.00	0.32	226.01	0.11	294.02	0.07		
175.01	0.49	227.00	0.25	295.03	0.20		
176.01	0.06	228.01	0.26	297.03	0.03		
177.01	0.06	229.02	1.58	301.01	0.07		
179.03	0.29	230.02	0.19	302.00	0.12		
180.02	0.09	231.01	0.09	305.02	0.27		
181.02	0.67	232.99	4.12	306.03	0.14		
182.03	0.11	234.00	1.89	307.03	73.87		
183.00	1.30	235.01	0.21	308.03	8.17		
184.01	0.26	236.01	0.05	309.04	0.82		
				314.01	0.13		

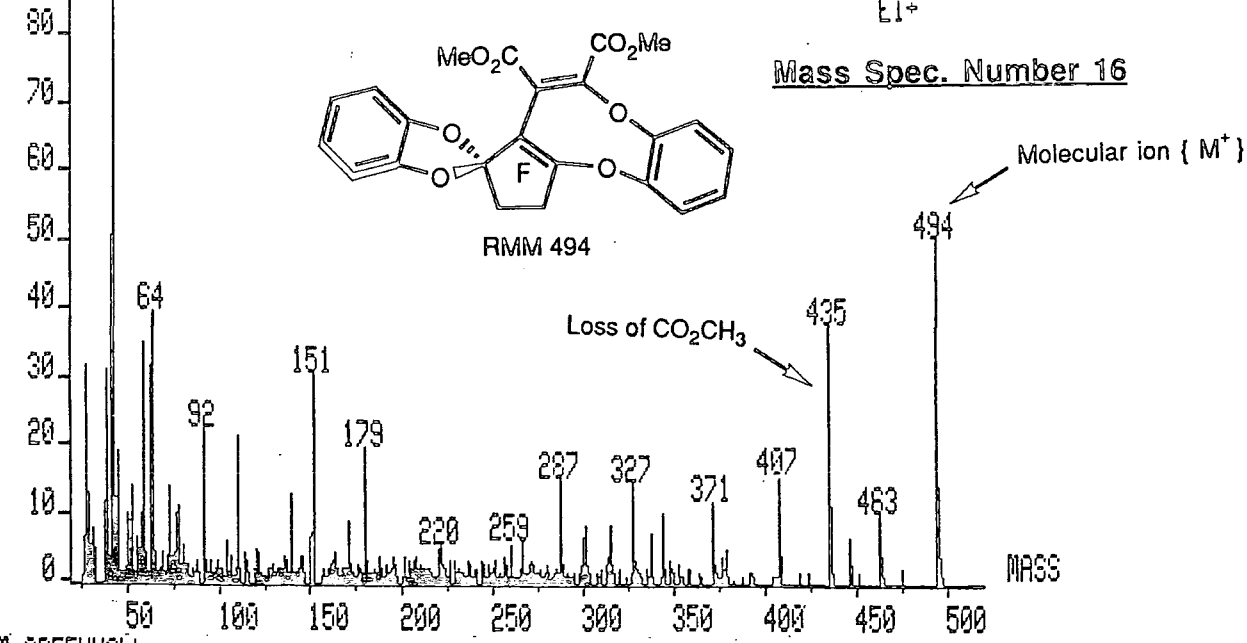


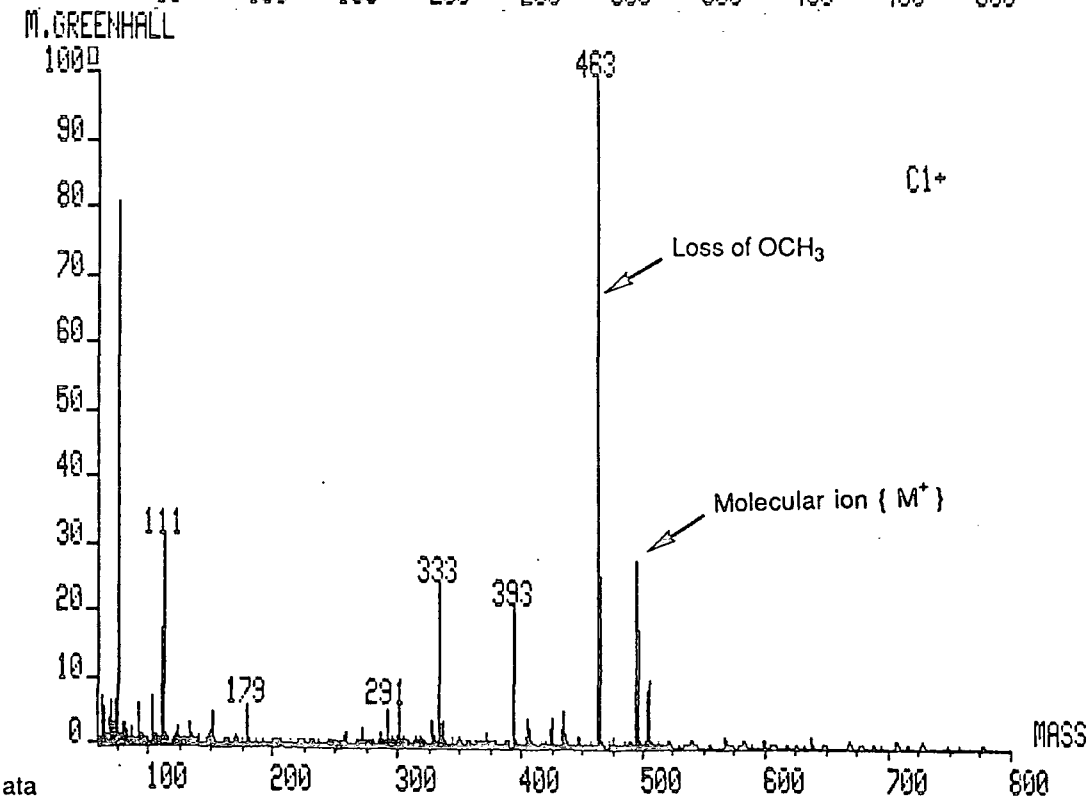




EI+ Data

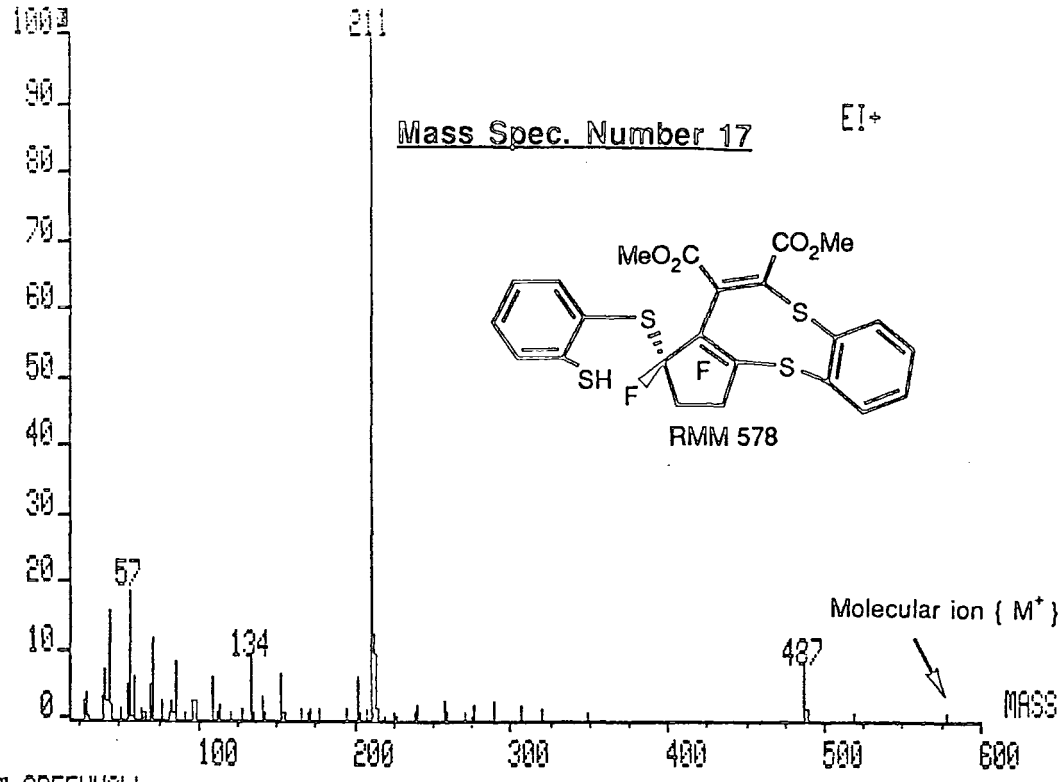
Mass	% Base
107.93	3.79
110.93	4.42
117.93	2.66
129.93	7.95
130.94	3.40
258.92	6.58
282.91	2.11
286.90	10.30
317.00	100.00
317.94	13.08
318.94	6.19
328.97	12.40
347.97	9.27
348.98	12.14
349.97	2.06



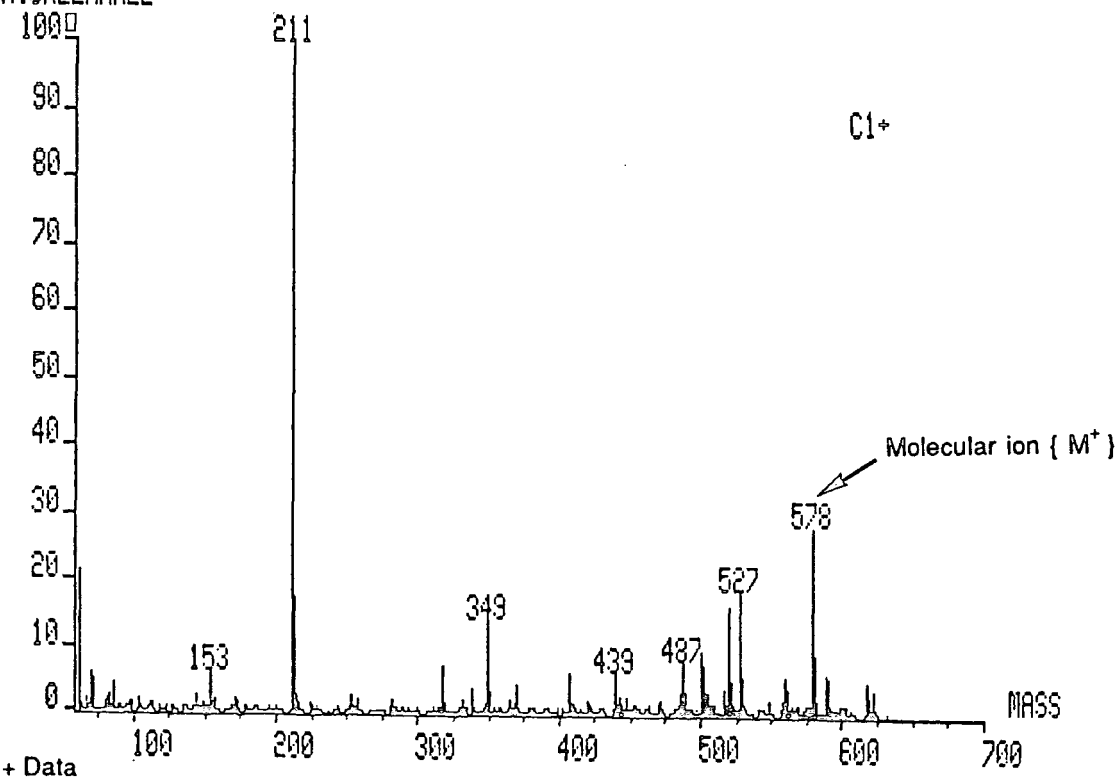


EI+ Data

Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
60.03	3.97	91.05	2.94	135.04	3.43	179.02	19.32	225.00	2.65	277.97	1.29
61.02	1.19	92.03	22.05	136.02	2.63	180.02	2.84	227.99	2.73	279.00	2.06
62.03	3.47	93.03	2.62	137.02	1.32	181.02	1.88	229.00	1.29	280.97	1.01
63.03	31.56	95.03	3.07	138.03	1.41	182.01	1.27	231.00	1.49	283.00	1.03
64.04	39.39	97.11	1.93	139.03	12.85	184.02	1.68	231.51	1.11	283.98	1.85
65.05	4.07	98.00	1.24	141.07	1.19	185.01	1.34	236.01	2.58	284.98	1.55
66.05	1.14	99.01	2.93	143.02	1.59	187.02	3.43	237.00	2.48	285.99	1.11
67.07	1.55	100.03	1.73	144.02	3.51	188.02	1.73	239.01	1.47	286.98	14.78
69.01	1.42	101.03	1.78	145.03	3.33	191.01	2.40	241.00	1.65	287.99	2.08
69.08	3.99	102.00	1.80	149.02	6.26	192.03	1.23	243.00	2.86	294.99	1.26
70.09	1.41	104.03	5.84	150.02	6.88	193.02	1.88	243.99	2.30	296.96	1.37
71.10	3.24	105.03	1.19	151.03	30.37	194.01	3.48	246.99	2.17	297.99	2.27
72.06	1.45	107.05	3.53	152.03	2.94	195.01	2.34	248.00	1.10	298.98	6.03
73.06	13.45	109.01	1.49	157.01	1.47	200.01	3.42	249.00	1.93	326.97	14.29
74.02	3.33	110.04	20.89	159.03	1.49	201.01	2.22	249.97	2.62	334.99	1.72
74.06	1.03	111.03	1.57	160.00	2.03	203.01	2.99	251.00	1.59	336.97	6.85
75.03	3.82	112.04	1.42	161.00	1.83	204.02	1.85	253.00	1.42	342.96	9.50
76.04	9.63	114.00	4.12	162.02	2.88	206.00	2.68	255.98	3.15	370.92	11.39
77.04	11.05	115.01	1.19	163.03	3.87	207.01	3.42	256.98	2.12	371.93	2.03
78.05	1.90	115.06	2.73	164.04	1.63	208.02	1.50	258.94	5.36	406.96	15.07
79.02	2.32	117.00	1.06	166.01	1.81	209.01	2.53	264.00	1.75	407.97	3.68
79.06	2.57	119.01	1.83	167.01	1.21	209.99	1.50	264.99	5.62	434.93	37.64
80.03	5.30	120.02	4.54	168.03	1.49	212.01	1.60	266.01	1.50	435.93	10.82
81.03	2.48	121.03	3.87	169.02	1.70	213.01	1.81	266.99	1.13	436.93	1.16
81.07	1.37	123.03	1.06	170.01	8.29	214.04	1.52	267.97	1.06	446.05	6.52
82.05	1.31	126.00	1.73	171.02	1.78	215.99	1.01	268.98	1.06	462.91	9.79
83.02	2.04	128.03	1.83	172.00	2.50	219.01	4.67	269.98	2.40	463.92	3.25
83.09	1.72	129.03	2.08	173.02	1.27	220.02	5.28	270.96	3.11	464.92	0.51
85.11	1.81	130.04	1.03	175.02	2.40	221.02	2.65	271.95	2.42	474.94	1.95
86.01	1.05	133.02	1.68	176.05	1.60	222.00	2.53	272.96	1.37	493.91	50.39
88.03	2.62	134.05	1.49			223.03	1.91	276.01	1.73	494.93	13.84



M.GREENHALL

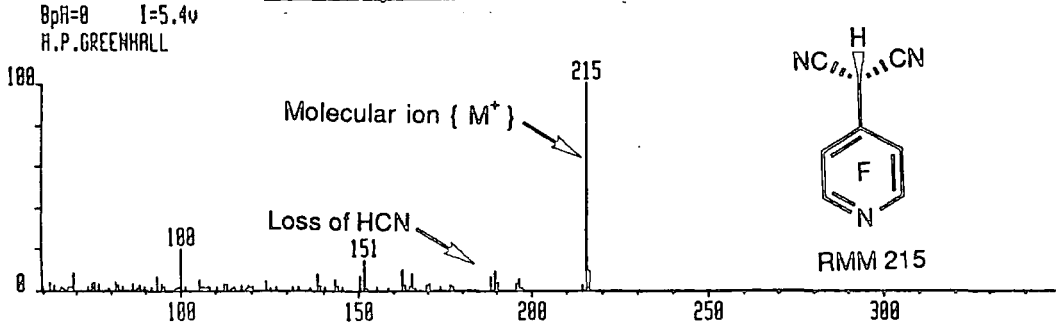


EI+ Data

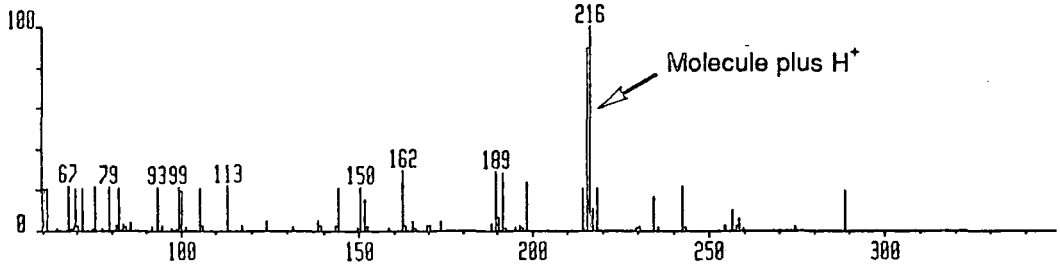
Mass	% Base		
68.91	4.35	218.90	0.27
69.00	3.09	224.92	0.57
71.02	11.52	225.93	0.22
76.99	2.22	237.90	0.32
83.05	2.08	238.89	1.68
85.06	7.99	256.88	2.18
95.97	2.09	257.88	0.37
97.06	2.39	269.88	0.35
99.08	2.57	274.90	0.24
107.96	5.53	275.90	1.69
133.98	8.35	288.88	2.47
139.93	2.76	306.86	1.59
151.92	4.48	318.86	0.91
152.94	6.21	347.84	0.72
201.90	5.70	486.82	7.28
202.90	0.33	487.83	1.37
206.93	0.52	488.82	0.98
207.90	1.03	518.74	0.84
210.91	100.00	577.80	0.62
211.91	11.90		
212.90	9.37		
213.91	1.14		
214.90	1.30		

Mass Spec. Number 18

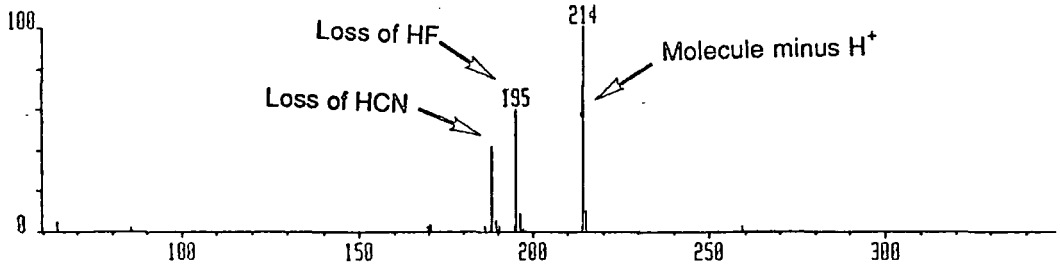
HPGE9C028◊ x1 EI+
BpH=0 I=5.4v
H.P.GREENHALL



HPGE9C025◊ x1 C1+
BpH=0 I=10v
H.P.GREENHALL



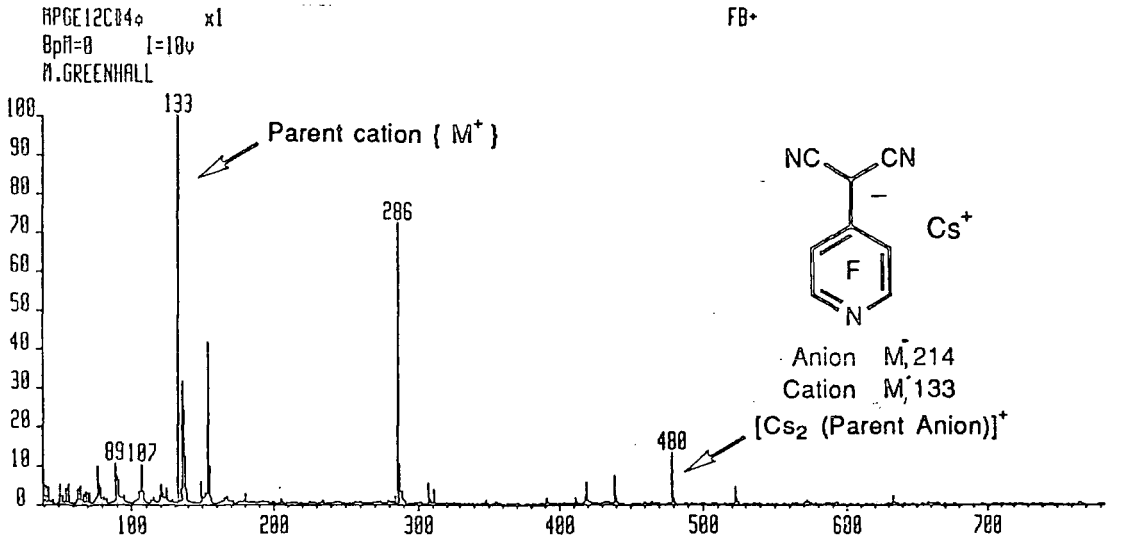
HPGE9C029◊ x1 C1-
BpH=0 I=3.1v
H.P.GREENHALL

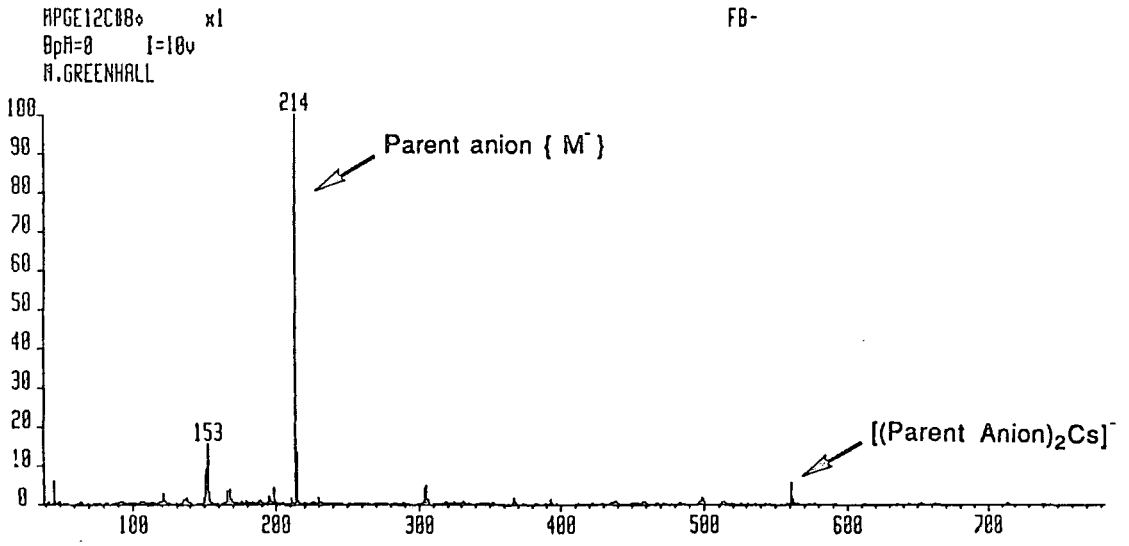


EI+ Data

Mass	% Base						
62.15	3.53	108.25	1.62	139.30	2.03	176.92	1.29
63.16	2.02	109.25	0.05	139.39	0.06	176.96	1.28
69.15	8.01	110.23	1.28	139.41	0.03	176.99	0.09
74.17	3.69	110.25	0.06	139.42	0.06	177.31	1.53
75.18	3.13	112.25	2.73	139.44	0.04	177.47	0.05
76.17	2.39	113.26	2.84	140.32	1.51	177.50	0.08
81.19	3.37	114.26	0.61	143.30	4.80	177.54	0.08
82.20	2.36	115.27	1.31	144.31	1.88	177.58	0.06
86.20	2.43	117.25	1.91	145.32	1.16	177.63	0.07
88.21	2.07	118.26	0.70	146.32	0.28	177.90	0.05
93.21	6.34	119.26	2.04	149.34	0.29	178.37	0.07
94.22	2.90	120.21	1.23	150.31	6.43	178.40	0.06
100.11	0.03	120.27	1.27	151.32	14.37	183.39	0.13
100.22	19.59	121.28	0.19	152.33	0.67	184.40	0.24
101.23	1.50	124.27	4.08	155.33	1.30	188.38	5.37
102.24	0.11	125.28	0.91	157.33	0.21	195.24	0.06
105.23	4.45	126.28	0.29	158.34	0.69	189.39	8.73
105.29	0.05	126.64	0.05	159.34	0.08	190.40	3.62
106.11	1.28	126.72	0.04	160.19	0.07	191.41	0.26
106.13	0.05	127.00	0.05	162.33	9.47	195.39	2.36
106.17	0.07	127.04	1.29	163.34	1.92	196.41	4.60
106.24	1.34	127.09	0.05	164.35	1.58	197.42	0.60
106.29	0.06	127.29	0.13	164.49	0.06	198.42	0.06
106.32	0.07	130.27	0.08	164.53	0.05	213.48	0.03
106.34	1.29	130.30	0.04	164.59	0.09	214.17	0.04
106.36	0.05	131.22	0.05	164.65	0.06	214.22	0.04
106.39	0.05	131.29	1.43	164.74	0.08	214.25	0.05
106.40	0.05	132.29	0.35	164.80	0.06	214.42	1.90
106.43	0.07	133.29	1.33	164.83	0.05	215.42	100.00
106.44	1.27	136.24	0.05	164.87	0.06	215.82	0.06
106.48	0.04	136.29	0.63	164.89	0.06	215.92	1.29
106.52	0.05	137.30	0.17	164.97	1.28	215.96	0.05
106.54	0.06	138.30	7.22	165.02	0.08	216.09	0.06
106.56	1.29	139.04	0.07	165.14	0.04	216.12	0.03
107.24	1.33	139.06	0.05	165.35	7.35	216.25	0.05
107.70	1.29	139.08	0.06	166.36	0.73	216.44	8.64
107.75	0.79	139.14	0.06	167.37	0.13	217.44	0.43
		139.18	0.06	169.35	2.32		

Mass Spec. Number 19



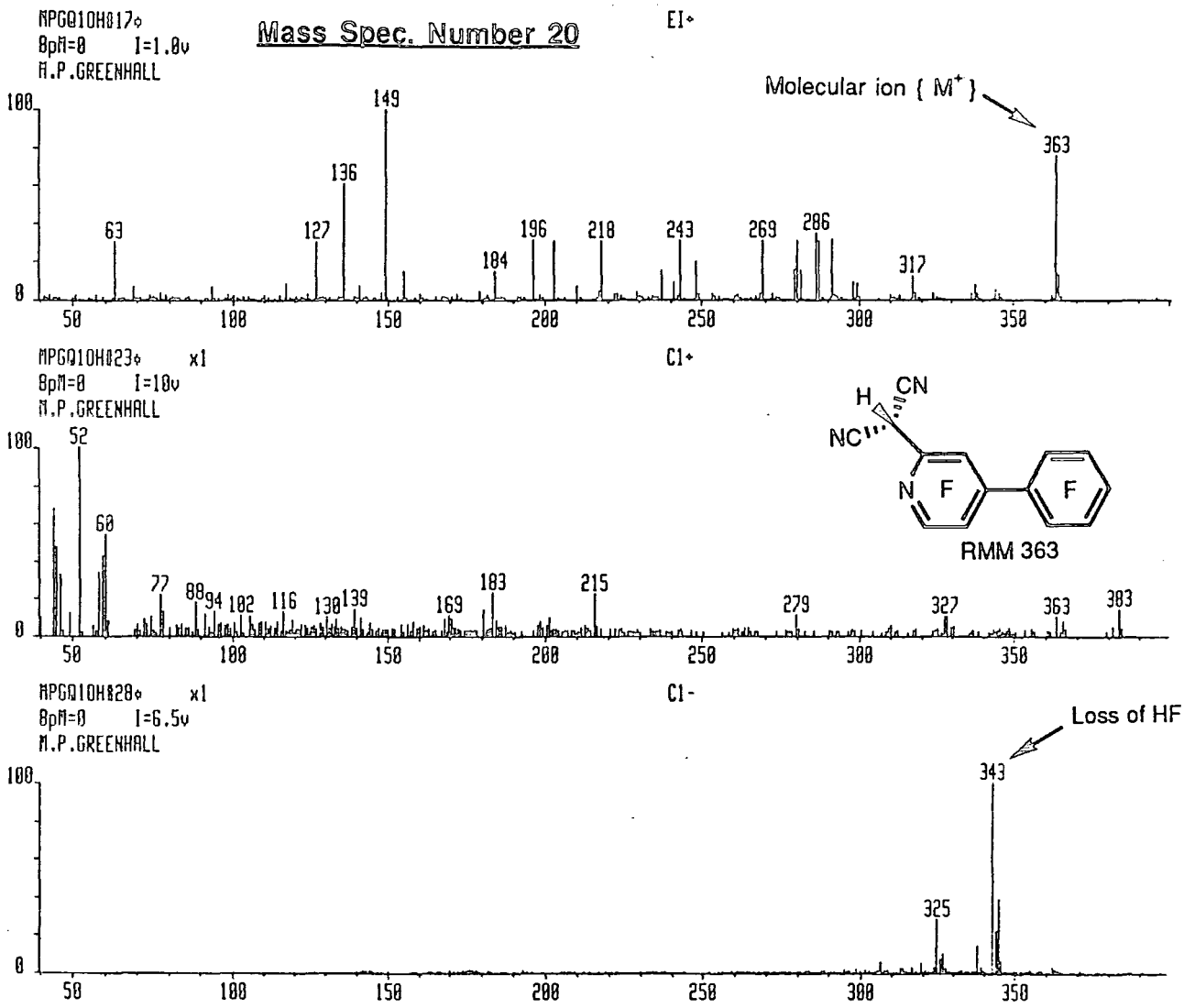


FAB Positive ion data

Mass	% Base		
88.99	10.35	165.98	1.33
90.00	7.22	166.97	1.75
91.01	5.94	180.02	2.55
92.00	1.65	205.04	1.21
93.00	1.83	284.77	1.82
94.00	1.32	285.81	72.22
95.01	2.24	286.82	10.00
103.99	1.14	287.84	1.44
104.99	3.24	288.94	3.35
105.99	2.96	306.94	5.28
107.00	10.02	307.90	1.04
108.00	3.20	311.65	3.63
113.06	1.03	311.90	1.37
115.00	1.93	391.10	1.28
119.00	2.14	410.89	1.57
119.99	5.02	417.67	1.90
121.00	2.74	418.67	5.44
122.00	1.59	438.81	7.27
123.01	1.96	439.82	1.61
123.99	3.97	479.61	12.78
125.00	1.17	480.62	1.24
132.88	100.00	522.97	4.26
134.99	3.81	523.99	1.13
135.98	31.48	601.65	0.04
136.99	24.08	601.77	0.05
137.99	12.12	602.87	0.04
139.00	4.07	602.96	0.04
148.96	5.71	603.02	0.04
149.97	1.73	603.07	0.04
150.97	1.00	606.94	0.04
151.98	2.94	607.88	0.04
152.98	2.31	612.65	0.03
153.98	41.33	612.80	0.04
154.98	9.63	612.86	0.05
155.99	1.67	612.94	0.04
164.99	1.42	613.96	0.04

FAB Negative ion data

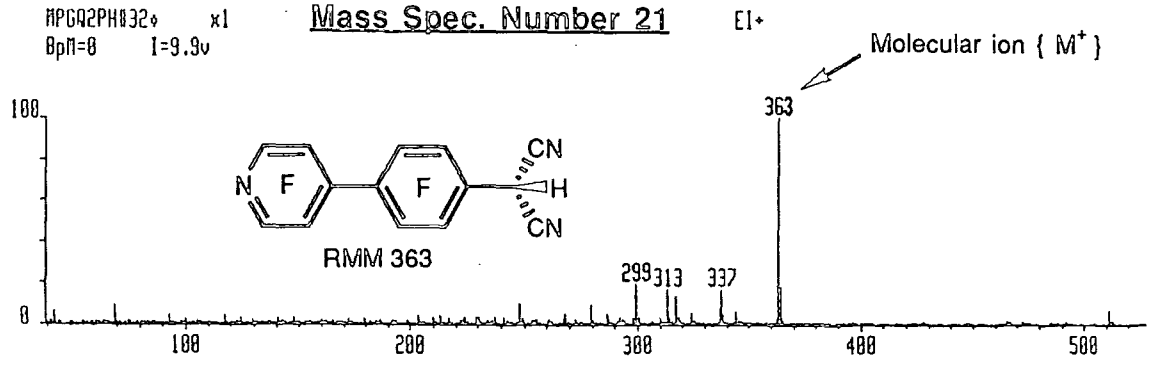
Mass	% Base
45.91	5.77
121.88	2.54
135.88	1.20
136.88	1.22
137.86	1.45
149.85	1.44
150.87	7.57
151.87	8.83
152.88	15.52
153.88	2.79
165.83	3.08
167.84	3.47
168.84	1.07
194.78	1.66
195.78	1.69
198.83	3.83
210.77	1.45
213.77	100.00
214.78	13.39
229.76	1.30
304.81	4.06
305.82	4.48
366.79	1.45
499.71	1.42
560.65	5.20
561.65	1.09

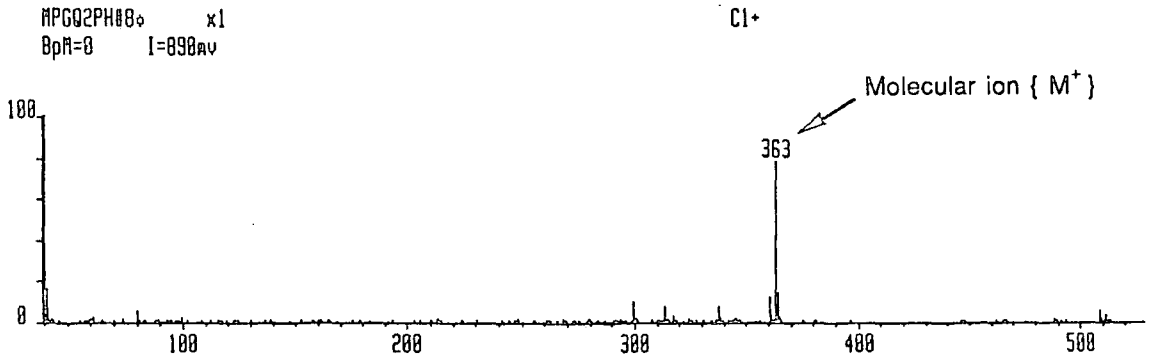


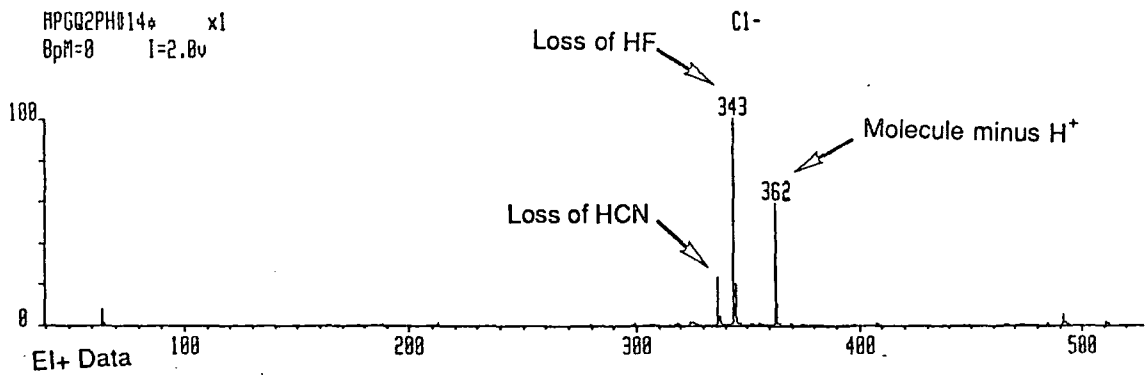
EI+ Data

Mass	% Base	Mass	% Base	Mass	% Base
27.00	1.90	203.12	30.16	338.18	2.51
29.03	2.29	210.14	6.60	344.19	4.51
31.00	10.02	217.15	3.95	345.20	2.63
43.07	1.71	218.17	30.14	352.30	0.26
51.08	1.80	222.15	2.55	362.02	0.21
57.13	1.83	223.16	2.96	362.19	1.90
59.11	1.66	224.16	1.52	362.69	0.33
63.10	30.23	229.15	3.40	362.73	0.33
69.06	6.76	237.19	14.63	363.19	75.58
74.07	1.83	241.15	8..86	364.20	12.83
77.11	3.68	243.17	30.35	365.19	1.40
79.08	1.84	248.16	19.41	396.21	0.39
93.08	6.88	249.17	2.48		
98.09	2.48	253.15	2.82		
100.10	1.80	261.16	1.93		
110.10	1.86	268.17	2.46		
115.16	1.77	269.14	30.08		
117.10	8.30	272.16	2.70		
122.11	1.68	279.17	15.76		
124.11	2.76	280.19	30.29		
127.14	30.17	281.17	14.54		
136.09	61.12	286.16	34.37		
141.13	6.69	286.24	2.54		
148.12	3.46	287.18	30.64		
149.15	100.00	291.17	30.97		
153.12	1.55	292.17	2.11		
155.15	14.93	293.17	1.68		
160.12	2.78	298.16	8.86		
172.13	2.94	299.16	8.14		
179.13	4.00	310.17	2.08		
181.64	1.98	313.19	1.78		
184.21	14.69	317.17	12.38		
186.14	1.60	318.19	3.14		
196.17	30.97	324.18	2.40		
198.14	1.72	336.17	3.00		
		337.18	7.50		

Mass Spec. Number 21



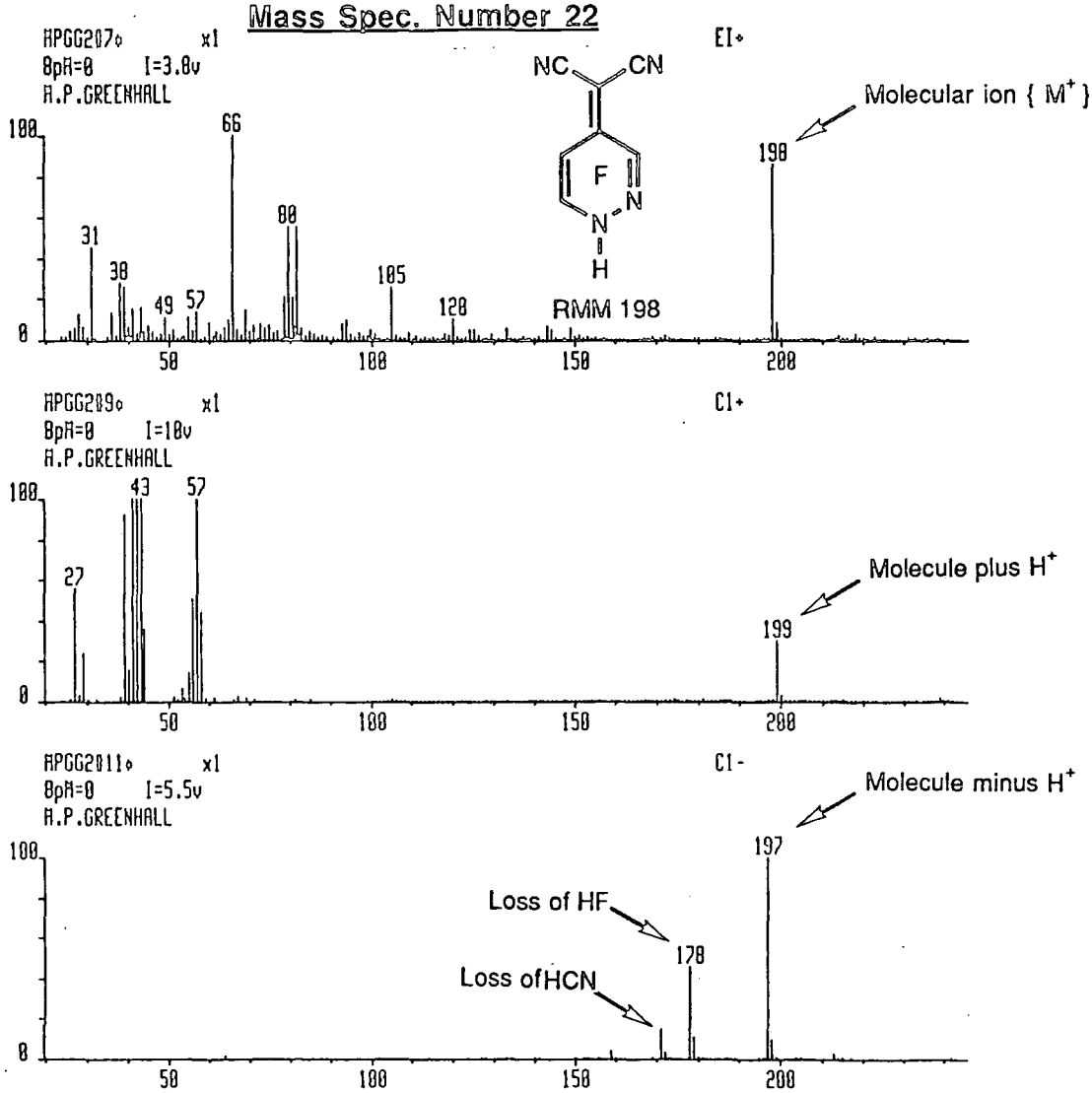




EI+ Data

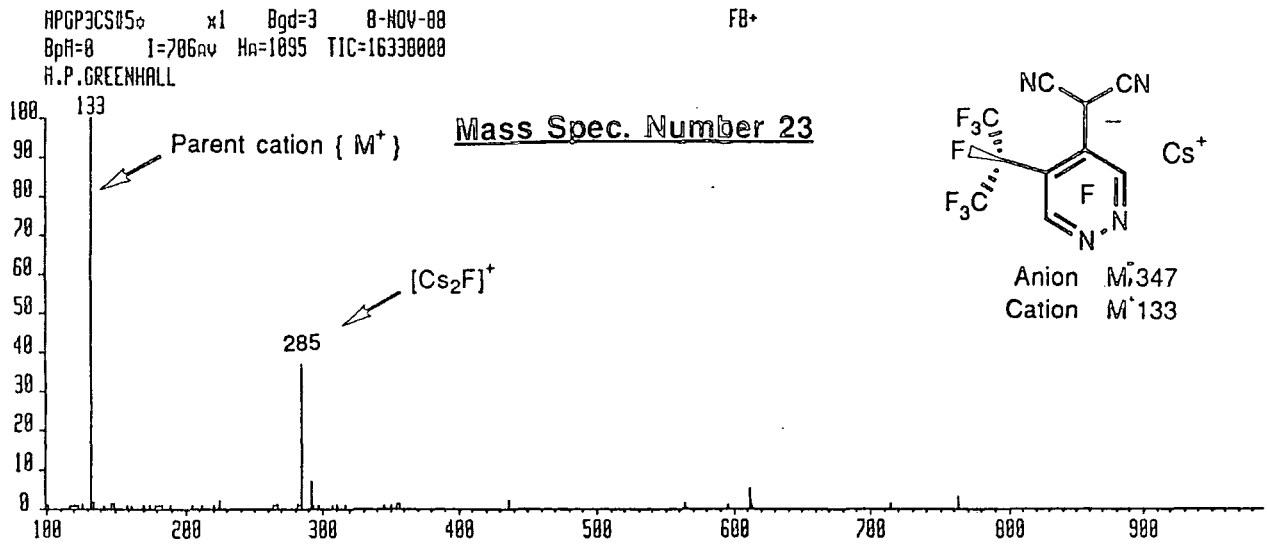
Mass	% Base				
41.08	1.18	248.25	9.23	344.35	5.13
43.06	5.51	249.26	1.88	345.36	1.64
69.07	8.71	253.24	1.11	362.35	2.29
75.08	1.02	254.26	1.52	363.28	40.89
93.09	4.06	255.26	1.75	363.39	100.00
98.10	1.43	260.26	1.25	364.30	6.79
100.10	2.18	261.27	2.00	364.40	17.33
105.11	1.37	262.26	1.21	365.38	1.61
117.12	3.95	267.27	2.03	465.45	1.07
122.12	1.06	268.27	4.52	491.50	1.01
124.13	2.43	272.27	2.33	511.53	6.09
129.13	1.11	279.27	8.67	512.53	1.35
141.14	2.93	280.28	1.60		
143.14	1.17	286.29	4.90		
148.15	2.80	287.29	1.97		
160.16	1.33	291.29	1.48		
165.17	1.37	292.30	2.67		
172.17	1.85	293.30	2.22		
179.18	1.99	294.30	1.16		
181.68	1.01	298.29	2.81		
186.19	1.54	299.24	7.41		
192.20	1.46	299.32	19.03		
193.20	1.33	300.30	2.44		
198.20	1.09	310.30	2.61		
203.20	3.47	313.25	6.71		
210.21	2.82	313.34	15.96		
213.22	3.30	314.32	2.37		
217.22	2.63	317.25	4.66		
222.22	1.12	317.33	12.67		
223.23	1.74	318.32	2.56		
224.22	2.46	324.32	4.77		
229.22	2.64	325.33	1.02		
230.23	2.81	336.33	1.66		
234.23	1.03	337.26	7.24		
236.24	1.26	337.34	16.55		
237.25	2.78	338.33	3.76		
241.24	3.00				
242.25	1.45				

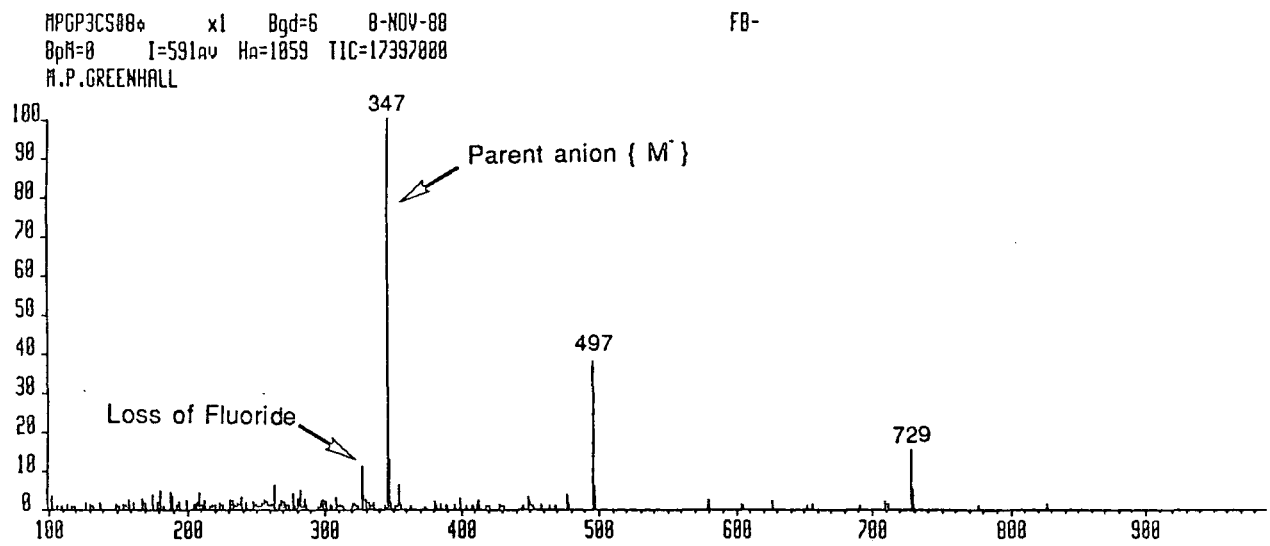
Mass Spec. Number 22



EI+ Data

Mass	% Base		
61.00	1.89	93.97	9.65
61.98	4.12	95.01	2.84
62.99	2.83	96.04	1.57
63.98	6.25	97.03	3.63
65.00	9.29	98.03	1.73
66.00	100.00	99.00	1.76
67.01	4.63	99.96	4.59
68.01	2.61	100.98	2.61
68.97	12.02	104.95	25.42
69.04	14.28	105.96	2.22
70.03	3.75	106.99	1.30
71.05	6.83	108.99	3.37
73.00	7.64	111.04	2.02
73.97	5.70	113.00	1.46
74.98	6.58	115.01	1.52
75.98	3.20	117.95	2.82
77.00	3.80	118.96	2.24
78.00	1.00	119.96	10.17
78.88	21.02	120.98	1.33
78.99	1.23	123.03	1.21
79.89	55.27	123.96	4.51
80.87	20.27	124.98	4.40
80.96	6.33	125.97	1.76
81.03	5.90	129.03	2.54
81.88	55.07	132.95	5.35
81.97	7.38	137.06	1.46
82.04	2.59	141.00	1.02
83.03	5.43	142.94	7.29
84.03	1.69	143.94	4.47
85.06	4.31	148.96	5.24
85.97	2.43	149.96	1.32
86.99	1.56	150.96	1.82
87.97	1.74	152.98	1.13
88.98	1.41	168.94	1.49
91.01	1.09	171.95	2.01
92.96	7.56	197.92	85.93
		198.93	7.92





FAB Positive ion data

Mass	% Base
125.83	1.19
132.65	100.00
134.70	1.40
149.70	1.08
224.56	1.62
266.60	1.04
280.66	1.08
284.39	36.96
291.41	6.83
354.60	1.17
356.44	1.10
436.30	1.88
612.42	5.08
714.34	1.02
762.46	3.00

FAB Negative ion data

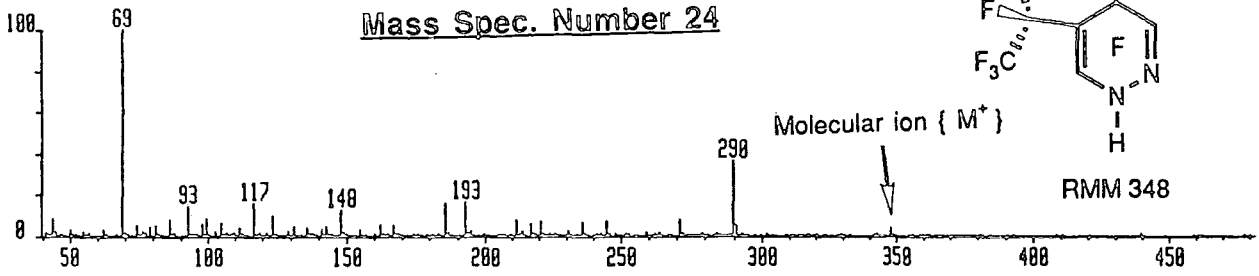
Mass	% Base
101.70	3.28
127.66	1.47
130.65	1.14
130.67	1.14
137.63	1.37
149.61	1.01
154.64	1.08
156.60	1.03
158.62	1.99
161.57	1.32
168.57	2.43
170.57	1.37
175.55	3.66
178.55	1.86
180.53	4.67
187.52	4.39
189.52	3.17
194.53	1.86
199.50	2.27
206.47	1.42
208.48	4.00
211.47	1.16
213.49	1.99
218.48	1.24
220.48	1.03
223.48	1.55
225.49	1.06
230.48	1.99
232.47	2.22
236.45	1.55
237.47	1.24
239.48	2.68
242.45	1.37
247.43	1.75
253.42	1.34
256.44	2.17
258.45	1.96
261.43	1.16
263.45	6.04
266.42	1.08
268.41	2.01
270.45	1.91
277.43	3.97
280.41	2.37
282.42	4.67
285.41	2.48
296.41	1.29
297.44	1.01
298.40	2.22
299.35	2.04
301.40	1.81
304.46	1.06
308.41	2.84
311.46	1.03
320.42	1.34
322.40	1.03
327.38	10.58
328.39	3.38
329.43	1.55
330.35	2.24
332.38	1.57
335.37	1.52
346.35	100.00
347.37	12.59
348.36	1.60
353.33	1.14
354.35	5.93
355.36	1.19
380.33	1.83
399.32	2.32
412.29	1.03
413.32	2.04
427.33	1.14
448.31	2.84
449.36	1.60
477.32	3.64
478.32	1.60
496.27	37.87
497.29	5.75
579.24	2.01
626.27	1.63
709.35	1.75
728.24	14.99
729.24	5.11

Calibration error -

All masses should be rounded up

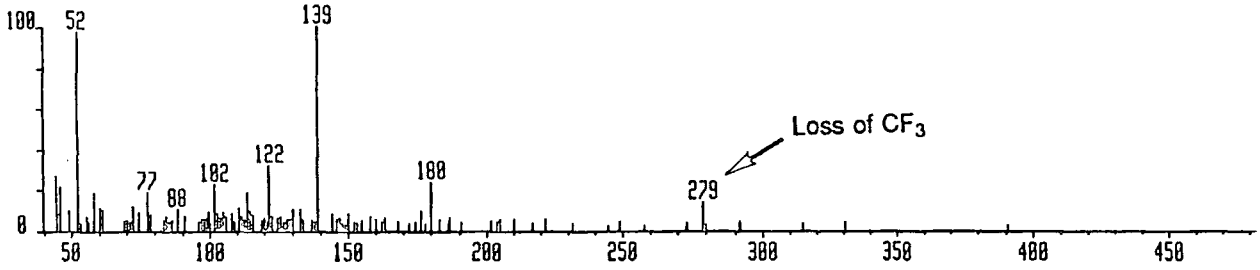
HPGP3H05◆ x1 Bgd=1 24-OCT-88 EI◆
BpM=0 I=4.9v Ha=479 TIC=174138000
H.P.GREENHALL

Mass Spec. Number 24

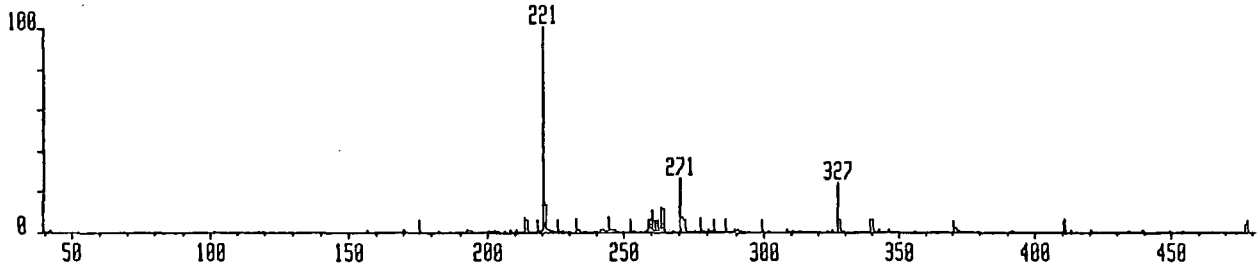


RMM 348

HPGP3H010◆ x1 Bgd=6 24-OCT-88 C1◆
BpM=0 I=10v Ha=398 TIC=73937000
H.P.GREENHALL



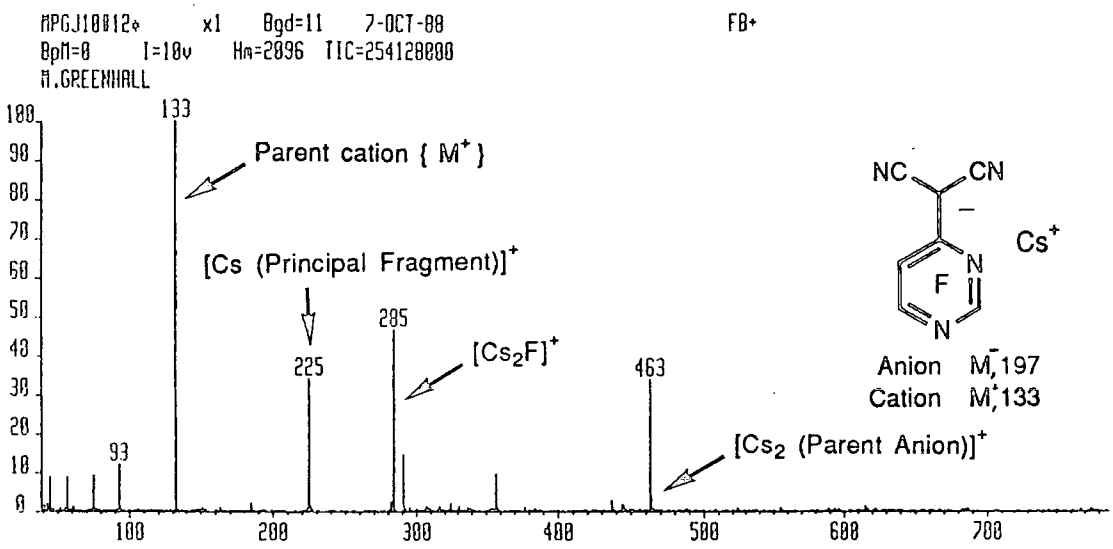
HPGP3H014◆ x1 Bgd=11 24-OCT-88 C1-
BpM=0 I=1.3v Ha=478 TIC=35628000
H.P.GREENHALL

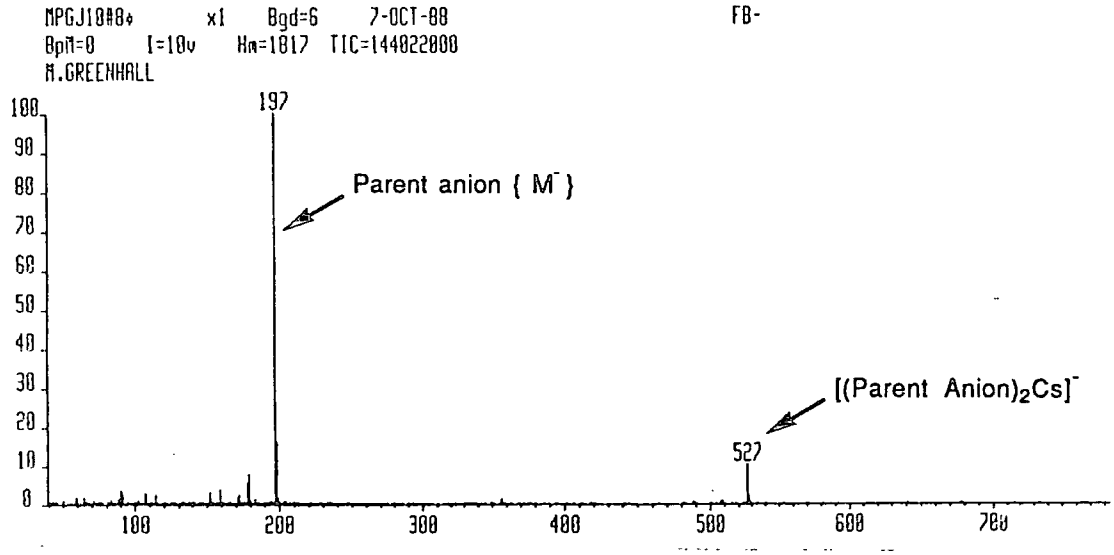


EI+ Data

Mass	% Base				
25.96	3.07	154.82	2.56	327.75	0.31
26.96	7.14	161.82	5.01	328.67	0.12
27.95	2.79	166.82	4.46	328.77	0.11
30.94	35.88	185.78	15.53	329.45	0.04
37.94	1.30	186.78	1.31	329.76	0.51
40.97	1.21	192.79	16.09	330.73	0.19
42.94	1.42	193.80	1.48	330.79	0.11
42.98	1.30	194.80	2.33	332.76	0.12
43.92	7.84	211.79	7.55	341.78	0.06
44.93	2.18	213.79	2.00	342.74	0.36
49.92	2.44	216.78	5.13	347.62	0.06
54.92	2.14	220.79	6.64	347.75	3.41
56.98	1.27	230.78	2.19	348.75	0.32
61.91	2.38	235.77	6.18	354.73	0.05
68.89	100.00	244.78	6.90		
69.89	1.36	245.78	1.01		
73.89	4.45	258.77	1.27		
75.89	2.13	263.76	1.12		
76.93	1.14	270.77	7.70		
78.89	3.82	289.76	35.66		
80.89	4.65	290.77	4.45		
85.88	7.57	301.78	0.38		
87.89	1.08	302.11	0.07		
92.87	13.96	303.78	0.16		
97.87	5.14	304.72	0.06		
99.87	8.24	304.76	0.05		
102.86	1.70	308.75	0.18		
104.87	6.06	308.96	0.09		
106.86	1.17	310.77	0.12		
109.86	1.53	311.75	0.13		
111.86	3.06	313.76	0.32		
116.85	15.77	314.77	0.07		
118.85	1.14	316.70	0.06		
121.85	1.15	316.74	0.26		
123.85	9.36	317.75	0.05		
128.84	1.98	319.73	0.07		
130.85	3.79	320.73	0.07		
135.84	3.71	322.73	0.03		
140.83	2.53	322.77	0.04		
142.83	3.96	323.78	0.11		
147.83	12.13	325.71	0.04		
148.85	1.36	325.74	0.07		

Mass Spec. Number 25





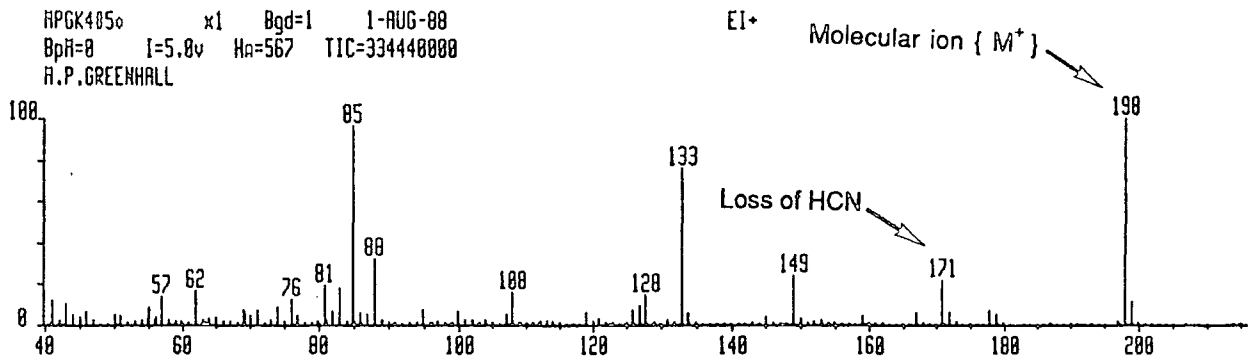
FAB Positive ion data

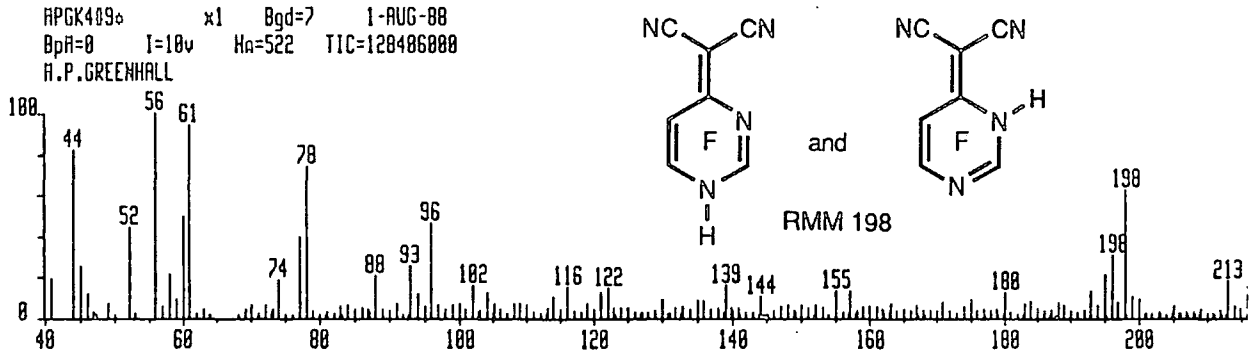
Mass	% Base
27.00	1.82
28.98	1.98
29.01	4.26
30.99	4.84
41.02	1.54
43.00	1.92
45.02	8.49
57 02	8.68
61.02	1.15
75.02	8.98
93.03	11.72
132.92	100.00
185.06	1.63
224.89	33.99
225.91	1.16
282.75	2.14
284.74	46.49
291.75	14.26
307.75	1.06
316.92	1.12
324.76	1.63
330.83	1.13
356.78	9.17
436.64	2.65
443.69	1.48
444.76	1.34
462.75	33.50
463.75	3.72

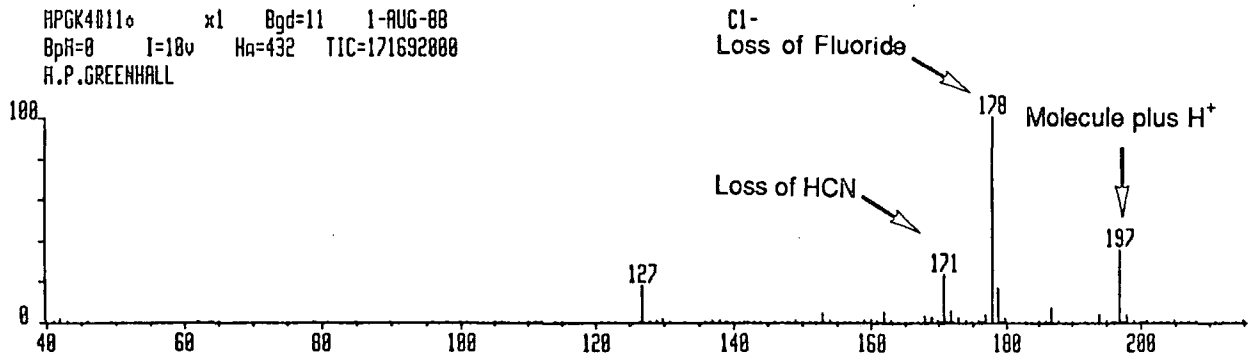
FAB Negative ion data

Mass	% Base
25.93	3.13
58.93	1.30
63.93	1.27
89.90	3.09
90.93	2.16
106.90	2.40
113.89	2.21
151.88	2.99
158.87	3.44
170.85	1.48
171.86	2.11
177.84	5.33
178.84	7.62
196.91	100.00
197.85	15.83
198.85	1.55
355.82	1.04
526.72	10.16
527.72	1.99

Mass Spec. Number 26



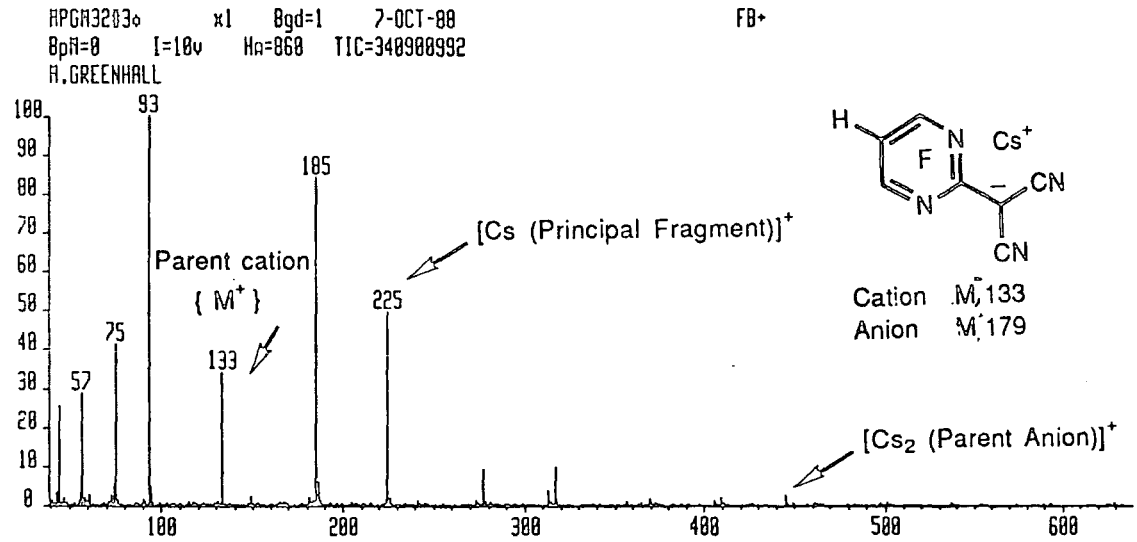


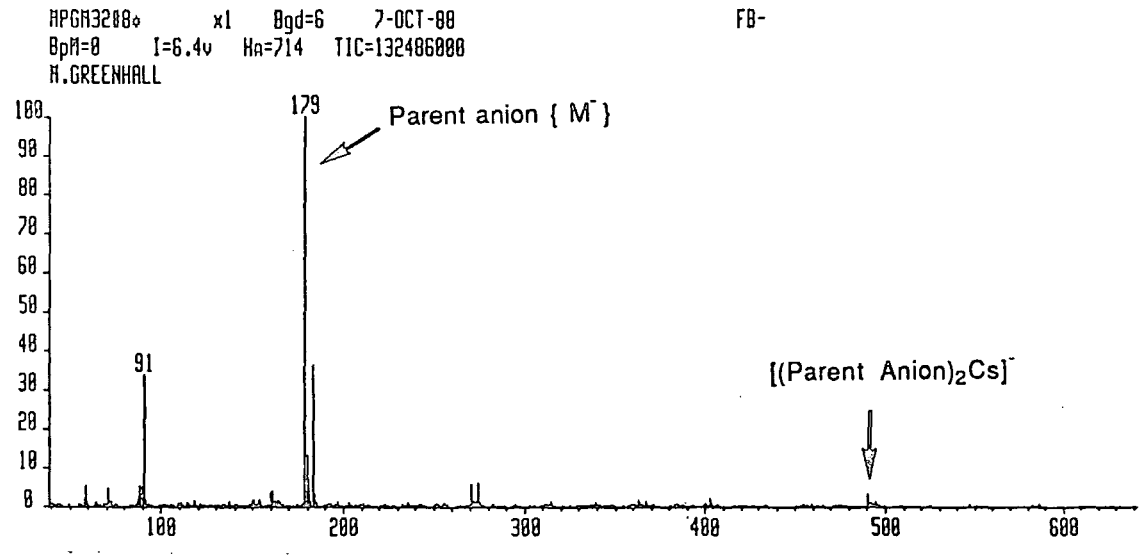


EI+ Data

Mass	% Base				
40.99	11.39	86.90	3.78	197.08	0.05
41.99	2.30	86.98	4.75	197.14	0.09
42.97	4.38	87.93	31.56	197.37	0.08
43.01	10.32	94.94	6.64	197.87	100.00
43.95	4.75	99.93	5.83	198.06	0.06
44.95	3.44	100.93	2.27	198.49	0.08
44.99	2.86	101.93	2.02	198.68	0.06
45.97	6.00	106.93	5.01	198.88	11.10
49.96	4.93	107.93	15.46	199.03	0.15
50.98	3.86	113.05	2.02	199.10	0.09
54.97	2.58	118.92	5.54	199.88	0.71
55.01	8.11	120.94	2.50		
55.97	2.09	125.91	6.74		
56.02	3.37	126.81	8.63		
56.97	4.69	126.92	2.16		
57.03	13.55	127.82	14.38		
57.97	2.23	132.90	75.48		
61.96	15.90	133.91	5.73		
62.97	2.17	144.90	3.54		
63.97	2.48	148.92	23.57		
64.98	3.29	149.92	2.72		
68.95	7.08	152.90	2.15		
69.02	5.37	158.89	3.96		
69.96	2.35	166.91	5.40		
70.03	4.25	170.88	21.47		
70.95	3.33	171.89	5.14		
71.03	6.68	177.89	6.60		
73.94	3.04	178.89	4.83		
73.98	7.94	190.04	0.09		
75.95	11.95	190.88	0.09		
76.96	4.11	191.05	0.09		
80.93	18.92	191.69	0.09		
81.95	6.38	192.05	0.05		
82.91	6.81	192.88	0.12		
82.94	17.25	193.08	0.09		
83.02	3.89	194.07	0.10		
84.90	96.03	194.89	0.17		
85.91	5.62	196.87	1.07		
		196.97	0.13		

Mass Spec. Number 27





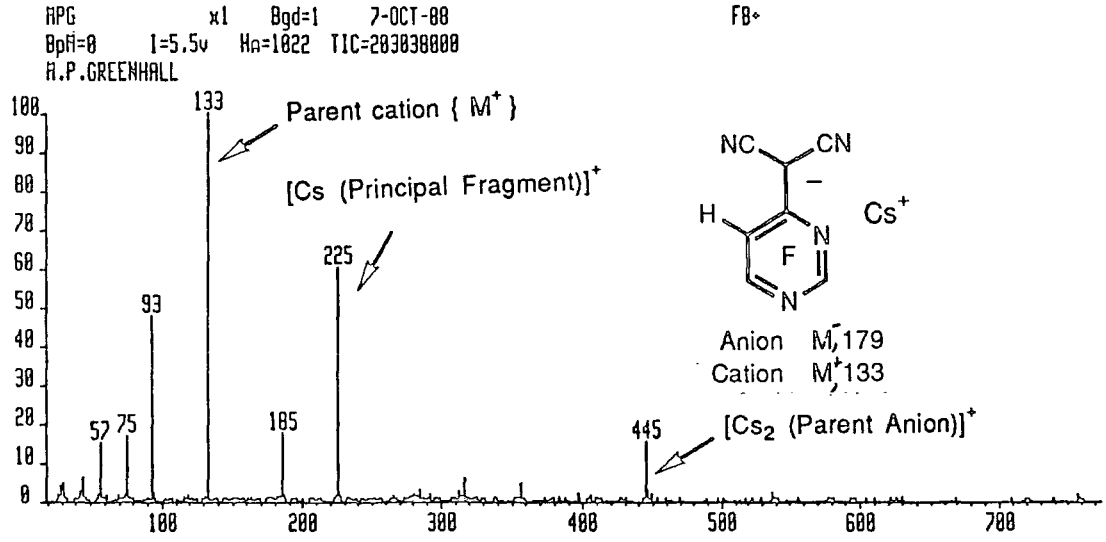
FAB Positive ion data

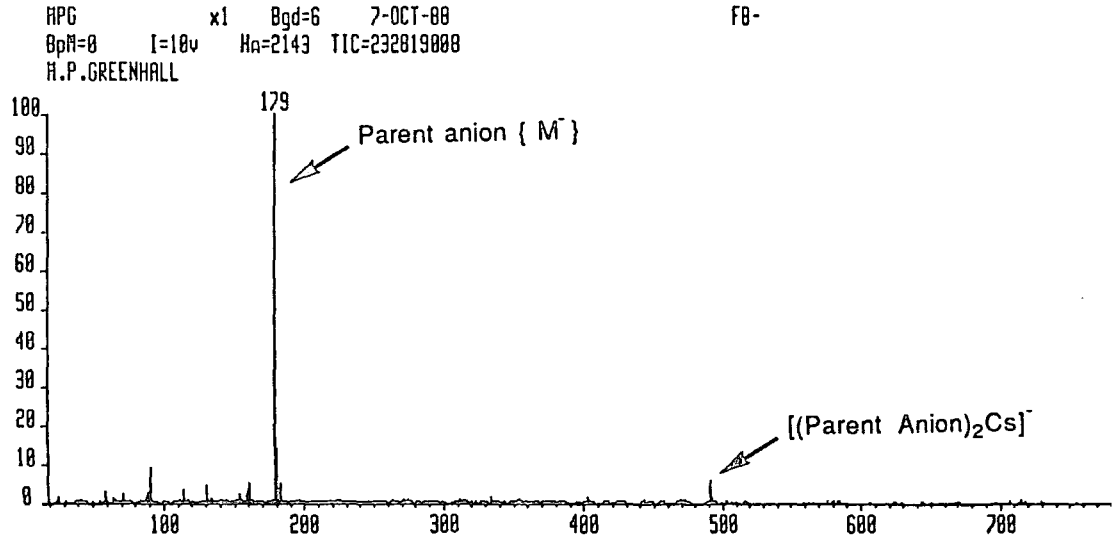
Mass	% Base		
27.00	1.60	273.03	1.11
28.01	1.45	277.10	8.98
28.98	2.29	312.87	3.48
29.02	9.11	316.94	9.81
31.00	4.07	369.13	1.50
41.03	1.08	404.91	1.05
43.01	3.34	408.96	1.81
44.01	1.55	444.76	2.54
45.02	25.48		
47.01	1.68		
55.02	1.19		
56.02	2.75		
57.02	28.64		
58.03	1.63		
61.02	2.45		
73.02	2.33		
74.02	4.84		
75.03	41.21		
76.03	1.41		
90.02	1.27		
93.06	100.00		
94.04	4.80		
132.89	33.99		
149.05	2.23		
181.00	1.65		
185.06	84.02		
186.06	5.60		
187.07	1.21		
223.90	1.26		
224.90	49.21		
225.90	1.83		

FAB Negative ion data

Mass	% Base
57.92	1.33
58.93	4.99
70.92	4.34
72.93	1.20
87.90	1.93
88.91	5.15
89.91	4.74
90.93	33.44
91.93	1.30
150.90	1.60
153.86	1.34
159.87	3.11
160.87	3.50
162.90	1.02
163.91	1.41
164.91	1.23
178.83	100.00
179.83	12.94
180.89	6.84
182.91	36.05
183.91	2.83
196.82	1.20
270.86	5.18
271.87	1.12
272.91	1.05
274.92	5.67
362.89	1.27
366.95	1.09
402.73	1.96
490.68	2.85
494.75	1.05

Mass Spec. Number 28





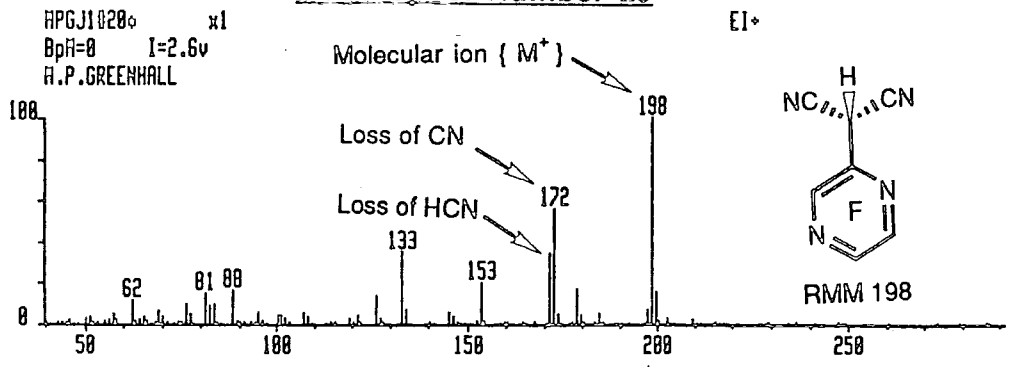
FAB Positive ion data

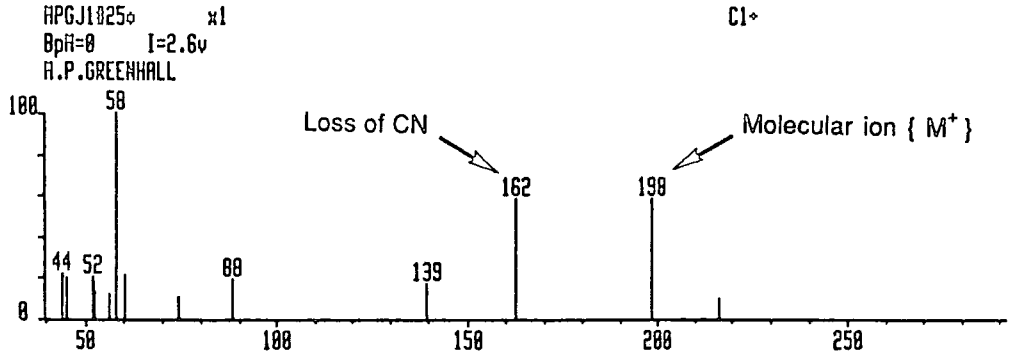
Mass	% Base
27.01	1.67
28.02	1.01
28.99	1.65
29.03	4.05
31.01	4.54
41.04	1.03
43.02	2.60
44.03	1.01
45.04	6.23
47.02	1.08
55.06	1.63
56.03	1.66
57.04	15.12
58.05	1.09
61.04	1.58
69.05	1.29
73.05	1.09
74.05	1.70
75.05	16.92
76.06	1.04
93.07	47.89
94.07	2.19
115.06	1.02
118.08	1.28
131.06	1.03
132.93	100.00
177.00	1.07
181.05	1.13
183.08	1.27
185.12	17.36
186.13	1.38
223.96	1.35
224.97	60.20
225.97	2.19
226.98	1.09
264.94	1.32
277.17	1.08
279.21	1.31
281.02	1.75
282.86	1.42
284.85	2.82
291.85	1.67
312.97	2.64
314.88	1.27
315.02	1.01
317.04	5.72
324.87	1.14
337.87	1.02
356.91	4.81
383.20	1.24
396.88	2.03
405.06	1.21
406.10	1.33
409.12	1.18
444.91	15.50
445.92	2.74
448.99	1.71

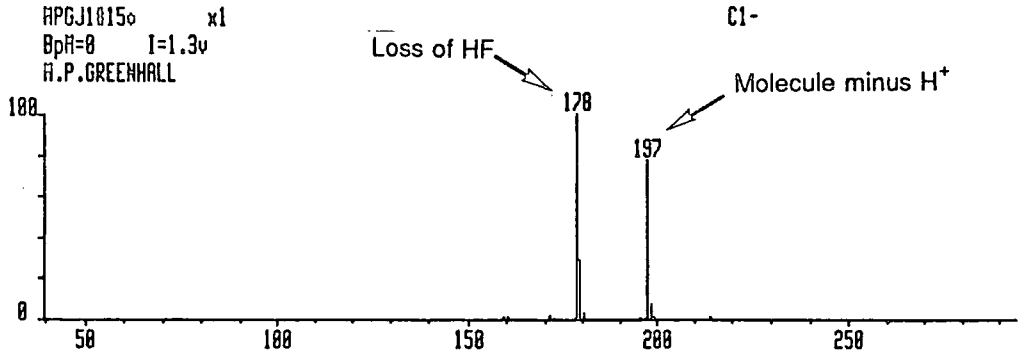
FAB Negative ion data

Mass	% Base
25.94	1.49
58.95	2.74
63.94	1.19
70.93	2.15
87.92	1.48
88.93	2.60
89.93	2.62
90.95	8.96
113.92	3.19
130.90	4.24
133.91	1.05
152.90	1.14
153.90	2.26
158.89	1.76
159.89	2.80
160.90	5.12
178.92	100.00
179.89	13.91
180.90	3.64
182.95	4.98
333.81	1.27
402.83	1.60
490.76	5.66
491.78	1.28

Mass Spec. Number 29







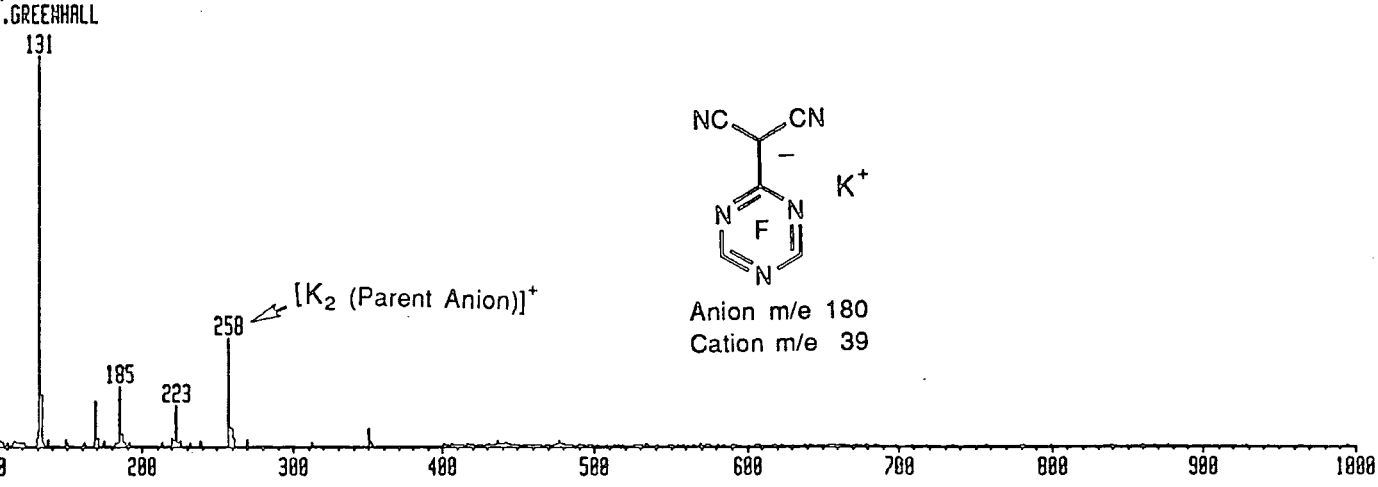
EI+ Data

Mass	% Base				
26.08	1.73	100.23	4.07	215.39	0.76
27.09	1.02	101.24	3.85	286.48	0.59
28.09	41.56	102.24	2.55	298.48	0.84
31.09	55.05	103.25	0.61	305.49	0.54
32.08	9.64	107.24	5.21		
36.10	0.65	108.25	3.20		
37.11	0.66	114.25	0.77		
38.11	7.85	115.26	0.82		
39.12	2.24	119.25	2.77		
40.07	0.74	120.27	0.56		
45.12	0.85	121.26	4.08		
46.13	2.31	122.27	0.80		
50.13	2.56	126.28	13.43		
51.15	3.60	127.28	2.83		
55.14	1.39	133.28	35.21		
56.15	2.28	134.29	7.01		
57.15	4.76	145.30	5.66		
58.16	2.11	146.31	3.32		
62.15	11.51	152.31	1.38		
63.17	1.33	153.32	20.19		
64.17	1.84	154.33	1.69		
65.18	3.61	164.32	0.67		
66.18	1.17	171.33	34.40		
69.17	5.89	172.34	56.21		
70.18	3.09	173.35	4.60		
75.19	0.61	178.35	17.07		
76.19	9.44	179.35	3.84		
77.20	4.88	180.36	0.57		
81.19	15.12	183.35	0.68		
82.21	8.66	184.36	4.79		
83.20	9.58	185.36	0.50		
84.21	0.56	197.37	6.65		
88.21	15.91	198.38	100.00		
89.22	1.29	199.39	15.80		
93.21	0.87	200.39	1.08		
95.22	5.60	202.38	2.73		
96.23	1.33	209.38	2.18		

PGK11K04◇
pH=0
.GREENHALL

FB◇

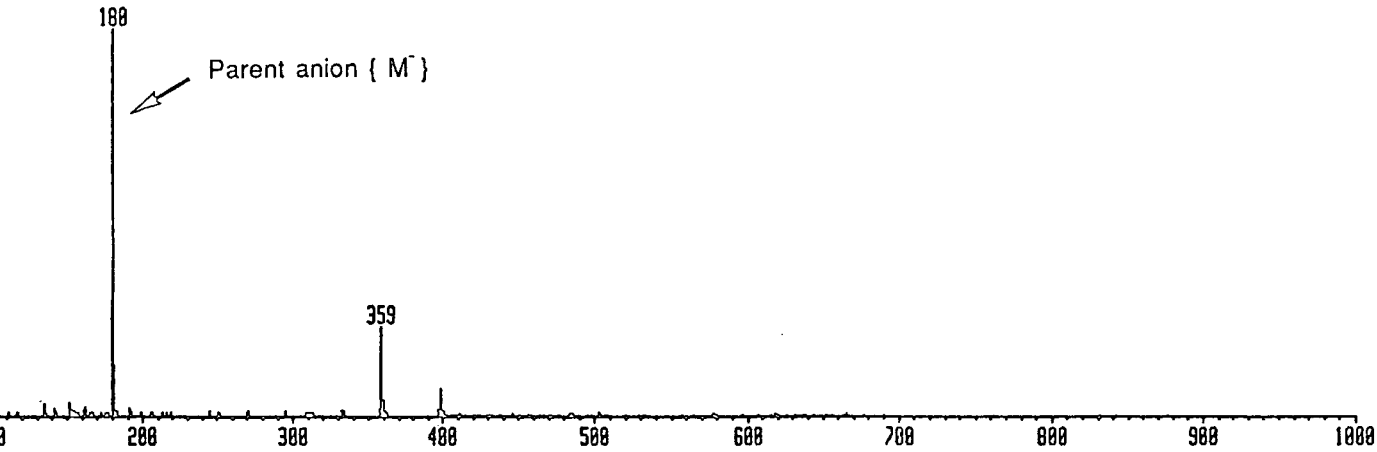
Mass Spec. Number 30



Anion m/e 180
Cation m/e 39

PGK11K09◇
pH=0
.GREENHALL

FB-



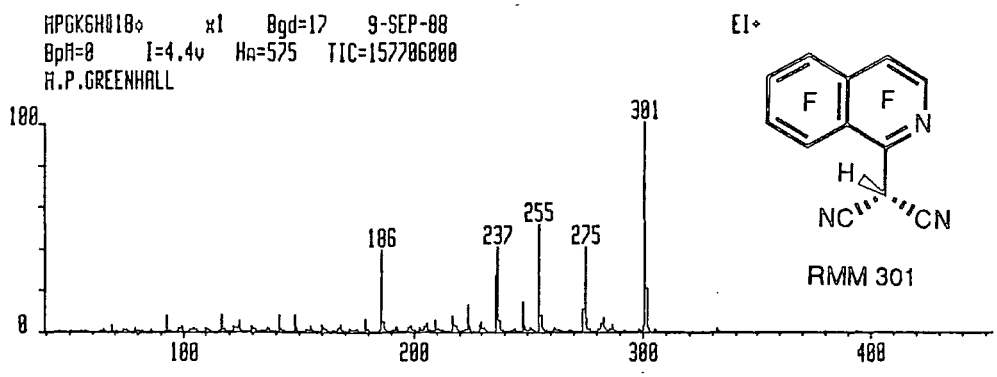
Positive ion data

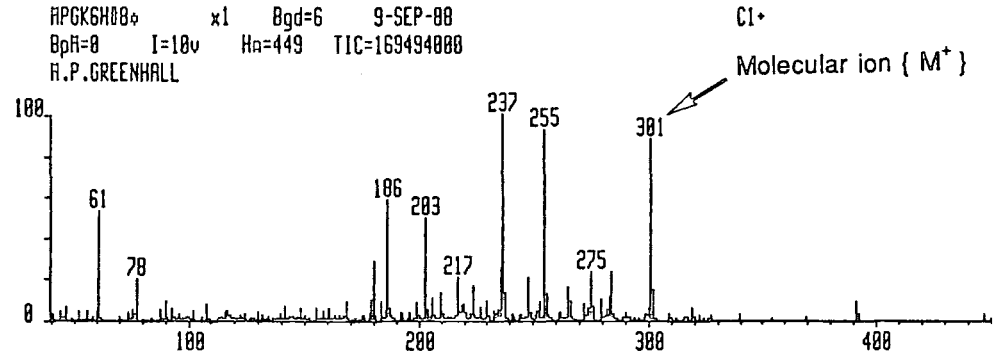
ss	% Base		
82.96	0.30	166.88	0.45
89.96	0.91	167.85	1.20
90.96	0.62	168.89	11.53
91.96	0.45	169.89	0.47
92.98	79.86	170.89	1.66
93.98	3.43	174.81	1.06
94.86	1.16	181.94	0.76
95.00	0.73	182.98	0.39
96.85	8.04	183.97	0.67
98.86	1.43	185.02	15.27
98.95	1.02	186.02	0.99
99.93	0.81	186.96	2.79
03.86	4.93	188.91	0.86
05.86	1.06	190.95	0.71
07.87	0.68	195.91	0.39
10.01	0.55	202.94	0.32
11.92	0.42	204.95	0.46
12.95	0.46	206.89	0.41
13.94	0.65	212.76	0.77
14.97	1.21	219.89	1.96
16.98	0.74	220.92	1.08
18.98	0.62	221.92	0.94
19.86	0.52	222.95	10.27
20.88	0.55	223.94	0.62
28.94	1.76	224.94	0.97
29.94	3.74	231.90	0.56
30.94	100.00	238.86	0.92
31.95	5.81	239.84	0.75
32.94	12.91	241.87	0.47
33.96	0.54	257.82	27.80
35.88	0.42	258.83	4.54
36.88	1.28	259.82	4.31
38.88	0.34	349.84	4.32
41.87	0.36	350.87	0.94
42.89	0.45	351.87	0.79
48.98	1.39	352.89	0.33
49.88	0.51	387.80	0.35
50.89	0.31	400.88	0.31
57.98	0.42	430.85	0.30
60.95	0.65	436.80	1.22

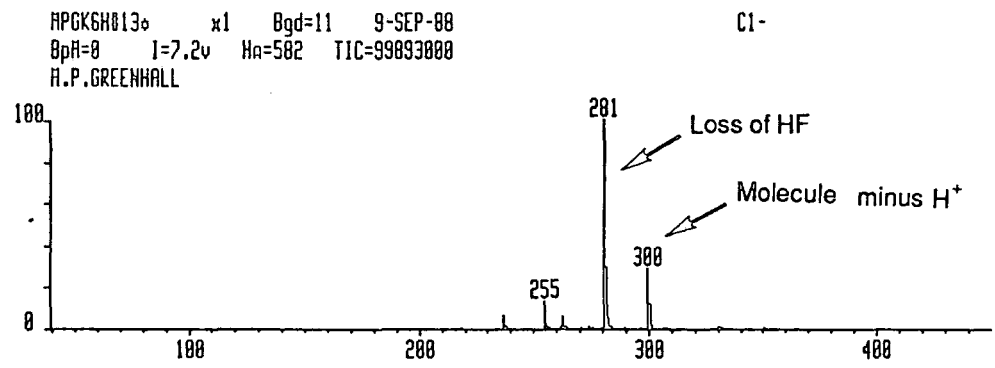
FAB Negative ion data

Mass	% Base		
79.89	0.64	206.78	0.67
80.79	0.56	210.83	0.31
86.84	0.64	212.92	0.58
88.86	0.79	215.75	0.62
89.84	19.02	218.75	0.67
90.86	3.48	220.80	0.34
91.86	0.73	225.77	0.43
96.81	0.55	244.70	0.98
99.98	0.55	250.75	0.73
110.86	0.82	251.75	0.68
116.85	0.71	269.74	0.64
133.88	0.52	270.73	0.95
134.82	2.76	289.70	0.42
135.83	0.50	294.69	1.05
141.82	1.76	308.68	0.70
142.82	0.54	309.67	0.59
151.79	3.25	310.68	0.84
153.81	1.34	312.68	0.66
154.80	1.22	318.70	0.31
155.83	0.55	332.68	1.47
157.81	0.68	333.68	0.91
160.81	1.38	352.66	0.40
161.81	2.18	353.67	0.34
164.87	0.59	357.66	1.68
165.80	0.55	358.66	22.84
166.84	0.55	359.66	4.02
172.81	0.61	360.69	1.13
175.80	0.58	361.65	0.57
176.81	0.67	370.69	0.45
177.79	0.39	376.63	0.43
179.78	100.00	380.66	0.35
180.78	13.22	396.59	1.34
181.80	1.58	397.61	0.33
182.84	0.96	398.60	6.66
191.80	1.71	399.60	1.56
192.80	0.71	400.62	0.96
198.82	0.68	410.63	0.37
203.81	0.33	484.57	0.39
205.77	0.80	502.56	0.64
		577.72	0.35
		617.86	0.34

Mass Spec. Number 31



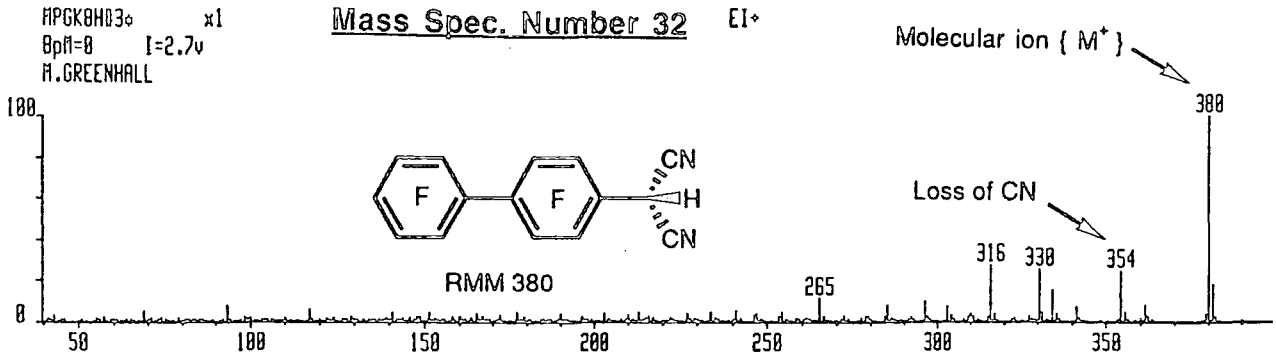


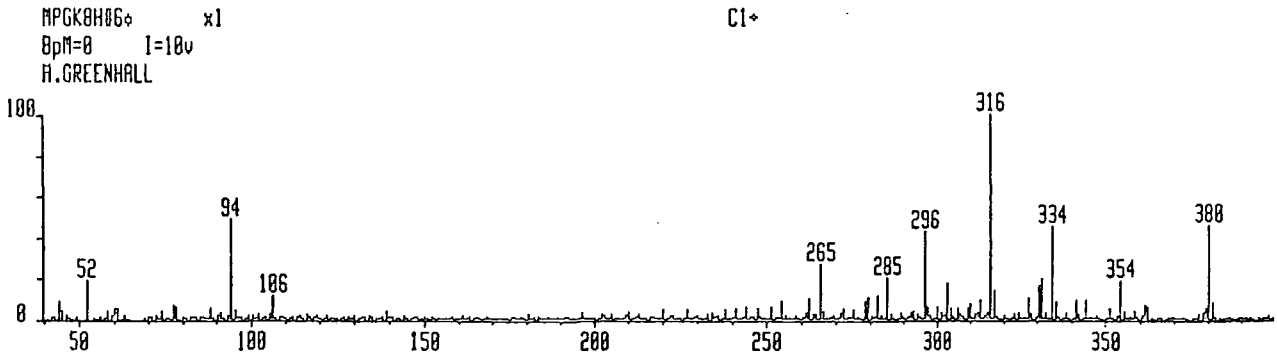


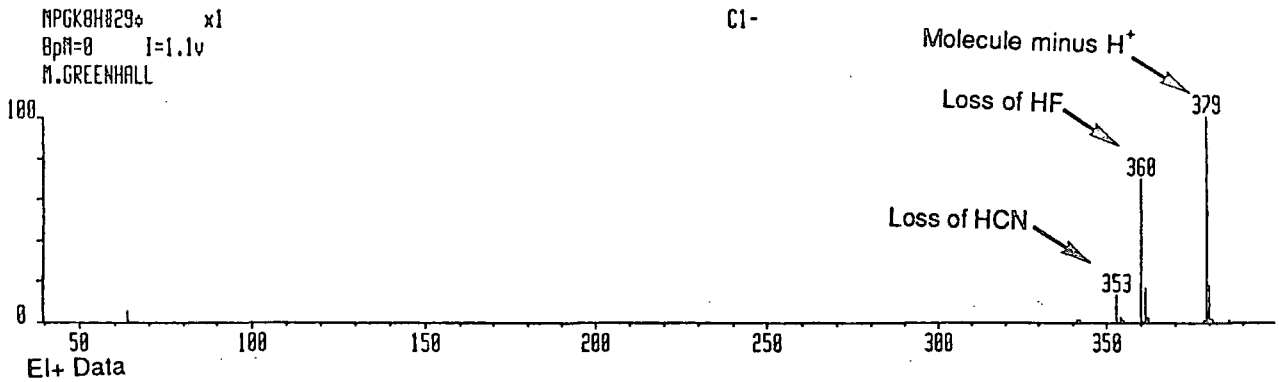
EI+ Data

Mass	% Base
30.97	5.11
38.92	1.06
68.92	2.51
78.93	1.08
92.92	7.47
97.92	1.46
98.92	1.13
99.92	2.30
104.92	1.06
109.91	1.55
116.91	7.11
121.91	1.93
122.92	1.27
123.91	4.92
128.91	2.15
129.91	1.41
135.90	1.31
140.90	7.72
147.90	7.31
148.91	1.02
154.90	2.32
159.89	2.94
160.90	1.52
166.90	1.67
167.90	2.88
178.88	5.25
185.89	38.46
186.89	3.96
191.89	1.07
192.89	1.24
197.88	1.30
198.89	2.05
202.89	1.06
204.88	1.70
205.89	3.71
209.88	4.62
216.89	6.82
217.89	2.73
218.90	1.74
223.88	11.97
224.89	1.76
228.88	2.67
229.89	4.39
230.89	1.39
235.88	26.45
236.88	39.68
237.89	4.79
247.88	13.36
248.88	1.77
250.89	1.40
254.88	50.75
255.89	7.17
256.90	1.45
261.89	1.13
273.88	10.29
274.89	39.79
275.89	5.59
281.89	3.39
282.90	6.22
283.91	1.48
286.89	2.48
299.88	2.29
300.89	100.00
301.89	20.52
302.90	1.67
304.88	0.67
305.88	0.07
331.90	1.59
332.90	0.13
379.89	0.08
393.89	0.25

Mass Spec. Number 32







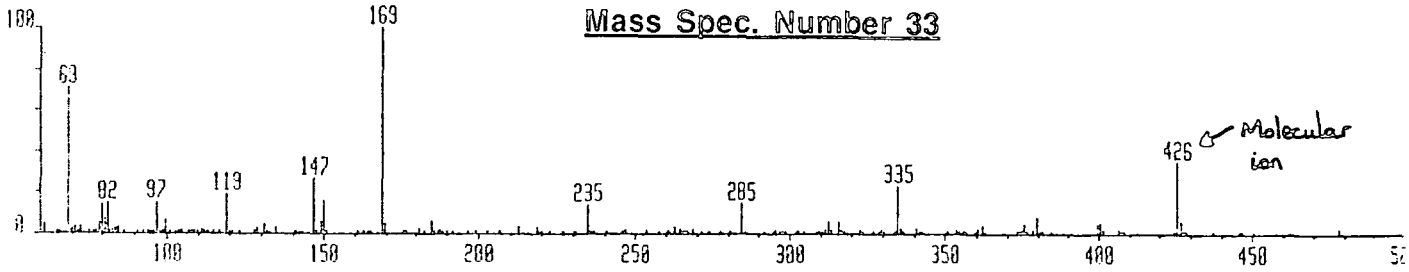
EI+ Data

Mass	% Base						
29.05	1.26	203.10	3.64	310.16	3.36	343.17	0.31
31.01	6.23	210.10	2.43	311.17	2.15	343.30	0.18
41.06	1.27	213.11	3.82	312.17	0.58	348.20	0.24
43.04	2.59	215.10	1.64	312.26	0.14	353.17	0.99
43.08	1.59	216.11	1.97	313.19	0.11	353.30	0.15
55.08	1.17	217.10	1.24	315.16	1.79	353.77	0.10
57.10	2.00	222.10	1.30	315.72	0.11	354.19	24.32
69.02	5.00	227.10	3.09	316.16	26.83	355.19	4.23
71.11	1.29	234.11	3.89	316.47	0.12	356.19	0.35
74.03	1.09	235.13	1.25	316.82	0.13	358.16	0.11
79.04	1.28	241.11	4.45	317.17	3.69	360.05	0.15
86.04	1.01	246.11	2.95	317.52	0.17	360.19	1.22
93.04	7.10	247.12	3.29	318.18	0.28	360.69	0.10
98.04	2.24	253.11	1.84	322.11	0.22	361.20	7.13
99.05	1.07	254.12	4.22	322.14	0.14	362.20	2.03
100.05	1.09	258.12	1.64	322.21	0.39	363.21	0.44
110.05	1.50	261.13	1.56	322.49	0.10	378.31	0.13
117.05	5.26	265.12	10.86	323.07	0.13	378.58	0.20
122.06	1.40	266.13	2.10	323.19	1.18	378.93	0.14
124.06	1.42	272.12	2.89	325.23	0.11	379.19	3.39
129.06	1.90	277.12	1.20	327.16	1.76	380.20	100.00
139.07	1.02	278.14	2.24	328.16	0.48	380.45	0.11
141.06	4.08	279.14	2.36	328.47	0.08	380.55	0.14
144.07	1.12	284.14	2.13	328.71	0.12	380.65	0.14
146.07	1.25	285.15	7.52	329.19	0.41	380.76	0.15
148.07	2.19	286.14	1.30	329.48	0.12	380.89	0.10
149.09	1.78	292.16	1.85	329.77	0.10	380.98	0.23
151.57	4.23	296.14	9.42	330.19	25.23	381.21	17.62
153.07	1.06	297.15	2.25	331.19	4.05	381.82	0.13
158.07	1.93	300.07	0.08	332.19	0.39	382.21	1.73
160.07	2.08	302.20	0.17	332.78	0.13	382.35	0.07
163.57	1.67	302.67	0.10	333.20	0.20	383.23	0.22
165.08	3.66	303.15	7.01	333.26	0.10	390.27	0.16
167.08	1.77	304.15	2.37	334.17	14.73		
172.08	2.74	305.11	0.26	334.96	0.10		
177.08	4.23	305.18	0.43	335.18	3.04		
179.10	2.29	308.06	0.19	336.19	0.63		
190.09	3.42	308.17	0.73	341.18	6.83		
196.09	2.20	309.16	2.06	342.19	1.18		
				342.50	0.21		

MPGM6H2018◆ x1
BpM=0 I=785mV
M.P.GREENHALL

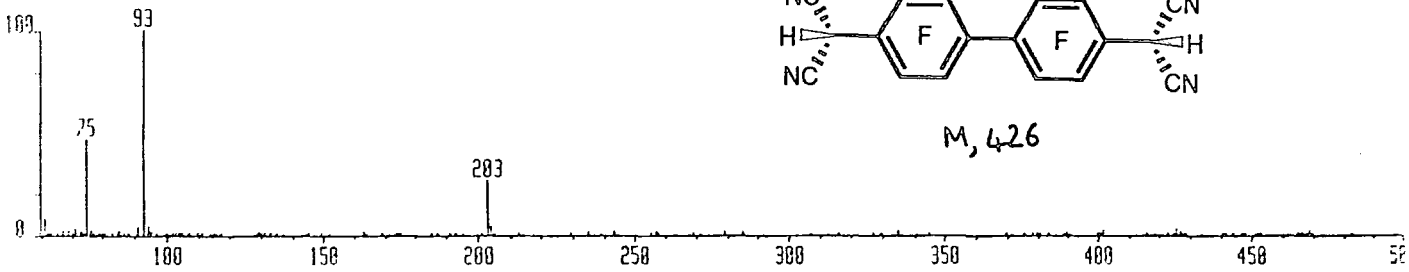
EI+

Mass Spec. Number 33



MPGM6H2#18◆ x1
BpM=0 I=10v
M.P.GREENHALL

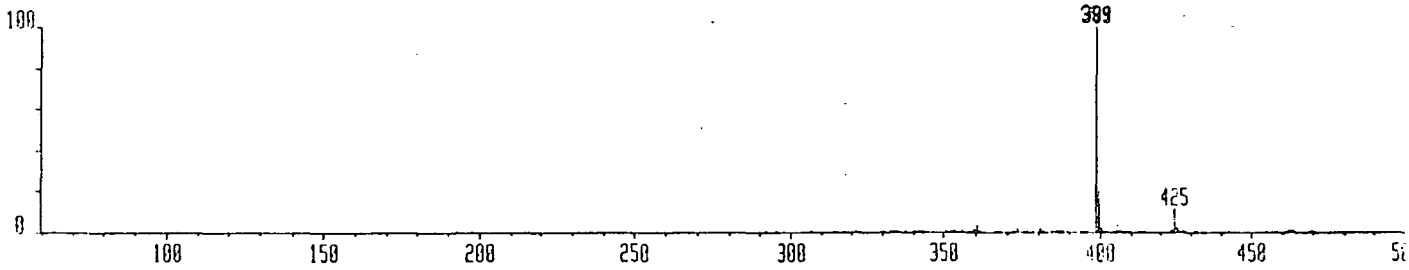
CI+



M, 426

MPGM6H2N#3◆ x1
BpM=0 I=7.5v
M.P.GREENHALL

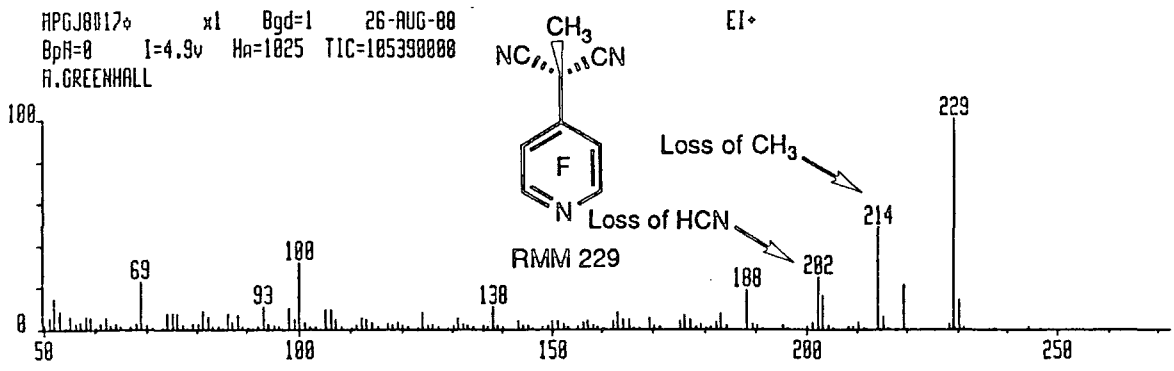
CI-

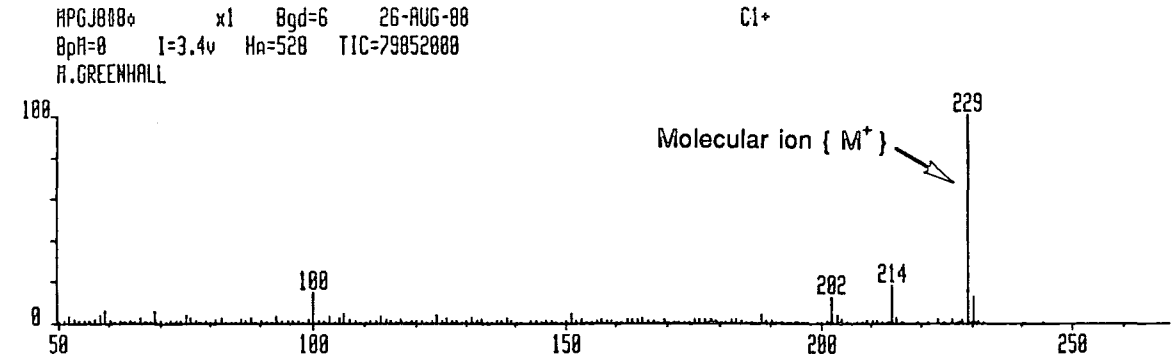


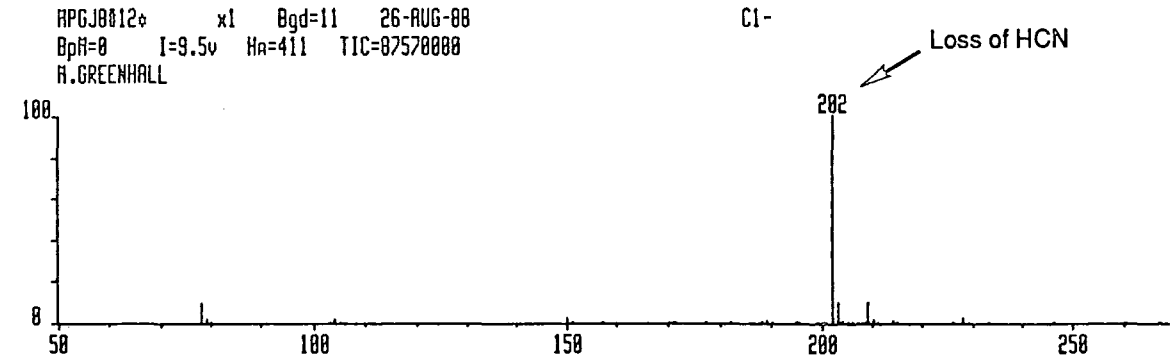
EI+ Data

Mass	% Base
311.61	1.17
312.56	5.87
313.53	1.38
313.58	0.41
315.59	5.44
316.58	1.30
317.60	0.58
322.58	1.61
323.60	0.58
326.55	0.39
326.58	0.54
328.60	0.41
329.59	1.53
330.52	0.37
333.58	0.95
334.10	0.64
334.54	22.77
335.56	2.06
336.02	0.43
336.58	0.95
340.56	1.79
341.59	0.41
342.58	0.54
350.62	0.64
353.55	1.26
354.56	0.87
355.60	0.49
356.55	0.68
359.55	0.37
360.54	2.18
361.55	3.40
362.51	0.64
362.55	0.43
368.49	0.31
373.51	0.43
373.56	0.39
374.57	1.15
375.55	3.98
376.58	0.45
378.48	1.19
379.53	7.52
380.52	0.89
381.54	0.74
384.47	0.84
399.52	3.94
400.51	4.82
401.50	1.17
406.54	1.07
407.55	0.54
408.53	0.70
412.54	0.33
424.48	0.84
425.51	34.37
426.52	5.19
427.51	0.64
428.46	0.45
437.48	0.43
445.61	0.89
446.60	0.76
446.65	0.35
450.43	0.72
462.43	0.72
478.40	2.14
500.37	8.33
501.37	1.59
505.22	0.33
516.34	0.33
566.35	1.17
616.30	0.31
666.24	0.78
682.29	0.56
849.45	0.47

Mass Spec. Number 34



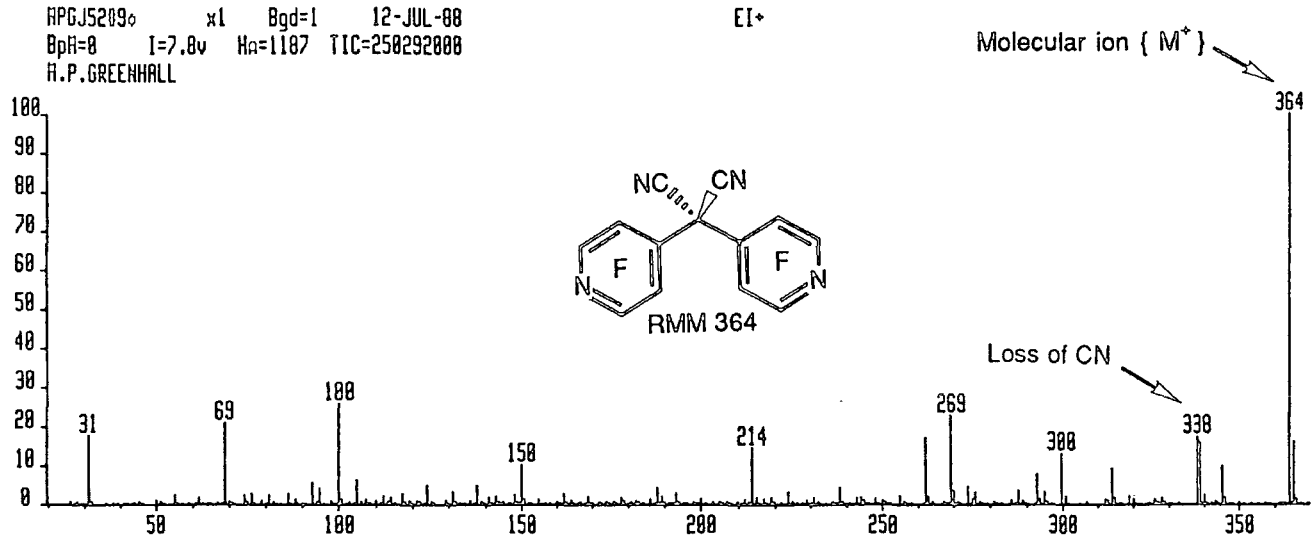


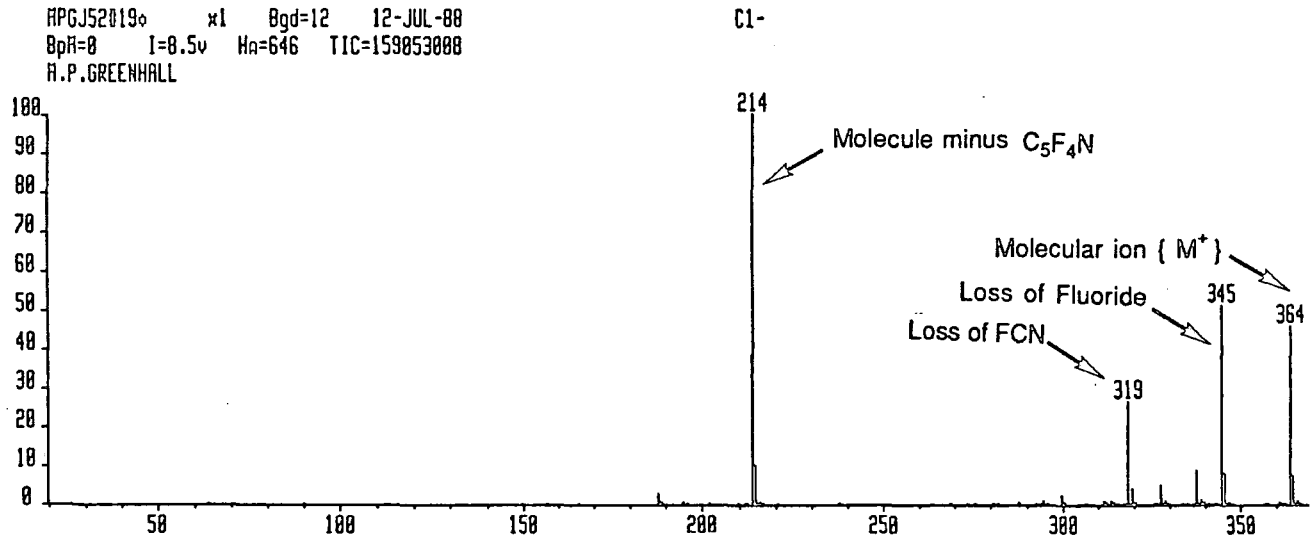


EI+ Data

Mass	% Base	Mass	% Base
26.06	1.19	165.23	1.21
28.07	1.32	169.22	1.57
31.05	15.29	176.23	1.81
42.10	1.86	177.24	1.17
51.08	1.43	183.25	2.05
52.09	4.43	188.24	5.82
53.10	2.45	200.26	0.15
55.07	1.72	201.26	0.95
58.11	1.77	202.27	7.72
59.13	1.56	203.28	4.84
62.08	1.57	204.29	0.46
69.08	7.08	205.28	0.04
74.09	2.05	208.27	0.23
75.10	2.06	209.29	0.31
76.10	2.10	210.29	0.86
81.11	2.45	211.30	0.08
82.12	1.64	214.27	15.12
36.11	2.07	215.28	1.71
88.13	1.81	216.29	0.07
93.12	3.28	219.30	6.30
98.13	3.05	228.30	0.70
99.14	1.36	228.42	0.08
100.13	9.74	228.85	0.05
105.14	2.81	228.96	0.04
106.15	2.79	229.32	31.49
107.15	1.31	229.64	0.05
112.14	1.50	230.33	4.21
113.16	1.38	231.33	0.25
124.16	2.38	237.35	0.06
131.17	1.54	244.36	0.17
138.18	3.19		
143.18	1.09		
150.19	1.01		
151.20	1.15		
157.21	1.04		
162.20	1.00		
163.22	2.43		
164.22	1.18		

Mass Spec. Number 35

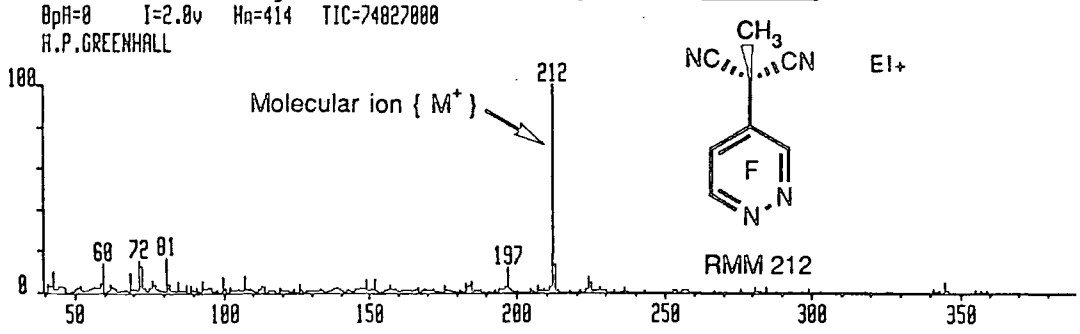


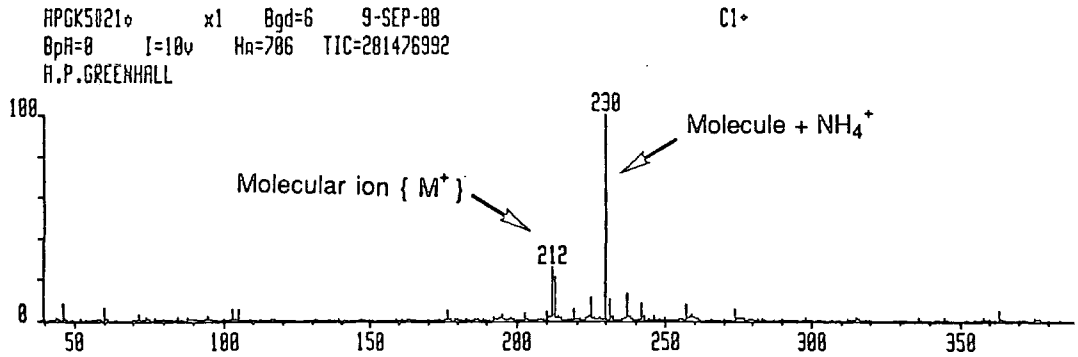


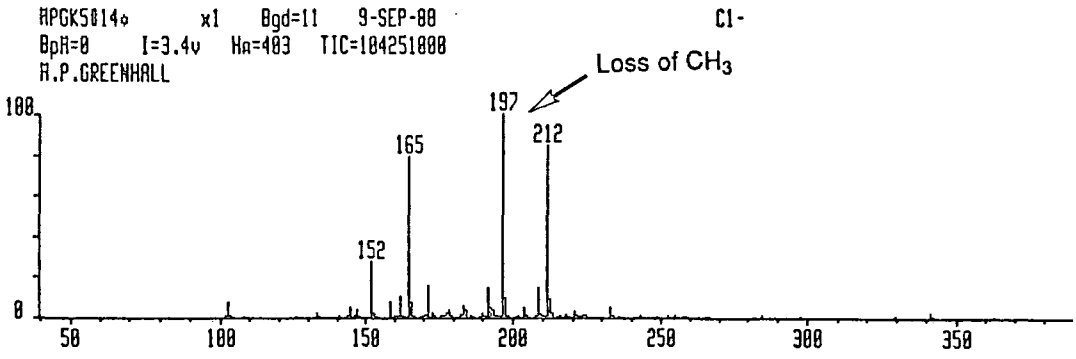
EI+ Data

Mass	% Base
30.98	17.37
54.97	2.27
61.97	1.33
68.96	20.71
73.96	2.28
75.96	2.38
80.96	2.24
85.96	2.33
92.95	5.25
94.95	3.99
99.96	25.88
100.96	1.20
104.95	5.93
106.96	1.06
111.95	1.95
113.95	1.52
116.95	2.37
123.95	4.47
130.94	2.76
137.94	4.69
140.94	1.28
142.94	1.90
147.94	2.08
149.93	10.15
154.93	1.13
161.93	2.44
168.93	1.93
177.92	1.36
187.93	4.08
188.94	1.61
192.93	2.46
199.92	1.01
211.92	1.05
213.92	14.16
214.92	1.35
216.91	1.10
218.91	1.39
223.91	2.79
230.92	1.53
237.92	4.03
242.91	1.43
243.91	1.31
247.90	1.04
254.90	1.71
261.90	16.91
262.90	1.82
268.91	22.34
269.91	3.28
273.90	4.19
274.91	1.11
275.91	2.78
287.90	3.17
292.89	7.50
293.90	1.04
294.91	2.68
299.90	12.74
300.91	1.80
311.90	1.22
313.90	8.85
314.91	1.33
318.90	1.64
325.90	1.08
327.89	1.36
337.88	17.13
338.88	15.54
339.89	2.01
344.90	9.65
345.91	1.48
363.91	100.00
364.92	15.70
365.93	1.22

Mass Spec. Number 36



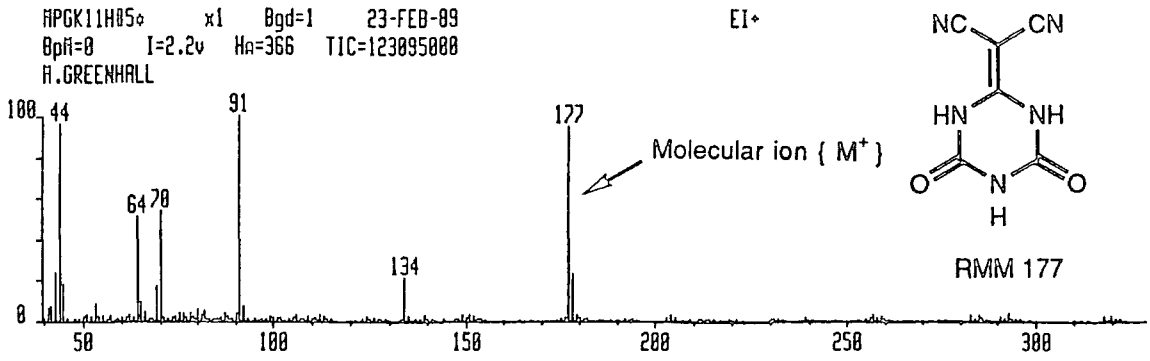


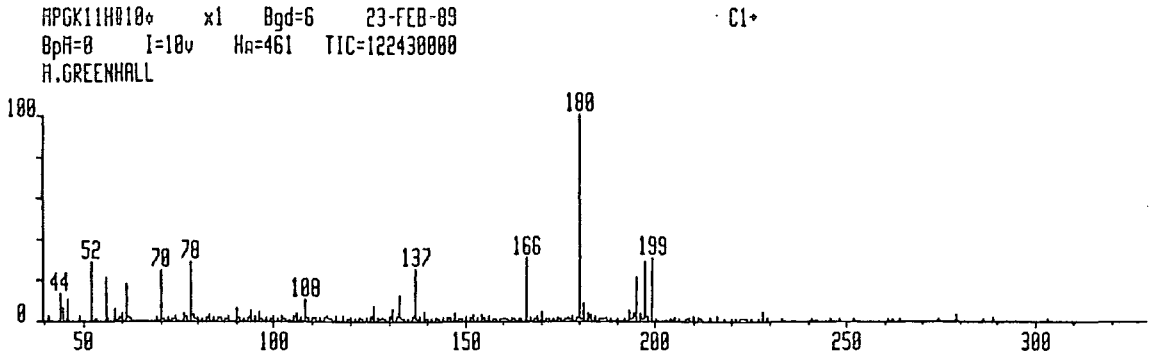


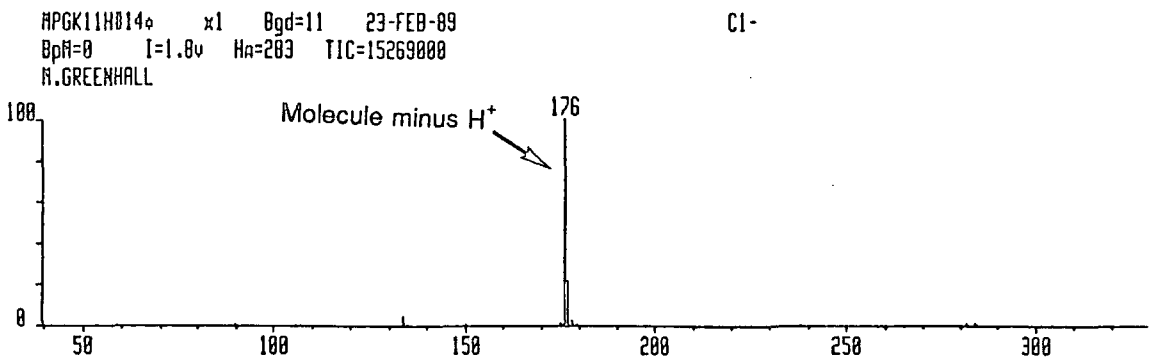
EI+ Data

Mass	% Base				
25.98	6.20	71.01	1.54	145.91	1.21
26.98	30.28	71.96	15.18	146.95	1.78
27.99	8.37	72.97	12.28	147.92	1.23
28.97	2.04	73.92	2.30	148.91	5.48
29.00	2.40	74.93	1.94	150.93	1.37
30.97	19.63	75.93	5.14	151.89	5.85
32.98	5.43	76.94	3.61	155.92	1.20
37.96	1.81	77.94	1.29	156.90	3.56
38.97	1.05	80.92	16.02	157.90	1.57
39.98	3.09	81.92	3.58	158.91	1.23
40.99	3.39	84.89	4.82	165.91	1.09
41.99	2.41	87.93	3.60	166.91	2.10
42.99	9.44	88.93	2.43	168.89	1.52
43.95	1.24	90.94	2.02	171.89	1.02
44.01	1.24	92.92	4.66	175.90	2.81
44.96	2.50	93.92	1.36	182.88	4.15
45.96	2.97	94.92	2.28	183.89	2.56
46.93	2.12	95.93	1.71	184.90	4.89
49.95	1.36	99.91	6.57	193.90	1.30
50.95	1.80	100.92	1.43	194.90	1.05
51.96	2.37	101.92	2.16	195.90	2.92
54.94	1.48	104.92	1.17	196.87	11.64
54.99	1.36	106.91	7.45	197.88	1.36
55.95	1.96	107.92	1.16	204.88	1.12
56.95	2.20	108.93	1.02	205.90	0.23
57.01	2.87	111.90	1.61	206.90	2.58
57.97	2.32	112.91	2.65	207.91	0.89
58.95	3.96	113.92	2.37	208.90	1.65
59.96	13.69	118.91	2.26	209.91	0.95
61.93	3.29	123.90	1.21	210.89	2.78
62.94	1.84	125.90	3.09	211.89	100.00
63.94	1.59	132.90	1.23	212.90	13.07
66.96	1.00	136.91	1.31	213.89	0.93
68.92	8.78	137.89	2.23	217.92	0.10
69.93	1.30	138.90	2.13	220.94	0.95
70.00	1.12	139.91	1.02	222.91	1.65
70.93	1.05	144.90	1.36	223.92	6.68
				224.91	4.30

Mass Spec. Number 37



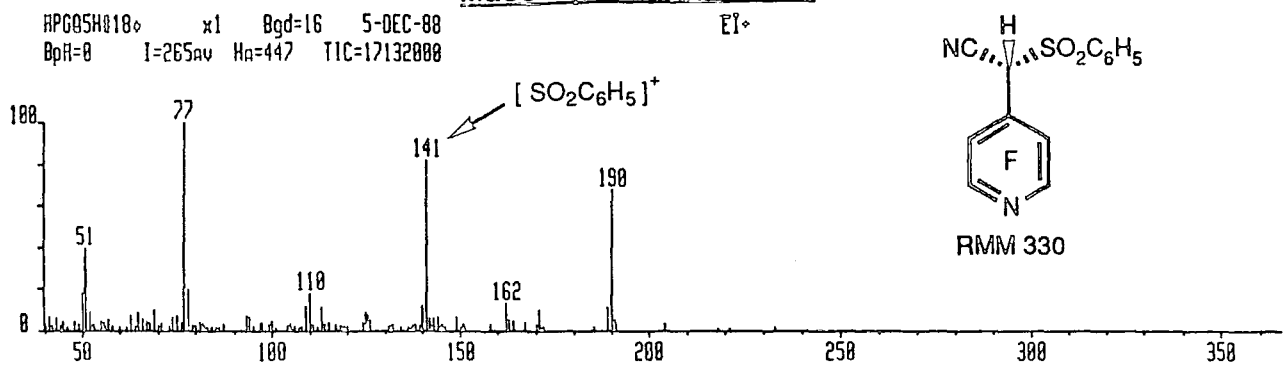




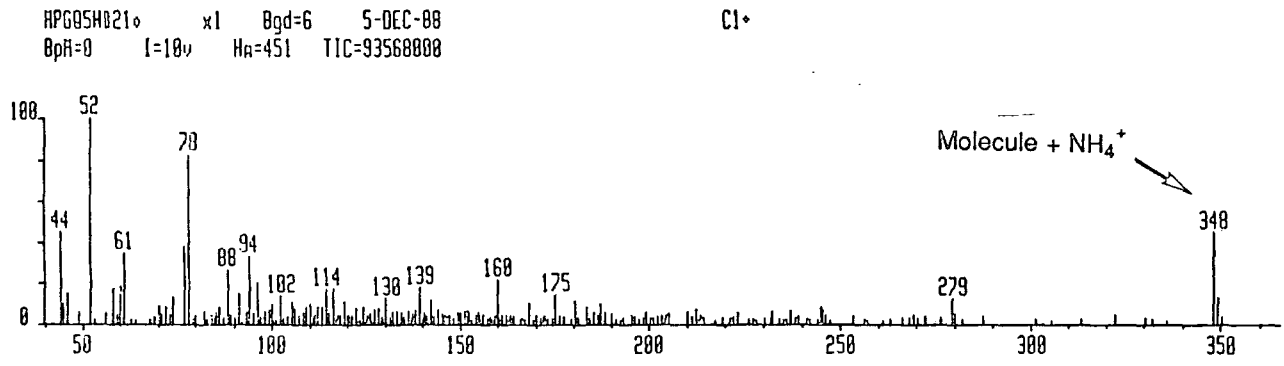
EI+ Data

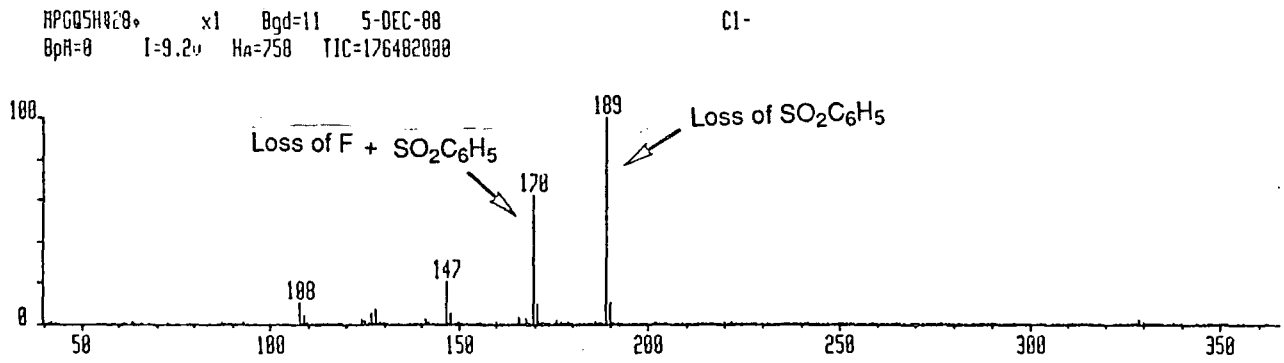
Mass	% Base		
41.02	5.99	86.00	1.18
41.05	3.86	87.01	3.57
42.02	6.74	88.01	2.33
43.01	23.57	90.00	3.34
43.06	3.74	91.00	100.00
44.02	95.62	92.01	6.90
45.03	17.55	99.00	1.86
50.01	2.22	100.00	1.40
51.01	2.56	101.00	1.23
52.01	1.84	102.01	1.03
53.01	7.91	105.03	1.35
53.99	2.10	105.98	2.90
55.01	1.01	106.06	2.15
55.05	2.54	109.01	1.76
57.06	2.44	110.99	1.47
60.02	1.43	112.00	2.51
61.01	1.47	113.00	1.84
62.00	2.76	123.99	2.29
63.00	1.61	125.00	1.01
63.99	50.84	126.00	1.21
65.00	8.73	134.00	21.27
66.01	3.73	135.00	1.93
68.99	16.63	139.00	2.70
69.05	1.17	148.99	2.55
69.97	53.24	149.99	1.66
70.98	1.48	151.00	2.44
71.07	1.02	152.00	2.25
73.01	1.44	175.99	1.61
74.00	2.16	176.99	94.89
75.00	3.70	177.99	22.74
76.00	3.12	179.00	2.37
77.01	1.25	180.01	1.24
78.00	3.34	202.97	1.05
78.90	1.98	203.98	2.88
79.91	5.39	204.98	1.10
80.90	2.49	238.95	1.17
81.91	4.43	255.86	1.44

Mass Spec. Number 38



RMM 330





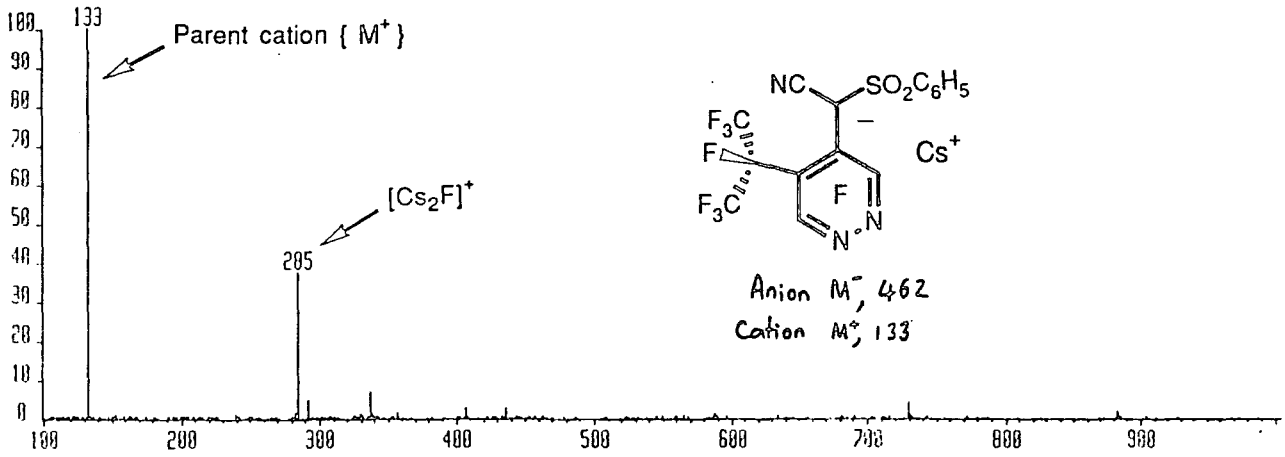
EI+ Data

Mass	% Base	Mass	% Base
28.95	3.05	93.00	6.50
28.99	3.45	94.02	6.39
30.96	11.57	97.03	3.45
31.94	3.28	97.11	3.57
36.99	5.12	100.00	4.37
38.00	3.74	109.00	11.68
39.01	8.98	110.01	17.84
41.02	4.37	113.00	11.05
41.03	6.21	115.06	3.22
43.02	3.28	124.00	3.05
43.05	5.64	124.98	8.17
44.98	3.74	125.02	7.08
47.97	4.37	126.01	4.66
50.01	17.26	140.00	11.57
51.02	39.18	140.99	81.47
52.02	9.03	141.97	5.41
55.05	4.26	142.96	5.29
56.01	3.51	143.97	3.74
57.07	5.47	144.02	5.98
63.01	6.96	148.99	5.93
65.04	8.11	149.04	5.06
66.03	5.58	162.00	12.77
67.05	4.03	162.97	4.83
68.00	3.68	163.02	3.74
68.98	9.15	163.99	4.37
69.06	6.73	166.96	3.68
71.08	3.34	170.99	9.21
74.00	6.33	189.01	10.59
75.01	6.44	189.99	67.26
76.00	3.39	190.97	5.06
76.03	4.32		
77.03	100.00		
78.04	19.28		
81.05	4.26		
81.09	3.68		
81.99	3.62		
82.02	3.68		

MPGP9CS#14+ **Mass Spec. Number 39** FB+

BpM=0

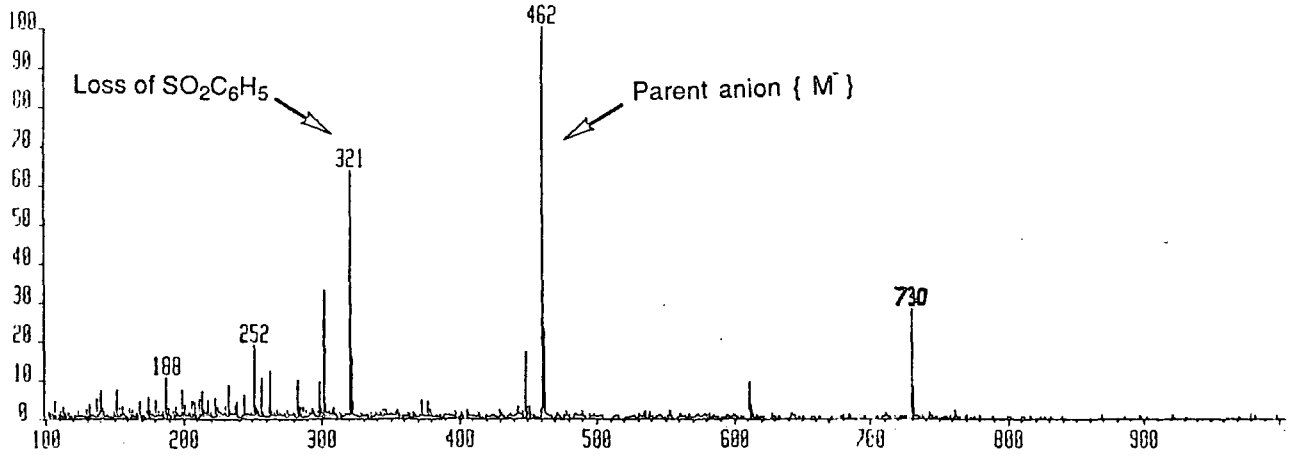
M.P.GREENHALL



MPGP9CS#19+ FB-

BpM=0

M.P.GREENHALL



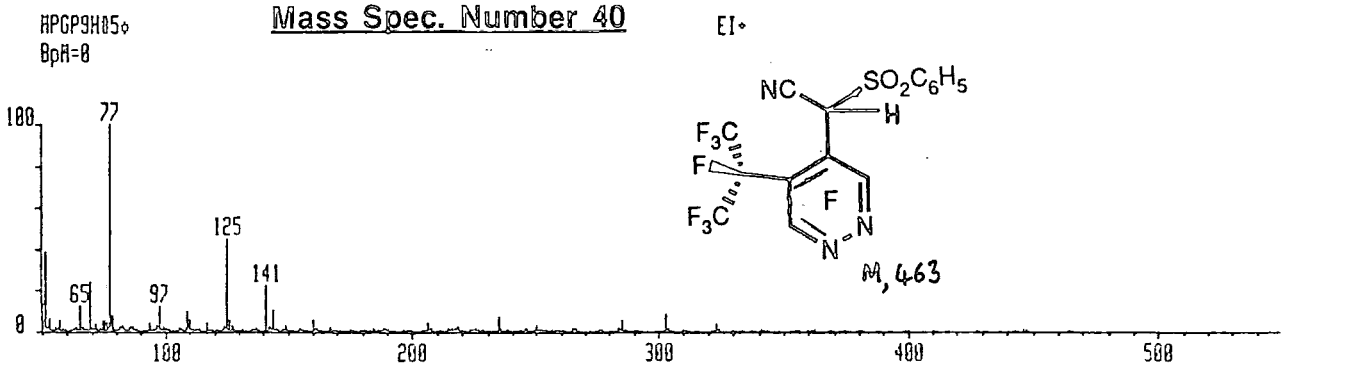
FAB Negative ion data

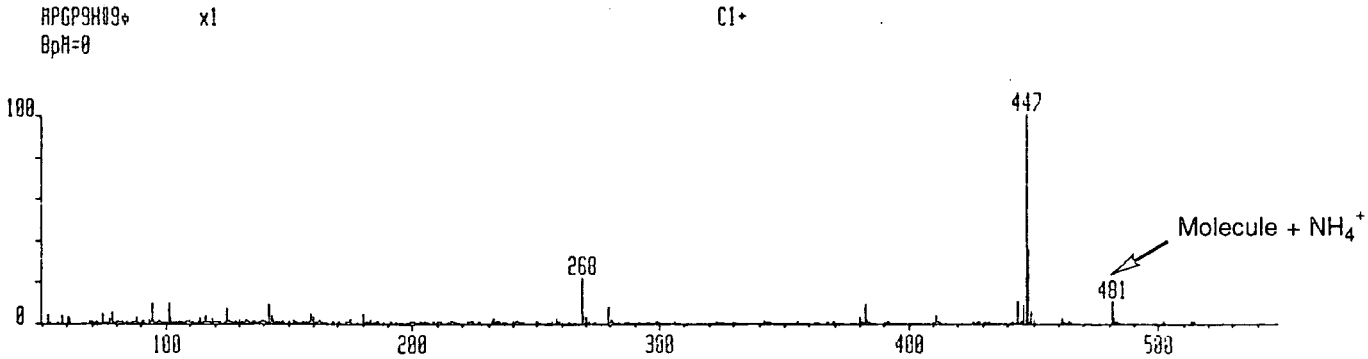
Mass	% Base
106.89	4.27
113.90	2.89
130.87	2.28
132.88	3.69
137.88	4.98
140.87	7.25
141.88	2.54
149.86	2.20
151.86	7.06
152.88	2.01
154.87	2.46
156.86	3.01
161.86	2.38
163.86	2.13
168.84	4.35
175.84	5.25
180.83	4.50
187.83	10.49
189.84	2.55
194.84	2.91
199.83	7.28
201.83	3.07
206.81	4.33
208.81	4.03
211.82	4.86
213.82	6.73
214.83	2.05
218.81	4.49
223.80	5.23
225.82	2.89
230.79	3.28
232.82	8.43
233.80	2.07
237.82	3.19
239.78	4.22
244.80	6.04
251.79	18.55
252.81	2.75
253.80	2.20
256.80	10.48
263.79	12.11
268.80	2.24
275.82	2.17
282.79	10.14
283.80	2.76
284.79	2.54
285.76	2.89
287.78	2.70
289.80	2.20
293.81	2.65
298.77	9.19
299.74	2.56
301.76	32.90
302.76	3.68
309.80	2.96
320.75	63.51
321.76	15.59
322.76	4.27
344.78	2.01
346.77	2.27
355.77	2.02
373.73	4.70
377.79	4.22
379.75	2.15
406.72	2.30
429.74	2.03
443.75	2.75
448.71	16.79
449.75	2.95
451.70	2.92
460.70	2.33
461.73	100.00
462.73	22.91
463.74	6.28
612.02	9.22
613.02	3.05
730.08	27.75
731.08	7.72
761.59	2.10

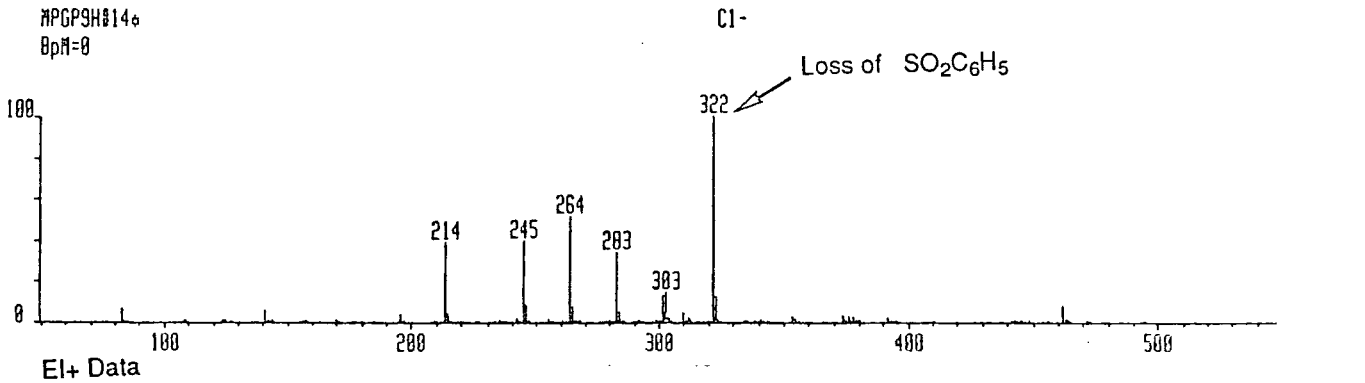
FAB Positive ion data

Mass	% Base
132.83	100.00
284.64	37.61
291.65	4.66
336.96	6.76
406.56	2.35
436.48	2.64
728.91	4.08

Mass Spec. Number 40







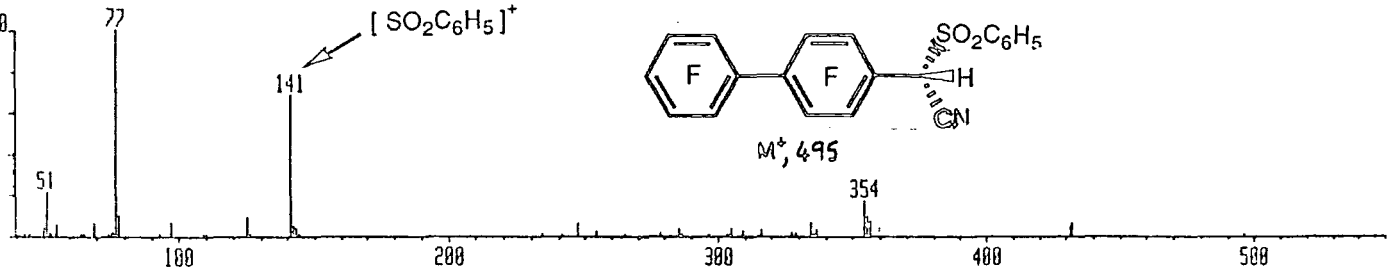
EI+ Data

Mass	% Base
20.01	7.58
27.03	4.34
31.00	5.84
37.01	2.14
38.02	3.03
39.02	7.96
41.04	2.77
43.02	3.87
43.05	3.78
43.99	6.04
44.98	4.49
47.97	2.38
50.02	12.68
51.03	38.27
53.04	6.33
55.05	2.11
57.07	4.94
63.03	2.19
65.04	11.93
68.99	23.85
69.07	2.02
71.05	3.28
74.01	4.83
75.02	4.42
76.03	4.08
77.04	100.00
78.05	7.69
82.01	2.85
86.00	2.00
93.02	4.17
96.04	3.47
97.02	11.99
99 01	2.07
109.01	9.53
110.02	5.62
117.00	3.75
124.00	2.38
125.01	45.26
126.02	5.25
127.01	3.02
141.00	22.38
144.01	9.86
149.02	2.49
159.99	5.21
166.99	2.03
206.00	4.28
218 02	2.32
234.01	7.08
250.01	2.57
285.01	5 31
302.99	8.24
323.00	3.69
354.00	0.28
355.04	0.12
356.08	0.08
359.00	0.08
359.96	0.18
360.05	0.16
360.93	0 11
362.04	0.65
363.01	0.11
368.34	0.13
368.92	0.14
371.99	0.12
373.03	0.16
373.98	0.12
379.02	0.34
380.06	0.29
381.01	0.16
387.04	0.14
391.92	0.10
391.97	0.10
392.03	0.08
399.00	0.27
399.08	0.10
400.02	0.30
409.99	0.43
410.98	0.18
415.03	0.10
415.09	0.09
416.02	0.13
427.95	0.11
430.99	0.12
442.98	0.34
443.93	0.15
444.08	0.06
446.14	0.59
447.14	0.41
447.24	0.11
463.96	0.46
465.00	0.07
489.06	0.11
521.95	0.10
526.16	0.09
547.95	0.14

MPGPSH#17
BpM=0
M.GREENHALL

Mass Spec. Number 41

EI+

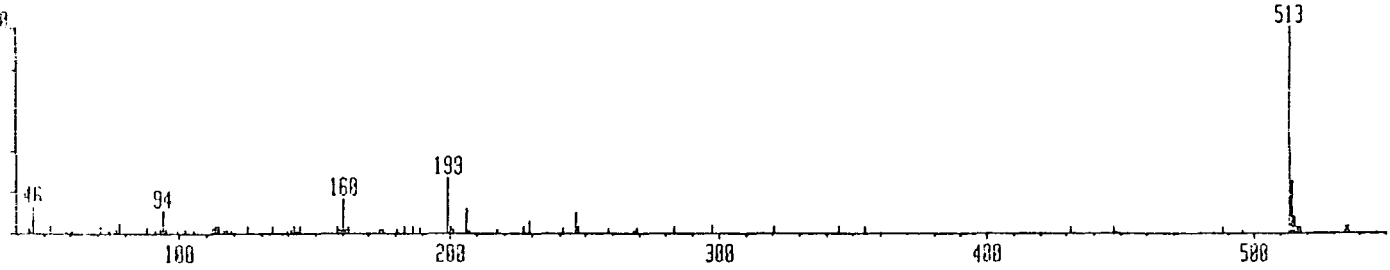


M^+, 495

MPGPSH#22
BpM=0
M.GREENHALL

CI+

Molecule + NH_4^+



MPGPSH#20
BpM=0
M.GREENHALL

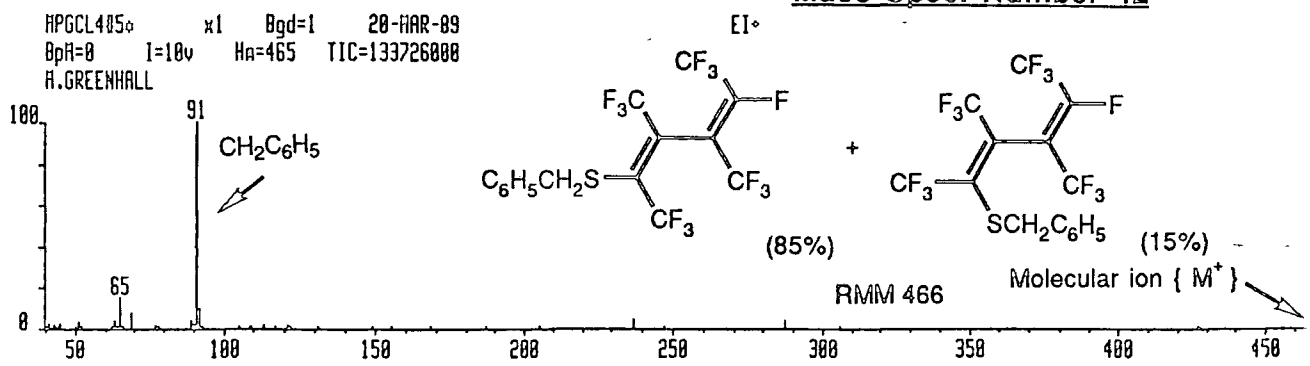
CI-

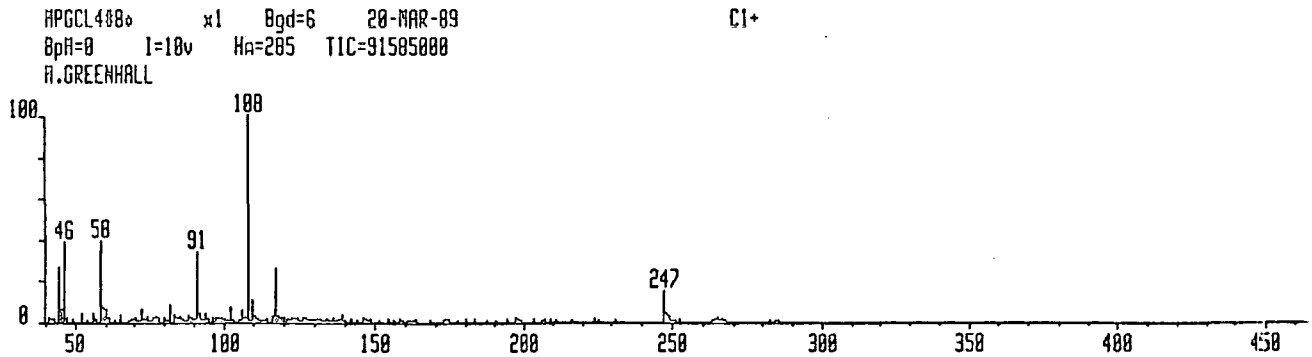
Loss of $SO_2C_6H_5$

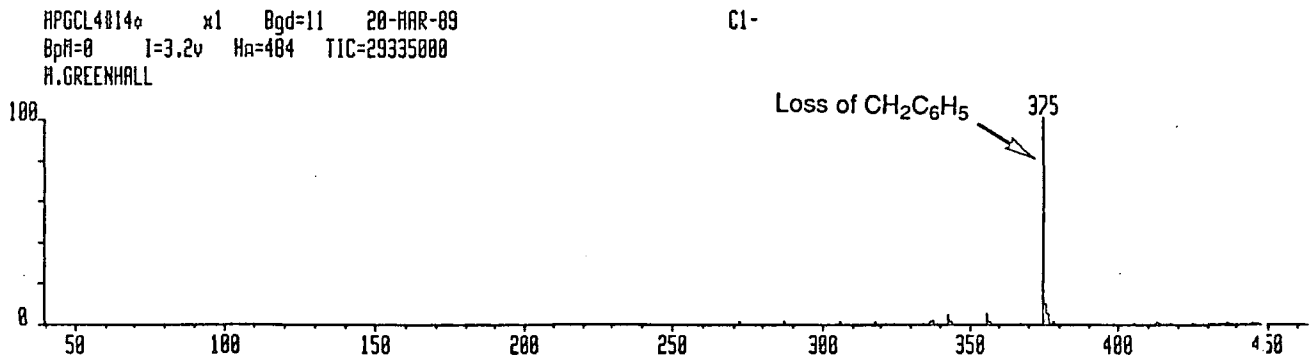
EI+ Data

Mass	% Base				
27.02	**1.44**	141.04	68.29	334.13	6.12
29.04	**0.43**	142.04	4.71	335.13	0.54
31.00	**0.39**	143.04	3.11	336.15	2.55
91.02	**0.35**	144.05	0.72	354.12	16.89
39.03	**1.92**	165.04	0.28	355.13	9.78
40.03	0.20	179.05	0.25	356.14	6.42
41.05	0.27	188.07	0.47	431.24	4.12
43.03	0.79	203.08	0.39	432.24	6.14
43.06	0.39	210.05	0.26	496.26	0.35
44.99	0.48	223.06	0.23		
45.04	0.18	227.08	0.26		
47.98	0.42	234.07	0.72		
50.03	3.72	235.07	0.44		
51.03	20.83	240.06	0.26		
52.04	1.04	241.07	0.70		
53.05	0.58	247.09	5.77		
55.06	5.65	253.09	0.38		
57.08	0.37	254.09	1.89		
63.03	0.44	255.09	0.43		
63.97	0.72	258.08	0.37		
65.05	0.67	259.10	0.26		
69.00	5.81	265.09	0.94		
71.10	0.23	266.09	0.37		
74.03	0.89	267.12	0.20		
75.03	1.11	272.10	0.27		
76.04	1.41	273.10	1.10		
77.06	100.00	284.10	0.31		
78.06	9.35	285.11	3.48		
93.02	0.76	286.08	0.27		
94.07	0.25	286.13	0.55		
94.08	0.15	298.10	0.88		
97.04	6.13	303.11	0.99		
109.03	0.73	304.13	0.70		
110.04	0.51	305.14	3.16		
117.02	0.49	306.14	0.42		
117.09	0.22	309.12	2.23		
125.04	8.79	310.12	0.27		
126.04	0.54	316.12	2.69		
127.04	0.39	317.15	0.33		
137.05	0.26	327.11	1.17		
139.03	0.27	329.13	1.28		

Mass Spec. Number 42



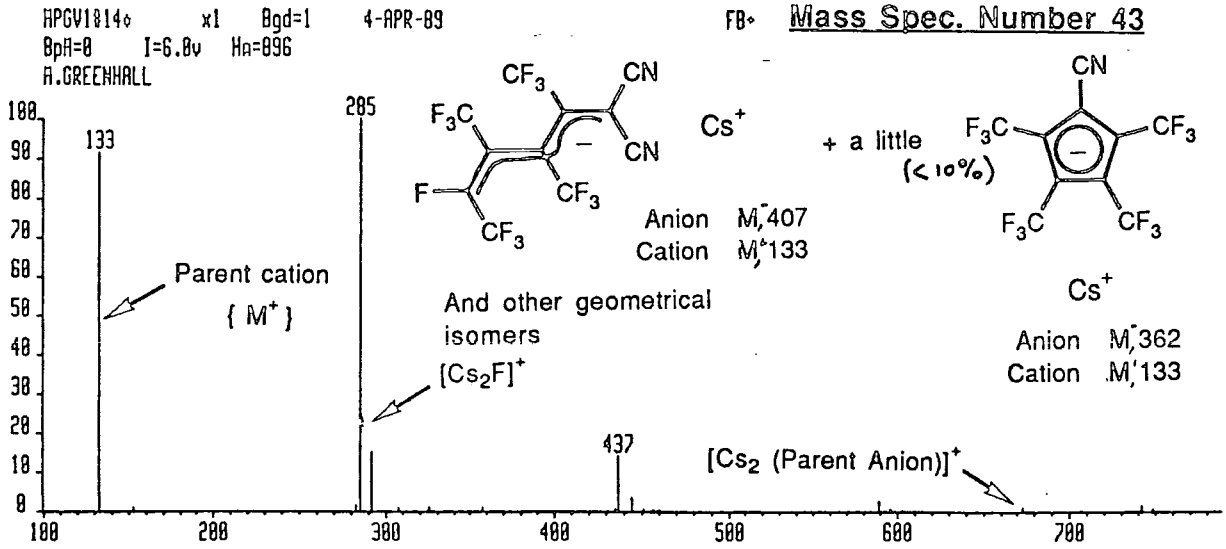


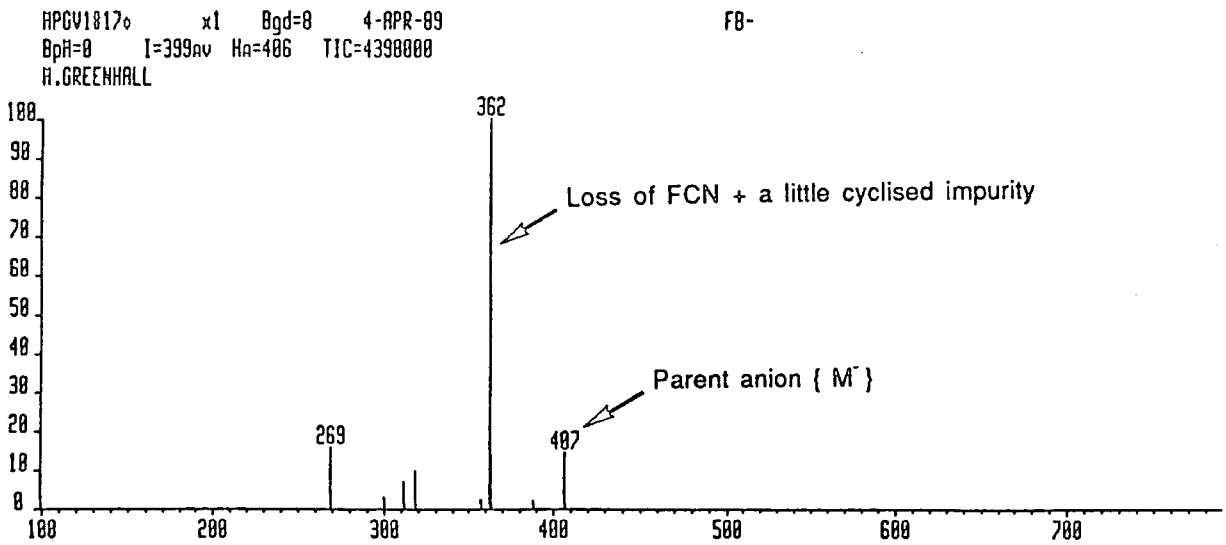


EI+ Data

Mass	% Base				
41.08	1.70	193.05	0.33	288.96	0.19
43.06	1.39	193.12	0.04	292.96	0.09
45.02	1.92	194.05	0.04	305.94	0.88
51.06	2.58	195.06	0.05	306.97	0.11
63.06	3.43	199.01	0.23	307.95	0.03
65.07	14.78	202.12	0.04	318.94	0.09
69.03	7.49	205.03	0.60	324.94	0.09
77.08	1.22	206.03	0.05	336.80	0.03
89.09	3.39	218.00	0.18	336.88	0.32
90.09	1.86	219.01	0.07	337.90	0.05
91.11	100.00	223.04	0.08	342.85	0.07
92.11	9.53	224.05	0.04	355.90	0.16
113.02	1.36	225.02	0.05	388.91	0.04
121.07	1.64	233.10	0.08	426.75	0.03
150.03	0.09	235.14	0.28	426.86	0.36
155.04	0.69	236.14	0.11	427.88	0.08
155.10	0.04	236.98	3.85	464.83	0.08
155.15	0.04	238.00	0.44	465.84	0.11
159.10	0.04	238.99	0.27		
159.14	0.04	243.01	0.36		
167.05	0.09	243.09	0.05		
168.02	0.66	244.02	0.06		
169.02	0.08	245.07	0.05		
169.13	0.07	246.14	0.04		
170.02	0.05	247.14	0.71		
174.05	0.09	248.14	0.26		
175.03	0.13	249.12	0.07		
178.13	0.10	255.01	0.14		
179.13	0.05	255.99	0.32		
181.04	0.12	256.98	0.08		
182.06	0.06	263.13	0.19		
186.04	0.08	264.12	0.14		
187.02	0.59	265.13	0.05		
187.09	0.06	274.98	0.05		
189.03	0.05	286.96	3.15		
189.07	0.06	287.96	0.32		

Mass Spec. Number 43





FAB Positive ion data

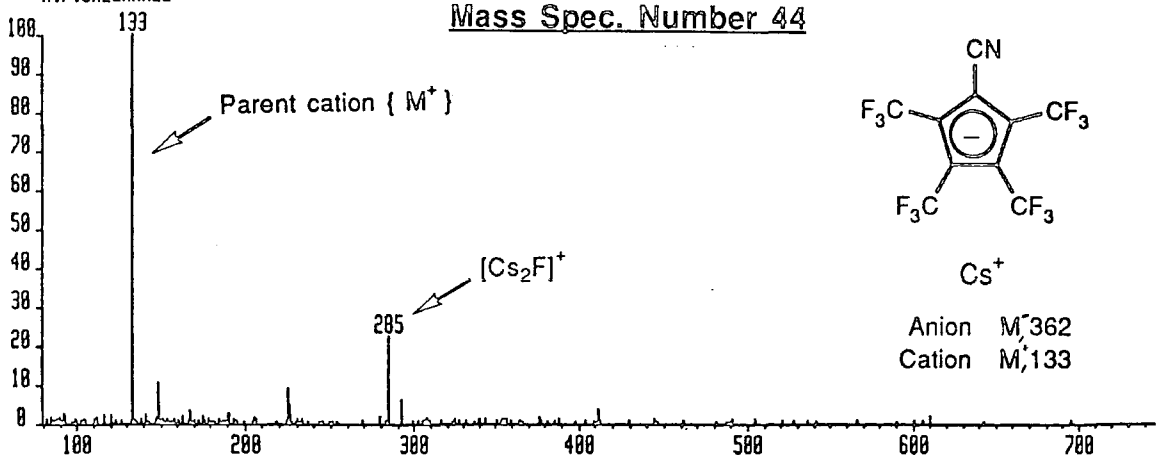
Mass	% Base
132.94	91.46
282.89	1.53
284.89	100.00
291.91	15.17
304.87	0.06
304.90	0.13
304.94	0.25
304.99	0.19
306.84	0.07
306.91	0.23
307.91	0.77
308.98	0.08
310.84	0.16
310.88	0.19
310.93	0.15
310.95	0.15
310.99	0.19
315.86	0.14
315.90	0.23
315.95	0.16
323.97	0.07
324.94	0.55
329.93	0.30
356.98	0.83
434.83	0.18
434.91	0.14
436.87	13.94
443.89	3.13
450.86	0.29
450.96	0.17
456.94	0.13
459.94	0.08
588.83	2.07
595.85	0.47
602.83	0.14
673.25	0.88
741.67	0.94
748.79	0.24

FAB Negative ion data

Mass	% Base
268.85	15.67
299.80	2.87
311.72	1.15
311.82	6.61
318.81	9.67
356.85	2.22
361.81	100.00
362.82	13.68
387.81	1.91
406.81	14.29

HPG07F05o x1 Bgd=1 10-FEB-89 FB+
BpM=0 I=1.1v Ha=694 TIC=21994000
H.P.GREENHALL

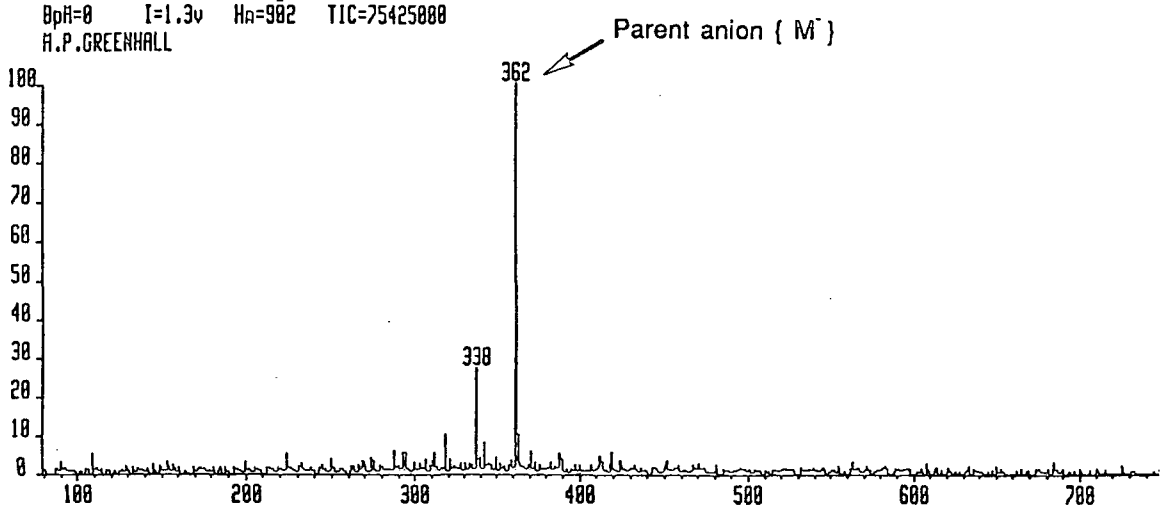
Mass Spec. Number 44



Cs^+

Anion M^- 362
Cation M^+ 133

HPG07F08o x1 Bgd=6 10-FEB-89 FB-
BpM=0 I=1.3v Ha=982 TIC=75425000
H.P.GREENHALL



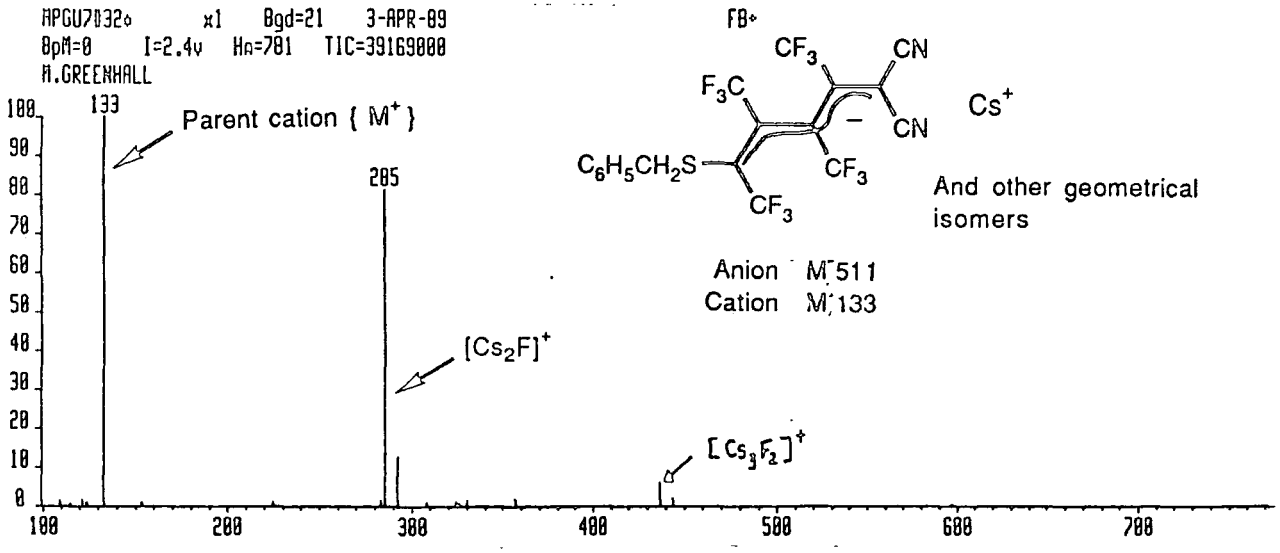
FAB Positive ion data

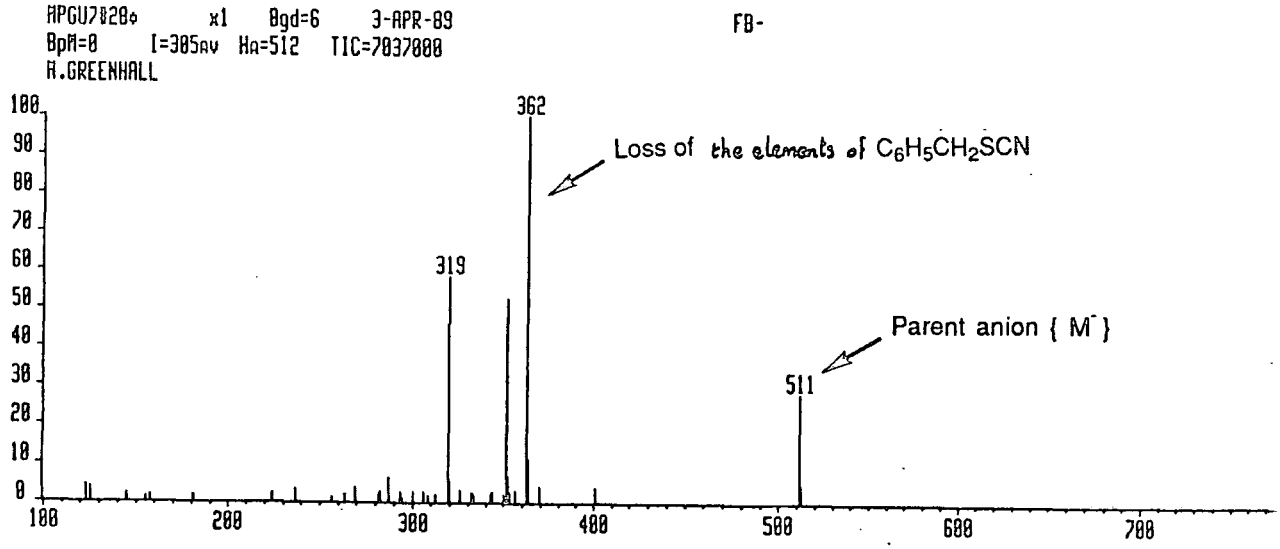
Mass	% Base
92.08	2.46
93.06	1.81
116.09	2.15
120.01	2.15
132.91	100.00
141.03	2.25
149.02	10.39
162.93	1.90
167.19	3.30
175.01	1.66
190.01	2.35
191.06	2.45
224.92	8.95
225.98	4.63
278.97	1.83
284.78	22.60
291.80	6.01
411.07	3.49
609.92	1.94

FAB Negative ion data

Mass	% Base
89.96	3.02
108.96	4.96
128.97	1.81
144.94	2.31
149.27	1.61
153.98	2.99
154.94	1.64
156.95	2.10
199.93	2.96
223.93	5.07
230.95	1.62
232.96	2.33
244.96	2.24
249.92	3.63
261.93	1.71
263.99	1.92
265.92	2.31
266.96	1.71
268.96	3.09
269.94	2.80
270.99	2.29
273.93	4.06
275.96	3.21
278.94	2.04
280.95	1.63
287.93	5.67
288.92	1.75
289.95	2.02
292.93	5.39
293.94	2.53
294.95	5.38
299.93	2.99
302.96	2.62
306.96	3.74
308.98	2.24
310.96	3.33
311.94	5.54
313.97	1.75
318.92	9.99
320.90	3.70
323.94	1.83
327.96	2.58
330.92	2.64
332.95	2.64
333.89	1.67
334.96	2.31
337.92	27.19
338.95	3.42
339.98	3.77
342.93	7.68
343.93	2.00
344.98	2.43
346.94	2.11
349.96	4.07
351.94	2.48
354.96	1.64
356.96	1.99
358.98	3.26
360.95	1.93
361.93	100.00
362.94	9.96
363.93	2.62
364.98	1.68
366.97	1.92
368.94	2.25
369.95	1.94
370.96	5.67
373.95	2.99
376.00	2.16
382.96	2.86
385.90	1.87
388.02	4.85
390.03	3.66
397.87	2.28
399.97	2.16

Mass Spec. Number 45





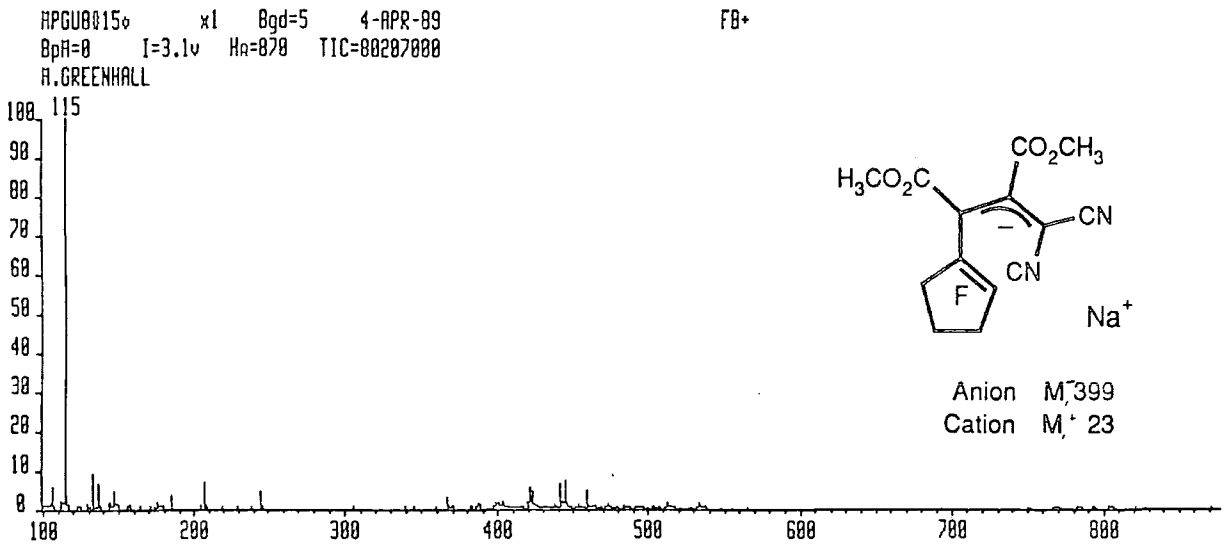
FAB Positive ion data

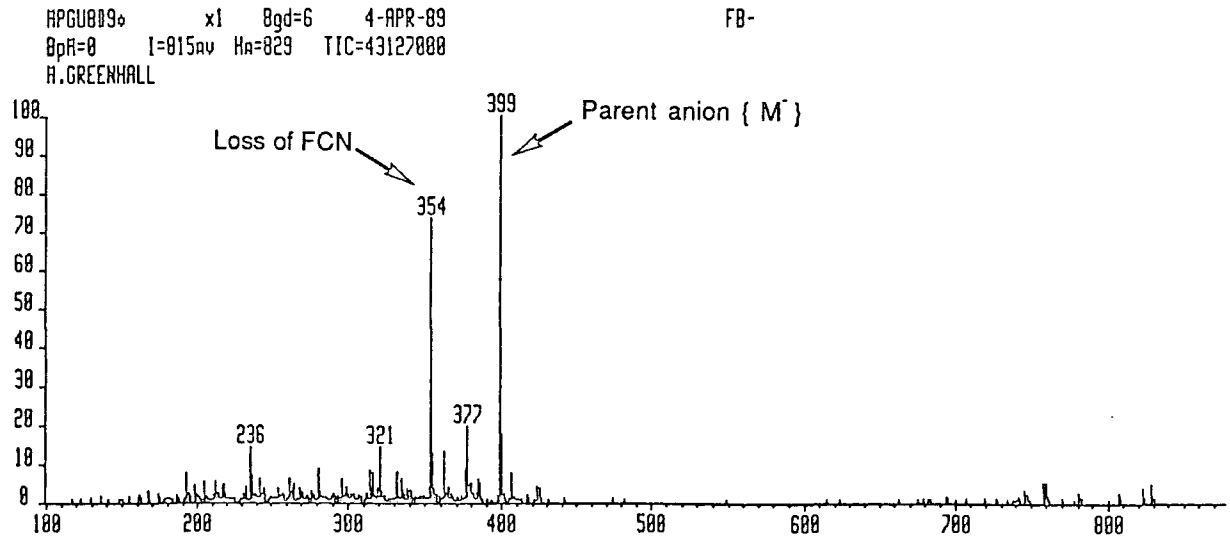
Mass	% Base
89.15	2.78
91.16	22.65
133.06	100.00
285.07	81.15
292.08	12.61
437.11	5.65
780.18	2.41

FAB Negative ion data

Mass	% Base
123.07	3.90
125.00	3.60
224.05	2.20
237.01	3.25
269.08	3.75
282.06	2.65
287.00	6.19
293.07	2.45
300.06	2.55
306.05	2.40
319.05	58.24
320.07	5.49
325.04	3.00
332.01	2.20
332.14	2.10
343.07	2.35
351.04	52.45
352.06	6.29
353.02	2.60
356.04	2.95
362.05	100.00
363.08	10.99
369.06	3.85
401.05	3.75
511.36	27.87
512.31	4.40

Mass Spec. Number 46





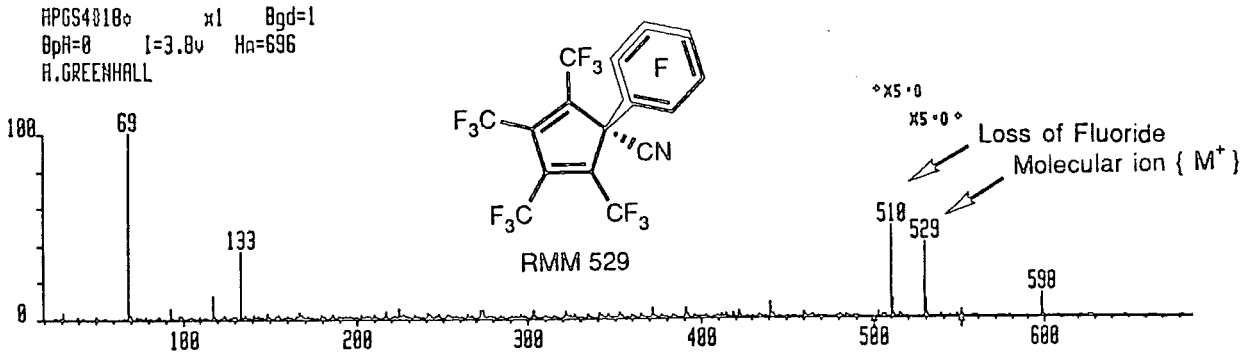
FAB Positive ion data

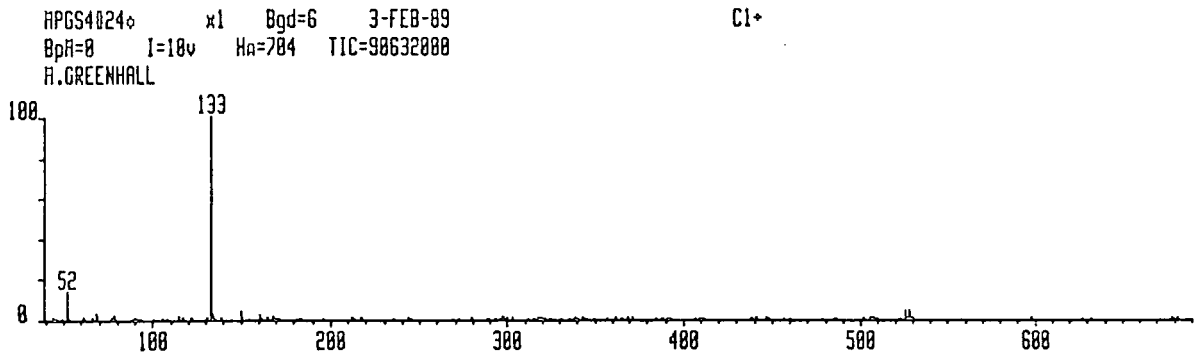
Mass	% Base
93.05	16.71
94.96	2.08
97.02	2.14
106.98	5.55
111.97	2.20
115.05	100.00
116.04	3.61
132.92	8.78
137.03	6.36
146.97	4.49
185.11	3.49
207.08	6.71
245.13	4.68
367.05	2.75
421.06	5.49
423.06	4.21
441.07	6.26
445.05	7.22
459.09	4.81

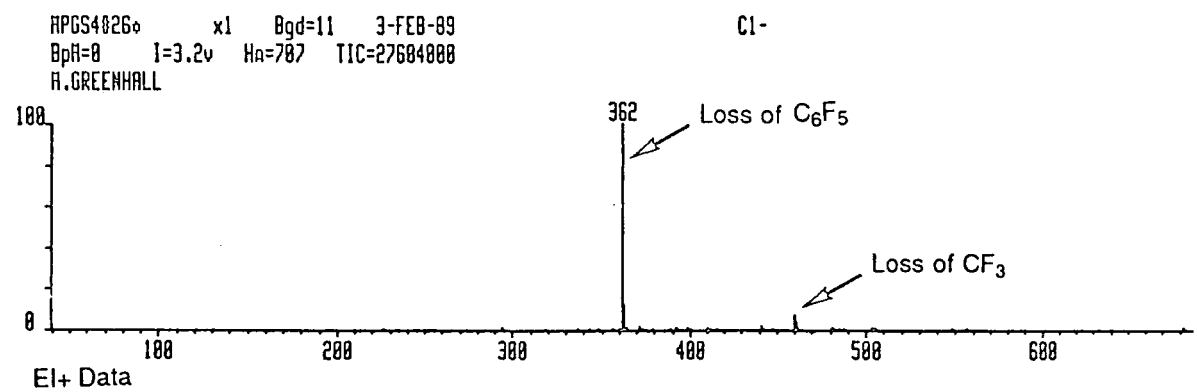
FAB Negative ion data

Mass	% Base	Mass	% Base	Mass	% Base
166.84	2.77	310.76	2.24	398.70	100.00
173.84	2.06	311.74	2.62	399.71	17.62
192.81	7.54	313.72	8.17	401.68	2.21
193.82	2.32	314.74	2.17	406.69	7.52
197.81	4.19	315.75	7.41	423.64	4.00
204.80	5.52	318.74	3.96	424.70	3.68
209.80	2.28	320.73	14.23	745.48	3.10
211.80	5.29	321.74	2.69	747.51	2.11
213.80	2.62	330.75	5.46	757.64	5.14
216.79	3.96	331.73	7.97	759.70	5.16
217.80	4.79	334.74	6.21	779.97	2.60
230.79	2.26	335.72	3.22	806.38	2.39
232.77	3.80	336.74	2.28	822.76	3.65
235.76	14.33	338.74	3.44	828.82	4.62
236.77	6.83	339.74	2.45		
237.76	2.02	340.74	3.25		
239.79	2.17	341.71	2.97		
242.77	6.04	352.69	3.82		
244.79	3.65	353.72	73.50		
254.77	3.72	354.73	12.66		
257.77	2.23	355 72	3.52		
261.77	5.95	357 74	2.21		
262.78	2.00	361.70	12 20		
263.76	2.97	362.72	2.60		
264.78	4.68	363.71	2.19		
268.77	3.65	364.72	3.98		
270.77	2.62	366.74	2.09		
275.78	2.75	375.74	8.53		
280.75	8.40	376.72	19.81		
281.76	2.67	377.74	3.65		
290.77	2.23	378.70	4.49		
295.75	6.13	379.74	5.05		
297.77	2.32	380.73	2.34		
298.75	4.06	381.73	2.02		
299.76	2.08	383.72	2.38		
301.76	2.26	384.72	6.12		
303.74	2.02	385.70	4.83		

Mass Spec. Number 47



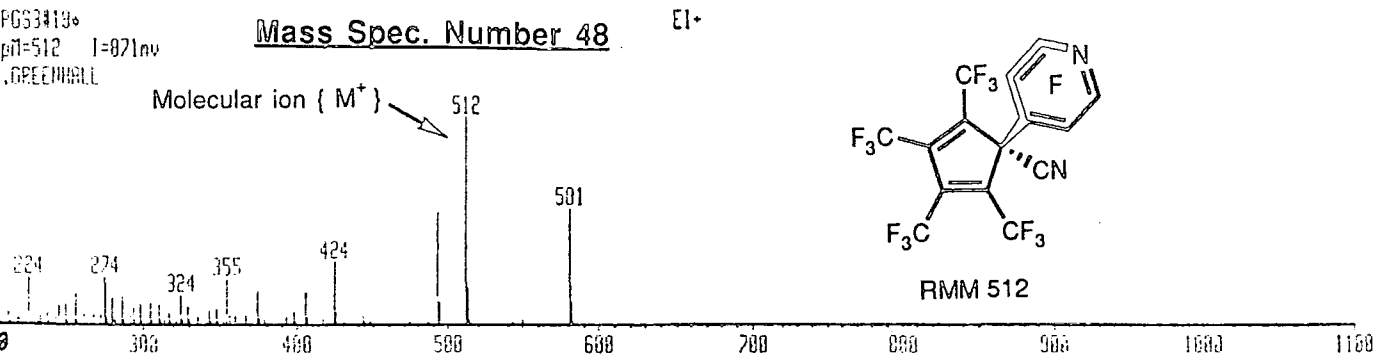




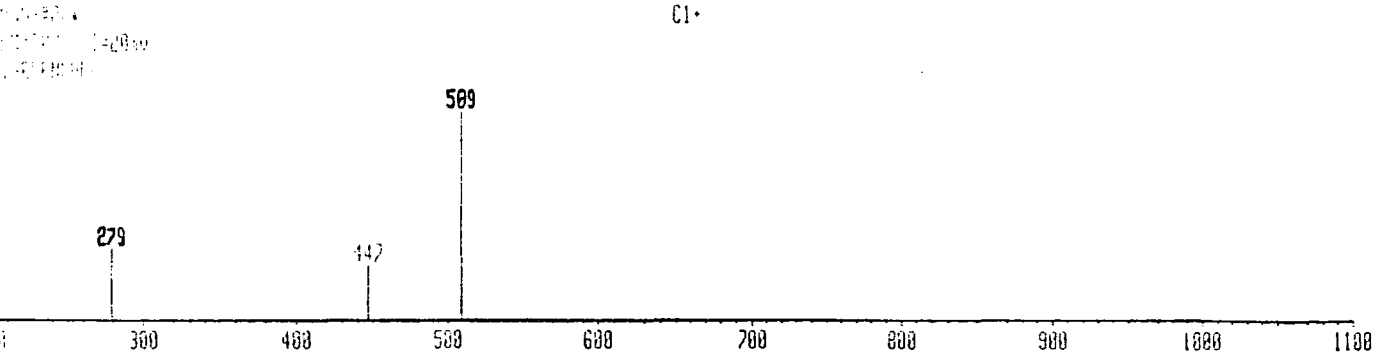
EI+ Data

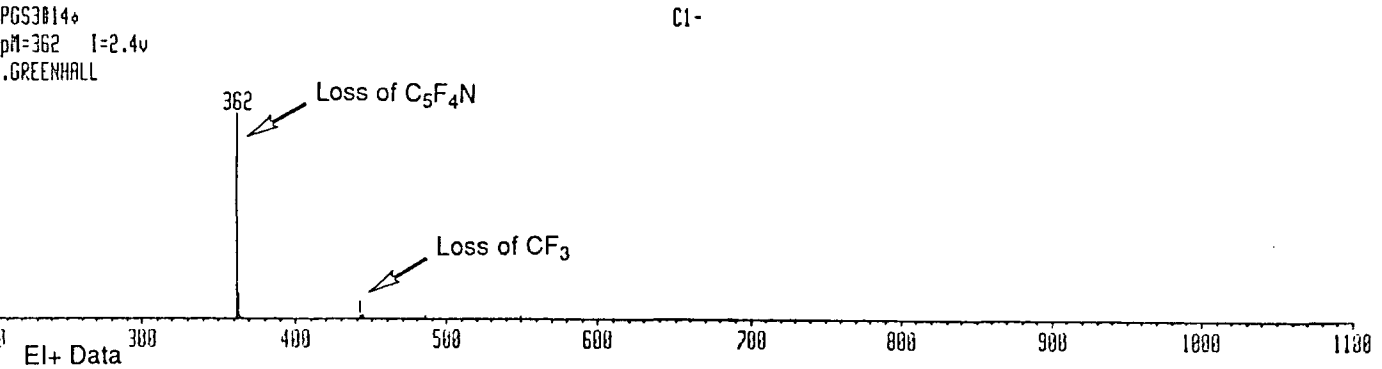
Mass	% Base				
49.99	0.69	223.99	4.29	342.86	0.61
68.98	100.00	225.01	0.51	345.89	1.33
69.98	1.23	226.99	1.41	352.95	2.01
78.99	0.65	228.99	0.52	359.96	0.91
85.99	0.54	233.99	1.35	364.94	1.41
92.99	4.89	240.98	2.33	371.95	4.72
97.99	1.39	242.98	1.56	372.95	0.87
100.00	0.82	245.98	0.65	383.93	0.72
105.00	0.74	247.97	1.27	389.94	0.60
116.99	11.91	252.97	1.52	390.94	4.20
118.00	0.75	253.98	0.54	391.94	1.29
124.00	1.88	257.97	0.75	395.94	0.57
129.00	0.55	264.96	1.61	402.95	0.55
130.99	0.60	266.95	0.62	409.93	0.86
132.90	36.23	271.95	3.88	411.94	1.13
135.99	1.16	272.97	0.79	414.93	1.27
140.99	1.68	273.96	4.10	418.92	1.93
142.99	0.52	274.97	0.54	421.93	2.88
147.99	2.13	276.96	0.78	422.93	0.56
154.99	1.45	278.96	0.69	433.92	0.83
159.99	0.54	290.95	0.77	440.93	7.40
164.99	0.96	292.95	0.83	441.93	1.35
166.99	3.28	295.95	1.72	459.93	2.00
168.00	1.44	297.95	0.51	464.93	0.61
172.00	0.94	301.95	0.91	483.93	0.91
178.99	1.35	302.95	3.85	509.92	9.84
181.00	0.58	303.96	0.60	510.92	1.85
185.99	1.63	309.95	0.60	528.90	8.00
189.00	0.58	314.94	0.99	529.91	1.61
193.00	0.86	320.96	0.78	549.94	0.54
196.00	0.62	321.96	2.82	597.89	12.38
202.99	1.57	322.96	0.61	598.90	2.30
204.99	0.80	323.96	1.06		
205.99	0.58	326.95	1.20		
209.99	1.23	333.94	1.26		
216.99	3.14	340.88	2.26		
221.99	0.51	341.88	0.65		

Mass Spec. Number 48



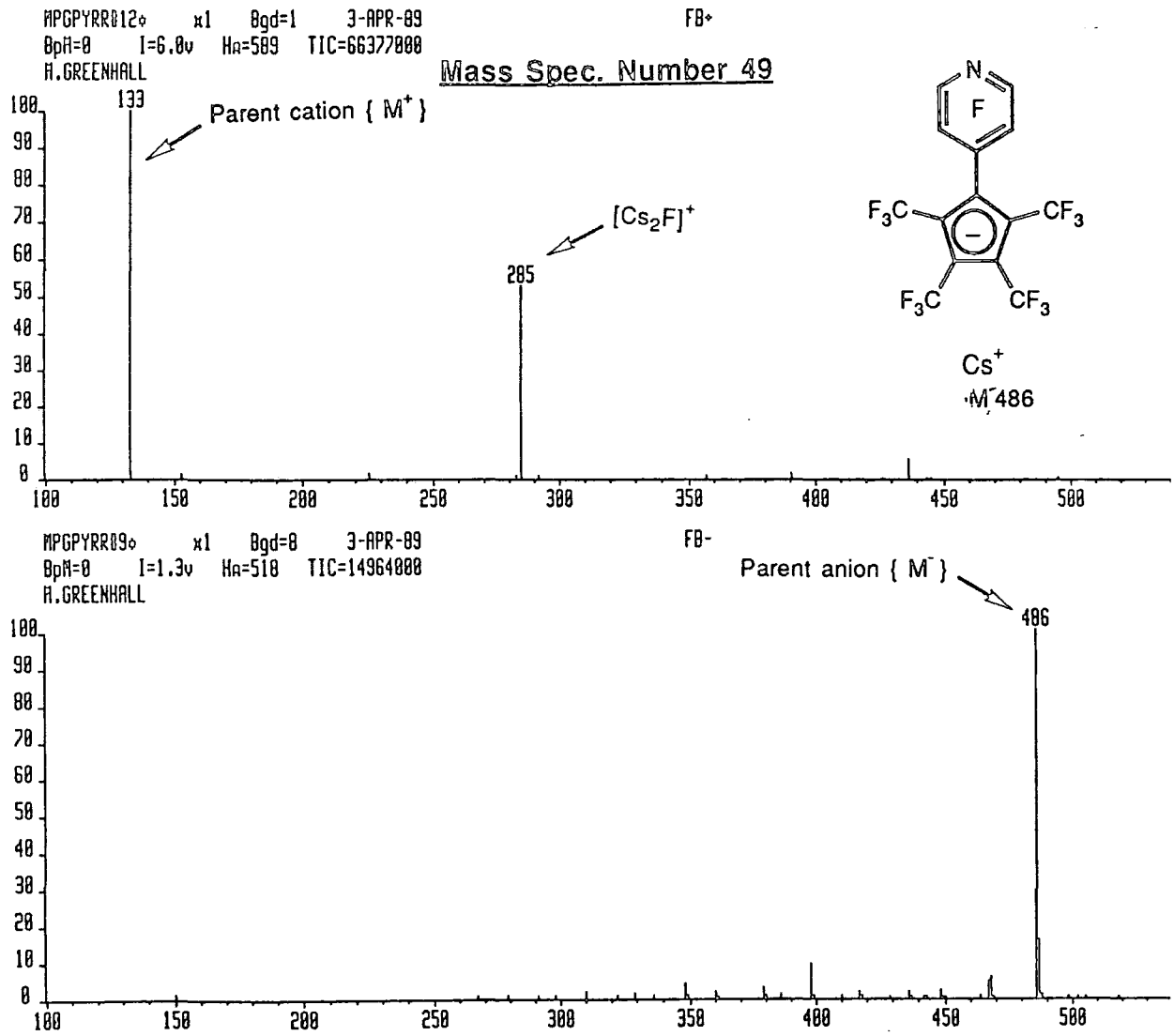
RMM 512





EI+ Data

Mass	% Base				
200.00	3.22	299.01	0.95	443.03	3.43
203.01	2.14	303.00	2.86	444.03	0.68
205.00	4.36	304.01	0.46	448.01	0.75
206.01	0.51	305.02	9.36	474.01	0.91
210.01	5.47	306.02	1.30	486.03	0.98
211.02	0.60	310.01	9.00	493.04	53.78
212.01	1.33	311.01	1.21	494.05	9.62
215.01	0.44	314.03	1.36	512.02	100.00
217.01	3.83	317.01	4.89	513.02	16.77
222.01	0.91	318.01	1.00	514.03	1.49
224.01	22.41	322.00	2.52	543.02	0.44
225.01	1.35	324.02	13.54	543.10	0.61
226.01	5.03	325.02	1.69	550.04	1.30
230.02	0.72	329.02	7.90	581.02	56.18
231.02	3.05	330.02	1.16	582.03	9.88
234.01	1.26	336.01	2.87	583.02	0.72
236.02	4.56	340.99	0.91	583.97	0.39
237.01	0.65	343.01	5.82		
241.01	3.31	344.01	0.51		
243.01	8.55	348.01	6.66		
248.01	9.02	348.05	0.56		
249.02	1.10	353.01	1.02		
253.00	1.61	355.01	21.72		
255.01	14.19	356.02	3.15		
256.01	1.58	360.00	3.42		
260.01	3.96	367.00	3.07		
262.01	1.52	371.97	0.49		
265.02	1.12	372.03	0.39		
267.01	3.80	374.02	15.56		
272.01	3.73	375.02	1.84		
274.01	22.06	379.01	1.63		
275.02	2.45	393.02	2.58		
279.02	12.25	398.01	5.40		
280.02	1.05	399.00	0.51		
281.01	1.09	405.02	14.66		
286.02	12.58	406.04	2.84		
287.03	1.58	417.02	2.26		
291.01	3.40	424.02	29.61		
293.02	7.25	425.02	4.43		
294.02	1.14	431.04	0.58		
298.01	8.57				



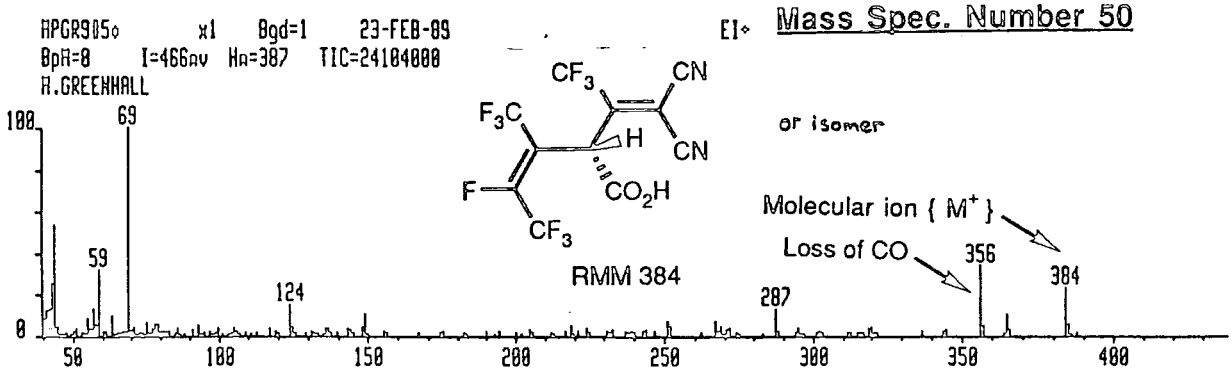
FAB Positive ion data

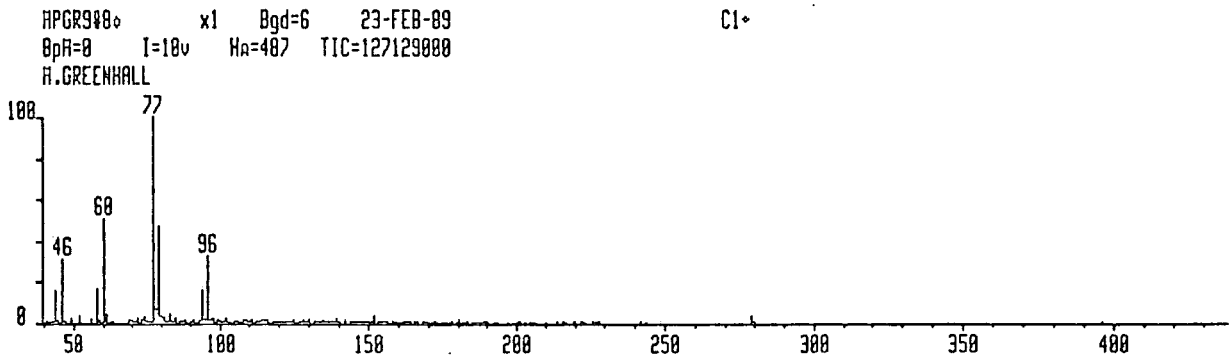
Mass	% Base
132.98	100.00
225.02	1.36
265.88	0.07
282.86	0.64
284.85	52.66
291.87	0.89
295.89	0.11
304.84	0.26
307.82	0.07
307.86	0.08
308.86	0.08
308.93	0.07
310.86	0.19
323.87	0.14
324.84	0.27
345.80	0.12
356.86	0.79
374.01	0.10
374.07	0.07
390.80	1.61
391.91	0.08
392.01	0.09
392.94	0.11
425.97	0.18
436.69	5.20
443.64	0.07
444.99	0.08
494.76	0.20
542.89	0.25
589.03	0.34

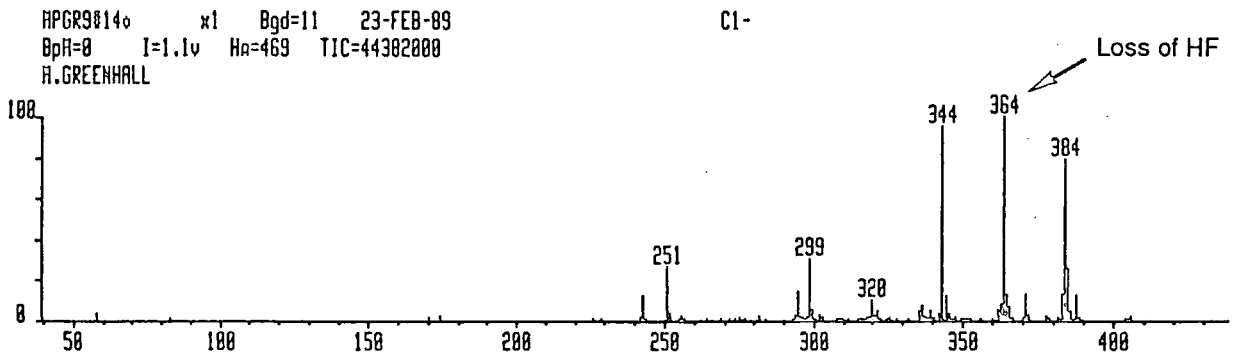
FAB Negative ion data

Mass	% Base
150.01	1.20
259.98	0.30
267.01	0.61
278.99	0.61
290.99	0.80
291.04	0.37
297.99	0.83
309.98	1.64
316.99	0.43
322.01	0.54
326.05	0.46
328.98	1.46
329.94	0.39
336.02	0.73
347.98	3.99
348.99	0.69
360.00	1.68
361.01	0.53
379.00	2.69
379.96	0.73
385.96	1.09
391.07	0.31
397.99	9.16
399.01	0.84
410.02	0.77
416.97	1.85
417.19	0.31
418.01	0.86
428.97	0.30
429.00	0.28
429.04	0.48
436.00	1.78
436.99	0.45
442.04	0.44
443.03	0.47
443.07	0.32
448.03	2.07
449.07	0.45
450.10	0.31
463.83	0.39
464.01	0.80
467.04	4.59
468.03	5.76
469.07	0.41
486.07	100.00
487.09	15.71
488.10	0.90
498.15	0.28
498.21	0.44
502.17	0.30
505.16	0.41
518.15	0.43
518.21	0.37

Mass Spec. Number 50







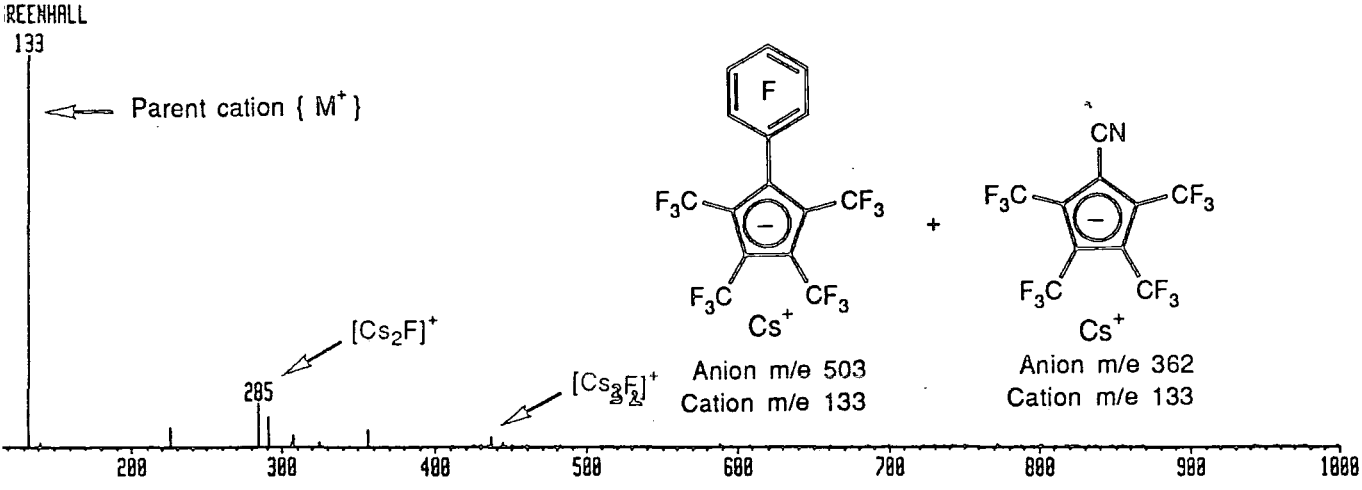
EI+ Data

Mass	% Base						
40.00	8.12	70.02	2.65	125.94	1.31	250.88	6.94
41.01	11.88	71.03	4.22	128.93	1.41	251.87	4.29
42.00	12.73	72.97	1.11	130.93	2.00	266.86	6.58
42.99	25.00	72.99	1.37	131.93	1.01	267.86	2.00
43.03	9.29	73.94	1.31	135.92	3.24	268.86	3.89
43.98	53.27	74.95	6.09	136.94	3.30	269.86	0.62
44.03	3.30	75.94	1.51	137.92	1.64	270.87	2.95
44.95	3.93	75.97	1.18	139.94	1.37	271.85	3.04
44.97	3.70	76.97	3.47	142.91	3.50	273.86	1.37
45.01	1.93	77.96	5.33	143.43	1.41	274.88	0.98
45.03	1.41	78.95	5.53	143.92	2.68	282.86	0.72
47.93	1.34	79.95	1.87	144.92	1.11	286.86	12.86
49.96	1.83	80.95	2.23	147.91	3.73	287.85	2.00
49.98	1.31	81.01	1.05	148.94	9.95	293.86	1.21
50.97	3.30	81.95	2.23	154.91	1.96	294.84	3.08
53.00	1.24	83.03	1.90	155.92	1.11	311.83	1.08
53.99	1.05	85.04	1.47	166.91	1.57	312.80	1.01
54.00	1.15	85.95	3.08	173.91	1.24	314.86	1.57
55.01	8.05	91.00	2.62	174.92	1.87	315.84	1.15
56.02	3.08	92.94	3.08	181.92	1.28	316.83	1.64
57.03	12.60	93.00	4.55	182.93	0.59	318.83	3.66
58.03	5.37	95.02	1.05	189.92	1.83	319.83	3.73
58.99	31.51	97.04	1.93	192.91	0.92	320.84	1.41
59.03	2.09	98.94	1.54	193.90	2.26	321.85	1.08
60.00	2.23	99.94	3.08	199.91	1.01	336.78	2.13
60.97	1.77	103.97	1.21	201.90	0.95	343.72	1.70
62.94	9.52	104.94	3.27	204.87	2.42	344.74	2.45
64.99	1.44	105.94	1.87	205.88	1.28	355.82	34.03
65.96	1.57	106.01	1.41	211.89	1.24	356.82	5.01
66.95	1.93	109.03	1.44	212.90	0.85	363.79	1.51
67.00	2.26	112.93	1.34	216.89	1.83	364.80	10.14
67.96	1.90	116.93	3.57	218.89	4.81	365.79	2.78
68.01	1.08	118.93	1.77	219.90	0.79	383.78	22.94
68.94	100.00	119.94	1.57	220.91	1.80	384.79	5.46
69.01	3.73	123.93	14.89	223.89	3.08	385.81	0.62
69.95	1.18	124.94	4.06	224.90	1.08	387.78	1.15

S484◇
I=8
GREENHALL

Mass Spec. Number 51

FB◇



S488◇
I=8 I=704AV
GREENHALL

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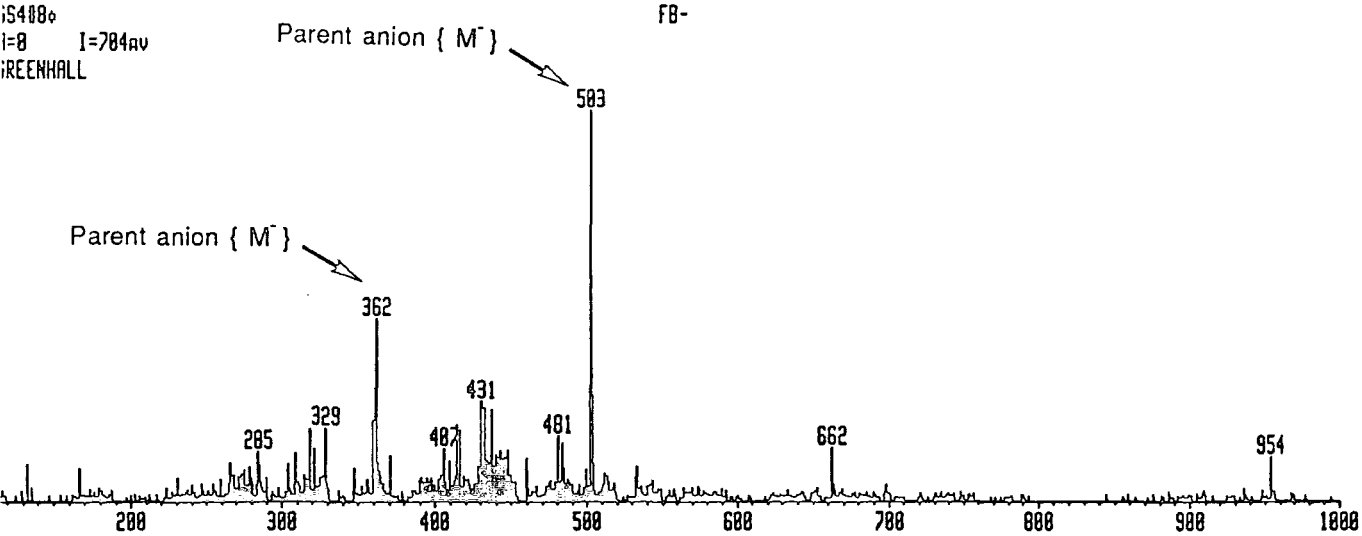


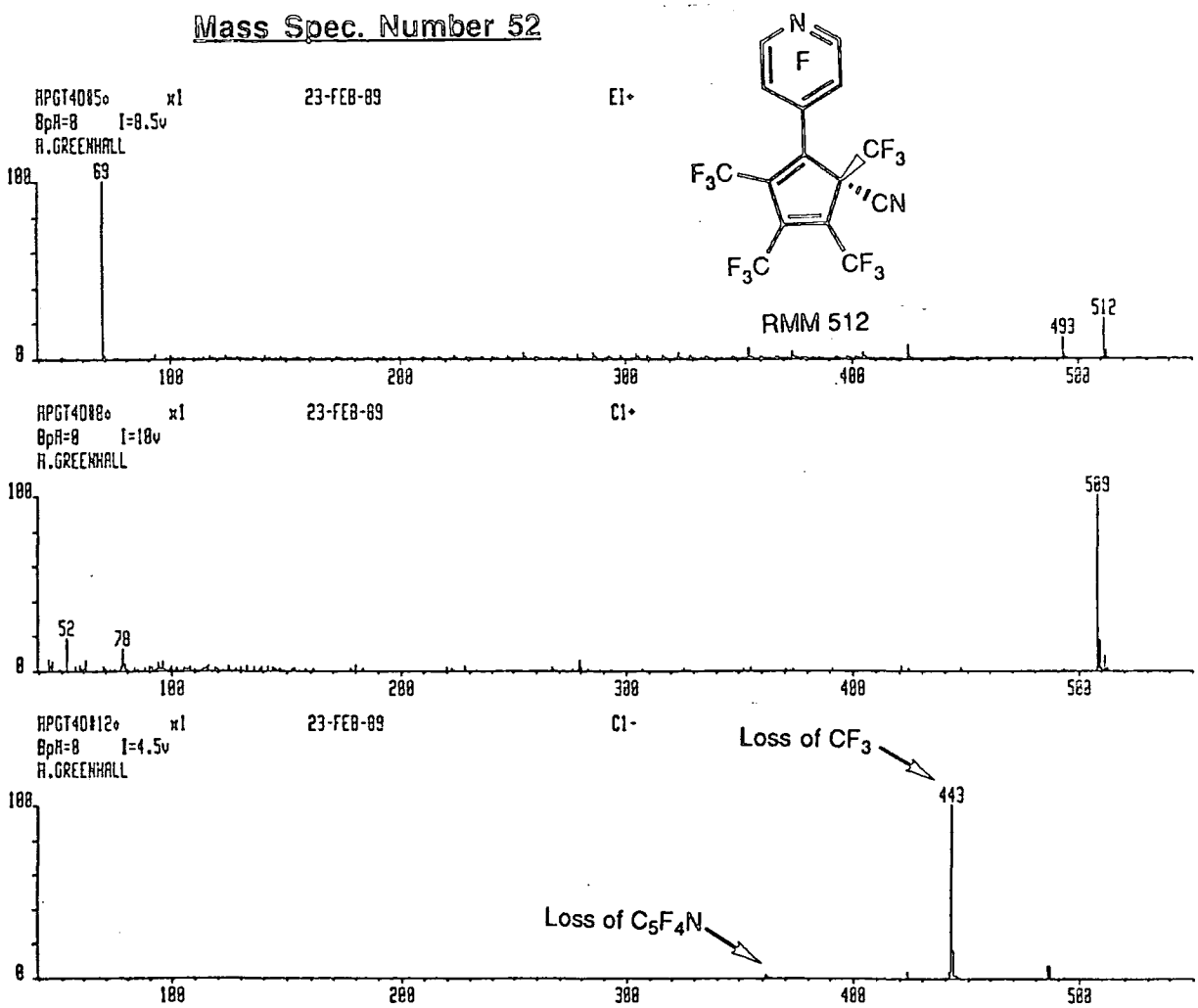
FAB Positive ion data

Mass	% Base
97.94	0.33
132.90	100.00
140.96	0.60
224.88	4.67
284.68	10.87
291.71	7.04
300.70	0.35
304.73	0.40
306.72	0.70
307.70	2.44
308.75	0.34
309.77	0.42
310.72	0.34
324.73	0.82
356.74	3.80
436.60	2.05
443.61	0.72

FAB Negative ion data

Mass	% Base
92.84	11.83
97.85	7.20
111.84	7.24
132.82	9.15
166.80	8.11
230.74	5.72
259.72	5.29
265.72	9.54
266.73	6.35
268.72	6.35
271.71	6.13
273.72	6.85
275.72	7.69
278.72	8.43
279.73	5.77
284.69	12.48
285.71	8.93
290.71	5.55
304.69	9.38
309.67	12.18
314.66	6.44
316.69	5.18
318.68	18.14
321.68	13.07
325.69	5.68
326.65	6.20
328.66	18.57
347.65	8.30
356.64	5.22
359.65	20.35
361.64	46.62
362.65	9.49
363.67	7.41
364.63	6.13
371.64	11.60
391.64	5.61
394.62	5.85
397.63	5.57
402.65	5.48
404.61	6.42
406.63	13.18
409.61	9.95
412.61	5.07
413.63	5.90
414.61	19.12
415.63	6.35
416.61	18.01
419.60	5.94
422.62	5.53
428.57	8.47
430.58	25.21
431.61	7.65
432.59	23.49
433.59	10.27
434.60	9.86
435.59	9.69
436.62	5.66
437.59	23.21
438.61	8.84
440.60	11.94
441.59	11.18
442.59	12.79
444.58	10.81
445.61	11.10
447.61	12.70
448.59	5.07
449.61	6.59
459.57	10.88
480.59	16.28
483.56	14.61
484.56	8.21
487.56	5.53
499.56	7.87
502.54	100.00
503.55	26.81
504.55	9.30
511.60	6.96
513.60	5.96
532.56	5.55
533.64	8.45
662.19	13.44
954.07	11.18

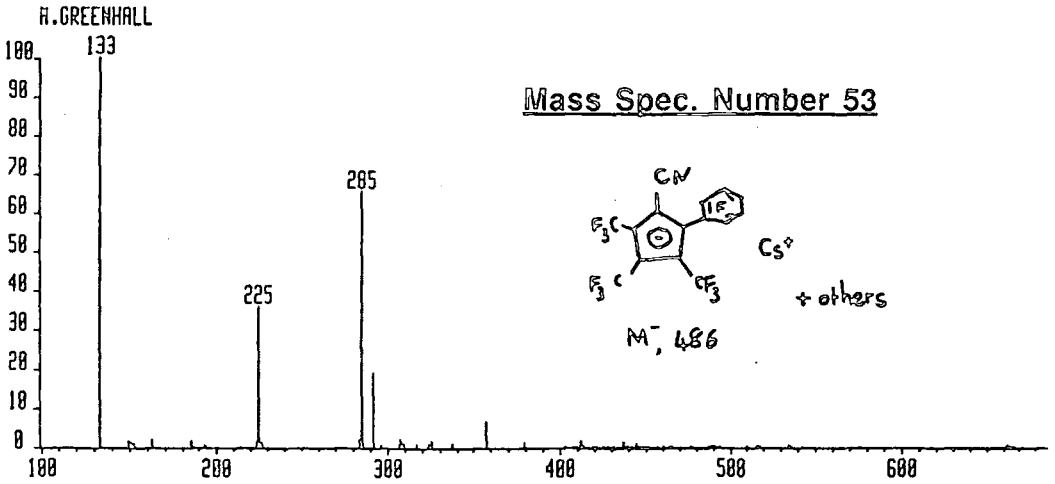
Mass Spec. Number 52



EI+ Data

Mass	% Base						
68.97	100.00	302.84	0.32	373.77	3.56	470.64	0.16
69.98	1.22	303.85	0.04	374.77	0.65	473.65	0.12
92.97	1.71	304.84	1.91	375.73	0.03	485.63	0.13
99.98	1.06	305.85	0.34	375.81	0.03	492.62	11.16
116.97	1.15	309.84	1.68	378.77	0.28	493.62	1.87
123.97	1.14	310.84	0.23	379.76	0.07	494.63	0.18
140.96	1.07	316.83	1.05	379.81	0.05	510.58	0.04
223.91	1.22	317.84	0.14	382.76	0.08	510.68	0.04
247.89	1.51	321.82	0.27	385.74	0.07	510.89	0.05
254.89	2.66	323.83	2.56	392.74	0.40	511.59	22.01
260.88	0.13	324.83	0.31	393.72	0.05	512.59	3.88
261.89	0.11	328.82	1.48	393.78	0.05	513.60	0.31
264.88	0.11	329.83	0.17	397.74	0.84	580-581	13.87
266.87	0.40	333.76	0.03	398.75	0.14		2.48
267.87	0.05	335.78	0.66	401.74	0.41		
271.87	0.44	336.78	0.13	402.73	0.10		
272.87	0.04	340.73	0.13	404.75	2.93		
273.87	0.63	342.71	0.33	405.75	0.48		
274.87	0.09	347.74	0.77	416.71	0.27		
278.86	1.79	348.76	0.10	417.72	0.05		
279.86	0.25	351.80	0.04	423.71	7.34		
280.87	0.07	352.78	0.16	424.71	1.12		
283.87	0.08	353.81	0.03	425.71	0.14		
285.86	2.63	354.80	5.40	442.69	0.82		
286.87	0.37	355.80	0.81	443.70	0.17		
290.85	0.34	356.81	0.06	444.69	0.05		
291.87	0.05	359.79	0.47	447.67	0.18		
292.85	0.49	360.79	0.10	454.67	0.04		
293.86	0.05	366.78	0.34	466.66	0.33		
297.84	1.14	367.77	0.05	467.67	0.04		
298.85	0.13	371.77	0.10				

FB+



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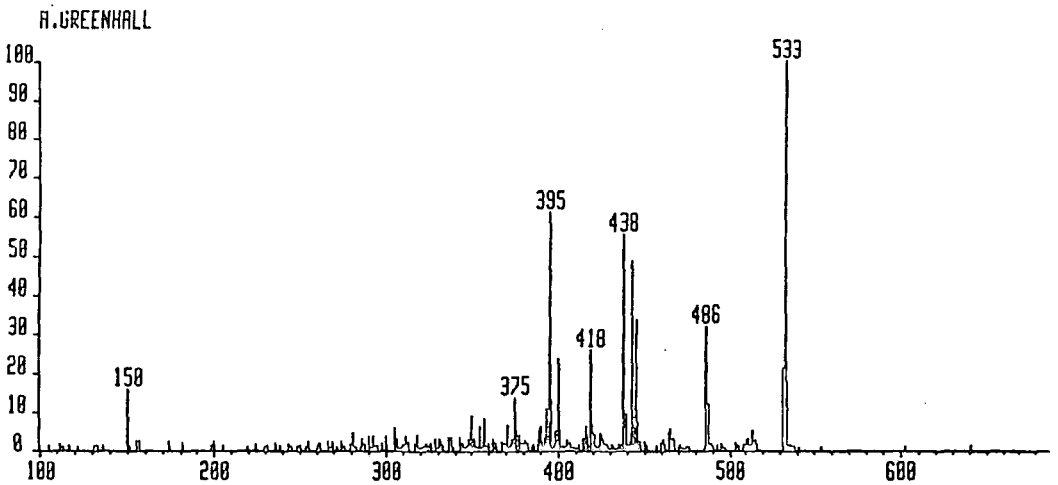


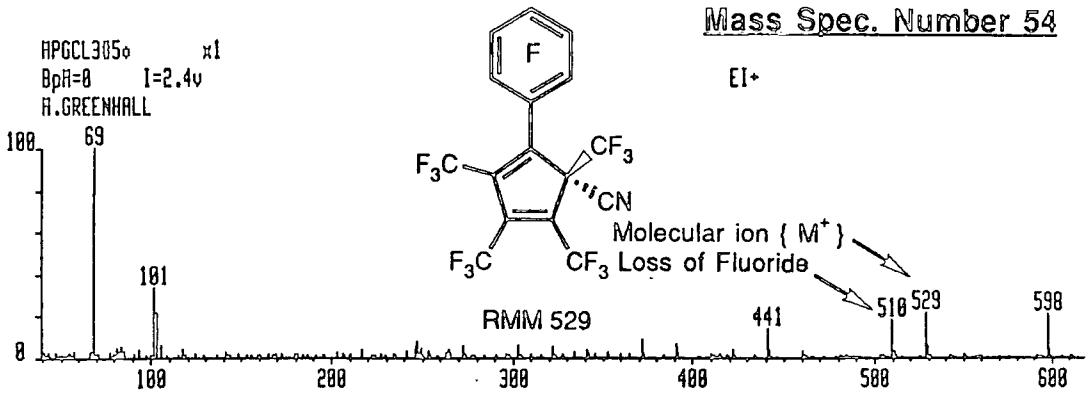
Mass	% Base
93.15	9.34
133.10	100.00
225.14	35.61
285.03	65.49
292.04	19.05
357.11	6.50

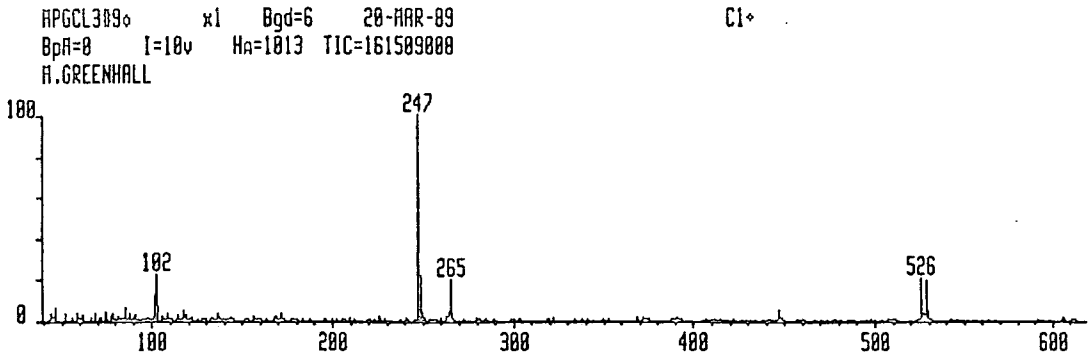
Mass	% Base
87.00	3.83
150.02	15.73
155.03	2.48
157.02	2.39
174.02	2.25
200.00	2.27
267.01	2.10
269.01	2.01
273.99	2.05
281.00	4.30
286.01	3.01
289.99	3.51
292.99	3.65
300.01	3.74
304.98	5.69
306.99	2.82
311.99	3.44
313.99	2.25
319.00	3.78
328.98	2.89
331.01	2.99
332.00	2.20
336.01	3.36
337.99	3.10
342.98	3.14
347.98	2.89
349.98	9.09
350.98	2.86
354.99	5.90
356.99	8.08
361.99	2.89
366.99	2.05
370.99	6.60
372.99	3.01
373.97	2.93
375.00	13.51
375.99	5.05
377.00	3.78
380.99	2.33

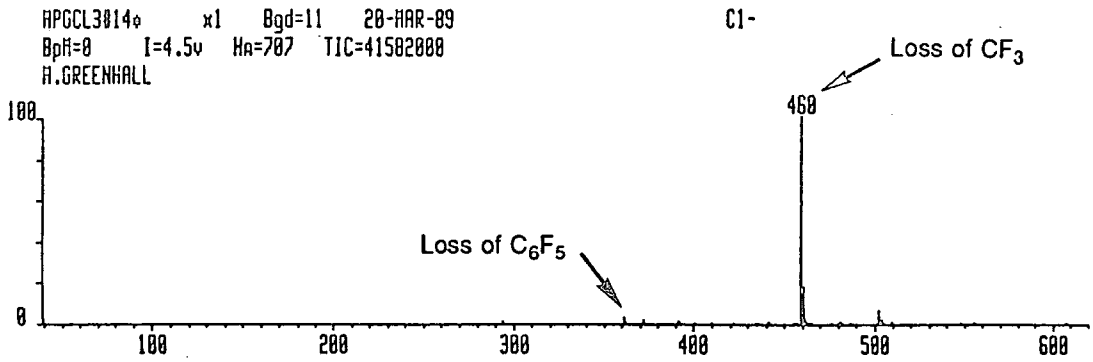
Mass	% Base
388.99	5.15
390.00	6.18
390.98	2.22
391.99	3.21
392.97	10.58
393.99	2.61
394.98	61.12
395.99	12.70
397.97	5.11
399.03	2.12
399.99	23.64
400.99	4.83
404.98	2.42
414.02	2.89
415.98	6.20
416.98	3.18
417.99	25.57
418.99	6.29
420.02	4.13
420.98	4.06
424.00	4.25
425.00	3.66
426.06	2.39
438.00	55.43
439.01	9.15
442.99	48.61
444.00	8.61
445.00	33.56
446.02	7.29
448.01	2.25
450.06	2.29
461.04	2.67
464.04	4.40
465.03	5.32
466.05	2.16
467.05	2.86
468.04	2.57
486.07	31.94
487.09	8.55

Mass	% Base
488.09	11.61
510.21	2.48
511.19	3.03
514.19	4.85
515.21	2.37
531.24	21.12
533.21	100.00
534.26	17.34

Mass Spec. Number 54







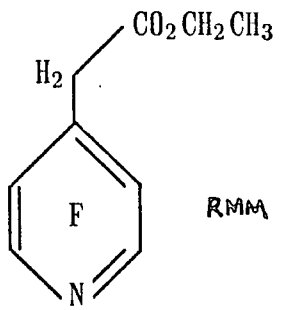
EI+ Data

Mass	% Base		
41.08	2.17	249.12	4.26
43.06	2.17	253.03	2.43
47.01	1.98	263.13	1.90
55.09	1.69	264.14	3.59
57.11	2.93	265.09	1.82
66.00	1.92	272.02	5.71
67.09	2.93	303.00	5.18
69.03	100.00	321.99	5.06
77.08	1.75	333.96	1.80
81.12	4.07	340.90	3.69
82.13	2.67	352.95	2.05
84.11	4.76	371.95	8.50
85.12	2.75	372.95	1.56
91.10	1.63	390.92	6.38
93.05	3.39	391.92	1.90
100.99	32.81	421.88	3.71
102.99	21.20	440.87	13.66
104.99	3.90	441.87	2.95
105.09	5.16	459.85	2.85
117.05	3.12	509.79	17.39
141.05	2.00	510.79	2.94
169.12	1.63	528.77	20.74
203.05	1.98	529.77	4.48
217.04	3.09	597.66	20.12
234.04	1.67	598.67	3.70
241.03	2.84		
246.13	4.98		
247.15	7.17		
248.11	1.95		

EI+ Data

Mass	% Base
51.07	2.23
52.09	0.17
55.06	0.20
56.06	0.67
57.07	1.27
60.06	0.26
62.03	0 22
63.04	0.40
64.05	1.76
68.01	1.44
69.00	6.23
70.01	0.55
73.02	1.22
73.99	0.87
75.00	2.85
76.00	0.80
78.98	0.19
79.99	0.36
80.99	0.47
81.98	2.38
82.99	0.15
85.97	0.32
86.98	1.02
87.99	1.23
88.99	0.11
92.97	3.32
93.98	1.31
94.99	1.30
95.98	0.42
97.97	0.24
98.98	4.19
99.98	1.43
100.99	0.20
104.97	0.23
105.98	0.55
111.97	0.22
112.97	3.56
113.98	5.67
114.98	1.28
116.95	1.09
117.95	2.20
118.96	5.96
119.95	0.74
123.94	0.28
124.95	0 16
125.97	0 22
131.95	0.36
132.96	1 10
133.97	0.38
135.94	0.22
136 95	2.54
137.95	7.03
138.96	0.28
139.99	0.11
140.07	0.13
140.14	0.11
141.97	0.21
143.96	2 61
144.97	3.05
145.98	0.65

Mass	% Base	
146.98	0.16	
150.96	0.15	
160.96	1.58	
161.95	0.44	
162.95	2.87	
163.78	0.76	
163.96	100.00	← $-CO_2CH_2CH_3$
164.71	0.10	
164.82	0.49	
164.97	63.58	
165.97	4.20	
166.96	0.23	
171.98	0.10	
173.98	0.11	
177.97	1.22	
179.96	0.24	
180.97	0.74	
188.95	0.41	
189.96	0.15	
190.94	2.66	
191.77	0.22	
191.95	32.55	← $-OCH_2CH_3$
192.96	3.10	
193.96	0.24	
201.95	0.12	
208.93	6.33	
209.94	0.97	
210.94	0.10	
217.96	0.61	
221.94	0.46	
236.75	0.16	
236.97	20.41	← M^+
237.97	3.04	
238.97	0.22	



RMM 237

Mass Spec. Number 55

APPENDIX IV

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:

(A) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(B) lectures organised by Durham University Chemical Society;

(C) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

(D) details of the postgraduate induction course.

(those attended are marked *)

29.10.86 Prof. E.H. Wong (University of New Hampshire, U.S.A.), '*Coordination Chemistry of P-O-P Ligands*'.

5.11.86 Prof. D. Dopp (University of Duisburg), '*Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes*'.

26.11.86 Dr. N.D.S. Canning (University of Durham), '*Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis*'.

3.12.86 Dr. J. Miller (Dupont Central Research), '*Molecular Ferromagnets: Chemistry and Physical Properties*'.

8.12.86 Prof. T. Dorfmuller (University of Bielefeld), '*Rotational Dynamics in Liquids and Polymers*'.

28.1.87 Dr. W. Clegg (University of Newcastle-upon-Tyne), '*Carboxylate Complexes of Zinc: Charting a Structural Jungle*'.

4.2.87 Prof. A. Thomson (University of East Anglia), '*Metalloproteins and Magnetooptics*'.

11.2.87 Dr. T. Shepherd (University of Durham), '*Pteridine Natural Products: Synthesis and Use in Chemotherapy*'.

17.2.87 Prof. E.H. Wong (University of New Hampshire, U.S.A.), '*Symmetrical Shapes from Molecules to Art and Nature*'.

4.3.87 Dr. R. Newman (University of Oxford), '*Change and Decay: A Carbon-13 CP/MAS NMR Study of Humification and Coalification Processes*'.

11.3.87 Dr. R.D. Cannon (University of East Anglia), '*Electron Transfer in Polynuclear Complexes*'.

17.3.87 Prof R.F. Hudson (University of Kent), '*Aspects of Organophosphorus Chemistry*'.

18.3.87 Prof. R.F. Hudson (University of Kent), '*Homolytic Rearrangements - Free Radical Stability*'.

6.5.87 Dr. R. Bartsch (University of Sussex), '*Low Co-ordinated Phosphorus Compounds*'.

7.5.87 Dr. M. Harmer (I.C.I. Chemicals & Polymer Group), '*The Role of Organometallics in Advanced Materials*'.

11.5.87 Prof. S. Pasynkiewicz (Technical University, Warsaw), '*Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium*'.

27.5.87 Dr. R.M. Blackburn (University of Sheffield), '*Phosphonates as Analogues of Biological Phosphate Esters*'.

24.6.87 Prof. S.M. Roberts (University of Exeter), '*Synthesis of Novel Antiviral Agents*'.

26.6.87 * Dr. C. Krespan (E.I. Dupont de Nemours), '*Nickel (0) and Iron (0) as Reagents in Organofluorine Chemistry*'.

4.11.87 Mrs. M. Mapletoft (Durham Chemistry Teachers' Centre), '*Salters' Chemistry*'.

19.11.87 Dr. J. Davidson (Herriot-Watt University), '*Metal Promoted Oligomerisation Reactions of Alkynes*'.

10.12.87 * Dr.C.J. Ludman (University of Durham), '*Explosives*'.

16.12.87 Mr. R.M. Swart (I.C.I.), '*The Interaction of Chemicals with Lipid Bilayers*'.

16.3.88 Mr. L. Bossons (Durham Chemistry Teachers' Centre), '*GSCE Practical Assessment*'.

7.4.88 Prof. M.P. Hartshorn (University of Canterbury, New Zealand), '*Aspects of Ipso-Nitration*'.

13.4.88 Mrs. E. Roberts (SATRO Officer for Sunderland), Talk - Durham Chemistry Teachers' Centre, '*Links Between Industry and Schools*'.

18.4.88 Prof. C.A. Nieto de Castro (University of Lisbon and Imperial College), '*Transport Properties of Non-polar Fluids*'.

25.4.88 Prof. D. Birchall (I.C.I Advanced Materials), '*Environmental Chemistry of Aluminium*'.

27.4.88 Dr. J.A. Robinson (University of Southampton), '*Aspects of Antibiotic Biosynthesis*'.

27.4.88 Dr. R. Richardson (University of Bristol), '*X-Ray Diffraction from Spread Monolayers*'.

28.4.88 Prof. A. Pines (University of California, Berkeley, U.S.A.), '*Some Magnetic Moments*'.

11.5.88 Dr. W.A. McDonald (I.C.I. Wilton), '*Liquid Crystal Polymers*'.

11.5.88 Dr. J. Sodeau (University of East Anglia), Durham Chemistry Teachers' Centre Lecture, '*Spray Cans, Smog and Society*'.

8.6.88 Prof. J.-P. Majoral (Universite Paul Sabatier), '*Stabilisation by Complexation of Short-Lived Phosphorus Species*'.

29.6.88 * Prof. G.A. Olah (University of Southern California), '*New Aspects of Hydrocarbon Chemistry*'.

18.10.88 Dr. J. Dingwall (Ciba Geigy), '*Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products*'.

18.10.88 Mr. F. Bollen (Durham Chemistry Teachers' Centre), '*The Use of SATIS in the classroom*'.

18.10.88 * Dr. C.J. Ludman (Durham University), '*The Energetics of Explosives*'.

9.11.88 Dr. G. Singh (Teesside Polytechnic), '*Towards Third Generation Anti-Leukaemics*'.

16.11.88 Dr. K.A. McLauchlan (University of Oxford), '*The Effect of Magnetic Fields on Chemical Reactions*'.

2.12.88 Dr. G. Hardgrove (St. Olaf College, U.S.A.), '*Polymers in the Physical Chemistry Laboratory*'.

9.12.88 Dr. C. Jaeger (Friedrich-Schiller University GDR), '*NMR investigations of Fast Ion Conductors of the NASICON Type*'.

14.12.88 Dr. C. Mortimer (Durham University Teachers' Centre), '*The Hindenberg Disaster - An Excuse for Some Experiments*'.

12.88 Dr. G. Hardgrove (St. Olaf College, U.S.A.), '*Polymers in the Physical Chemistry Laboratory*'.

25.1.89 * Dr. L. Harwood (University of Oxford), '*Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry Under Pressure*'.

1.2.89 *Mr. T. Cressey and Mr. D. Waters (Durham Chemistry Teachers' Centre), 'GCSE Chemistry 1988: A Coroner's Report'.*

13.2.89 * Prof. R.R. Schrock (M.I.T.), '*Recent Advances in Living Metathesis*'.

15.2.89 * Dr. A.R. Butler (St. Andrews University), '*Cancer in Linxiam: The Chemical Dimension*'.

22.2.89 Dr. G. MacDougall (Edinburgh University), '*Vibrational Spectroscopy of Model Catalytic Systems*'.

1.3.89 Dr. R.J. Errington (University of Newcastle-upon-Tyne), '*Polymetalate Assembly in Organic Solvents*'.

9.3.89 Dr. I. Marko (Sheffield University), '*Catalytic Asymmetric Osmylation of Olefins*'.

14.3.89 Mr. P. Revell (Durham Chemistry Teachers' Centre), '*Implementing Broad and Balanced Science 11-16*'.

15.3.89 Dr. R. Aveyard (University of Hull), '*Surfactants at your Surface*'.

20.4.89 Dr. M. Casey (University of Salford), '*Sulphoxides in Stereoselective Synthesis*'.

27.4.89 Dr. D. Crich (University College London), '*Some Novel Uses of Free Radicals in Organic Synthesis*'.

3.5.89 Mr. A. Ashman (Durham Chemistry Teachers' Centre), 'The Chemical Aspects of the National Curriculum'.

3.5.89 Dr. P.C.B. Page (University of Liverpool), '*Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides*'.

10.5.89 Prof. P.B. Wells (Hull University), '*Catalyst Characterisation and Activity*'.

11.5.89 Dr. J. Frey (Southampton University, '*Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl*'.

16.5.89 Dr. R. Stibr (Czechoslovak Academy of Sciences), '*Recent Developments in the Chemistry of Intermediate-Sited Carboranes*'.

17.5.89 Dr. C.J. Moody (Imperial College), '*Reactive Intermediates in Heterocyclic Synthesis*'.

23.5.89 Prof. P. Paetzold (Aachen), '*Iminoboranes XB≡≡NR: Inorganic Acetylenes ?*'.

14.6.89 Dr. M.E. Jones (Durham Chemistry Teachers' Centre), '*GCSE and A-level Chemistry 1989*'.

15.6.89 Prof. J. Pola (Czechslovak Academy of Sciences), '*Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry*'.

28.6.89 Dr. M.E. Jones (Durham Chemistry Teachers' Centre), '*GCSE and A-level Chemistry 1989*'.

11.7.89 Dr. D. Nicholls (Durham Chemistry Teachers' Centre), '*Liquid Air Demonstration*'.

(B) Lectures organised by Durham University Chemical Society 1986-1989

(those attended are marked *)

16.10.86 * Prof. N.N. Greenwood (University of Leeds), '*Glorious Gaffes in Chemistry*'.

23.10.86 Prof. H.W. Kroto (University of Sussex), '*Chemistry in Stars, between Stars and in the Laboratory*'.

30.10.86 Prof. D. Betteridge (B.P. Research), '*Can Molecules Talk Intelligently*'.

6.11.86 * Dr. R.M. Scrowston (University of Hull), '*From Myth and Magic to Modern Medicine*'.

13.11.86 Prof. Sir G. Allen (Unilever Research), '*Biotechnology and the Future of the Chemical Industry*'.

20.11.86 * Dr. A. Milne and Mr. S. Christie (International Paints), '*Chemical Serendipity - A Real Life Case Study*'.

27.11.86 * Prof. R.L. Williams (Metropolitan Police Forensic Science), '*Science and Crime*'.

22.1.87 Prof. R.H. Ottewill (University of Bristol), '*Colloid Science: A Challenging Subject*'.

5.2.87 Dr. P. Hubberstey (University of Nottingham), '*Demonstration Lecture on Various Aspects of Alkali Metal Chemistry*'.

12.2.87 Dr. D. Brown (I.C.I. Billingham), '*Industrial Polymers from Bacteria*'.

19.2.87 * Dr. M. Jarman (Institute of Cancer Research), '*The Design of Anti-Cancer Drugs*'.

5.3.87 Prof. S.V. Ley (Imperial College), '*Fact and Fantasy in Organic Synthesis*'.

9.3.87 * Prof. F.G. Bordwell (Northeastern University, U.S.A.), '*Carbon Anions, Radicals, Radical Anions and Radical Cations*'.

12.3.87 Dr. E.M. Goodger (Cranfield Institute of Technology), '*Alternative Fuels for Transport*'.

15.10.87 * Dr. M.J. Winter (University of Sheffield), '*Pyrotechnics (Demonstration Lecture)*'.

22.10.87 * Prof. G.W. Gray (University of Hull), '*Liquid Crystals and their Applications*'.

29.10.87 * Mrs. S. van Rose (Geological Museum), '*Chemistry of Volcanoes*'.

5.11.87 Dr. A.R. Butler (University of St. Andrews), '*Chinese Alchemy*'.

12.11.87 Prof. D. Seebach (E.T.H. Zurich), '*From Synthetic Methods to Mechanistic Insight*'.

19.11.87 Prof. P.G. Sammes (Smith, Kline and French), '*Chemical Aspects of Drug Development*'.

26.11.87 Dr. D.H. Williams (University of Cambridge), '*Molecular Recognition*'.

3.12.87 Dr. J. Howard (I.C.I. Wilton), '*Liquid Crystal Polymers*'.

21.1.88 * Dr. F. Palmer (University of Nottingham), '*Luminescence (Demonstration Lecture)*'.

28.1.88 Dr. A. Cairns-Smith (University of Glasgow), '*Clay Minerals and the Origin of Life*'.

11.2.88 Prof. J.J. Turner (University of Nottingham), '*Catching Organometallic Intermediates*'.

18.2 88 * Dr. K. Borer (University of Durham Industrial Research Laboratories), '*The Brighton Bomb - A Forensic Science View*'.

25.2.88 Prof. A. Underhill, (University of Bangor), '*Molecular Electronics*'.

3.3.88 Prof. W.A.G. Graham (University of Alberta, Canada), '*Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds*'.

6.10.88 * Prof. R. Schmutzler (University of Braunschweig), '*Fluorophosphines Revisited - New Contributions to an Old Theme*'.

21.10.88 Prof. P. von Rague Schleyer (University of Erlangen), '*The Fruitful Interplay Between Calculational and Experimental Chemistry*'.

27.10.88 * Prof. W.C. Rees (Imperial College), '*Some Very Heterocyclic Compounds*'.

10.11.88 Prof. J.I.G. Cadogan (B.P. Research), '*From Pure Science to Profit*'.

24.11.88 Dr. R.W. Walker and Dr. R.R. (University of Hull), '*Combustion - Some Burning Problems*'.

1.12.88 Dr. R. Snaith (University of Cambridge), '*Egyptian Mummies - What, Where, Why and How ?*'.

26.1.89 Prof. K.R. Jennings (University of Warwick), '*Chemistry of the Masses*'.

2.2.89 * Prof. L.D. Hall (Addenbrookes' Hospital), '*NMR - A Window to the Human Body*'.

9.2.89 * Prof. J. Baldwin (University of Oxford), '*Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis*'.

16.2.89 Prof. J.B. Aylett (Queen Mary College), '*Silicon-based Chips: The Chemists Contribution*'.

23.2.89 Dr. B.F.G. Johnson (University of Cambridge), '*The Binary Carbonyls*'.

(C) Conferences attended and papers presented

The following conferences have been attended:

R. S. C. Review Symposium, University of Salford, July 1987;
Postgraduate Heterocyclic Symposium, Keele, July 1987;
Graduate Symposium, Durham, April 1987;
21st Sheffield Symposium on 'Modern Aspects of Stereochemistry', Sheffield, December 1987;
Graduate Symposium, Durham, April 1988;
22nd Sheffield Symposium on 'Modern Aspects of Stereochemistry', Sheffield, December 1988.

In addition work has been presented by the author at:

Postgraduate Heterocyclic Symposium, Nottingham, July 1988;
12th. International Symposium on Fluorine Chemistry, Santa Cruz, California, U.S.A., August 1988;
Graduate Symposium, Durham, April 1989.

(D) First year induction course. October 1986

This course consists of a series of one hour lectures on the services available in the department.

Departmental organisation: - Dr. E. J. F. Ross.
Safety matters: - Dr. M. R. Crampton.
Electrical appliances: - Mr. B. T. Barker
Chromatography and microanalysis: - Mr. T. F. Holmes.
Atomic absorptiometry and inorganic analysis: - Mr. R. Coult
Library facilities: - Mr. R. B. Woodward.
Mass spectroscopy: - Dr. M. Jones.
Nuclear magnetic resonance spectroscopy: - Dr. R. S. Matthews.
Glassblowing techniques: - Mr. R. Hart and Mr. G. Haswell.

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