Part I: Co-telomerisation reactions of fluorinated olefins Part II: Physical and chemical properties of some fluorinated aromatic compounds

Smith, Thomas Wardley

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THE UNIVERSITY OF DURHAM

A THESIS

entitled

PART I: CO-TELOMERISATION REACTIONS OF FLUORINATED OLEFINS.

PART II: PHYSICAL AND CHEMICAL PROPERTIES OF SOME FLUORINATED AROMATIC COMPOUNDS.

submitted by

THOMAS WARDLEY SMITH, B.Sc.

(HATFIELD COLLEGE)

A candidate for the degree of Doctor of Philosophy.

1966.

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1962 and September 1965. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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PART II.

CHAPTER I : INTRODUCTION.

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SUMMARY.

PART I. Cross-linking reactions of two co-telomer alcohol mixtures have been investigated. The co-telomer alcohols contained (1) hexafluoropropylene, vinylidene fluoride, and methanol; (2) octafluorocyclohexa-1,4-diene, vinylidene fluoride, and methanol. Both mixtures eliminated hydrogen fluoride on standing.

Co-telomer (1) has been successfully cross-linked and stabilised by a primary amine, several primary diamines, and a tertiary amine with a dithiol, as indicated by the infra-red spectra, molecular weights, and fluorine content, of the products.

Products from reactions of co-telomer (2) with diamines had increased viscosity but still eliminated hydrogen fluoride.

Mechanisms have been put forward for the cross-linking reactions.

PART II. The electric dipole moments of some members of the series C_6F_5X and 2,3,5,6-H.C_6F_4X (where X is any substituent) have been measured in order to investigate the ground state electron distribution of these compounds.

The dipole moments of the corresponding members of the series 4-F.C_6H_4.X have been measured and calculated, in order to provide comparative values for the series C_6F_5X, and values for the series C_6H_5X have been obtained from the literature in order to provide comparative values for the series 2,3,5,6-H.C_6F_4.X.

The results show that the high electronegativity of fluorine causes the pentafluorophenyl nucleus to act as an electron sink, facilitating movement of electrons from electron donating groups into the ring and reducing electron withdrawal by electron attracting groups. The resonance of nitro and N-dimethyl groups is shown to be reduced by steric hindrance, due to the presence of the two fluorine atoms ortho to the groups.

In an attempt to prepare a partially fluorinated indole derivative, the reactions between the sodium salts of polyfluoroanilines and chloracetic ester have been investigated. N-(pentafluorophenyl)-glycine, N-(2,3,5,6-tetrafluorophenyl)-glycine, and N-(2,3,4,5-tetrafluorophenyl)-glycine have been prepared. An attempted cyclisation of N-(2,3,4,5-tetrafluorophenyl)-glycine with polyphosphoric acid did not give the desired 4,5,6,7-tetrafluoroindoxyl.

PART I.

CHAPTER I: INTRODUCTION

I.1. Fluoro-olefin reactions, telomerisation.

Nucleophilic addition is characteristic of the reactions of fluoro-olefins, in contrast to hydrocarbon olefins, because of the electron withdrawal by the strongly electronegative fluorine atoms.[1] Free radical attack on the double bond of a fluoro-olefin proceeds smoothly, and the direction of addition (for an unsymmetrical olefin) and the reactivity can be correlated with the steric and polar factors involved.[2]

In 1947, Miller and his co-workers [3] were using a free radical polymerisation process in order to make fluorocarbon oils with the reactive monomer olefin, $CF_2 = CFCl$. An oil with a puzzlingly high chlorine content was obtained. The solvent in the reaction was chloroform and they deduced that the extra chlorine was coming from the solvent, i.e. the solvent was acting as a terminator in a chain transfer process and telomerisation was occurring. They postulated the following mechanism:

(i) $CHCl_3 \xrightarrow[R^\bullet]{\text{peroxide}} CCl_3^\bullet + HR$

(ii) $CCl_3^\bullet + CF_2{:}CFCl \longrightarrow CCl_3.CF_2.CFCl^\bullet$ initiatio

(iii) $CCl_3.CF_2.CFCl^\bullet + CF_2{:}CFCl \longrightarrow$

$CCl_3.CF_2.CFCl.CF_2.CFCl^\bullet$ propagation

(iv) $CCl_3(CF_2CFCl)_n^{\bullet} + CHCl_3 \longrightarrow CCl_3(CF_2.CFCl)_nH + CCl_3^{\bullet}$
etc.

chain transfer

The growing polymer chain reacts with a solvent molecule by transfer, with the formation of a free radical from the solvent. The chain transfer step (iv) competes with the propagation step (iii), and, by careful selection of the proportions of reagents, can become the dominant step. Telomerisation occurs only in a polymerising system, and a non-homopolymerisable olefin will not undergo telomerisation.

Telomerisation reactions are usually assumed to proceed by a radical-chain mechanism as represented above, although, a mechanism which involves a stepwise series of additions of iodide to olefin, has been suggested by Hauptschein [4] for the telomerisation (thermal) of $CF_3CF{=}CF_2$ with $n\text{-}C_3F_7I$. There are several methods of initiation for telomerisation reactions. Organic free radical initiators such as bis(trifluoromethyl) peroxide [5] and di-t-butyl peroxide,[6,7] irradiation in the form of ultra-violet rays,[8,9] X-rays and γ -rays,[10,11] and thermal initiation,[4,12] have all been used.

I.2. Fluoro-olefins/methanol cotelomerisations of Musgrave and Plimmer.

The first part of this thesis is an extension of the work of Musgrave and Plimmer,[13] who extended the idea of telomerisation into systems, not simply of an olefin and chain-transfer agent (C.T.A.), but of a pair of fluoro-olefins and a C.T.A. The reactions were initiated with γ radiation from a cobalt^{60} source. C.T.A.'s such as CH_3 CHO, $(CH_3)_2CO$, C_2F_5I, CF_3COOH, CH_3OH, and CH_3SH were used, and various pairs of fluoro-olefins, having first ascertained that copolymers were formed by the olefins under the conditions used.

With CH_3OH as the C.T.A. for the Viton ($CH_2{:}CF_2/CF_3CF{:}CF_2$) copolymer system, chain shortening occurred with total conversion of olefins to form a mixture of viscous liquid products. It was deduced from the infra-red spectrum of this mixture, by a wide band at 3436 cm^{-1}, that hydroxyl groups were present. These cotelomer alcohols could be distilled into crude fractions, up to 160° C, at reduced pressure. The viscous residue formed at 160°C was assumed to be the result of HF elimination, followed by a certain amount of polymer formation. All the crude fractions distilled at reduced pressure had peaks in the region 5 - 6·5μ in their infra-red spectra, indicating unsaturated centres, plus the band at 3436 cm^{-1} showing the presence of an -OH group. Molecular weight determinations varied from 300 to 800 corresponding to a chain length of up to 4 units (1 unit = $- CF_2.CF(CF_3)CH_2CF_2 -$). The byproduct wasalways the 1:1 adduct $CH_2(OH)CF_2CFH(CF_3)$. The mechanism of this telomerisation, based on experimental evidence, was postulated as:

$$\text{a)} \quad CH_3OH \longrightarrow {}^{\bullet}CH_2OH + H^{\bullet}$$

$$\left.\begin{array}{llllll} \text{b)} & {}^{\bullet}CH_2OH & + & CH_2{:}CF_2 & \longrightarrow CH_2(OH)CH_2CF_2^{\bullet} & B \\ \text{c)} & \dot{C}H_2OH & + & C_3F_6 & \longrightarrow CH_2(OH)(C_3F_6)^{\bullet} & A \end{array}\right\} \text{Initiation}$$

$$\text{d)} \quad CH_2(OH)(C_3F_6)^{\bullet} \xrightarrow{CH_3OH} CH_2(OH)(C_3F_6)H \qquad \text{Transfer A}$$

Initiation A is not likely to lead to cotelomer formation since step (d) is very efficient.[14] The intermediate free radical from initiation B can attack either olefin present to give:

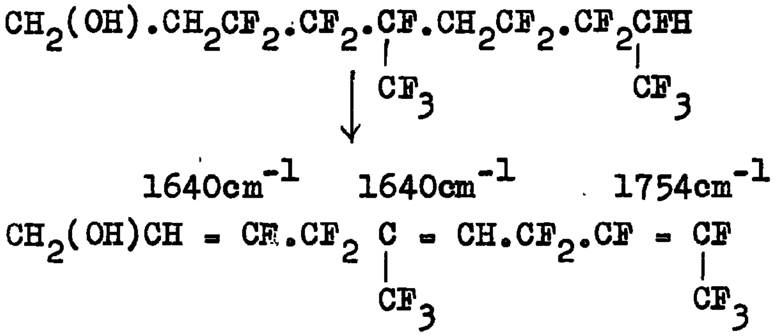
$$CH_2(OH)CH_2CF_2^{\bullet} \xrightarrow{CH_2CF_2} CH_2(OH)CH_2CF_2CH_2CF_2^{\bullet}(1) \xrightarrow{\text{either olefin}}$$

$$\xrightarrow{C_3F_6} CH_2(OH)CH_2CF_2CF_2\dot{C}F(CF_3)(2) \text{ or } \xrightarrow[CH_3OH]{CH_2CF_2}$$

The former (1) can attack either olefin present to continue the copolymer chain. The latter (2) can <u>only</u> attack $CH_2{:}CF_2$, or undergo chain transfer by abstracting a hydrogen atom as in(d) forming the n = 1 cotelomer. The final longest chain copolymer which will form will be (D) where l,m, and p, are either one or two:

$$CH_2OH(CH_2CF_2)_l(C_3F_6)(CH_2CF_2)_m(C_3F_6)(CH_2CF_2)_pCF_2\dot{C}F(CF_3) \qquad (D)$$

Radical attack on $CH_2:CF_2$ is exclusively on the $:CH_2$,[15] and on C_3F_6, exclusively on the $= CF_2$.[16] This copolymer (D) now undergoes chain transfer to form a cotelomer by hydrogen abstraction as in (d). No homopolymer of vinylidene fluoride was detected in the product. The slight unsaturation in the crude fractions was taken as corresponding to HF elimination from structures such as (E) giving (F) as an extreme example.



$$CH_2(OH).CH_2CF_2.CF_2.\underset{\displaystyle CF_3}{\underset{|}{CF}}.CH_2CF_2.CF_2\underset{\displaystyle CF_3}{\underset{|}{CFH}} \qquad (E)$$

$$\downarrow$$

$$CH_2(OH)CH \overset{1640cm^{-1}}{=} CF.CF_2\underset{\displaystyle CF_3}{\underset{|}{C}} \overset{1640cm^{-1}}{=} CH.CF_2.CF \overset{1754cm^{-1}}{=} \underset{\displaystyle CF_3}{\underset{|}{CF}}$$

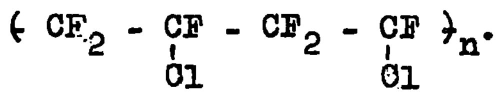
The peaks which arise in the unsaturation region were explained as follows:[13]

cm^{-1}	unsaturation	
1640	$- CF = CH_2$	linear
	$- CH = CFH$	"
1754	$- CF = CF -$	"
	$- CF = CF_2$	

I.3. Fluoro-polymers.

The presence of fluorine in a polymer molecule gives it marked chemical and thermal stability. This is due to the high C - F bond dissociation energy, the shielding effect of the fluorine atoms, and the high electronegativity of fluorine. Fluorine is a slightly larger atom than hydrogen (van der Waals radius, 1·35A; cf. hydrogen, 1·2A), and, in a large fluorocarbon molecule, these atoms form a compact shield around the carbon chain, protecting it from chemical attack. Fluoropolymers have been the subject of several reviews.[17,18,19]

The best known organic fluoropolymer is polytetrafluoroethylene (P.T.F.E.) a homopolymer of tetrafluoroethylene. It shows remarkable resistance to chemical attack, and because of its high softening point (327° C) and high thermal stability may be used over a wider range of temperature than any other simple addition polymer. X-ray diffraction measurements [20] show that the zig-zag chains in P.T.F.E. are not planar as in normal paraffins, but are twisted to relieve repulsions between fluorine atoms on alternate carbon atoms. P.T.F.E. is classed as a thermoplastic, but, mainly because of the high viscosity of its melts, cannot be moulded.

The resinous nature of P.T.F.E. can be reduced in two ways. Heterogeneity can be introduced by replacing some of the fluorine atoms by bulky atoms or groups as in polychlorotrifluoroethylene, the structure of which has been shown to be [21]  $\left(CF_2 - \underset{Cl}{CF} - CF_2 - \underset{Cl}{CF} \right)_n$. This polymer has its crystallinity broken by the pendant chlorine atom. Its softening point (216° C) is lower than P.T.F.E. and it can be moulded, i.e. it is a true thermoplastic.

The tightly coiled polymer backbone of P.T.F.E. can be converted to a more mobile structure by the inclusion of methylene (CH_2) units in the chain as in polyvinylidene fluoride which consists of alternate - CH_2 - and - CF_2 - units i.e. $\left(CH_2 - CF_2 \right)_n$[15]. The rigidity of the backbone is broken by the alternating - CH_2 - units, and it has a lower softening point (about 171° C) which limits its thermal stability. The presence of the - CH_2 units also provides sites for crosslinking i.e. the use of amines in the curing of fluoro rubbers containing CH_2:CF_2.[22,23,24,25] The order of thermal stability for hydrogen-containing fluoropolymers is:[26]

$$(C_2F_4)_n > (CF_2{:}CH_2)_n > (CF_2{:}CHF)_n > (C_2H_4)_n > (CH_2{:}CHF)_n$$

Copolymerisation of one of these 'reactive' (homopolymerisable) monomers with an 'unreactive' (non-homopolymerisable) monomer leads to the formation of copolymers with 'tailormade' properties i.e. the properties can be varied by altering the ratio of the two monomers. The copolymer of reactive $CF_2 = CF_2$ and non-reactive $CF_3CF = CF_2$

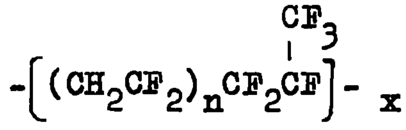
is a true thermoplastic with a working range up to 200° C and a softening point of 285° C. The backbone remains rigid, but the thermally stable, bulky, pendant $-CF_3$ group breaks up the crystallinity (50%, cf. P.T.F.E.,95%) of the chain.

The most thermally stable elastomer so far produced is a copolymer of $CH_2 = CF_2$ and $CF_3CF = CF_2$, Viton A [28] (Trade name: E.I. Du Pont de Nemours & Co., U.S.A.). The $- CH_2 -$ units break down the rigidity of the backbone and act as a site for cross-linking. The $- CF_3$ group reduces the crystallinity. It keeps its elastic properties down to about - 25° C and can be used indefinitely at 204°C and up to 315° C for 48 hours.

I.4. The cross-linking of Viton A.

a) Industrial Cures.

Viton A is a copolymer of vinylidene fluoride and hexafluoropropylene. Its structure (I) consists of alternating $- CH_2 -$ and $- CF_2 -$ groups interspersed with very short branched fluorocarbon chains.[29] The copolymer



$$-\left[(CH_2CF_2)_nCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F\right]-_x \quad (I)$$

is of little use until it has been converted to a cross-linked vulcanisate. The chemical stability conferred by its structure (I) makes the formation of cross-links difficult. Several methods have been used to cross-link Viton A although only one, using derivatives of aliphatic amines, has been found to be commercially feasible.

The actual procedure used [23] is to compound Viton A on normal rubber processing equipment, with filler metal oxide acceptor, and curing agent. The stock is then moulded in a press for 5-60 mins. at 100-150° C. The partially vulcanised stock is then oven-cured in an air circulating oven at 200° C for up to 24 hours. It is important that sufficient cross-links are formed during the press cure to prevent sponging by release of decomposition products during the oven cure, without causing scorching during the compounding.

Cross-links may be introduced by 3 general methods: by the action of aliphatic amines, high energy radiation, or peroxides. Primary, secondary, and tertiary mono-amines can be used, but press cures of up to 200° C are necessary.[23] This is sometimes called a thermal cure. Tertiary mono-amines are effective co-curing agents with diamines [23] and dithiols.[30,31] Presumably the tertiary amine eliminates HF and the dithiol forms cross-links across the double bonds so formed. Diamines such as $NH_2(CH_2)_6NH_2$ and $NH_2(CH_2)_2NH_2$ are very scorchy but do form effective vulcanisates.[23] When their amine functions are blocked in order to reduce this tendency to scorch they are by far the most widely used curing agents. Inner carbamates and bis-cinnamylidene derivatives are those most commonly used.[23,24,25,30,32]

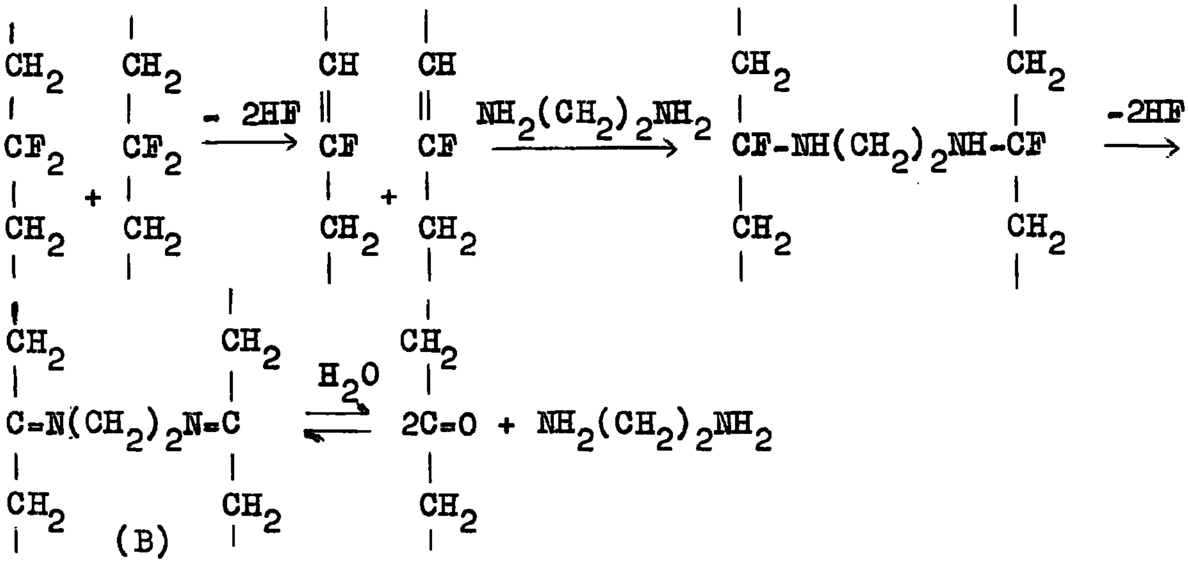
The use of high energy radiation has all the obvious disadvantages inherent therein without producing an improved vulcanisate. The radiation causes unsaturation similar to that caused by the action of amines and the unsaturated polymer is considered to crosslink at high temperature by mutual interaction of the unsaturated centres.[23]

Benzoyl peroxide [24,32] is a very scorchy curing agent, yet leads to only a moderate state of cure. It is also somewhat impractical due to poor processing safety.

Acid acceptors such as magnesium oxide, zinc oxide, or basic lead phosphite, are essential ingredients in the curing process of Viton A.[23,33] It has been shown by Smith [33] that the oven cure of Viton A is dependent upon the elimination of water from the polymer and he concludes that the water is derived from the neutralisation of HF, which is eliminated during the cure, by the magnesium oxide:

$$MgO + 2HF \longrightarrow MgF_2 + H_2O \qquad (A)$$

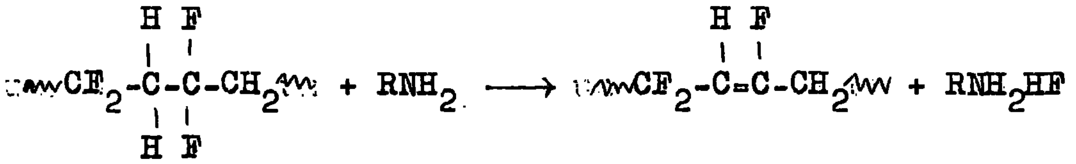
By assuming the stoichiometry of equation (A) and measuring the quantity of water evolved, he was able to show that 4 moles of HF were eliminated per mole of curing agent. On the basis of this information he proposed the following mechanism:


(B)

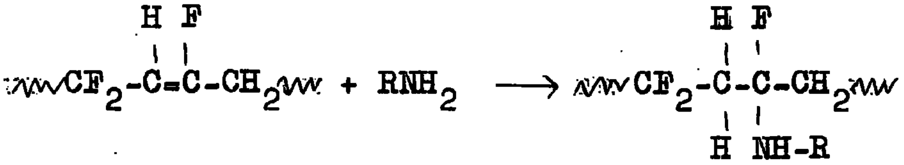
In a 3-stage process, 2 moles of HF are eliminated to form double bonds, then the diamine forms crosslinks across the double bonds, and finally 2 moles of HF are eliminated to give a di-imine structure (B). It should be possible to hydrolyse (B) if it is present, and, in fact, 20% of the original amine was obtained on hydrolysis.

b) Solution Studies.

Several solution studies of the reactions of fluoroelastomers with amines have been undertaken. An early study by Bro [22] of the embrittlement and colour changes caused by adding strips of polymer to refluxing amines, led him to postulate the following reaction reaction sequence:

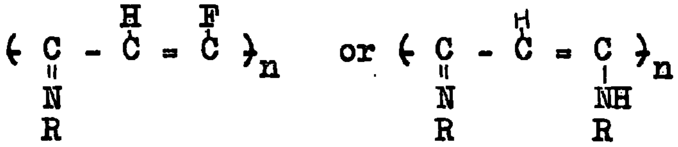


$$\sim CF_2-\overset{H}{\underset{H}{C}}-\overset{F}{\underset{F}{C}}-CH_2\sim + RNH_2 \longrightarrow \sim CF_2-\overset{H}{C}=\overset{F}{C}-CH_2\sim + RNH_2HF \qquad (1)$$



$$\sim CF_2-\overset{H}{C}=\overset{F}{C}-CH_2\sim + RNH_2 \longrightarrow \sim CF_2-\overset{H}{\underset{H}{C}}-\overset{F}{\underset{NH-R}{C}}-CH_2\sim \qquad (2)$$

He suggested that the product from (2) may react with excess amine to give conjugated imine structures of the type:



$$\left(\underset{\underset{R}{N}}{\overset{\|}{C}} - \overset{H}{C} = \overset{F}{C}\right)_n \quad \text{or} \quad \left(\underset{\underset{R}{N}}{\overset{\|}{C}} - \overset{H}{C} = \underset{\underset{R}{NH}}{C}\right)_n$$

or the product from (2) may add to a double bond on another chain and crosslink giving considerable stiffening of the films.

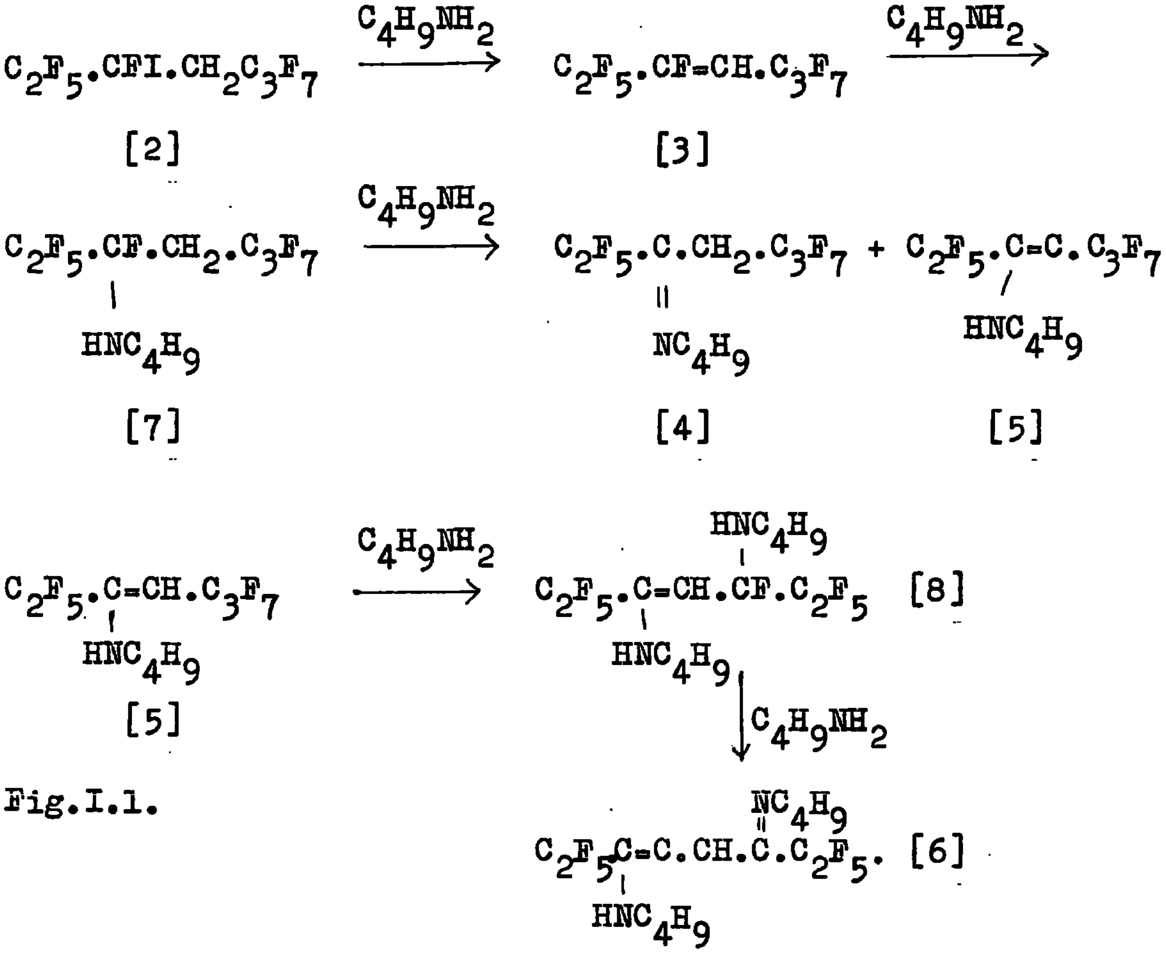
Pakiorek [34] examined the reactions of Viton A and Kel F elastomer (trade name: Minnesota Mining and Manufacturing Co., U.S.A. for CF_2:CFCl/CF_2:CH_2) by dissolving them in diglyne and adding amines under varying conditions. Addition of amines to Kel F caused discolouration and precipitation of amine hydrochloride. Fluoride ion was only obtained when excess amine was present, which indicates the relative ease of dehydrohalogenation of HCl and HF. Primary amines were the most reactive and tertiary amines the least reactive, as cross-linking took place at room temperature with primary amines and at 180-90° with tertiary amines. This conclusion is confirmed [23] by the results of a study of the rate of elimination of HF, in the treatment of Viton A in tetrahydrofuran, with amines, for periods of several weeks, at room temperature.

When Viton A was treated with tertiary amines [23] it was possible to demonstrate that chain scission occurred during the reaction by plotting the time of reaction against the viscosity of the solution and noting the gradual fall in viscosity. It was suggested that similar degradation occurred in reactions with primary and secondary amines, but this could not be demonstrated because of the formation of gels during isolation of the polymer samples.

An attempt to establish the presence of unsaturation in amine-treated Viton A by ozonolysis [23] caused no reduction in molecular weight. $KMnO_4$ and Br_2 could not be used as double bond reagents because Viton A was attacked by them in solution. However, infra-red spectra of pressed films of Viton A after treatment with trimethylamine showed 2 new absorbtion peaks at 5·8 and 5·95 microns which were assigned to double bonds.[23] The infra-red spectra of Viton A after treatment with primary and secondary amines showed similar but more pronounced changes.

c) Model Compound Studies.

The reactions of model compounds containing structures resembling those of fluoroelastomers, with various amines, have been studied in order to elucidate the mechanism of curing in the fluoroelastomers. Two model compounds, 1,5,5-trihydro-4-iodoperfluorooctane [1] and 4,4-dihydro-3-iodoperfluoroheptane [2], were synthesised by Pakiorek,[35] and their reactions with amines investigated. Their structures are similar to that of Kel F polymer except that chlorine is replaced by iodine. At room temperature high yields of amine hydroiodide were obtained with butylamine, dibutylamine, and trethylamine, and rates of reaction were the same as for Kel F and amines, i.e. primary $>$ secondary $\gg$ tertiary amines. The olefin formed by reaction of [2] with $C_4H_9NH_2$ was [3], the presence of - CF = CH - being indicated by infra-red absorption bands at $5{\cdot}80\mu$ and $3{\cdot}22\mu$ similar to those exhibited by amine treated polymers. When [3] was treated with an equimolar quantity of $C_4H_9NH_2$, the amine added across the double bond. A further equimolar quantity of amine caused the precipitation of $C_4H_9NH_2.HF$ and a mixture of tautomers [4] and [5] was obtained. Infra-red absorptions at 5·93μ, ascribed to C = C, and at 5·86μ, ascribed to the imino group, indicated the presence of the tautomers. Treatment of a mixture of [4] and [5] with more $C_4H_9NH_2$ gave [6]. The reaction mechanism is shown in fig.I.1.



$$C_2F_5.CFI.CH_2C_3F_7 \xrightarrow{C_4H_9NH_2} C_2F_5.CF{=}CH.C_3F_7 \xrightarrow{C_4H_9NH_2}$$

[2] [3]

$$C_2F_5.\underset{\underset{HNC_4H_9}{|}}{CF}.CH_2.C_3F_7 \xrightarrow{C_4H_9NH_2} C_2F_5.\underset{\underset{NC_4H_9}{\|}}{C}.CH_2.C_3F_7 + C_2F_5.\underset{\underset{HNC_4H_9}{/}}{C}{=}C.C_3F_7$$

[7] [4] [5]

$$C_2F_5.\underset{\underset{HNC_4H_9}{|}}{C}{=}CH.C_3F_7 \xrightarrow{C_4H_9NH_2} C_2F_5.\underset{\underset{HNC_4H_9}{|}}{C}{=}CH.\overset{\overset{HNC_4H_9}{|}}{CF}.C_2F_5$$

[5] [8]

$$\Big\downarrow C_4H_9NH_2$$

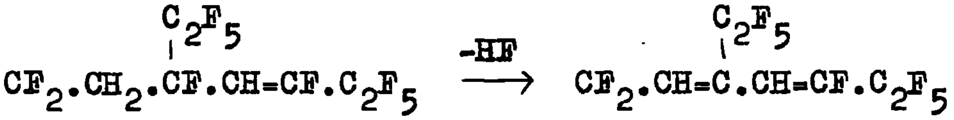
$$C_2F_5\underset{\underset{HNC_4H_9}{|}}{C}{=}C.CH.\overset{\overset{NC_4H_9}{\|}}{C}.C_2F_5.$$

[6]

Fig.I.1.

The non isolation of the intermediates [7] and [8] is not unexpected as it has been shown [36] in a study of the reaction of $C_4H_9NH_2$ with $CFCl = CF_2$ that a structure containing the element $-\mathrm{NH}-\overset{|}{\mathrm{C}}\mathrm{F}-$ readily eliminates HF. A similar reaction sequence was obtained using dibutylamine [35] but with a slower rate of addition of the amine to the olefin formed by dehydroiodination.

Further work by Pakiorek [35] has shown that KOH and amines will eliminate a tertiary fluorine atom as HF from the unsaturated model compound $CF_2.CH_2.CF(C_2F_5)CH{=}CF.C_2F_5$:



$$CF_2.CH_2.\overset{C_2F_5}{\overset{|}{C}}F.CH{=}CF.C_2F_5 \xrightarrow{-HF} CF_2.CH{=}\overset{C_2F_5}{\overset{|}{C}}.CH{=}CF.C_2F_5$$

Work in these laboratories [37] on the reactivity of the saturated model compounds [1], [2], and [3], of which [1] contains tertiary fluorine has

$$[(CF_3)_2CF.CH_2.CF_2]_2, \quad [n.C_3F_7.CH_2CF_2]_2, \quad [C_2F_5.CH_2.CF_2]_2$$

[1] [2] [3]

shown that whereas primary and secondary amines eliminate HF from [1] and [3] at room temperature, extensive decomposition occurs, in reactions with KOH. Reaction of [1] with 1 mole of $(C_4H_9)_3N$ at 130° [38] causes dehydrofluorination to give a diene,

$$(CF_3)_2CF{-}CH = CF.CF_2.CH = C(CF_3)_2,$$

in which one double bond only is formed by the release of tertiary fluorine. Some unidentified polymeric material was also formed which was highly fluorinated and contained nitrogen, and it was suggested that the formation of this compound corresponds to the formation of cross-links in Viton A.

The treatment of a simpler model compound $(CF_3)_2CFCH_2CF_3$ with 2 moles of tri.n-butylamine at 130° for 24 hours gave as the main product $(CF_3)_2CHCH_2CF_3$ (38) i.e. instead of the usual elimination of HF, fluorine has been replaced by hydrogen. This type of replacement had not previously been demonstrated and may be a factor in the cross-linking of fluoroelastomers.

PART I

CHAPTER II: DISCUSSION AND EXPERIMENTAL

Discussion.

II.1. Introduction.

Previous work in these laboratories[13] led to the preparation of various co-telomer alcohol mixtures from pairs of olefins and methanol as a chain transfer agent (C.T.A.) or telogen. The reactions led to the formation of a complex mixture of co-telomer products of various chain lengths, and it was found to be impossible to separate such a mixture into its components for characterisation. Two co-telomer alcohol mixtures have been used in this thesis, those containing $CF_3CF{:}CF_2$, $CH_2{:}CF_2$ and MeOH (Viton-MeOH), and 1,4-C_6F_8, CH_2CF_2, and MeOH. Both mixtures eliminate HF on standing. Part I of this thesis concerns the attempt to stabilise these co-telomer alcohols, and increase their molecular weight by crosslinking, for possible use as plasticisers, lubricants, or heat exchangers.

Various methods have been used in industry to crosslink Viton A copolymers (see p. 8.). The most successful of these methods have been those involving the use of primary diamines, diamine derivatives, and tertiary amines with dithiols. These reagents have now been used to crosslink the co-telomer alcohol mixtures. Most of the work concerns the Viton-MeOH co-telomers.

The products from these reactions have been investigated by average molecular weight determination (ebullioscopically), measurement of infra-red spectra, and analysis of fluorine content.

II.2. Reagents and Solvents.

The preliminary reactions were carried out with excess n-butylamine and triethylamine using the Viton-MeOH co-telomer alcohols in ether solutions. Ethylene diamine and hexamethylene diamine, whose Schiff's bases (e.g. $R.CH=N(CH_2)_6N=CH.R$) have both had commercial acceptance as curing (crosslinking) agents, [23] are only slightly soluble in ether, and an attempted crosslinking by the addition of a suspension of ethylene diamine in ether to the co-telomers, gave a very low yield because of the difficulty in extracting the product from the aqueous layer, after the ethereal solution was acidified with dilute HCl and then neutralised. The product from the aqueous layer from a similar crosslinking reaction with hexamethylene diamine could not be extracted with ether, benzene, or carbon tetrachloride. The diamines were found to be soluble in monoglyme (1,2-dimethoxy ethane), and later reactions were carried out in this solvent. Monoglyme is miscible with dilute HCl which prevented the removal of excess amine by washing with aqueous acid. However, smaller molar ratios of co-telomers:diamine were now used (mainly 2:1), anhydrous potassium carbonate was added as an acid-acceptor to take up the HF eliminated (cf. MgO etc. as industrial acid-acceptors[23,33]), and acid-washing of the reaction mixture was felt to be unimportant.

Reaction	Co-telomer Alcohols	Cross-linking Agent	Time/temp. of Reaction	m.wt. Reactant	m.wt. Product	%F Reactant	%F Product	% F (Reactant) -% F (Product)
(a)	1	Et_3N	50°C/2 hr	409	488	62·8	60·6	2·2
(b)	1	$n.C_4H_9NH_2$	20°C/18 hr	583	1100	64·0	56·8	7·2
(c)1	1	$NH_2(CH_2)_2NH_2$	20°C/18 hr	355	397	64·4	54·5	9·9
(c)2	1	"	20°C/18 hr	355	480	64·4	54·9	9·5
(c)3	1	"	150°C/3 hr	355	764	64·4	57·5	6·9
(c)4	1	"	100°C/3 hr	355	520	64·4	57·1	7·3
(c)5	1	"	170°C/3 hr	399	785	57·9	51·5	6·4
(d)1	1	$NH_2(CH_2)_6NH_2$	100°C/3 hr	330	-	59·9	47·5	12·4
(d)2	1	"	50°C/18 hr	330	1130	59·9	50·8	9·1
(e)	1	$NH_2(CH_2)_3NH_2$	100°C/3 hr	330	556	59·9	46·6	13·3
(f)	1	$Et_3N/SH(CH_2)_3SH$	50°C/18 hr	330	835	59·9	53·4	6·5
(g)	2	$NH_2(CH_2)_6NH_2$	50°C/18 hr	-	-	55·9	43·6	12·3
(h)	2	$NH_2(CH_2)_2NH_2$	20°C/18 hr.	-	0	55·9	38·9	17·0

Co-telomer Alcohols:- 1 : $C_3F_6/CH_2CF_2/MeOH$

2 : 1,4-$C_6F_8/CH_2CF_2/MeOH$

Table II.1. Summary of Cross-linking Reactions.

II.3. Cross-linking Reactions.

Cross-linking of Viton-MeOH Co-telomer Alcohols with Primary Mono-amines and Diamines.

When the Viton-MeOH co-telomers were treated with excess n-butylamine in ether, and the excess amine was removed with aqueous acid, a stabilised (non HF-smelling) brown oil of much increased viscosity was obtained. The increase in molecular weight (583 ⟶ 1,110; 90%), showed that cross-linking had taken place and a product of the desired type had been obtained. The infra-red spectrum of the starting material had peaks at 3436 cm^{-1} [(broad), O-H stretch], 2985 cm^{-1} [(S), C-H stretch], and showed slight unsaturation at 1757 cm^{-1} (w) and 1639 cm^{-1} (w). The alcohol portion was shown to be still present in the infra-red spectrum of the product, stronger absorption at 2985 cm^{-1} indicated the presence of $n\text{-}C_4H_9\text{-}$, and absorption at 1757 cm^{-1} (s) and 1639 cm^{-1} (broad) indicated a large amount of unsaturation. The product was tested by sodium fusion and ferrous sulphate for nitrogen and gave a positive result, showing that the amine is present in the crosslinked structure. Amine hydrofluoride was precipitated in the reaction, showing that HF is eliminated, and leading to unsaturation. The reduction in fluorine content (see Table II.1) obtained can be explained as resulting from both the elimination of HF and by the inclusion of amine in the cross-links formed.

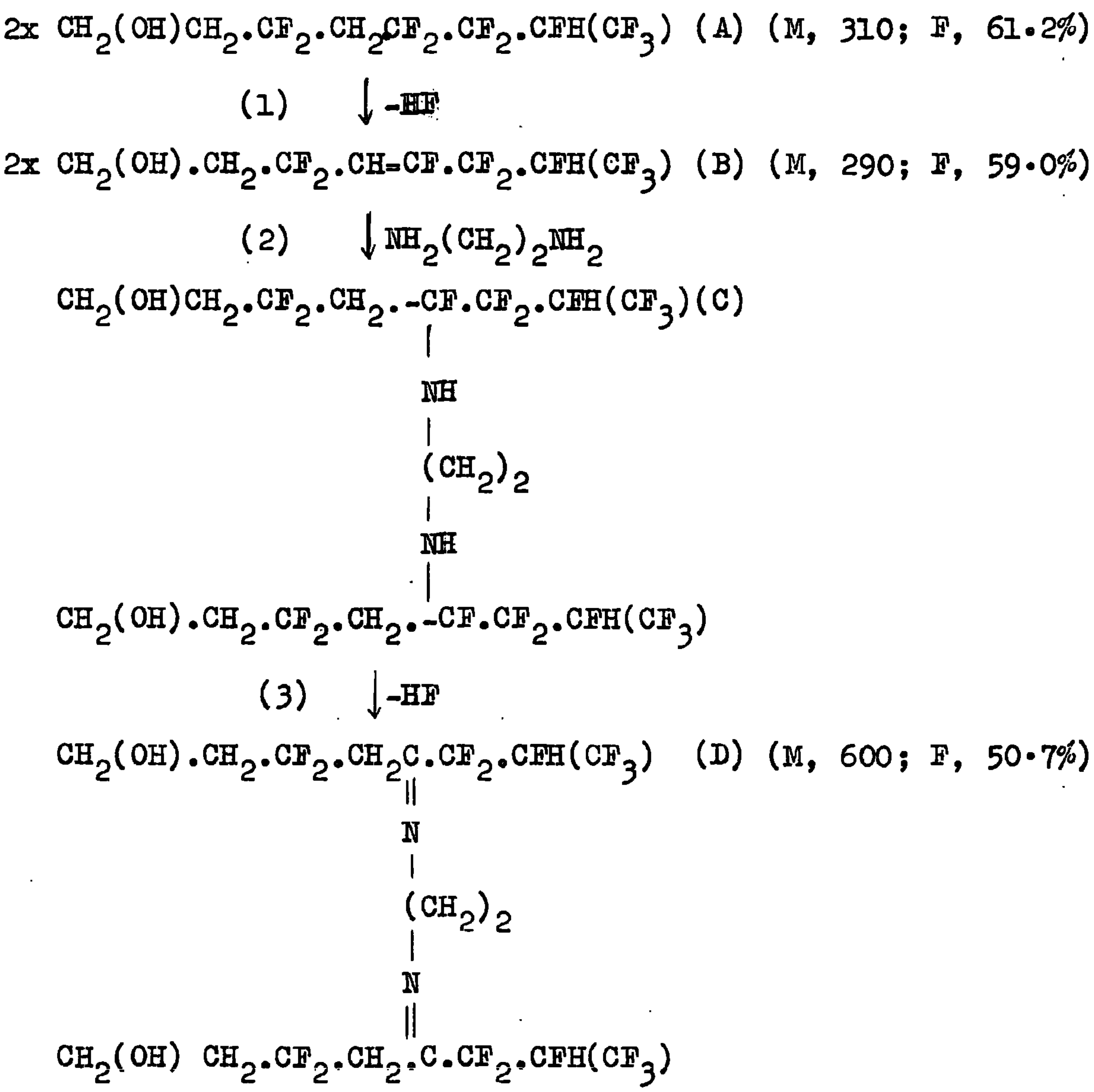
The Viton-MeOH co-telomers were then treated with ethylene diamine in monoglyme under various reaction conditions. A molar ratio of 2:1 for co-telomers:diamine was used in each reaction except the first (4:1). It was considered that this molar ratio (2:1) would be best if one molecule of diamine cross-linked two co-telomer chains by interaction of each of the amino groups of the diamine with a separate co-telomer chain. Anhydrous potassium carbonate was added asan acid acceptor, just as MgO etc. are added in the curing of Viton A.[23,33]

The products obtained at room temperature were pleasant-smelling, red oils of increased viscosity. From reactions in Carius tubes at 100-170° C, brown-black,semi-solid products were obtained. At this temperature degradation occurred and carbon was filtered off from the reaction mixture. Cross-linking increased with temperature, as indicated by the increase in average molecular weight from 355 to 480 (35%) at room temperature to 355 to 764 (115%) at 150° C. Nitrogen was shown to be present in the products by sodium fusions and ferrous sulphate. All the products showed a large amount of unsaturation with peaks at 1724 cm^{-1} (s) and 1613 cm^{-1} (s) in their infrared spectra. The alcohol portion was still present and the C-H stretching absorption was increased.

The average molecular weight of the co-telomers used in reactions with ethylene diamine was 355. The actual co-telomer molecule with the nearest molecular weight to this contains 1 C_3F_6:$2CH_2CF_2$:1 MeOH (M, 310.), and will have the following structure (after Plimmer [13]):

$CH_2(OH).CH_2.CF_2.CH_2CF_2.CF_2.CFH(CF_3)$ (M, 310; F, 61·2%)

It is possible to postulate a mechanism for the reaction of this molecule with ethylene diamine and correlate it with average molecular weights and fluorine analyses, as in fig. II.1. It is believed that dehydrofluorination is the first step, followed by addition of the amine to the resulting double-bond, with concurrent or subsequent hydrogen fluoride elimination. The evidence in support of this mechanism is as follows: the elimination of HF on standing from the Viton-MeOH co-telomers, and the formation of amine hydrofluoride in the reaction of excess n-butylamine with co-telomers points to dehydrofluorination as the main process in stage (1). This is supported by evidence from other workers who found that dehydrohalogenation was the first step in the reaction of Viton-like polymers [22,34]



$$2x\ CH_2(OH)CH_2.CF_2.CH_2CF_2.CF_2.CFH(CF_3)\ (A)\ (M,\ 310;\ F,\ 61{\cdot}2\%)$$

$$(1)\ \downarrow -HF$$

$$2x\ CH_2(OH).CH_2.CF_2.CH{=}CF.CF_2.CFH(CF_3)\ (B)\ (M,\ 290;\ F,\ 59{\cdot}0\%)$$

$$(2)\ \downarrow NH_2(CH_2)_2NH_2$$

$$\begin{array}{l} CH_2(OH)CH_2.CF_2.CH_2.\text{-}CF.CF_2.CFH(CF_3)(C) \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad NH \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad (CH_2)_2 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad NH \\ \qquad\qquad\qquad\qquad\quad | \\ CH_2(OH).CH_2.CF_2.CH_2.\text{-}CF.CF_2.CFH(CF_3) \end{array}$$

$$(3)\ \downarrow -HF$$

$$\begin{array}{l} CH_2(OH).CH_2.CF_2.CH_2C.CF_2.CFH(CF_3)\quad (D)\ (M,\ 600;\ F,\ 50{\cdot}7\%) \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad N \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad (CH_2)_2 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad N \\ \qquad\qquad\qquad\qquad\quad \| \\ CH_2(OH)\ CH_2.CF_2.CH_2.C.CF_2.CFH(CF_3) \end{array}$$

Fig. II.1.

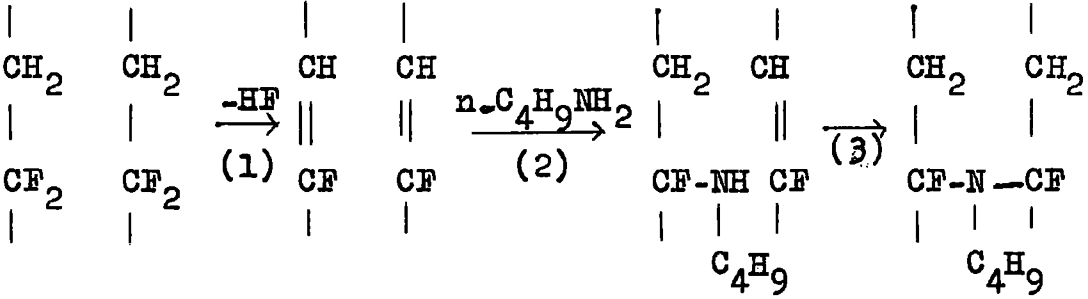
and model compounds [35,38,38] with primary amines. The increase in molecular weight, the presence of nitrogen and increased C-H absorption (infra-red) in the products indicates that the amine takes part in the cross-linking. The unit $-\overset{|}{C}F-NH-$, which is present in structure (C) has been shown to be unstable and to eliminate HF to form $-\overset{|}{C}=N-$.[36], and it is suggested that this occurs at stage (3) to give structure (D). The increse in molecular weight in going from A to D is from 310 to 600 which agrees well with the comparative figures for the co-telomer reactions at 150° C and 170° C, e.g. at 150° C, the molecular weight increase is from 355 to 764; and the decrease in fluorine content (10•5% - Table II.1), is of the order of that obtained in the co-telomer reactions at 150° C and 170° C (6•9%, 6•4%). These observations also confirm the postulated mechanism. The decrease in fluorine content is greater for the lower temperature reactions (9•5% at room temperature). This can be explained by suggesting that as there is less cross-linking at this temperature, co-telomer chains attached to diamines, the second amino group of which will not havereacted, will be present. Thus, with molecules present in which one diamine is attached to only one co0telomer chain, the fluorine content of the molecule will be reduced.

The infra-red spectrum of the products indicates different kinds of unsaturation. This corresponds to elimination of HF at several sites in A, e.g.

$$CH_2(OH)CH{=}CF.CH{=}CF.CF.{=}CF(CF_3)$$

as well as the C=N unsaturation suggested above, and addition of amine could take place at any of these sites. Pakiorek [35] has shown that unstable structures of the type $-\ CH_2\ -\ \overset{|}{C}F\ -\ NH\ -$ can eliminate HF to give $-\ CH\ =\ \overset{|}{C}\ -\ NH$ as well as $-\ CH_2\ -\ \overset{|}{C}\ =\ N\ -$ and the former structure is therefore also likely to be present in the products.

In order to explain the cross-linking in the n-butylamine product, it is necessary to postulate (1) removal of HF from two co-telomer chains, (2) addition of

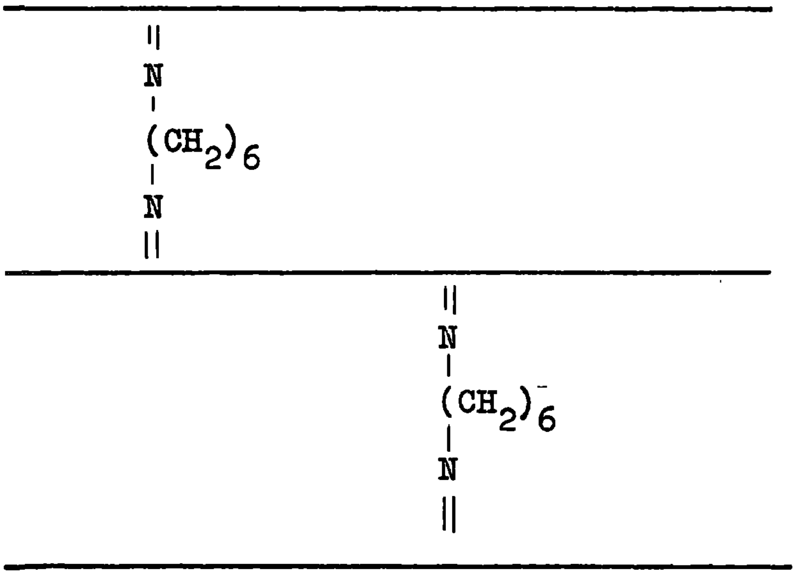


amine to one chain, (3) interaction of the - NH group with the other chain. This type of mechanism has been suggested before to explain the reactions of primary amines with Viton-like structures obtained after removal of HCl from Kel F elastomer. The average molecular weight of the starting material is 583, and a calculation of the molecular weight of the product formed in the cross-linking of two of these chains with n-butylamine gives the following result:

$$(2 \times 583) - 40\ (2HF) + 73\ (n\text{-}C_4H_9NH_2) = 1{,}199$$

This value is very close to actual molecular weight of the product (1,110).

At 100° C, the product from the reaction of hexamethylene diamine with Viton-MeOH co-telomers was a black solid. Its molecular weight could not be determined as it was insoluble in boiling acetone. However, its molecular weight must have been much greater than 1,130 which was the molecular weight of the semi-solid obtained from the reaction at 50° C. The infra-red spectrum of the former product and that from the reaction of trimethylene diamine with co-telomers were very similar to those described above for the ethylene diamine reaction products. In order to obtain a product of molecular wt. 1,130 from a starting material of average molecular wt. 330 it is necessary to postulate structures involving three co-telomer chains cross-linked by two molecules of hexamethylene diamine, e.g.



The line ——— represents a co-telomer chain. A molecular weight calculation gives the following result: (3 x 330) + [2 x 112 ($NH_2(CH_2)_6NH_2$)] - 160 (8HF) = 1,054, which is close to the experimental value (1,130). It is also possible to postulate that two chains are cross-linked by two or more amines. This would also lead to increases in molecular weight. If the reactivities of the diamines towards reaction with co-telomer chains are expressed in terms of the ratio + m.wt. product/m.wt. reactant, the following results are obtained:-

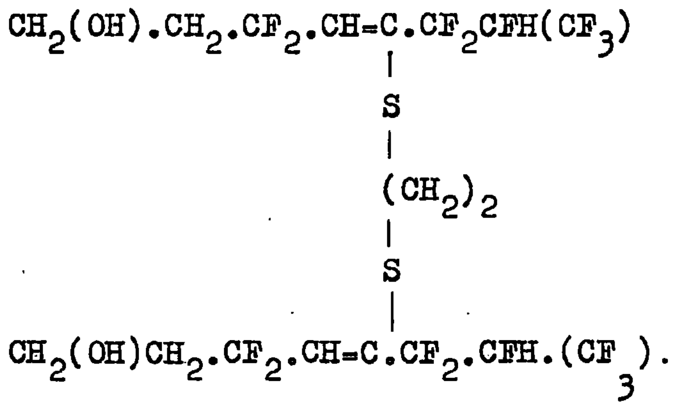
Ethylene Diamine , 100°C + 520/355 = 1·50
Trimethylene Diamine, 100°C : (556-14)/330 = 1·64 [14=CH_2]
Hexamethylene Diamine, 50° C: (1,130-112)/330 = 3·08
[112 = 2 x $(CH_2)_4$]

Allowances were made for the molecular weights of the diamines and the postulate that two molecules of hexamethylene diamine will cross-link three co-telomers chains. Thus, the order of reactivity is found to be:-

Hexamethylene Diamine $\gg$ Trimethylene Diamine $>$ Ethylene Diamine

Cross-linking of Viton-MeOH Co-telomer Alcohols with a Tertiary Amine and Dithiol.

When a tertiary amine (Et_3N) was treated with co-telomers for two hr. in ether at 50° C, the molecular weight of the brown product obtained was increased only slightly (409 to 488). The infra-red spectrum showed little change with only a very slight increase in unsaturation. When propane-1,3-dithiol in monoglyme, a more polar solvent, was added, at the same temperature, in the presence of potassium carbonate, considerably more reaction took place. The molecular weight of the starting material was increased by 153% (330 to 835), and the fluorine content was reduced by 6.5% (Table II.1). The infra-red spectrum was similar to those of the diamine products, showing a large amount of unsaturation [1724 cm^{-1} (s), 1639 cm^{-1} (broad)], and increased C-H stretch absorption [2985 cm^{-1}(s)]. No S-H absorption in the region around 2564 cm^{-1} could be observed. Sodium fusion followed by sodium nitroprusside showed that sulphur was present in the product. Thus, the following type of structure can be postulated for the product, involving cross-linking of two co-telomer chains (A) by the dithiol:

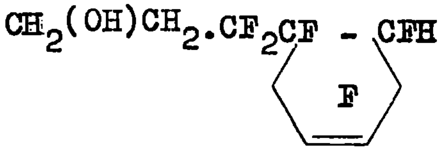


$$\begin{array}{l} CH_2(OH).CH_2.CF_2.CH{=}\underset{|}{C}.CF_2CFH(CF_3) \\ \qquad\qquad\qquad\quad\;\; S \\ \qquad\qquad\qquad\quad\;\; | \\ \qquad\qquad\qquad\quad\;\; (CH_2)_2 \\ \qquad\qquad\qquad\quad\;\; | \\ \qquad\qquad\qquad\quad\;\; S \\ \qquad\qquad\qquad\quad\;\; | \\ CH_2(OH)CH_2.CF_2.CH{=}C.CF_2.CFH.(CF_3). \end{array}$$

The reaction mechanism will be similar to that suggested in fig.II.1. As before, the cross-linking could take place at several sites on a co-telomer chain and involve more than one dithiol and more than two co-telomer chains.

Cross-linking of 1,4-Octafluorocyclohexadiene/Vinylidene Fluoride/MeOH Co-telomer Alcohols with Diamines.

Plimmer[13] suggested that these co-telomers contained structures of the type:-



The infra-red spectrum contains peaks in the unsaturation range at the following wave numbers 1757 cm^{-1}(w), 1754 cm^{-1}

(s), and 1695 cm^{-1} (w). The 1754 cm^{-1}(s) peak was attributed [13] to the - CF = CF - cyclic double bond and the other peaks can be attributed to the HF elimination, which occurs on standing.

The co-telomers were treated with ethylene diamine at room temperature to give a red-brown oil of increased viscosity, and with hexamethylene diamine at 50° C to give a black solid. Both the starting material (copiously) and the product, eliminated HF on standing. It was impossible to obtain molecular weights for these compounds, and it seems likely that the ebulliometer was affected by the HF released. The increased viscosity of the products, and the large reductions in fluorine content (Fig.II.1) due to HF elimination and inclusion of amine, showed that cross-linking had occurred, and strong absorption at 1695 cm^{-1} in the infra-red spectrum showed that unsaturation had increased. The mechanism for these reactions will be similar to that postulated for the Viton-MeOH co-telomer reactions with diamines.

Experimental

II.4. Molecular Weights.

The instrument used to determine these was a Gallenkamp semi-micro ebulliometer, suitable for the determination of molecular weights on 200 mg. samples. The limitations of the method are that the compound to be determined must (a) have a negligible vapour pressure (b) be soluble in acetone, ether, or benzene (c) have a molecular weight below 1,000.

Procedure. The apparatus was set up as described in the instruction leaflet. The samples were injected in the form of weighed pellets (solids), or on a looped copper wire (semi-solids and viscous liquids). The apparatus was first calibrated using naphthalene as a standard. Once the solvent (dry acetone) had reached a condition of steady boiling, pellets of naphthalene (approx. 50 mg. each) were weighed accurately, and added to the solvent at three minute intervals, noting the resistance change with each addition, by bringing the galvanometer deflection back to zero.

Results and Calculation. For naphthalene the results were tabulated as follows:

R	Δ R	$\Sigma\Delta$ R	Δ Wt	$\Sigma\Delta$ Wt
2085				
2012·5	72·5	72·5	0·057	0·057
1920	92·5	165	0·081	0·138
1851·5	68·5	233·5	0·050	0·188
1784	67·5	301	0·053	0·241
1697	87·0	388	0·075	0·316

Where R = resistance

ΔR = change in resistance caused by addition of ΔWt g. solute.

$\Sigma\Delta$Wt = the sum of ΔWt corresponding to $\Sigma\Delta$R

A graph was drawn of $\Sigma\Delta$R vs. $\Sigma\Delta$Wt, the slope of which, $\Sigma\Delta R/\Sigma\Delta Wt = S$, was proportional to the molecular weight of the compound used (see Fig. II.2).

i.e. K = Mol.wt. x S.

Hence for the naphthalene standard,

$K = 128{\cdot}17 \times S.$

K is a constant for the apparatus under these conditions. From Fig.II.2, for naphthalene S = 1237·5, where K = 158,600. For any unknown compound, the above procedure was repeated, and a value S^x obtained for the slope of the graph. Thus:

$$M = \frac{K}{S^*}$$

$$= \frac{158{,}600}{S^*}$$

The accuracy of the method was checked using benzoic acid. From the graph of $\Sigma \Delta R / \Sigma \Delta Wt$ of benzoic acid in acetone, $S^* = 1{,}350$, $\therefore M = 158{,}600/1{,}350 = 117{\cdot}5$ (Calc: 122·1; error = 3·8%).

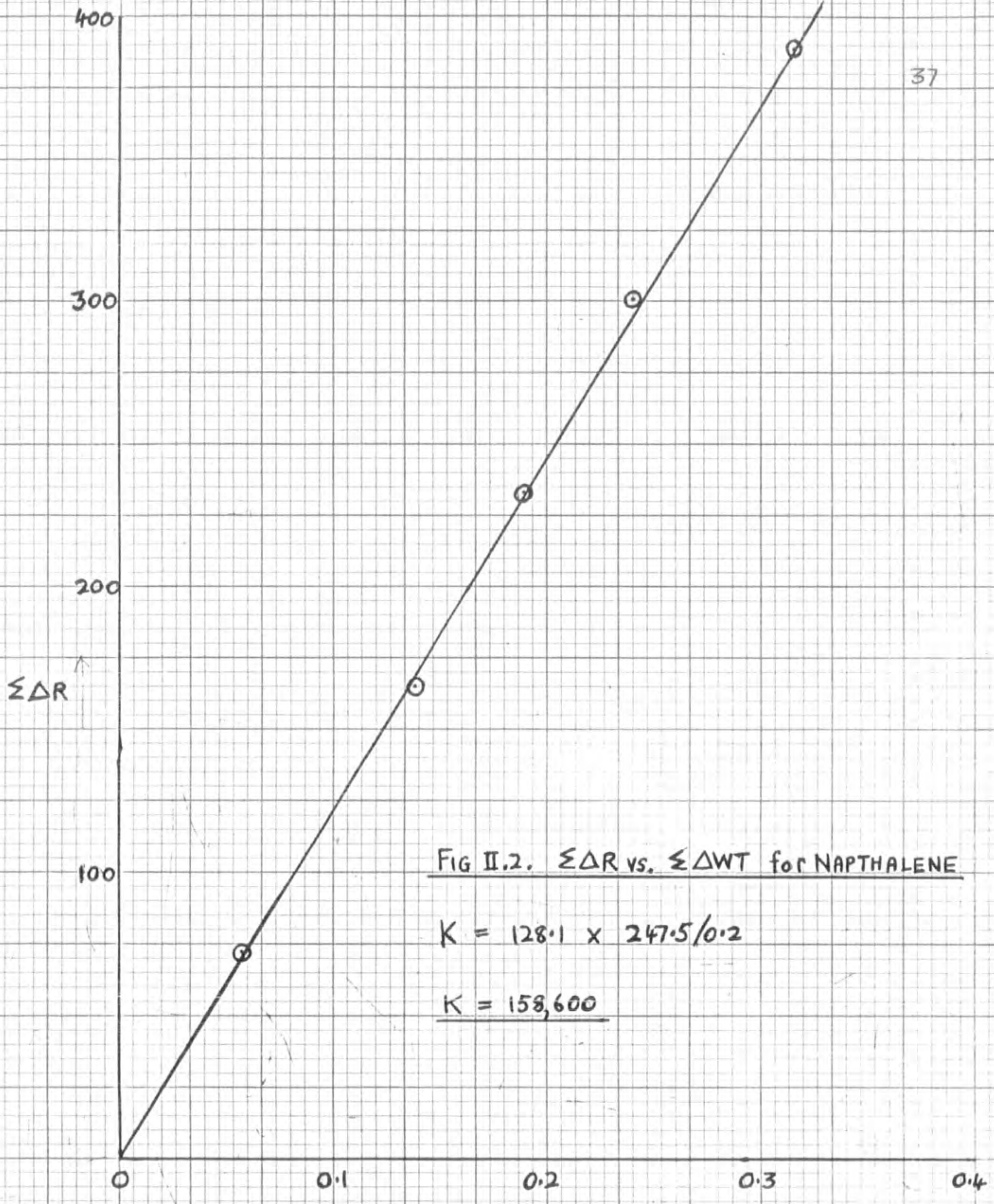


FIG II.2. ΣΔR VS. ΣΔWT for NAPTHALENE

K = 128·1 x 247·5/0·2

K = 158,600

II.5. Infra-Red Spectroscopy.

The infra-red spectra of all compounds have been recorded. A Grubb-Parsons, Type G.S.2A infra-red spectrometer operated by Miss D. Chapman, has been used to obtain the spectra. The sample was usually in the form of a thin contact film between potassium bromide discs.

Infra-Red Data. (See p. 53 for Infra-red spectra). Bands are quoted for the regions 2-5 μ and 5-7 μ (unsaturation).

Viton-MeOH Co-telomer Alcohols. 3690 cm^{-1} (m), 3436 cm^{-1} (broad) OH; 2985 cm^{-1} (s) C-H; 1757 cm^{-1} (w), 1724 cm^{-1} (w), 1639 cm^{-1} (w) unsaturation.

Spectral data from reactions of Viton-MeOH co-telomers are shown below. ED = Ethylene Diamine, HMD = Hexamethylene Diamine, TMD = Trimethylene Diamine.

$Et_3N/50^\circ$ C. Spectrum identical with starting material except for a slight broadening of the unsaturation peak.

$n.C_4H_9NH_2/20^\circ$. 3690 cm^{-1}(m), 3436 cm^{-1} (broad) OH; 2985 cm^{-1} (s) C-H; 1724 cm^{-1}(s), 1613 cm^{-1}(broad) unsaturation.

ED/20°. Mole ratios of co-telomers:diamine of 4:1 and 2:1 were used at this temperature. Both give the same spectrum 3690 cm^{-1}(m), 3436 cm^{-1} (broad) OH; 2985 cm^{-1}(s) C-H; broad band centred on 1613 cm^{-1} with shoulders at 1724 cm^{-1}; 1666 cm^{-1}; 1563 cm^{-1} unsaturation. The ED/100° C, 150°C, 170° C products give very similar spectra, except that the shoulders of the broad band at 1613 cm^{-1} become blurred as the molecular weight of the product increases.

HMD/50° C. 3436 cm^{-1} (broad) OH; 2985 cm^{-1} (vs) C-H; broad band centred on 1613 cm^{-1}, with shoulders at 1724 cm^{-1}, 1666 cm^{-1} unsaturation. No spectrum could be obtained for the HMD/100° C product.

TMD/100° C. 3436 cm^{-1} (broad) OH; 2985 cm^{-1} (vs) C-H; broad band centred on 1613 cm^{-1} with shoulders at 1757 cm^{-1}, 1563 cm^{-1} unsaturation.

$Et_3N/SH(CH_2)_3SH$/50° C. 3436 cm^{-1} (broad) OH; 2985 cm^{-1} (s) C-H; broad band centred on 1681 cm^{-1} and 1613 cm^{-1} unsaturation. (No SH absorption in the region 2525 cm^{-1} to 2575 cm^{-1}).

Octafluorocyclohexa-1,4-diene/Vinylidene Fluoride/MeOH Co-telomer Alcohols. 3436 cm^{-1} (broad) OH; 2985 cm^{-1} C-H; 1757 cm^{-1} (s), 1748 cm^{-1} (vs), 1639 cm^{-1} (broad) unsaturation. The peak at 1757 cm^{-1} occurs in 1,4-C_6F_8.

Spectral data from the reactions of these co-telomers are shown below.

<u>ED/20° C.</u> 3436 cm^{-1} (broad) OH; 2985 cm^{-1} (s) C-H; 1757 cm^{-1} (s), 1613 cm^{-1} (broad) unsaturation. No spectrum could be obtained for the HMD/50° C product.

II.6. Preparation of the Co-telomer Alcohols.

These reactions were carried out in a stainless-steel autoclave (volume 380 ml.) fitted with a stainless-steel insert, to accommodate a cobalt^{60} gamma-source guide tube (Fig.II.3).

Procedure - Anhydrous methanol was weighed directly into the autoclave, the insert was fitted, and the pressure head screwed down. The autoclave was then cooled in liquid air, the outlet arm was connected to a vacuum line with pressure tubing, and the autoclave was evacuated. The valve on the outlet arm was then closed, and the autoclave was allowed to warm up to room temperature in order to vapourise the telogen. After more cooling in liquid air the autoclave was evacuated again. Thus, oxygen, which might have inhibited the reaction, was removed. The olefins were now transferred from their cylinders into the autoclave via an evacuated three-litre bulb which was connected to the autoclave via the vacuum line. The amount of olefin transferred was controlled by noting the manometer pressure of the gas in the three-litre bulb and was determined by weighing the cylinders before and after transfer. The valve on the outlet arm was now closed and the autoclave allowed to warm to room temperature before being placed under the gamma source for irradiation.

Working up - After approx. 14 days the autoclave was taken off the gamma source and connected to a vacuum line. Any unreacted olefins were allowed to expand into a large bulb connected to the vacuum line, to which a vapour density bulb was attached. The average molecular weight of the volatile olefins was then determined and the relative amounts of recovered olefins estimated from this determination. The autoclave head was then removed, the remaining liquid was pipetted into a flask, and the telogen and olefin-methanol adduct (e.g. $CF_3.CFH.CF_2.CH_2OH$) removed by distillation under reduced pressure. The co-telomer mixture was then transferred to a one-piece distillation apparatus and distilled at 0·05 mm up to 200° C, the pressure being measured on a Piranivacuum gauge.

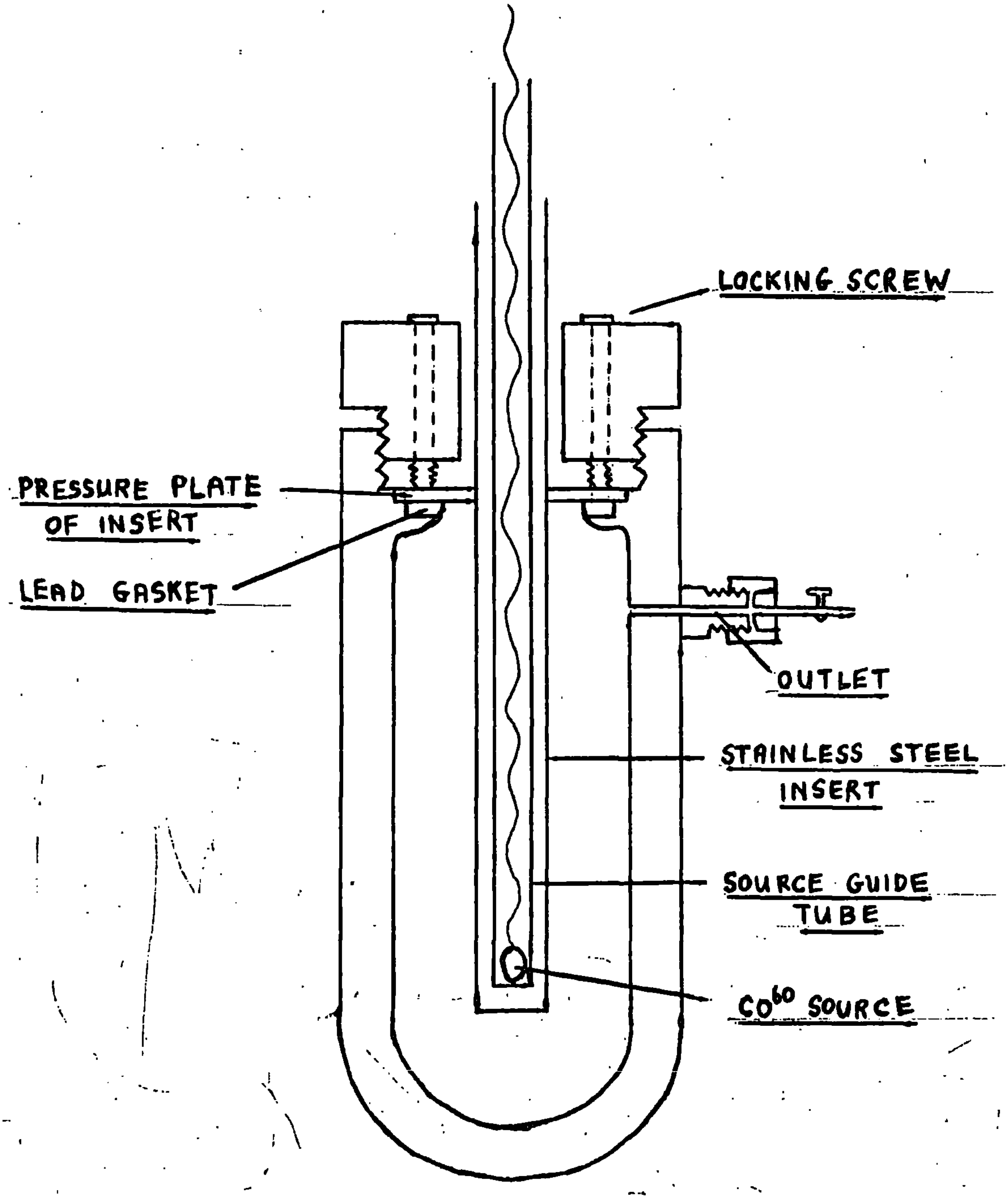


FIG II.3 AUTOCLAVE

Reactions (i) $C_3F_6/CH_2CF_2/MeOH$.

Reagents	MeOH	(52 g., 1·63 mole)
	C_3F_6	(60 g., 0·4 mole)
	CH_2CF_2	(26 g., 0·4 mole)
Irradiation	14 days on 500 curie source	
Recovered	MeOH	47·2 g.
	C_3F_6	4 g.
	CH_2CF_2	Nil
Reacted	MeOH	(4·8 g., 0·15 mole)
	C_3F_6	(56 g., 0·37 mole)
	CH_2CF_2	(60 g., 0·4 mole)

Distillation of the methanol + olefin-methanol adduct gave 12 g. $CF_3.CFH.CF_2.CH_2OH$. b.p. 114° C. This contains 9·9 g. C_3F_6 + 2·1 g. MeOH, therefore the co-telomer mixture contained:

C_3F_6:56-9·9 = 46·1 g., 0·30 mole
MeOH:4·8-2·1 = 2·7 g., 0·084 mole
CH_2CF_2 = 60 g., 0·40 mole

(ii) 1,4-$C_6F_8/CH_2CF_2/MeOH$.

Reagents	MeOH	(103·5 g., 3·23 mole)
	1,4-C_6F_8	(83·0 g., 0·37 mole)
	CH_2CF_2	(38·0 g., 0·59 mole)
Irradiation	14 days on 500 curie source.	

Recovered	MeOH	97·5 g.
	$1,4\text{-}C_6F_8$	48·1 g.
	CH_2CF_2	Nil
<u>Reacted</u>	MeOH	(6·0 g., 0·19 mole)
	$1,4\text{-}C_6F_8$	(34·9 g., 0·15 mole)
	CH_2CF_2	(38·0 g., 0·59 mole)

Distillation of the methanol + olefin-methanol adduct gave 21·4 g. $H(C_6F_8)CH_2OH$. b.p.164° C. This contains 18·72 g. $1,4\text{-}C_6F_8$ + 2·68 g. MeOH, therefore the co-telomer mixture contained:

$1,4\text{-}C_6F_8$:34·9-18·72 = 16·18 g., 0·07 mole
MeOH: 6·0-2·68 = 3·32 g., 0·10 mole
CH_2CF_2 = 38·0 g., 0·59 mole

II.7 Cross-linking Reactions.

Cross-linking Reactions of Viton-Methanol Co-telomer Alcohols with Amines -

a) Triethylamine. Co-telomer alcohols (6·5 g., 0·016 mole) in anhydrous ether (20 ml.) were placed in a three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. Triethylamine (9·9 g., 0·098 mole) in ether (10 ml.) was added dropwise over 30 min., and the reaction mixture was stirred for 12 hr. at room temperature. Finally the reaction mixture was heated under reflux for 2 hr. A small amount of precipitate formed and was filtered off. The brown ethereal solution obtained was filtered through activated charcoal, washed with dilute HCl to remove excess amine, and dried over $MgSO_4$. The ether was then pumped off and a brown viscous liquid (3 g.) remained (Found: F, 60·6%; M, 488. Original material contained: F, 62·8; M, 409).

b) n-Butylamine. Using the apparatus described above, co-telomer alcohols (11 g., 0·019 mole) in anhydrous ether (30 ml.) were placed in the flask, which was cooled to 0° C in an ice-bath, and n-butylamine (17·5 g., 0·246 mole) in ether (10 ml.) was added slowly, with stirring, over 45 min. The reaction mixture was then allowed to warm to room temperature and stirred for 21 hr. A white precipitate formed (3·7 g.) which was filtered off and washed with anhydrous ether (Found: F, 20·6%; Calc. for $C_4H_9NH_3F$: F, 20·4%). The dark brown solution was filtered through activated charcoal, washed with dilute HCl to remove excess amine, and then washed with water. After drying the solution over $MgSO_4$, the ether was removed under reduced pressure and the product was a dark-brown, viscous oil (8·4 g.) (Found: F, 56·8%; M, 1,110. Original material contained: F, 64·0%; M, 583).

c) Ethylene Diamine (1.) Using the apparatus described above, co-telomer alcohols (3 g., 0·008 mole), monoglyme (10 ml.) and anhydrous K_2CO_3 (0·55 g., 0·004 mole) were placed in the flask, which was cooled to 0° C in an ice-bath. Ethylene diamine (0·12 g., 0·002 mole) in monoglyme (15 ml.) was added slowly, with stirring, over 20 min. The resulting yellow solution was then allowed to warm to room temperature and stirred for 18 hr. The white residue, presumably containing K_2CO_3, KF, and some amine hydrofluoride, was filtered off from the brown solution. The monoglyme was removed at reduced pressure, and 2·4 g. of pleasant-smelling red oil of increased viscosity was obtained. (Found: F, 54·5%; M, 397. Original material contained: F, 64·4; M, 355).

(2) Using the procedure described above [(c)(1)] and changing the mole ratio of co-telomers to diamine gave the following result:

<u>Reagents</u> Co-telomer alcohols (3 g., 0·008 mole)
$NH_2(CH_2)_2NH_2$ (0·24 g., 0·004 mole)
K_2CO_3 (1·15 g., 0·008 mole)

<u>Time/Temp.</u> 18 hr./20° C.

<u>Product</u> 1·9 g. dark red oil of approx, doubled viscosity. (Found: F, 54·9%; M, 480; Original material contained: F, 64·4; M, 355).

(3) Reactions (3), (4), and (5) were carried out in carius, tubes, shaken in a mechanical shaker, and heated in a cylindrical heater. In each case monoglyme (30 ml.) was added as solvent. The working-up of the product was the same as that described above in c(1).

<u>Reagents</u> Co-telomer alcohols (4·2 g., 0·011 mole)
$NH_2(CH_2)_2NH_2$ (0·34 g., 0·0055 mole)
K_2CO_3 (1·61 g., 0·011 mole)

<u>Time/Temp.</u> 3 hr./150° C.

<u>Product</u> 2·0 g. brown-black, semi-solid. (Found: F, 57·5%; M, 764; original material contained: F, 64·4%; M, 355). Some degredation occurred and carbon was filtered off.

(4)

Reagents	Co-telomer alcohols.	(3 g., 0·008 mole)
	$NH_2(CH_2)_2NH_2$	(0·24 g., 0·004 mole)
	K_2CO_3	(1·15 g., 0·008 mole)
Time/Temp.	3 hr./100° C.	
Product	1·7 g. brown-black, extremely viscous oil. (Found: F, 57·1%; M, 520; original material contained: F, 64·4%; M, 355).	

(5)

Reagents	Co-telomer alcohols	(6 g., 0·015 mole)
	$NH_2(CH_2)NH_2$	(0·4 g., 0·0075 mole)
	K_2CO_3	(2·1 g., 0·015 mole)
Time/Temp.	3 hr./170° C.	
Product	2·0 g. brown-black, semi-solid. (Found: F, 51·5%; M, 785; original material contained: F, 57·9%; M, 399).	

d) Hexamethylene Diamine (1) Using the procedure described in c(1) gave the following results for d(1) and d(2):

Reagents	Co-telomer alcohols	(5 g., 0·015 mole)
	$NH_2(CH_2)_6NH_2$	(0·87 g., 0·0075 mole)
	K_2CO_3	(2·07 g., 0·015 mole)
Time/Temp.	3 hr./100° C.	
Product	3·4 g. black, semi-solid. (Found: F, 47·5%;	

M, - ; original material contained: F, 59.9%; M, 330). The product was unsoluble in boiling acetone and no molecular weight could be obtained.

(2)

Reagents	Co-telomer alcohols	(5 g., 0·015 mole)
	$NH_2(CH_2)_6NH_2$	(0·87 g., 0·0075 mole)
	K_2CO_3	(2·07 g., 0.015 mole)
Time/Temp.	18 hr./50° C.	
Product	3·5 g. brown-black, semi-solid. (Found: F, 50·8%; M, 1,130; original material contained: F, 59·9%; M, 330).	

Monoglyme was the solvent used for these [d(1) and (2)] and all further reactions.

e) Trimethylene Diamine. Using the procedure described in(c)(1) gave the following result:

Reagents	Co-telomer alcohols.	(5 g., 0·015 mole)
	$NH_2(CH_2)_3NH_2$	(0·55 g., 0·0075 mole)
	K_2CO_3	(2·07 g., 0·015 mole)
Time/Temp.	3 hr./100° C.	
Product	3·7 g. black, semi-solid. (Found: F, 46.6%; M, 556; original material contained: F, 59·9%; M, 330).	

f) Triethylamine and Propane-1,3-Dithiol. Using the procedure described in c(1), with propane-1,3-dithiol also in the flask gave the following result:

Reagents	Co-telomers alcohols	(5 g., 0·015 mole)
	$(C_2H_5)_3N$	(1·52 g., 0·015 mole)
	$HS(CH_2)_3SH$	(0·81 g., 0·0075 mole)
	K_2CO_3	(2·07 g., 0·015 mole)
Time/Temp.	18 hr./50° C.	
Product	2·8 g. red-brown oil. (Found: F, 53·4%; M, 835; original material contained: F, 59·9%; M, 330).	

Cross-linking Reactions of 1,4-Octafluorocyclohexadiene/ Vinylidene Fluoride/MeOH Co-telomer Alcohols with Diamines.

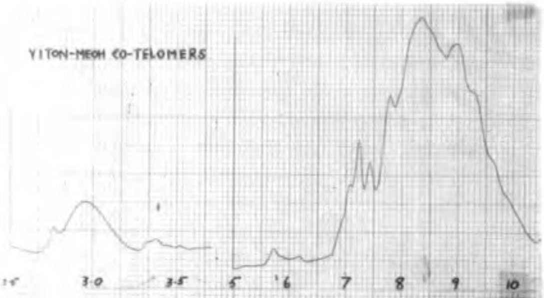
g) Hexamethylene Diamine. Using the procedure described in c(1) gave the following result:

Reagents	Co-telomer alcohols	(5 g., 0·017 mole [*])
	$NH_2(CH_2)_6NH_2$	(0·99 g., 0·0085 mole)
	K_2CO_3	(2·35 g., 0·017 mole)
Time/Temp.	18 hr./50° C.	
Product	1·8 g. HF-smelling black solid. (Found: F, 43·6%; M, - ; original material contained: F, 55·9%; M, 300[*]). It was not possible to obtain molecular weights in g) and h), probably due to HF elimination by	

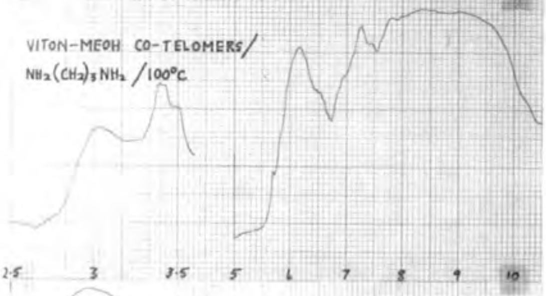
both original material and product.*
Molar quantities were based on molecular weights obtained by Plimmer [13] for the same fractions.

h) Ethylene Diamine. Using the procedure described in c(1) gave the following result:

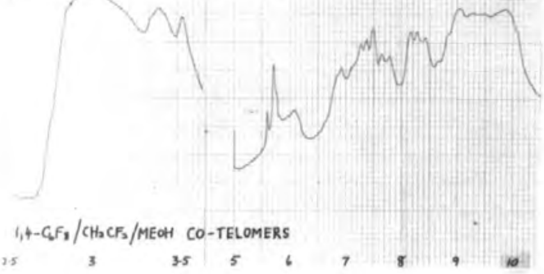
Reagents	Co-telomer alcohols	(5 g., 0·017 mole *)
	$NH_2(CH_2)_2NH_2$	(0·51 g., 0·0085 mole)
	K_2CO_3	(2·35 g., 0·017 mole)
Time/Temp.	18 hr./20° C.	
Product	2·1 g. HF-smelling, dark-red oil. (Found: F,55·9%; M, - ; original material contained: F, 38·9%, M, 300*).	



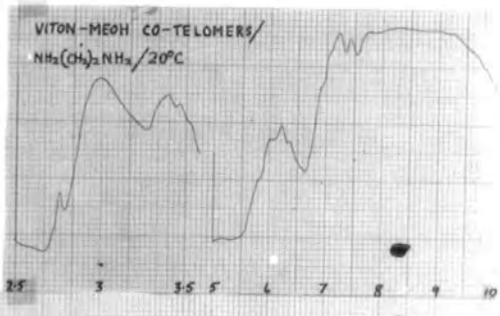
VITON-MEOH CO-TELOMERS



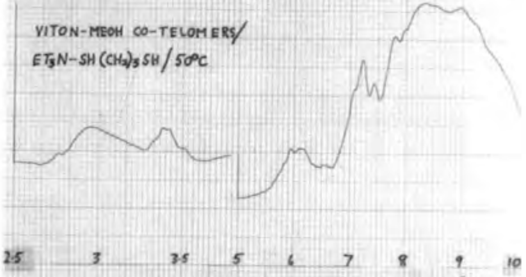
VITON-MEOH CO-TELOMERS/ $NH_2(CH_2)_3NH_2$ /100°C



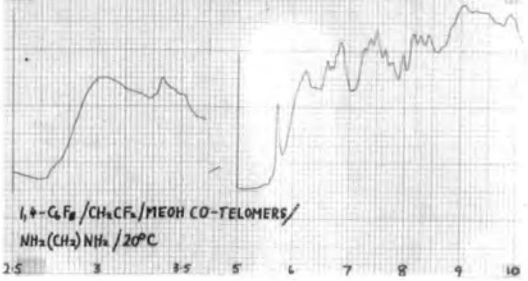
1,4-C_6F_8/CH_2CF_2/MEOH CO-TELOMERS



VITON-MEOH CO-TELOMERS/ $NH_2(CH_2)_2NH_2$/20°C



VITON-MEOH CO-TELOMERS/ ET_3N-$SH(CH_2)_3SH$/50°C



1,4-C_6F_8/CH_2CF_2/MEOH CO-TELOMERS/ $NH_2(CH_2)NH_2$/20°C

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PART II.

CHAPTER I: INTRODUCTION

I.1. Dipole Moment, Bond Moment and Group Moment; Sign, Angle, and Vector Summation of Moments.

A molecule is said to have a dipole moment if its centres of +ve and -ve charge do not coincide. If the +ve and -ve charges, $+\delta e$ and $-\delta e$, are separated by a distance l, then the dipole moment = $\delta e \times l$. As the moment acts in the direction of the line joining the two charges, that is, the axis of the dipole, it is a vector quantity. The electronic charge is $4{\cdot}8 \times 10^{-10}$ e.s.u. so that if an electron moves 1Å i.e. a distance of the order of one bond length, a moment of $4{\cdot}8 \times 10^{-18}$ e.s.u. is created. This is normally quoted as 4·8 Debye units or 4·8D.

The HCl molecule is a simple example of a molecular dipole which lies in the HCl bond with the +ve end towards the hydrogen and the -ve end towards the chlorine. It is often written $\overset{+\!\!\!\longrightarrow}{\mathrm{H{-}Cl}}$. This illustrates the fact that a chemical bond between atoms of different elements normally has a dipole moment acting in the direction of the bond, known as the bond moment. For a group such as the $-NO_2$ group we can define a characteristic group moment, which is more useful than the bond moment in the calculation of molecular moments, as the vector sum of the individual bond moments. Tables of bond and group moments have been published,[1,2] and collected values of dipole moments up to 1948 [3] and 1962 [4] are available.

It is necessary to assign directions to dipole moments. If the direction of the moment of any atom or group bonded to the benzene ring is known, then that of another atom or group can be determined from the moment of the compound in which the two groups are substituted para to each other on a benzene ring. The [illegible] negative pole of the C-Cl bond was assumed [5] to be at the chlorine atom because of the greater electronegativity of the chlorine than carbon. For p-Cl.$C_6H_4NO_2$, the moment would then be either the sum of the moments of C_6H_5Cl and $C_6H_5NO_2$ or the difference. The value obtained is 2·61D which is much closer to the difference (2·46D) than to the sum (5·56D), i.e. - NO_2 acts in the same direction as -Cl relative to carbon. This test is not very useful for the 'bent' groups such as - OH, - NH_2, but it is usually assumed that the more electronegative atom is the negative pole and no real anomalies have been found.

Because of the vector properties of dipole moments, when two or more groups are attached to the benzene ring, it is possible to calculate an expected value for the resultant moment - e.g. for the dichlorobenzenes the following values have been obtained and calculated [6]

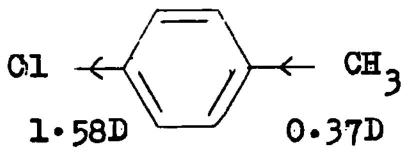
(C_6H_5Cl = 1·56D) in Table I.1.

	Observed (D)	Calculated (D)
o-$C_6H_4Cl_2$	2·25	2·70
m-$C_6H_4Cl_2$	1·48	1·56
p-$C_6H_4Cl_2$	0	0

Table I.1.

The angle between the vectors in the o-compound is 60°, in the m-compound 120°, and in the p-compound 180°. The para vectors cancel out, and the meta and ortho values are calculated using the cosine rule. The agreement between the measured and calculated values for p- and m-$C_6H_4Cl_2$ and the discrepancy for o-$C_6H_4Cl_2$ is typical of dihalo-substituted benzenes (see later). This is important when considering the dipole moments of C_6F_5X compounds where the C-F(4) and C - X moments are likely to be affected by the fluorine atoms ortho to them.

From the vector law, the moment of p-chlorotoluene would be expected to be the sum of the moments of chlorobenzene and toluene i.e. 1·58 + 0·37 = 1·95D

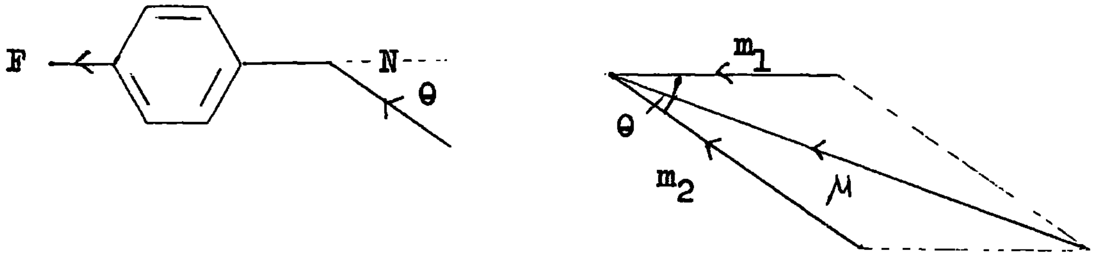


The observed value is 1·95D, which shows that the vector law holds and confirms the directions assigned to these groups. Since the vector law seems to hold for p-methyl groups, it seemed reasonable to assume that the moments of other groups which are not directed radially from the ring, e.g. - NMe_2, would be unaffected by the introduction of a p-methyl group, and that the vector law would still hold. Marsden and Sutton [8] used this approach to calculate θ, the angle between the dipole axis and the plane of the ring, for aniline, phenol, etc. An example of this is the calculation of θ for - NMe_2 from N-dimethyl aniline (1·58D) and dimethyl p-toluidine (1·29D). These values should be related to the dipole moment of toluene (0·37D) by the following relationship:-

$$\mu^2(NMe_2.C_6H_4.Me) = \mu^2(NMe_2AR) + \mu^2(ARMe) - 2.\mu(NMe_2AR).\mu(ARMe).\cos\theta$$

Substituting the numerical values gives $\theta = 34^\circ$. When large interactions are found to take place between groups in p-disubstituted benzenes, this type of calculation cannot be used.

The following calculation is an example of vector calculation using the cosine rule for 4-fluoro-aniline, where θ,[7] the angle between the dipole axis of the - NH_2 group and the plane of the ring is known. The aim is to obtain a calculated value for the molecule and the value is used later in the thesis. Fig. I.1a) shows the moment directions and I.1b) is a vector diagram for the calculation.



a) 4 F - C_6H_4-NH_2

b) vector diagram

C-F = m_1 = 1·45,[4] C - NH_2 = m_2 = 1·50,[4] θ = 48°,[7] μ = resultant moment

Fig.I.1.

$$\mu^2 = m_1^2 + m_2^2 - 2m_1\, m_2 \cos(180 - \theta)$$
$$= 1{\cdot}45^2 + 1{\cdot}50^2 + 2 \times 1{\cdot}45 \times 1{\cdot}50 \cos 48^\circ$$
$$= 7{\cdot}265$$
$$\therefore \underline{\mu = 2{\cdot}70D}$$

I.2. Inductive and Mesomeric Effects. (I_σ, I_π, M).

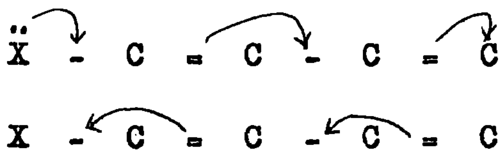
As the interpretation of dipole moments concerns the electronic effects which occur in organic molecules, it is necessary to define these effects.

The inductive effect I_σ concerns σ electrons and describes the tendency for a substituent to attract or repel electrons according to its electronegativity without changing the arrangement of electron pairs in the molecule. The effect decreases with distance from the source of the disturbance and may be represented:-[9a]

$$\begin{array}{ccccccccc} \delta- & & \delta+ & & \delta\delta+ & & \delta\delta\delta+ & & \\ X & \longleftarrow & C & \longleftarrow & C & \longleftarrow & C & & (-I_\sigma) \\ \delta+ & & \delta- & & \delta\delta- & & \delta\delta\delta- & & \\ X & \longrightarrow & C & \longrightarrow & C & \longrightarrow & C & & (+I_\sigma) \end{array}$$

δ^+ and δ^- denote small fractions of a charge unit.

The mesomeric effect, which occurs only in unsaturated molecules, describes the tendency of the substituent to extend the conjugation path by rearranging the electron pairs in the unsaturated molecules. This involves either donation of an electron to the molecule or acceptance of an electron from the molecule. It may be depicted as follows:-



(+ M)

(- M)

For halogen atoms attached to aromatic molecules, an inductive effect concerning π-electrons or I_π effect is important. It has been attributed to repulsion between the π-electrons on the substituted carbon atom and the halogen lone pair electrons (Fig.2)[10] and also to unfavourable penetration of filled orbitals containing the same type of electrons.[11]

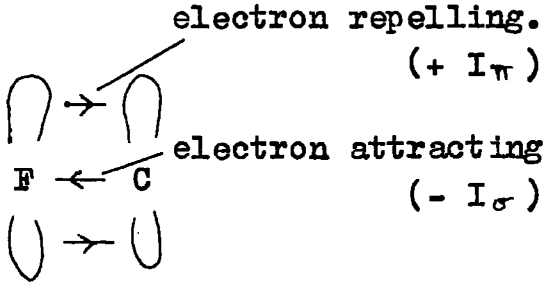
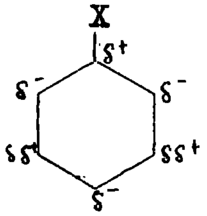
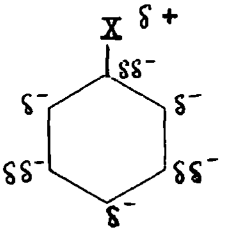


Fig.I.2

The changes in π electron density caused by + I_π and + M substituents in aromatic molecules may be shown as follows:-



+ I_π



+ M

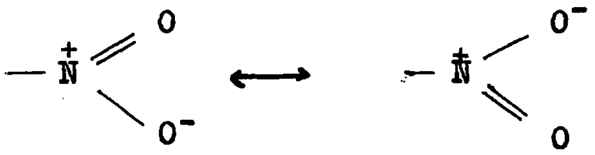
i.e. the + I_π effect removes π electrons from the position of substitution, building up electron density at o- and p- positions, reducing it slightly at m-positions. For the + M effect, valence bond theory predicts an increase in density at o- and p- and no change in m-positions, and molecular orbital theory predicts a slight increase in electron density at the m-position also.

Burdon[12] has used the + $I\pi$ effect of the halogens to rationalise nucleophilic substitutions in polyfluoro- and polychoro-aromatic systems. (see later).

I.3. The Electronic Ground State of the Substituent Groups.

From a molecular orbital standpoint, when resonance interaction is + M, the occupied orbital of the substituent associates with the molecular orbitals of the π- electrons of an aromatic nucleus increasing the electron density in the ring. Where it is - M, the π-orbitals of the substituent interact with the π-orbital system of the ring to give a π- system covering the ring and the substituent and the electron density in the ring is reduced. Both effects are conditioned by overlap of the orbital of the substituent and the P_π orbital of the carbon atom linked to it.

In the nitro group the three sp^2 hybrid orbitals of the nitrogen atom overlap with the carbon atom of the ring and two oxygen atoms to form σ bonds. The remaining p-orbital of the nitrogen atom, which at this stage will be doubly-occupied, can then release one of its electrons to fill the singly occupied orbital of one of the oxygen atoms, and form a π -bond with the singly occupied orbital of the other. Thus a valence-bond description of the group is as a resonance hybrid

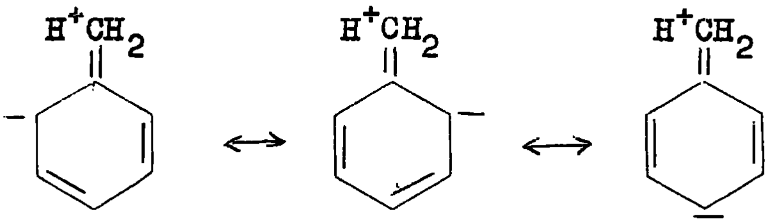


The formal structures are of equal energy and the two N-O bonds are identical. The three atoms bonded to the nitrogen are coplanar. For resonance with the ring to occur, overlap between the unhybridised p-orbitals of the nitrogen atom and of the α ring carbon atoms must be reasonably large, and therefore, for maximum possible overlap, the nitro group must become coplanar with the ring. It is not likely that the group will assume a fixed planar configuration as there will be the usual repulsion between already filled orbitals superimposed upon the resonance effect. It seems most likely that there will not be a random free rotation of the nitro group about the C - N bond but that there will be a preference for orientations near to coplanarity with the ring. The formyl (-CHO) group can be described on a similar basis except that its group moment is situated mainly in the C = O bond whereas that of the nitro group acts in the direction of the C - N bond. Both groups have $-I_\sigma$ and -M effects.[9]

In amines ($-NH_2$, $-NHCH_3$, $-N(CH_3)_2$), the bonding is more complex. In aliphatic amines the orbitals of the nitrogen atom can best be considered sp^3 hybridised and the lone pair occupies an sp^3 hybrid. When linked to an aromatic system the nitrogen orbitals must rearrange to give more p character if there is to be any interaction with the orbitals of the conjugated system. This would lead to a flatter disposition of the bonds of the nitrogen atom and a conformation with the two hydrogen atoms as nearly as possible coplanar with the ring. It is highly improbable that the lone pair becomes a pure p orbital as p-phenylene diamine and benzidine should in that case have a zero dipole moment and they do not.[4] Because of the resonance effect, therefore, the lone pair will have more p character in aromatic than in saturated aliphatic amines and there will be a preference for orientations in which the axis of this orbital makes a large angle with the plane of the ring. Each group has a $-I_\sigma$ inductive effect but this is outweighed by its strong + M effect.[9]

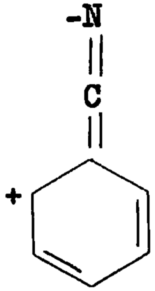
The H - O - H angle in water should be 90° if the bonding of the oxygen atom was pure P. The experimental value is 104½°, and Coulson [29] explains this by saying that, since H - H repulsions can only open out the angle to 95°, the bonding cannot be pure P. A slight admixture of S will give more strongly overlapping orbitals and involve an opening out of the angle. An assumption of a C- O - H angle of 115° in phenols has previously been made,[23,28] based on X-ray analyses and electron diffraction measurements, and this further opening out of the angle will require a larger proportion of S, The C - O - C angle in anisoles has been assumed to be 120°.[28] The axis of the remaining P orbital is at right angles to the plane of the oxygen atom and the two atoms to which it is linked so that the position is very similar to that arising for the nitro group, maximum overlap being attained when the two bonds from the oxygen atom are coplanar with the ring. The -OH group differs from the amino groupings in that it is not essential for a change of state of hybridisation to occur in order to achieve this. The group has a stronger $- I_\sigma$ effect and a weaker + M effect than the amino group.[9] The alkoxy and thiol groups can be discussed on a similar basis.

An alkyl group joined to a phenyl gives a molecule of small moment, which is shown by the moments of p-substituted toluenes to have its negative end toward the ring. The mechanism by which this shift of electrons occurs is termed hyperconjugation for which polar structures may be written as follows:-



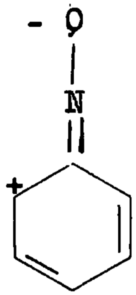
The methyl group also has a $+ I_\sigma$ effect.

The nitrile group is a linear sp hybridised group which is unlikely to be affected by steric or planarity factors. Its - M resonance may be described in terms of small contributions from polar structures such as the following:



It has a strong - I_σ effect.

The C - N - O angle in p-iodonitrosobenzene, a monomer, has been shown to be 125°.[14] It has been suggested by Smyth [29] that the angle is probably widened by resonance to 180°. This was indicated but not definitely established by the moments of the p-halogen and p-nitronitrosobenzenes, as the agreement between the observed and calculated values for p-nitro-nitrosobenzene points to linearity of the group dipoles.[29] A contributory resonance structure for nitrosobenzene is shown.



I.4. Dipole Moment Literature.

The dipole moments of numerous fluorine-containing aliphatic and aromatic compounds have been measured, by various methods.[4]

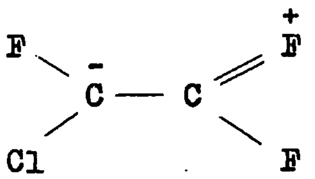
The following measurements were made in a study of the dipole moments in the vapour state, and molecular structures, of some highly fluorinated aliphatic hydrocarbons and ethers:[15]

CF_3Cl, 0·46; CF_3Br, 0·65D; CF_3I, 0·92D; CF_2CBr_2, 0·66 D.

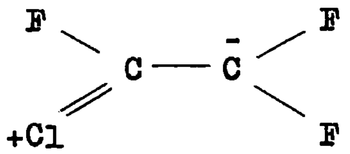
These moments are much larger than would be expected on the basis of the small differences between the four methyl halides in the vapour state,[4] from which the expected moment for, say CF_3Cl, should be less than 0·1D,

CH_3F, 1·82D; CH_3Cl, 1·88D; CH_3Br, 1·80D; CH_3I, 1·64D,

and were explained in terms of the induced charge shift resulting from the differences between the polarisabilities of the halogens. A value of 0·38D for the dipole moment of chlorotrifluoroethylene in the vapour state when the expected value was 0·1D was obtained in a study of aliphatic fluorine containing compounds. This was taken to indicate that contributions from structures such I are favoured over II to the extent of contributing 0·3D to the molecule



I

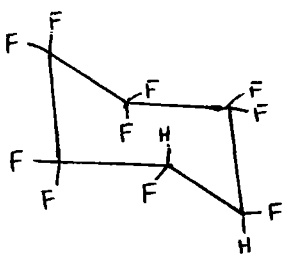


II

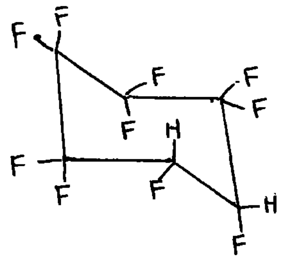
This conclusion was supported by evidence of the shortening of the C - F distances in various chlorofluorides.

Allocations of structure to several decafluorocyclohexanes have been confirmed by measurement of their dipole moments in benzene.[17,18] The following values were obtained for perfluorocyclohexane, un decafluorohexane and two 1H:2H decafluorocyclohexanes:

C_6F_{12}, 0D; C_6HF_{11}, 1·64D; $C_6H_2F_{10}$ (b.p.91°), 2·59D; $C_6H_2F_{10}$ (b.p. 70°), 0·88D.



I. b.p. 70°



II. b.p. 91°

The expected dipole moment of the two equivalent cis structures (1Ha:2He and 1He:2Ha), calculated from that of the decafluoride, is 2·69D. This is in reasonable agreement with the experimental value found for the isomer of b.p. 91° (II). In the case of the isomer of b.p. 70o(I) the low dipole moment (0·88D) confirmed that this structure must have the trans structure and that the conformation with the 2 axial hydrogen atoms predominates.

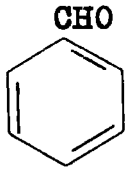
As the dipole moments of C_6F_5X compounds are studied in this thesis, it is necessary to examine previous dipole moment evidence concerning o-, p-, and polysubstituted benzenes. A determination of the dipole moments of p-halo toluenes, anisoles, and anilines, showed that the interaction moments were least for the fluorine-containing compounds.[8] Interaction moments are the differences between observed and calculated moments caused by interactions of the resonance effects of the substituents. The dipole moments of a series of p-fluoro aromatic compounds were then measured and the values used in determination of AR - X - AR bond angles in compounds such as p.p'-difluorodiphenyl ether because the low interaction moments would make the errors which might arise from interaction moments least for fluorine.[19] Halobenzenes with p-substituted - M groups show evidence of resonance interaction which is again small for fluorine. From a table of values of these compounds,[20] it is noted that the observed value for p-$F.C_6H_4NO_2$ (2·63D) is only 0·11D (4·4%) greater than the calculated value (2·52D). The contributing resonance structures can become much more important when a strongly attracting - M substituent is para to a strongly donating + M substituent, e.g. p-NO.C_6H_4.NMe_2, 6·90D;[4] (calculated value, 4·49D).

The dipole moments observed for o-dihalobenzenes are consistently lower than the calculated values. This discrepancy, often called the 'ortho effect', is about 1/3 as large for fluorine as for chlorine and increases with increasing size and polarisability of the halogen atoms.[2b] See Table I.2.

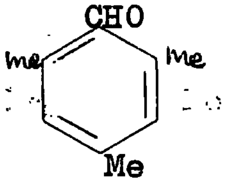
	Observed(D)	Calculated(D)
o-$C_6H_4F_2$	2·38	2·53
o-$C_6H_4Cl_2$	2·27	2·74
o-$C_6H_4Br_2$	2·10	2·67
o-$C_6H_4I_2$	1·70	2·24

Table I.2.

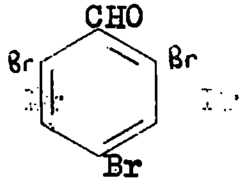
The chlorine atoms in o-$C_6H_4Cl_2$ and the bromine atoms in o-$C_6H_4Br_2$ have been shown to be bent out of the plane of the ring by 18° [20] which would account for some decrease in moment. o-$C_6H_4F_2$ is unlikely to be sterically affected and it has been shown that the ortho effect can be accounted for entirely by mutual inductive effects for all the o-halobenzenes.[21] Smith [22] has used dipole moment measurements to study the effects of o-halogen atoms and o-methyl groups on nitro, amine, formyl, and acetyl groups attached to a benzene ring. After allowances were made for the inductive effects of each dipole upon the electron clouds of the other substituents, it was found that one o-chlorine atom lowers the nitro group moment (4·01D) by 0·38D, and two o-bromine atoms lower it by 0·69D. This was explained by steric inhibition of resonance, partially in o-$ClC_6H_4NO_2$ and fully in 2,4,6-tribromonitrobenzene. The methyl group had much less effect and reduced the nitro group by only 0·16D. Two o-methyl groups were shown to have little effect on formyl and acetyl groups attached to benzene whereas two o-bromines cause considerable inhibition of resonance:-



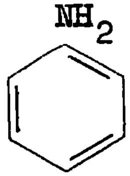
2·92D



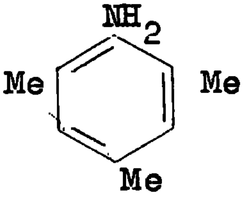
2·96D



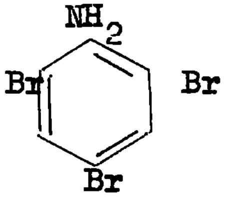
2.53D



1·53D



1·45D

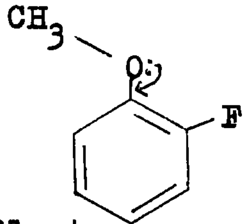


1·73D

The reverse was shown to be the case in aniline derivatives i.e. the effect caused by methyl groups is greater than that caused by bromine atoms. As the atomic radius of the bromine atom is only slightly larger than a methyl group it was inferred that the characteristics of the groups concerned, as well as their sizes, were significant, i.e. as repulsions between a halogen atom and an oxygen atom of the nitro or formyl groups are likely to be stronger than those between a halogen and hydrogen atom, the effective radius of a halogen atom may be smaller with respect to the approach of a hydrogen atom than with respect to that of an oxygen atom, while the reverse will hold for a methyl group. A comparison of the observed dipole moments for o-halo anisoles with the calculated moments has shown that the double bond character of the ring to oxygen bond is sufficient to lock these molecules in a trans configuration,[23] e.g.

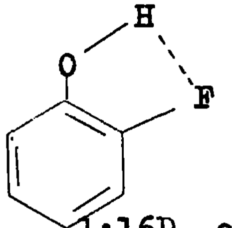
o-F.C_6H_4.OCH_3, 2·31D; calculated values: trans, 2·45D;
cis, 0·43D; free rotation, 1.78D.

The dipole moment values of the o-halophenols show that between 85-90% of these molecules have the -OH group in the cis position due to intramolecular hydrogen bonding. The configurations of the anisoles and phenols may be shown as follows:-



2·31, trans.

o-fluoroanisole

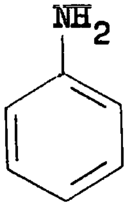


1·16D, cis.

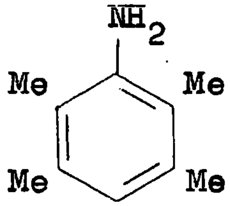
o-fluorophenol

.... indicates hydrogen bonding

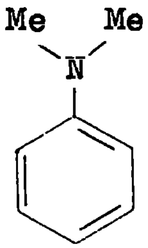
Studies of the dipole moments of polysubstituted benzenes are of particular relevance to this thesis. The classical studies of polymethyl substituted benzenes by Hampson and his co-workers [24,25] showed how the resonance of various groups could be strikingly inhibited by the presence of two o-methyl groups in their durenyl and mesityl derivatives, e.g. they found that the moment of aminodurene is 1·39D, as compared with 1·53D for aniline, and the dipole moment of dimethyl mesidine is 1·03D compared with 1·58D for dimethylaniline, i.e.



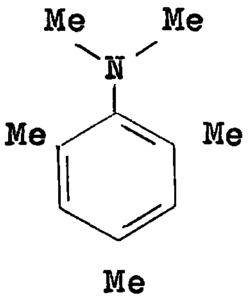
1·53D



1·39D



1·58D



1·03D

When both the 1- and 4-positions in durene contain polar substituents the differences between the moments of the durene and benzene derivatives are even more pronounced. The dipole moments of p-amino, p-hydroxy and p-dimethylamine nitrodurene are 4•98D, 4•08D, and 4•11D, respectively, compared with 6•10D, 5•04D, and 6•87D for the corresponding benzene derivatives.[24,25]

In the polychlorobenzenes, the ortho or inductive effect which explained the dipole moment values of o-dihalobenzenes is again evident. The observed and calculated values in Table I.3 for chloro-substituted benzenes were obtained by Smyth:-[26]

Substituents	Observed(D)	Calculated(D)
$1,2\text{-}Cl_2$	2•27	2•74
$1,2,3\text{-}Cl_3$	2•31	3•16
$1,2,3,4\text{-}Cl_4$	1•90	2•74
$1,2,3,5\text{-}Cl_4$	0•65	1•58
Cl_5	0•88	1•58
$(CH_3), Cl_5$	1•55	1•95
$(C_2H_5),Cl_5$	1•50	1•95

Table I.3.

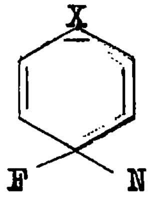
The moment of $1,2,3,4\text{-}C_6H_2Cl_4$ can be treated as the vector sum of the 2- and 3-C-Cl bonds. Its moment is considerably lower (by 0•84D) than the calculated value and lower than O-$C_6H_4Cl_2$ (2·27D) by 0·37D because of further induction of the 2- and 3- chlorines by the 1- and 4- chlorines. Thus, when the 2- and 3- chlorine atoms have one chlorine atom O- to them, they are O- to each other, the moment is lowered by 0·4D; and, when the 2- and 3- chlorine atoms have two O- chlorine atoms each, the moment is lowered by twice this amount. If the value for C_6H_5Cl (1·58D) is subtracted from that of 1,2,3-$C_6H_3Cl_3$ it should be equal to the moment of 1,2,3,5-$C_6H_2Cl_4$, i.e. 2·31 - 1·58 = 0·73D. The difference between this calculated value and the observed value (0·65D) is no more than the probable error. The observed moment of 1,2,3,5-$C_6H_2Br_4$ is about the same (0·7D)[4] for similar reasons. The moment of C_6Cl_5H, in the absence of induction, should be the same as C_6H_5Cl. The observed moment, however, is 0·88D, and is a measure of the inductive effects of the four chlorine atoms. This value is important because the value of the corresponding fluoro compound, C_6F_5H, is measured in this thesis. As C_6Cl_5H differs from $C_6Cl_5(CH_3)$, and $C_6Cl_5(C_2H_5)$ only in lacking the alkyl group, the moments of these compounds would be expected to be about 0·88 + 0·37 = 1·25D, ($C_6H_5(C_2H_5)$ = $C_6H_5(CH_3)$ = 0·37D), whereas they are in fact about 0·3D higher. A value has been obtained for $C_6Cl_5(OH)$ (2·14D) [4] which is close to the calculated value (2·27D) and again much higher than the value expected for C_6Cl_5H = 0·88D. Dipole moment values for C_6Cl_6, C_6F_6, and 1,2,3,4-$C_6H_2F_4$ have been obtained using the randomly oriented solid pellet technique.[27] The results were surprising in that C_6Cl_6 and C_6F_6 were shown to be polarised, and the value obtained for 1,2,3,4-$C_6H_2F_4$ (2·43D) is close to the calculated value (2.53D), whereas induction would be expected to lower this moment. It would be of interest to measure the dipole moments of the latter compound and other tri- and tetra-fluorobenzenes in CCl_4 solution, in order to check the latter value and to provide more information concerning ground state electron distribution in fluoroaromatic compounds.

PART II

CHAPTER II: DISCUSSION.

II.1. Introduction

There is considerable current interest [30] in the chemical properties of the series of polyfluoroaromatic compounds C_6F_5X, where X is any substituent, and the electric dipole moments of some members of this series have been determined in order to examine the trends in ground state electron distribution for different X substituents.



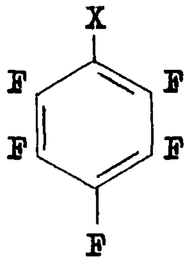
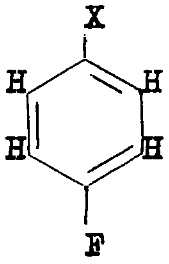
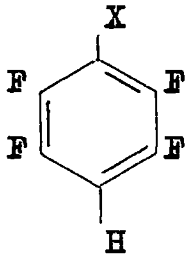
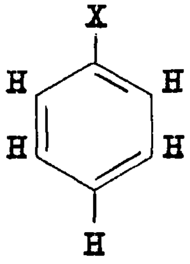
N = nucleophile

X = any substituent

Fig.II.1.

As the reactivity of a C_6F_5X compound towards nucleophilic replacement of fluorine depends on the difference in stability between the ground state and an intermediate of the type shown in Fig. II.1, it was considered that an attempt to examine ground state stability, as determined by the trends in electron distribution, which would be indicated by the dipole moment values, might lead to a clearer picture of reactivity and orientation of substitution in these compounds.

The Series which have been Measured and Calculated:

Series: I II and III IV V

Series I, II, and IV have been measured. Series III has been obtained by calculation using values from the literature.[4] Series V has been obtained from the literature.[4]

X = Substituent Group = NO_2, CN, NO, CHO, NH_2, NHMe, NMe_2, OH, OMe, SH, CH_3.

The C_6F_5X series (I) was the first to be measured. In a C_6F_5X molecule, the 2- and 3-(C-F) bond moments can be regarded as cancelling the 5- and 6-(C-F) bond moments. The dipole moment of the molecule will therefore be the vector sum of the 4-(C-F) bond moment and the X group moment, and will be a measure of the effects of the 2,3, 5, and 6-fluorine atoms on the 4-fluorine atom and the X group, and of this atom and group on each other. The 4.F.C_6H_4X series II was also prepared and measured, in order to provide comparative values for the resultant moments of a 4-(C-F) bond and X group, when not attached to a polyfluorinated ring. In a 4.F.C_6H_4.X molecule the four C-H bond moments will cancel across the ring, and the dipole moment is equal to the vector sum of the two substituent groups, as in the C_6F_5X series.

The dipole moments of some of the compounds in series II had been measured before,[4,19] but not in carbon tetrachloride which was the solvent used in all determinations. It is normally accepted that use of the same solvent and conditions provides a sound basis for the comparison of dipole moment values. Benzene is the solvent most frequently used in dipole moment determinations, but this could not be used for these measurements because it forms π-complexes with polyfluoro-aromatic compounds.[31] Carbon tetrachloride was used because of its good solvent properties, non-polarity, and the likelihood of no interaction between the halogen atoms of the solvent and solute.

Values for the 4.F.C_6H_4.X series (III) were also obtained by vector calculation, using values from tables [4] for the 4-(C-F) bond moment and the X group moment, as a check on the measured values of series II. Where the dipole axis is acting at an angle to the ring, the angle values used were those used by Smith [7] in similar calculations.

It was then decided to prepare, and measure the dipole moments of,the 2,3,5,6-H.C_6F_4.X series (IV) in order to examine the effect of 2,3,5- and 6-fluorine atoms on an X substituent when no 4-fluorine atom is present. The 2- and 3-(C-F) bond moments will cancel with the 5- and 6-(C-F) bond moments and the dipole moment will be the vector sum of the 4-(C-H) bond moment and the X group moment. There is some doubt as to the value and sign of the C-H bond moment in aromatic molecules, but its value is small, and the dipole moment of C_6H_5X is normally regarded as the group moment of X [2c] i.e. the X group moment includes the small moment of the 4-(C-H) bond. Thus the dipole moment of a 2,3,5,6-H.C_6F_4.X compound can be regarded as the X group moment. This procedure is adopted in this thesis. Of course, when the dipole moment of a p-disubstituted benzene is calculated from the values of two mono-substituted benzenes as in series III, any contributions from the C-H bonds will cancel. The values for the C_6H_5X series (V) have been obtained from tables [4] in order to provide comparative values for the X group moment when not attached to a 2,3,5,6-tetrafluoro substituted ring.

Table II.1. Dipole Moment Results in Debyes (D).

Series I		Series II		Series III	(C-X, θ, S, T,%EP, P)
C_6F_5		$4.F.C_6H_4$			
$-NH_2$	2·85	$-NH_2$	2·69	2·66	(1·50,48°,CCl_4,25°,0,196)
$-NHCH_3$	3·02	$-NHCH_3$	2·93	2·92	(1·67,41°, B ,25°,0,259)
$-N(CH_3)_2$	2·52	$-N(CH_3)_2$	2·91	2·90	(1·59,34°, B ,25°,0,299)
$-OH$	2·11	$-OH$	1·99	2·29	(1·46,76°,CCl_4,10-60°, 5,193)
$-OCH_3$	2·11	$-OCH_3$	2·14	2·13	(1·25,76°,CCl_4,25°,0,254)
$-SH$	1·44	$-SH$	1·20	-	
$-CH_3$	1·83	$-CH_3$	1·79	1·80	(0·35, 0°,CCl_4,25°,5,251)
C_6F_5		$4F.C_6H_4$			
$-NO$	1·39	$-NO$	-	1·72	(3·17, 0°, B ,25°,0,181)
$-CN$	2·34	$-CN$	2·67	2·57	(4·02, 0°,CCl_4,25°,5,233)
$-NO_2$	1·94	$-NO_2$	2·69	2·55	(4·00, 0°,CCl_4,25°,0,183)
$-CHO$	1·59	$-CHO$	2·13	-	
Series IV		**Series V**			
$2,3,5,6-H.C_6F_4$		C_6H_5			
$-NH_2$	1·74	$-NH_2$	1·50		
$-NHCH_3$	1·96	$-NHCH_3$	1·67		
$-N(CH_3)_2$	1·54	$-N(CH_3)_2$	1·59		
$-OCH_3$	1·47	$-OCH_3$	1·25		
$-NO_2$	3·28	$-NO_2$	4·00		
$-CN$	3·62	$-CN$	4·02		
C_6F_5H	1·34	$-F$	1·45	(1·47)	(1·45,0°,CCl_4,20°,5-25,180)

Also measured was C_6H_5F = 1·47D.

The dipole moments of Series I, II, and IV have been measured experimentally, and Series III has been calculated by vector summation using the C-X values given and C-F(4) as 1·45D (see p. 4 for an example of vector summation).

All C-X values are taken from McClellan's Dipole Moment Tables,[4] (measured as C_6H_5-X).

θ = angle between the moment anxis and the plane of the ring.[7]

S = solvent used for the measurement.

T = temperature °C used for the measurement.

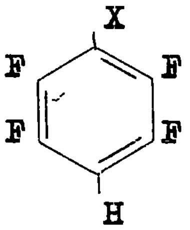
%EP = the % of the electron polarisation allowed for the atom polarisation.

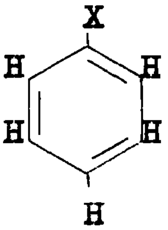
The series V values are those used for the substituent groups C-X in series III.

II.2. Results : Trends.

The following trends can be observed from Table II.1, (1) when the dipole moment values of the 2,3,5,6-H.C_6F_4.X series (IV) are compared with the corresponding values of the C_6H_5X series (V), and (2) when the values of the C_6F_5X series (I) are compared with the corresponding values of the 4.F.C_6H_4.X series:-

(1) 2,3,5,6-H.C_6F_4.X C_6H_5X





(a) The values of the 2,3,5,6-H.C_6F_4.X compounds in which X has a +M effect, are greater than the values of the corresponding C_6H_5X compounds e.g.

2,3,5,6-H.C_6F_4.NH_2(1·74D) $>$ $C_6H_5NH_2$(1·50D) by 0·24D(16%)

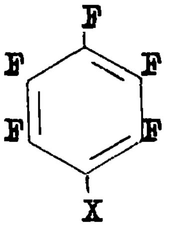
Exception: 2,3,5,6-H.C_6F_4.NMe_2(1·54) $<$ $C_6H_5NMe_2$(1·59D) by 0·05D (3%)

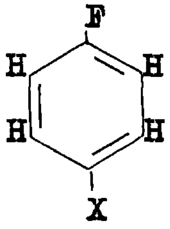
(b) The values of the 2,3,5,6-H.C_6F_4.X compounds, in which X has a -M effect, are less than the values of the corresponding C_6H_5X compounds e.g.

$2,3,5,6\text{-}H.C_6F_4.CN(3{\cdot}62D) < C_6H_5CN(4.02D)$ by 0·4D(10%)

(c) The value of C_6F_5H (1·34) is less than C_6H_5F (1·45) by 0·11D (8%).

(2) <u>C_6F_5X</u> <u>$4F.C_6H_4.X$</u>





(a) The values of the C_6F_5X compounds in which X has a +M effect are approx. equal to the values of the corresponding $4F.C_6H_4.X$ compounds.

Exception: $C_6F_5NMe_2(2{\cdot}52D) < C_6H_5NMe_2(2{\cdot}90D)$ by 0.38D(13%)

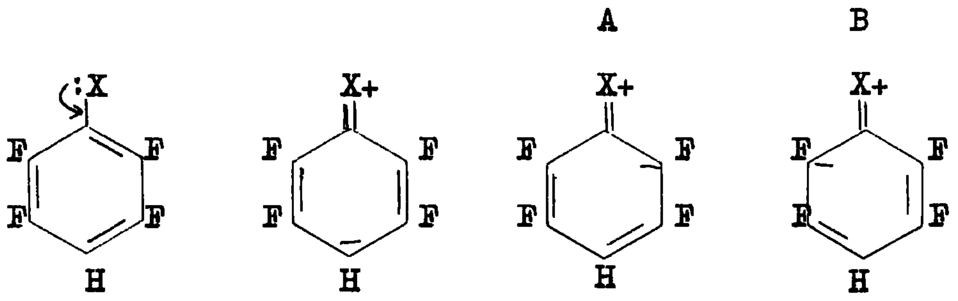
(b) The values of the C_6F_5X compounds in which X has a -M effect are less than the values of the corresponding $4F.C_6H_4.X$ compounds e.g.

$C_6F_5CN(2{\cdot}34D) < 4F.C_6H_4.CN(2{\cdot}67D)$ by 0·33D (12%)

II.3. Discussion of +M Substituents in 2,3,5,6-HC_6F_4X and C_6F_5X.

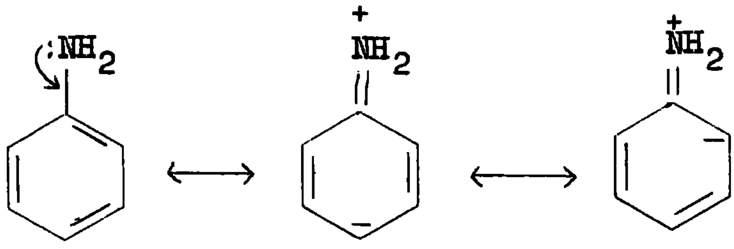
(a) 2,3,5,6-$H.C_6F_4.X$ compounds. - In the compounds in this series where X is NH_2, NHMe, OH, etc. the substituent X group moments are directed towards the ring, at an angle to the plane of the ring, and the main contribution to the moment is that of the lone pair of electrons on the nitrogen or oxygen atom conjugating with the π-electron cloud of the ring and causing an increase in π-electron density at the ortho and para positions.

We have seen that, in general, the moment values for the 2,3,5,6-$H.C_6F_4X$(+M) series (IV) are greater than the corresponding C_6H_5X(+M) values i.e. the X group moments are increased when attached to the 2,3,5,6-tetrafluorophenyl nucleus. It is possible to explain this by postulating that the presence of ortho fluorine atoms in the 2,3,5,6-$H.C_6F_4.X$ series would cause repulsion, by a $+I_\pi$ effect, of the π-electrons donated by the (+M)X group, and lead to a greater concentration of π-electrons at the 4-(C-H) bond (where there is no $+I_\pi$ repulsion from the hydrogen) without an actual increase in the amount of charge movement, i.e.



with very little contribution to the resonance hybrid from structures A and B. This would mean that the same amount of π-electron cloud had moved a greater distance, and, as the dipole moment is a measure of the product of charge and distance, this would lead to an increase in dipole moment.

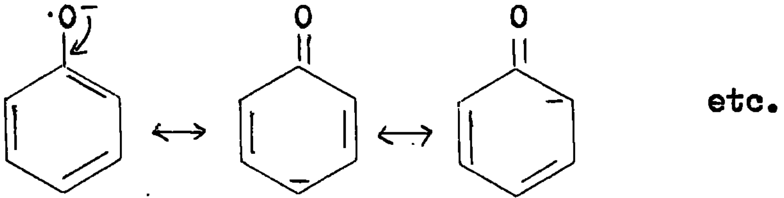
There is evidence to suggest that this explanation is not the correct one: (1) During the preparation of the compounds studied, it was found that the 2,3,5,6-tetrafluoro and pentafluoroanilines will only form salts with dry HCl gas in anhydrous ether and these salts are hydrolysed by water, i.e. the base strengths of the fluoro anilines are lower than that of aniline. This suggests that stronger resonance contributions of the type,



etc.

occur in polyfluoroanilines than in aniline.

(2) The ionisation constant of C_6F_5-OH is much greater than that of C_6H_5OH (C_6F_5OH: Ka = $3{\cdot}0 \times 10^{-6}$; C_6H_5OH + Ka = $1{\cdot}3 \times 10^{-10}$),[32] which suggests that the anion formed when a phenol loses a proton is being stabilised more effectively, by contributions of the type,



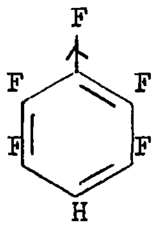
in $C_6F_5O^-$ than in $C_6H_5O^-$.

(3) $C_6F_5NH_2$ requires 220° C for replacement offluorine by NH_2^- [33] whereas $C_6F_5NO_2$, where the nitro group is electron attracting, reacts with ammonia at room temperature.[34]

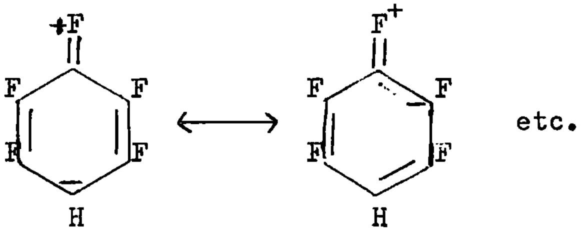
Each of these three points suggests that, where substituent group X has a +M effect, there is increased electron movement into the ring rather than the same amount of electron movement over a greater distance. There is no reason why the 4-(C-H) bond should not accept increased π-electron cloud and the dipole moment values of the 2,3,5,6-tetrafluoro compounds containing +M substituents can therefore be explained on the basis of increased resonance with the ring π-system.

An alternative explanation can be suggested from a consideration of the strong -Iσ inductive effects of the ortho fluorine atoms. The resultant group moment of the OH group in a phenol consists of a -Iσ contribution, directed away from the ring, due to the greater electronegativity of the oxygen atom, and a larger contribution towards the ring, due to the group's +M effect. The inductive effects of the ortho fluorine atoms could be considered to reduce the inductive contribution of the C-O bond, without changing the amount of +M donation. Thus although the contribution to the group moment due to the +M effect of the group is unchanged, that due to the -Iσ effect is reduced, and the resultant group moment will be increased. The reduction of the $N(Me)_2$ group moment in 2,3,5,6-$H.C_6F_4.NMe_2$ is considered later.

(b) <u>C_6F_5H.</u> - The 4-(C-F) bond moment in C_6F_5H can be regarded as the dipole moment of the molecule. The bond moment is directed radially away from the ring and is the resultant of (a) a large contribution due to the -Iσ effect of the fluorine atom, and (b) a smaller contribution directed into the ring due to the +M effect of the fluorine atom, i.e.



(a)



(b)

The 4-(C-F) bond moment in C_6F_5H is 1·34D compared with 1·45D in C_6H_5F, and this reduction can be explained by a decrease in the inductive contribution of the 4-fluorine atom in C_6F_5H caused by the $-I\sigma$ inductive effects of the two fluorine atoms ortho to this atom. It is possible to postulate an increase in the +M effect of the 4-fluorine atom, which would also lead to a decrease in the 4-(C-F) bond moment, but the +M effect of fluorine is small compared with that of the amino group, and an increase in the +M effect of fluorine would have little effect.

The reduction of the 4-(C-Cl) bond moment in C_6Cl_5H is much greater than that of the 4-(C-F) bond moment in C_6F_5H (1·58D in C_6H_5Cl to 0·88D in C_6Cl_5H) and has been similarly explained.[26] This is as expected, because the difference between the calculated and observed values for o-difluorobenzene has been shown to be only about 1/3 as large as it is for o-dichlorobenzene.[6]

(c) C_6F_5X compounds. - The dipole moment of a C_6F_5X compound with X a +M substituent can be regarded as the vector sum of the 4-(C-F) bond moment and the X group moment. If a vector calculation is made for $C_6F_5NH_2$, taking the 4-(C-F) bond moment as 1·34D (as in C_6F_5H), θ as 48° as in $C_6H_5NH_2$ [7] (θ = angle

The NH_2 and NHMe groups will achieve greater resonance by a change in hybridisation. The orbitals of the nitrogen atom will rearrange and move closer to sp^2 hybridisation, i.e. closer to co-planarity with the ring, and the orbital containing the lone pair of electrons will move closer to pure P thereby achieving increased overlap with the ring π-electron system. In OH groups etc. the P orbital of the oxygen at right angles to the plane of the ring simply overlams to a greater extent with the ring π-electron system in order to achieve increased resonance.

By analogy with the explanation suggested for the +M substituents, the moment value of $C_6F_5CH_3$ suggests that increased hyperconjugation of the methyl group also occurs when the methyl group is attached to the pentafluorophenyl nucleus i.e. using 4-(C-F) = 1·34D, the expected moment is 1·34 + 0·35 = 1·69D, whereas the actual moment of $C_6F_5CH_3$ is 1·83D.

Similar results have been noted for polychoro compound of the type C_6Cl_5X where X = OH, CH_3, ahd C_2H_5. The relevant dipole moment values are:- [26,4]

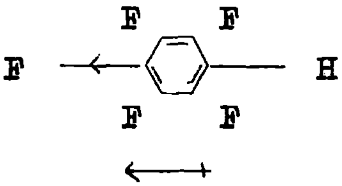
$C_6Cl_5.OH$	2·14D	$C_6H_5.CH_3$	0·35D
$C_6Cl_5.CH_3$	1·55D	$C_6H_5.C_2H_5$	0·35D
$C_6Cl_5.C_2H_5$	1·50D	$4Cl.C_6H_4OH$	2·14D
$C_6Cl_5.H.$	0·88D	$C_6H_5.Cl$	1·58D

The 4-(C-Cl) bond moment in C_6Cl_5H is 0·88D and the moments of $C_6Cl_5.CH_3$ and $C_6Cl_5.C_2H_5$ would be expected to be about 0·88 + 0·35 = 1·23D, whereas they are about 0·3D higher, and the moment of $C_6Cl_5.OH$ is actually equal to that of $4.Cl.C_6H_4.OH$ when the expected value would be much less that this on the basis of the 4-(C-Cl) bond moment in C_6Cl_5H. This suggests a similar explanation to that proposed earlier for the fluoro analogues i.e. increased resonance for OH and increased hyperconjugation of CH_3 and C_2H_5. The C-Cl bonds in polychloro compounds are known to be bent out of the plane of the ring (see Section I.4). This complicates the above calculations slightly but will not affect the conclusions.

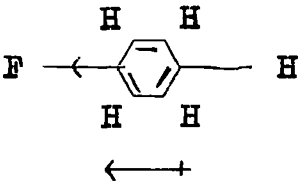
In both the 2,3,5,6-tetrafluoro and pentafluoro series, the X = NMe_2 values are less than the corresponding $C_6H_5NMe_2$ and $4F.C_6H_4NMe_2$ values. This is explained by steric interactions between the NMe_2 group and the ortho fluorine atoms. The fluorine atoms force the group away from the plane of the ring and decrease the resonance interaction of the group with the ring π-system, thus reducing the group moment.

II.4. Discussion of -M Substituents in 2,3,5,6-H.C_6F_4.X and C_6F_5X.

(a) Fluorobenzenes:

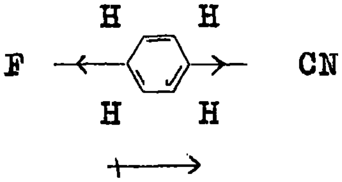


1·34D

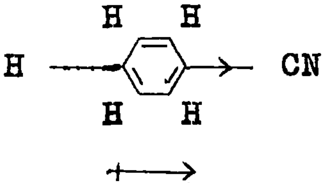


1·45D

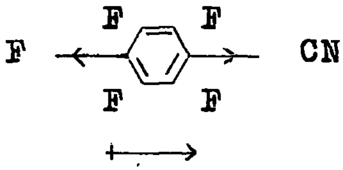
(b) Nitriles:



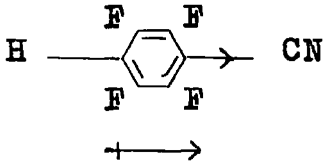
2·67D



4·02D

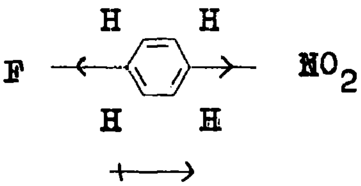


2·34D

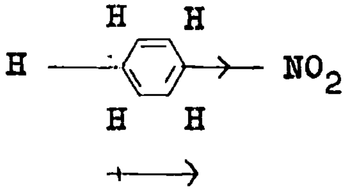


3·62D

(c) Nitro-compounds:



2·69D



4·00D

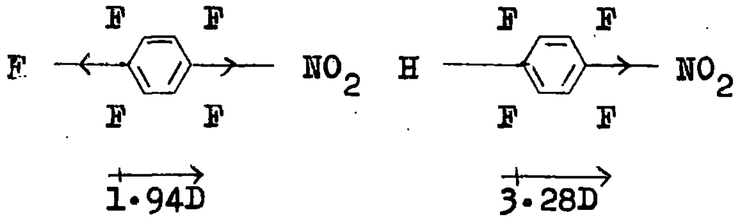


Fig.II.2 - Dipole Moments, and Bond and Group Moment directions for nitriles, nitro-compounds, and fluorobenzenes.

—<— Direction of bond and group moments which make contributions to the resultant dipole moment.

←—+ Direction of the resultant dipole moment of the molecule.

The group moments of nitro and nitrile groups are directed radially away from the benzene ring and both groups normally have group moments of approx. 4D to which their -Iσ and -M effects make contributions. Because of the similarities between these groups it is convenient to discuss the effects of -M substituents attached to the 2,3,5,6-tetrafluorophenyl and pentafluorophenyl nuclei by examination of the dipole moment values of compounds containing these groups. The relevant compounds and values are shown in Fig.II.2.

From Fig.II.2(b), the effect of the 2,3,5, and 6-fluorine atoms on the nitrile group in 2,3,5,6-H.C_6F_4.CN,

$= \mu(C_6H_5CN) - \mu(2,3,5,6\text{-}H.C_6F_4.CN) = 4{\cdot}02 - 3{\cdot}62 = 0{\cdot}4D$,

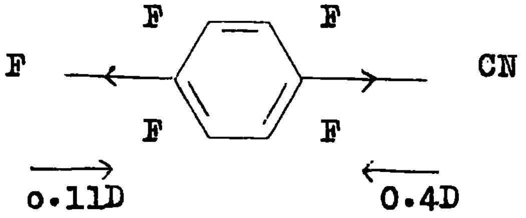
i.e. a reduction of 0·4D in the -CN group moment.

From Fig.II.2(a), the effect of the 2,3,5, and 6-fluorine atoms on the 4-(C-F) bond in C_6F_5H,

$= \mu(C_6H_5F) - \mu(C_6F_5H) = 1{\cdot}45 - 1{\cdot}34 = 0{\cdot}11D$,

i.e. a reduction of 0·11D in 4-(C-F) bond moment.

C_6F_5CN contains both a nitrile group and a 4-(C-F) bond affected by 2,3,5, and 6 fluorine atoms, and its dipole moment can be regarded as the vector sum of the nitrile group moment and the 4-(C-F) bond moment. As the nitrile and 4-(C-F) moments are directed in opposition to each other, the reduction in the nitrile group moment should partly cancel the reduction in the 4-(C-F) moment in C_6F_5CN as shown below:



and a difference of 0·4 - 0·11 = 0·29D would be expected for $\mu(4F.C_6H_4CN) - \mu(C_6F_5CN)$. The observed value for

C_6F_5CN is 2·34D, and the observed value of $4F.C_6H_4.CN$ is 2·67D, hence the difference

$$= \mu(4F.C_6H_4.CN) - \mu(C_6F_5CN) = 2{\cdot}67 - 2{\cdot}34 = 0{\cdot}33D,$$

Using the calculated value of $4F.C_6H_4.CN$ the difference

$$= \mu(4F.C_6H_4.CN) - \mu(C_6F_5CN) = 2{\cdot}57 - 2{\cdot}34 = 0{\cdot}23D,$$

These differences have the correct sign and are of the order expected. It is possible to make the same calculations for the nitro-compounds:

The effect of the 2,3,5, and 6-fluorine atoms on the nitro group in $2,3,5,6\text{-}H.C_6F_4NO_2$

$$= \mu(C_6H_5NO_2) - \mu(2,3,5,6\text{-}H.C_6F_4.NO_2) = 4{\cdot}00 - 3{\cdot}28$$
$$= 0{\cdot}72D$$

Thus, a difference of 0·72 - 0·11D = 0·61D would be expected for $\mu(4.F.C_6H.NO_2) - \mu(C_6F_5NO_2)$. The observed value for $C_6F_5NO_2$ is 1·94D, and hence, for the observed value of $4F.C_6H_4.NO_2$ (2·69D),

$$\mu(4F.C_6H_4.NO_2) - \mu(C_6F_5NO_2) = 2{\cdot}69 - 1{\cdot}94 = 0{\cdot}75D$$

Using the calculated value of $4.F.C_6H_4.NO_2$ (2·55D)

$$\mu(4F.C_6H_4.NO_2) - \mu(C_6F_5NO_2) = 2{\cdot}55 - 1{\cdot}94 = 0{\cdot}61D$$

Again the differences have the correct sign and are of the order expected. Thus, the differences between the observed and expected moment values for C_6F_5X, where X is -M, can be calculated on the basis of the C_6F_5H and 2,3,5,6-$H.C_6F_4.X$ moment values, i.e. the effects of the 2,3,5, and 6-fluorine atoms on the substituents are the same in C_6F_5X as in C_6F_5H and 2,3,5,6-$H.C_6F_4.X$.

We suggest that, in 2,3,5,6-$H.C_6F_4.CN$, the decrease in the nitrile group moment is caused by inductive withdrawal of σ electrons by the ortho fluorine atoms. The same kind of ortho inductive effects have been suggested earlier to explain the smaller reduction of the 4-(C-F) bond moment in C_6F_5H, and we conclude that the nitrile group and 4-(C-F) bond are similarly affected by the fluorine atoms ortho to them in C_6F_5CN.

The difference between the dipole moment values for 2,3,5,6-$H.C_6F_4.X$ and C_6H_5X is much greater for X = NO_2 than for X = CN, i.e.

$$\mu(C_6H_5NO_2) - \mu(2,3,5,6\text{-}H.C_6F_4.NO_2) = 4{\cdot}00 - 3{\cdot}28 = 0{\cdot}72D$$

and $\mu(C_6H_5CN) - \mu(2,3,5,6\text{-}H.C_6F_4.CN) = 4{\cdot}02 - 3{\cdot}62 = 0{\cdot}4D$

even though $C_6H_5NO_2$ and C_6H_5CN have very close dipole moment values. This is probably due to steric inhibition of the resonance of the nitro group by the fluorine atoms ortho to it. For maximum resonance to occur, the nitro group must be coplanar with the ring and examination of a scale molecular model of $C_6F_5NO_2$ shows that the oxygen atoms of the nitro group almost touch the ortho fluorine atoms, when the group is oriented coplanar with the ring. It has been suggested,[22] in a study of ortho effects and dipole moments, that interactions between oxygen and halogen atoms will be more strongly repulsive than those between, say, hydrogen and halogen atoms. The effective radius of a fluorine atom would therefore be larger with regard to the approach of an oxygen atom,and we suggest that this causes repulsion between the ortho fluorine atoms and the nitro group, and hence steric inhibition of the resonance of the nitro group. Thus, inductive and steric effects must be postulated to explain the dipole moment value of $C_6F_5NO_2$.

The difference between the values of $4F.C_6H_4.CHO$ and C_6F_5CHO (table II.1)

$$= \mu(4F.C_6H_4.CHO) - \mu(C_6F_5CHO) = 2.13 - 1.59 = 0.54D$$

This difference is very high and suggests that ortho steric effects are occurring for the formyl group also. Examination of a scale molecular model of C_6F_5CHO indicates non-coplanarity of the formyl group and confirms this conclusion.

It has been suggested [2C] from a study of the dipole moments of p-halo and p-nitro/nitroso benzenes that the C-N-O angle in nitrosobenzenes is 180°.

$$\mu(4F.C_6H_4.NO) - \mu(C_6F_5.NO) = 1{\cdot}72 - 1{\cdot}39 = 0{\cdot}33D,$$

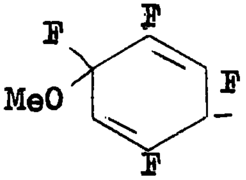
using the calculated value for $4.F.C_6H_4.NO$ in table II.1. Assuming the C-N-O angle is 180°, this value can be compared with the corresponding difference for nitriles (0·23D), and is of the same order. The value for C_6F_5NO can therefore be explained on the basis of the inductive effects of the 2,3,5,6-fluorine atoms as is that of C_6F_5CN.

II.5. Dipole Moments and Reactivity.

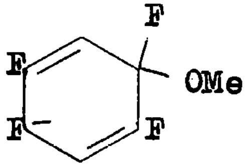
A phenyl group can act as electron source or as an electron sink, depending on the characteristics of the group or groups attached to it. It would be expected that the -Io effects of the fluorine atoms attached to the pentafluorophenyl and 2,3,5,6-tetrafluorophenyl nuclei, would lead to the removal of electrons from the nuclei and cause them to act as electron sinks. From the dipole moment results obtained, we have seen that the nuclei do act as electron sinks, leading to ease of electron movement into the nucleus for electron donating substituents, and causing difficulty in the withdrawal of electrons from the ring for electron attracting substituents.

The reactivity of a C_6F_5X compound, towards nucleophilic replacement of fluorine, depends on the difference in stability between the reaction intermediate (see Fig.II.1) and the ground state of the C_6F_5X compound. The ground state stability of a C_6F_5X compound depends on its ground state electron distribution which Burdon [35] has termed the electron deficiency because of the electron-sink effect of the five fluorine atoms, e.g. C_6F_5H is more stable than C_6F_6 [35] because it has less electronegative fluorine substituents and is therefore less electron deficient. When substituent X has a +M effect we would expect the electron donation indicated by the dipole moment results, to reduce the electron deficiency of the ring, thus increasing the ground state stability and decreasing the reactivity towards nucleophilic replacement of fluorine. We would therefore expect $C_6F_5NH_2$, for example, to be more stable, i.e. less reactive, than C_6F_6, and this is found to be the case.[33] Similarly, when X has a stronger electron attracting effect than fluorine we would expect the reactivity of C_6F_5X towards nucleophilic replacement of fluorine to be greater than C_6F_6. Again, this is found to be the case, e.g. $C_6F_5NO_2$ is considerably more reactive than C_6F_6.[33, 34] We have suggested that when substituent groups with +M effects are attached to a pentafluorophenyl nucleus, this electron donation is increased, with the 4-(C-F) bond as presumably the main repository, and this is important in view of present theories concerning nucleophilic substitution reactions in polyfluoro aromatic systems.

In an analysis of the ground state and spectroscopic evidence of the different inductive and mesomeric effects of the halogens, Hedder et.al.[10] question the assumption that inductive effects are necessarily the same for saturated and unsaturated systems, and show how spectroscopic evidence indicates the presence of a $+I_{\pi}$ effect for the halogens (see Section I.2). Burdon has used this concept to rationalise nucleophilic substitution reactions in polyfluoro, polychloro, and polyfluoropolycyclic aromatics,[35] explaining orientations of the replacement of fluorine in a series of tetrafluorobenzenes [12] by suggesting that transition state contributor [i] is more stable than [ii]:-



[i]



[ii]

i.e. that carbon bearing a negative charge is less stable when it is attached to fluorine than when it is attached to hydrogen. For the kind of resonance effect postulated earlier to explaine the dipole moment results of C_6F_5X compounds in which X has a +M effect, to take place, the $+I_{\pi}$ effect cannot be the most important effect in the ground state, as π-electrons would be repulsed by the 4-(C-F) bond if it was. The quantity of electron cloud which the 4-(C-F) bond is required to accept in the ground state is much less than that of the electron pair set free by the formation of the bond between the nucleophile and the carbon atom, which the 4-(C-F) bond is required to accept in contributor [ii] for example, and it is likely that the $+I_\pi$ effect of the fluorine will be more important in the latter case, and the larger charge will be repelled. Dewar[36] has suggested that π- inductive effects are more important in excited states of molecules than in their ground states which confirms this suggestion.

The dipole moment values of $C_6F_5NMe_2$ and 2,3,5,6-$H.C_6F_4.NMe_2$ have been explained by steric inhibition of the resonance of the NMe_2 group, whereas no steric effects are indicated by the dipole moment values of the corresponding compounds containing NH_2 and NHMe groups. As electron donation by substituent groups with +M effects is directed to the o- and p-positions of a pentafluorophenyl nucleus, we would expect that C_6F_5X compounds containing these groups would be deactivated in o- and p-positions towards the approach of a nucleophile. The tendency should therefore be for the nucleophile to replace fluorine at the m-position i.e. as the delocalisation of the lone pair increases, the m/pratio for replacement of fluorine will increase, and the reactivity of the molecule towards nucleophile replacement of fluorine will decrease. The m/p ratio for

$C_6F_5NH_2$: C_6F_5NHMe : $C_6F_5NMe_2$ is 7 : 1 : 0·07.[37] Thus, although, as expected, $C_6F_5NMe_2$ is the more reactive, C_6F_5NHMe is distinctly more reactive than $C_6F_5NH_2$, which would not be expected on the basis of the ground state stability of these molecules. The reduction in intensity ϵ_{max} in going from $C_6F_5NH_2$ to $C_6F_5NHCH_3$ and $C_6F_5N(CH_3)_2$ in the ultra-violet spectra results in table II.2A has been interpreted as showing that the $-N(CH_3)_2$ group is hindered to a lesser extent.[37]

	λ_{max}, $m\mu$,	ϵ_{max}.
$C_6F_5NH_2$	215	18,000
$C_6F_5NHCH_3$	225, 217	16,800
$C_6F_5N(CH_3)_2$	217	10,000

Table II.2A.

For $C_6H_5\overset{+}{N}H_3$ which cannot back-donate electrons, and for $C_6F_5NH_2$, which can, the wavelengths and intensities have been obtained for bands II and III of the benzene spectrum with C_6H_6 values for comparison [38] and are shown in Table II.2B.

	Band II ᴺ		Band III ᴺ	
	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
$C_6H_5NH_2$	230	8,600	280	1,430
$C_6H_5\overset{+}{N}H_3$	203	7,500	254	160
C_6H_6	203·5	7,400	254	204

ᴺ Braude notation[40]

Table II.2B.

From the intensity and wavelength values quoted it can be seen that the table II.2A figures relate to band II of the benzene spectrum. Intensity changes have been used previously [39] to show steric hindrance of resonance in ortho alkylated anilines, though normally a decrease in band III intensity and hypsochromic shifts in wavelength for bands II and III are used to indicate the disappearance of resonance, e.g. $C_6H_5\overset{+}{N}H_3$ shows a nine-fold intensity decrease from $C_6H_5NH_2$, and shifts to the blue of 27 mμ in band II and 16 mμ in band III. An examination of the band III figures for $C_6F_5NHCH_3$ etc. may therefore be of value. Changes in absorption frequency and intensity can be attributed to a change in the ground electronic state, a change in the upper electronic state, or a combination of the two. If it is accepted that the intensity change in band II for $C_6F_5NH_2/C_6F_5NHCH_3$ does indicate some steric interaction then for $C_6F_5NHCH_3$ this is likely to be due to a change in the upper electronic state as the dipole moment values obtained indicate no steric interaction in the ground state.

PART II

CHAPTER III: RESULTS AND EXPERIMENTAL

III.1 Introduction.

When a molecule is subjected to a uniform electric field it will become polarised. This polarisation is made up of three independent contributions as follows:-

1) The field displaces the electrons with regard to the nucleus giving riseto an induced dipole moment. This is called the ELECTRON POLARISATION (E.P.).

2) If the molecule contains polar bonds, its constituent atoms will carry different effective charges, and in an electric field the nuclei will be displaced relative to one another. This is known as ATOM POLARISATION (A.P.) and is much smaller than electron polarisation. Both A.P. and E.P. are temperature independent.

3) Molecules with a permanent dipole moment will tend to orientate themselves along the field but this tendency will be opposed by thermal motions. This is called the ORIENTATION POLARISATION (O.P.), and is temperature dependent.

4) The total polarisation of the molecule is the sum of these three terms, i.e.

$$TP = OP + AP + EP$$

The sum of (AP + EP) is sometimes called the distortion polarisation.

III.2. Calculation of Electric Dipole Moments.

(1) The following equation, due to Debye, relates the total polarisation (TP) to the molecular dipole moment, :

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = TP = \frac{4\pi N}{3}\left(\gamma + \frac{\mu^2}{3kT}\right) = EP + AP + OP \qquad \text{III.1}$$

M = molecular weight, d = density, N = Avogadro's number, k = Boltzmann constant, T = absolute temperature, ϵ = dielectric constant, $\frac{4}{3}\pi N \gamma$ represents the polarisation a molecule would have in the absence of a permanent dipole and this may be divided up into atom polarisation and electron polarisation; $4\pi N\mu^2/9kT$ is an expression for the orientation polarisation, i.e.

$$OP = \frac{4\pi N\mu^2}{9kT}$$

hence,

$$\mu = \sqrt{\frac{9kT.\ OP}{4\pi N}}$$

and at 25°C,

$$\mu = \underline{0{\cdot}2212\sqrt{OP}} \qquad \text{III.2}$$

Thus, the molecular dipole moment is obtained by substituting the value of the orientation polarisation in equation III.2.

(2) The electron polarisation (EP) of a molecule is equal

to its molar refraction R (extrapolated to very low frequency), i.e.

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = EP. \qquad n = \text{refractive index.}$$

(3) There is no experimental way of obtaining the atom polarisation (AP) of a molecule that is simple enough for routine use. Fortunately the AP is small and is approx. 5-10% of the magnitude of EP. For some time this relationship was widely used to estimate AP. Today most workers prefer to neglect AP, since EP, as determined from the refractive index for the sodium D-line is several per cent larger than the extrapolated zero-frequency value. The D-line molar refraction is commonly used as an approximation for AP + EP and this is the procedure used in this thesis.

(4) The expression for the polarisation of a solution, due to Debye is:-

$$P = P_1f_1 + P_2f_2 = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M_1f_1 + M_2f_2}{d} \qquad \text{III.3.}$$

where P_1 P_2 f_1 and f_2 are the total polarisations and mole fractions of solvent and solute respectively.

Halverstadt and Kumler [41] used specific volumes instead of densities and weight fractions instead of mole fractions. By assuming that the specific volume and dielectric constant of the solution are linear functions of the weight fraction (i.e. $\epsilon = a + \alpha W_2$ and $V = b + \beta W_2$, where a and b are the dielectric constant and specific volume of the solvent, W_2 is the weight fraction of the solute), they derived an expression for the specific total polarisation at infinite dilution of the solute P_2:-

$$P_2 = \frac{3\alpha V_1}{(\epsilon_1 + 2)^2} + \frac{\epsilon_1 - 1}{\epsilon_1 + 2}(V_1 + \beta) \qquad \text{III.4}$$

By plotting ϵ against W_2 and V against W_2, α and β may be evaluated.

In a similar manner the electron polarisation Ep_2 can be expressed as:-

$$Ep_2 = \frac{6\gamma n_1 V_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2}(V_1 + \beta) \qquad \text{III.5}$$

where the assumption is made that $n = n_1 + \gamma W_2$ where n_1 is the refractive index of the solvent.

To obtain dipole moments by measurements on solutions, the dielectric constant, refractive index, and density, of a number of solutions must be determined. By plotting ϵ , V, and n, against W_2, obtaining α , β , and γ , from the graphs, and fitting them in the equations, then the total polarisation and electron polarisation of the compound being studied may be obtained. At low concentrations ($W \ll 0.02$) the plots are usually very close to straight lines,[41] and linear plots of n against W_2 may be obtained at still higher concentrations.

III.3. Physical Measurements.

(a) Dilectric Constant Measurements. Carbon tetrachloride was used as the solvent in all determinations and the dielectric constants of air (ϵ_1) and carbon tetrachloride (ϵ_2) were assumed to be known. The principle used was the measurement of the change in capacitance which occurred when the dielectric of a condenser was changed.

The condenser was the cell (Fig.III.1), the dielectric of which could be changed easily by blowing out with dry nitrogen and replacing with the required solution. If ϵ_3 is the dielectric constant of the solution, and C_1, C_2, and C_3, the capacitances of the cell filled with air, carbon tetrachloride, and solution, respectively, then:-

$$\frac{C_3 - C_1}{C_2 - C_1} = \frac{\epsilon_3 - \epsilon_1}{\epsilon_2 - \epsilon_1}$$

and
$$\epsilon_3 = \left(\frac{C_3 - C_1}{C_2 - C_1}\right)(\epsilon_2 - \epsilon_1) + \epsilon_1$$

$$= \left(\frac{C_3 - C_2}{C_2 - C_1} + 1\right)(\epsilon_2 - \epsilon_1) + \epsilon_1 \qquad \text{III.6.}$$

A heterodyne beat capacitance meter, similar to the one

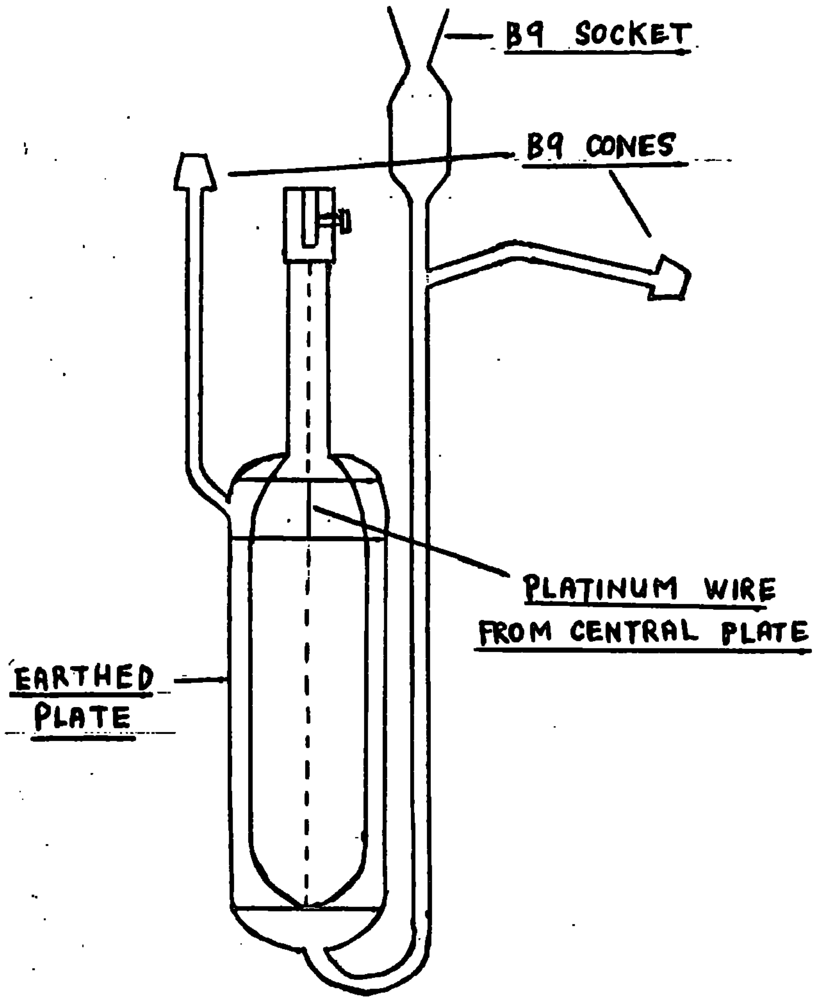


FIG III.1. DIELECTRIC CELL

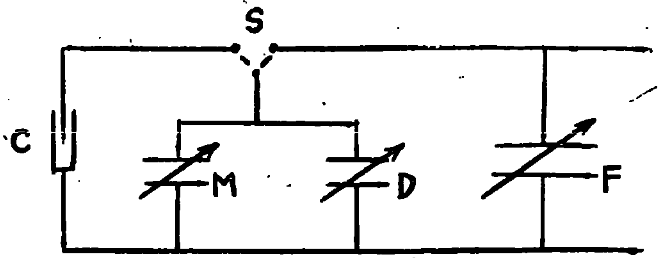


FIG III.2. MEASURING SYSTEM

designed by Hill and Sutton [42] was used to measure the capacitance change in the cell. The measuring system is shown in Fig.III.2. C was the cell, D an air-spaced, uncalibrated, variable condenser, as was F, and M was a calibrated, concentric cylinder, variable condenser, with a micrometer screw, having a capacitance change of 3·38 pfs. per cm. S was a switch by which the cell could be replaced by F and M. The cell was a modified form of the Sayce Briscoe type [43] with plates of platinum burnt onto the glass instead of deposited silver. This made the cell more robust and allowed washing out with strong acid if necessary. The capacitance was about 50 pfs. The cell was immersed in a 25° thermostat bath filled with transformer oil to reduce stray capacitances.

Procedure. The cell was washed out twice with carbon tetrachloride, blowing the solvent out with a stream of nitrogen. The cell was then filled with carbon tetrachloride, making sure that any air bubbles were removed, and allowed to come to thermal equilibrium (10 minutes was usually sufficient). F was then adjusted until the figure of eight was obtained on the cathode ray tube. D and M were then switched in and the figure of eight again obtained by adjustment. The cell was switched back in and the figure of eight again obtained, and then D and M switched in again and adjusted. As changes in capacitance in the circuit containing F and the cell caused slight changes in the frequency of the circuit containing F, D, and M, and vice-versa, it was always necessary to adjust each circuit twice at least. When a steady figure of eight was obtained on both sides of the switch indicating that the capacitances on both sides had the same value, then the reading on M was noted. As M was calibrated in centimeters in length (0 to 2·5) and as the capacitance of M increased as the reading in centimeters decreased it was always arranged that when a balance was obtained with carbon tetrachloride in the cell, M should read approximately 2·4 cms.

The carbon tetrachloride was then blown out with dry nitrogen and the cell filled with the solution under test. The process of adjustment was repeated but this time only F and M were adjusted so that the change in capacitance could be read off on M.

(b) Specific Volume Measurements. A Sprengel type pyknometer of about 4 ml. capacity fitted with ground glass taps to prevent evaporation was used.

Procedure. The dry pyknometer was filled and placed in a 25° C thermostat for 15 min. The meniscus of the liquid was adjusted to the graduation mark by applying a piece of filter paper to the tip of the opposite limb and the pyknometer was removed from the thermostat, dried with tissue paper, and the caps put in place. It was then hung on the balance for 20 min. to allow it to reach hygrometric equilibrium with the atmosphere, and then weighed.

(c) Refractive Index Measurement. A Pulfrich Refractometer with a divided cell, which was cemented by silicone rubber, was used. The refractometer was enclosed in a 25° C air thermostat which consisted of a large box (2 x 2 x 2 ft.) fitted with a glove and a terylene window through which readings could be taken and one could see to make adjustments without opening the box. The box was heated by an electrical sheet heater placed directly in front of a fan. The temperature was controlled by an a/c bridge thermo-regulator with a platinum resistance thermometer as the arm of the bridge inside the box. Temperature differences in particular places did not vary by more than 0.1° C.

Procedure. The solution was placed in one side of the divided cell and carbon tetrachloride in the other. A polythene cap was placed over the top of the cell to prevent evaporation and the liquids allowed to reach thermal equilibrium (usually taking about 20 min.). The extinction angles were read off from the refractometer, and the differences obtained by substraction. As differences rather than absolute refractivities were of primary importance, this technique minimised any errors which might be caused by temperature fluctuations.

III.4 Calculation of Results.

(1) Dielectric Constants. The change in capacitance in the cell was measured on the calibrated condenser M. The dielectric constant of carbon tetrachloride was taken as 2·2280 [44] and that of air 1·0006. The change in capacitance of the cell when filled with air and then with carbon tetrachloride was 28·20 pfs., and was measured by connecting an N.P.L. calibrated condenser in parallel with the cell and finding the necessary change in capacitance to restore the balance when the dielectric was changed from air to carbon tetrachloride.

From equation III.6:-

$$\epsilon_3 = \left(\frac{C_3 - C_2}{C_2 - C_1} + 1\right) (\epsilon_2 - \epsilon_1) + \epsilon_1$$

$\epsilon_1 = 1{\cdot}0006$, $\epsilon_2 = 2{\cdot}2280$, $C_2 - C_1 = 28{\cdot}20$ pfs.

$C_3 - C_2$ was the change in capacitance measured on M.

$$\epsilon_3 = \left(\frac{\Delta C}{28{\cdot}20} + 1\right) \quad 1{\cdot}2274 + 1{\cdot}0006$$

If l is the reading on the condenser in cm., as the capacitance change per cm. was 3·38 pfs., then:-

$$\epsilon_3 = \left(\frac{3\cdot 38\,\Delta l}{28\cdot 20} + 1 \right) 1\cdot 2274 + 1\cdot 006$$

$$\Delta\epsilon_3 = \left(\frac{3\cdot 38\,\delta l}{28\cdot 20} \right) 1\cdot 2274$$

$$\frac{d\epsilon}{dW} = \frac{1\cdot 2274 \times 3\cdot 38}{28\cdot 20} \cdot \frac{dl}{dW}$$

$$\frac{d\epsilon}{dW} = 0\cdot 14711 \frac{dl}{dW}$$

dl/dW is the slope of the graph obtained by plotting the reading on the calibrated condenser against weight fraction. $d\epsilon/dW$ corresponds to α in equation III.4.

(2) <u>Specific Volumes.</u> The volume of the Sprengel Pyknometer was 4·1458 ml.

$$\text{Hence Specific volume} = \frac{4\cdot 1458}{Wg}$$

where Wg is the weight of solution in the pyknometer.

$$V = b + \beta W_2 = \frac{4\cdot 1458}{Wg}$$

$$= \frac{d\left(4\cdot 1458/Wg\right)}{dW_2}$$

Thus β is the slope of the graph of specific volume against weight fraction. After repairs to the pyknometer the volume changed to 4·1544 ml.

(3) Refractive Indices. The relationship between the extinction angle and refractive index of a solution for the refractometer had been found to be:-[45]

1 min. of arc = 1087×10^{-7} for the sodium D-line.

A plot of Δn vs. W gave dn/dW which corresponds to γ in equation III.5.

(4) Total Polarisation. From equation III.4,

$$TP_2 = \frac{3\alpha V_1}{(\epsilon_1 + 2)^2} + \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\ (V_1 + \beta)$$

$\epsilon_1 = 2{\cdot}2280$, $V_1 = 0{\cdot}63123$,[46]

Then $TP_2 = 0{\cdot}10593\,\alpha + 0{\cdot}29044\ (0{\cdot}63123 + \beta)$ III.7.

(5) Electron Polarisation. From equation III.5,

$$EP_2 = \frac{6n_1 \gamma V_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{(n_1^2 + 2)}\ (V_1 + \beta)$$

$V_1 = 0{\cdot}63123$, $n_1 = 1{\cdot}45759$,[46]

Then $EP_2 = 0{\cdot}32450\,\gamma + 0{\cdot}27265\ (0{\cdot}63123 + \beta)$ III.8

(6) Error and Size of Moment. To find the dipole moment the sum of (EP + AP) must be subtracted from TP. If the moment is small large relative errors will result at this

stage. Bradford Thompson[47] has calculated the errors in moment which might arise from 1·7 ml. error in TP or in (EP + AP) for various dipole moments as follows:-

(D)	Error(D)	% Error
0	0·29	
1	0·041	4·1
2	0·020	1·0
3	0·013	0·4
4	0·010	0·25

He notes that both the absolute and relative errors increase as the moment decreases.

III.5. Results.

Specimen of Results and Calculation for Pentafluoronitrobenzene. $C_6F_5NO_2$.

Making up of Solutions.

1) wt.of flask	40·2224	41·3138	31·9376	37·9856
2) wt.of flask + $C_6F_5NO_2$	40·3272	41·5194	32·2301	38·3878
3) wt.of flask + $C_6F_5NO_2$ + CCl_4	80·5092	81·5025	72·5636	78·5183
4) wt.of $C_6F_5NO_2$	0·1048	0·2056	0·2925	0·4022
5) wt.of $C_6F_5NO_2$ + CCl_4	40·2868	40·1887	40·6260	40·1305
6) weight fraction	0·002601	0·005116	0·007200	0·009923

Specific Volume Measurements.

1) wt. of pyknometer + solution	27·1824	27·1828	27·1832	27·1836
2) wt.of pyknometer	20·5856	20·5856	20·5856	20·5856
3) wt.of solution	6·5968	6·5972	6·5976	6·5980
4) specific volume	0·628456	0·628418	0·628380	0·62834

Dielectric Constant Measurements.

1) zero reading (cm.)	2·385	2·385	2·385	2·385
2) solution reading (cm.)	2·322	2·265	2·217	2·155
3) Δc (cm.)	0·063	0·120	0·168	0·230

Refractivity Measurements.

The readings are in minutes and seconds of arc measured on the Pulfrich Refractometer for the Sodium D-line.

1) change in angle	55"	2'00"	2'50"	3'50"
2) $10^{7}\ \Delta\ n$	997	2174	3080	4167

From the graphs (see p. 73a, b, c.):-

$$\frac{d\epsilon}{dw} = \alpha = 3{\cdot}4350, \quad \frac{dv}{dw} = \beta = -0{\cdot}0154, \quad \frac{dn}{dw} = \gamma = 0{\cdot}04167$$

From equation III.7:-

$$TP_2 = M\,[0{\cdot}10593\alpha + 0{\cdot}29044\,(0{\cdot}63123 + \beta)\,]$$

$$= 213{\cdot}07\,[0{\cdot}10593 \times 3{\cdot}4350 + 0{\cdot}29044\,(0{\cdot}61583)]$$

$$= \underline{115{\cdot}64\ \text{ml.}}$$

From equation III.8:-

$$EP_2 = M\,[0{\cdot}32450\gamma + 0{\cdot}27265\,(0{\cdot}63123 + \beta)]$$

$$= M\,[0{\cdot}32450 \times 0{\cdot}04167 + 0{\cdot}27265\,(0{\cdot}61583)]$$

$$= \underline{38{\cdot}66\ \text{ml.}}$$

$$OP_2 = TP_2 - EP_2 = 115{\cdot}64 - 38{\cdot}66 = 76{\cdot}98\ \text{ml.}$$

$$\therefore \mu = 0{\cdot}2212\,\sqrt{76{\cdot}98}$$

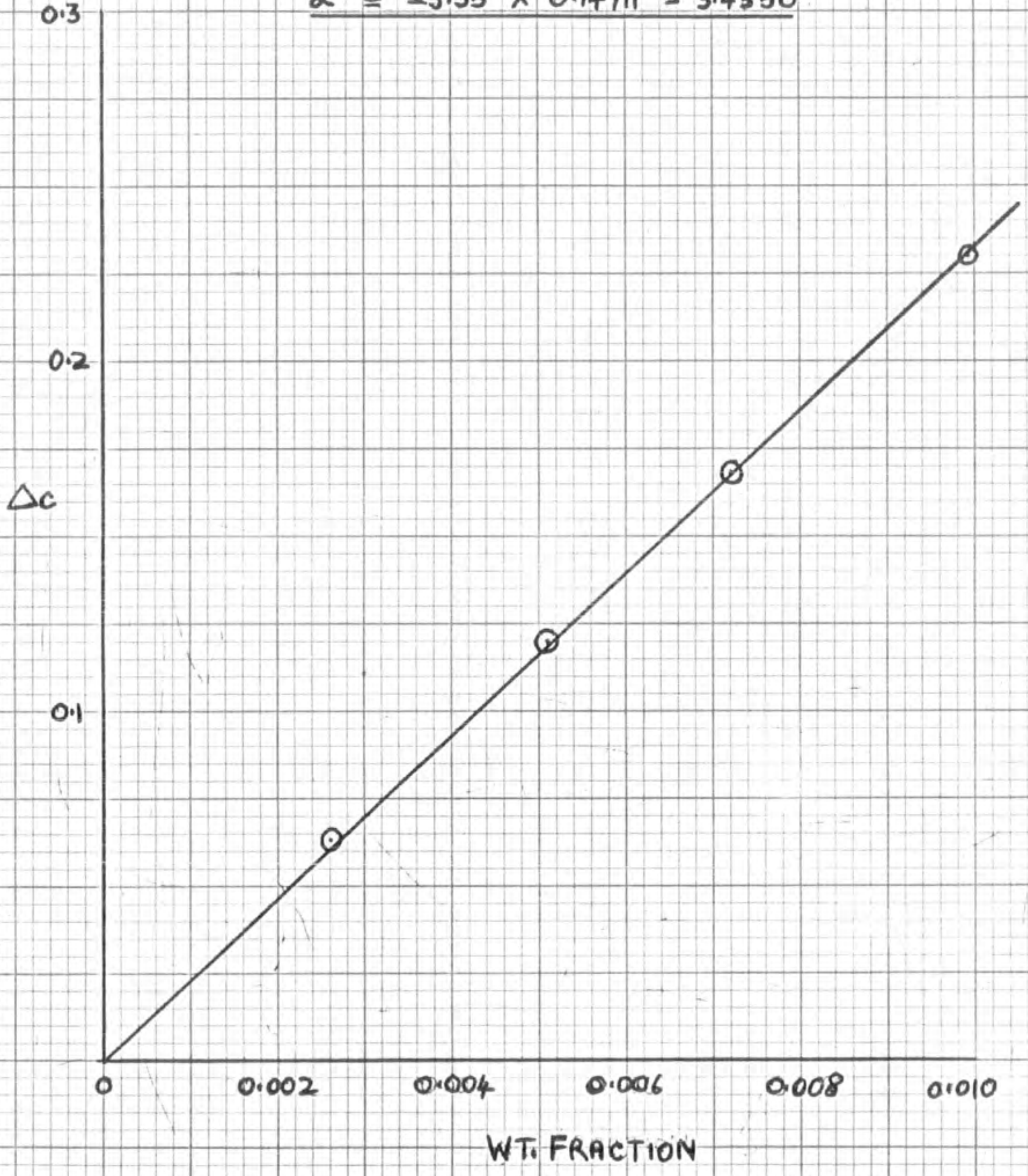
$$\mu = \underline{1{\cdot}94\ \text{D.}}$$

$C_6F_5NO_2$ in CCl_4 at 25°C.

Δc vs. WT. FRACTION

$$\frac{dl}{dw} = \frac{0.2335}{0.01} = 23.35$$

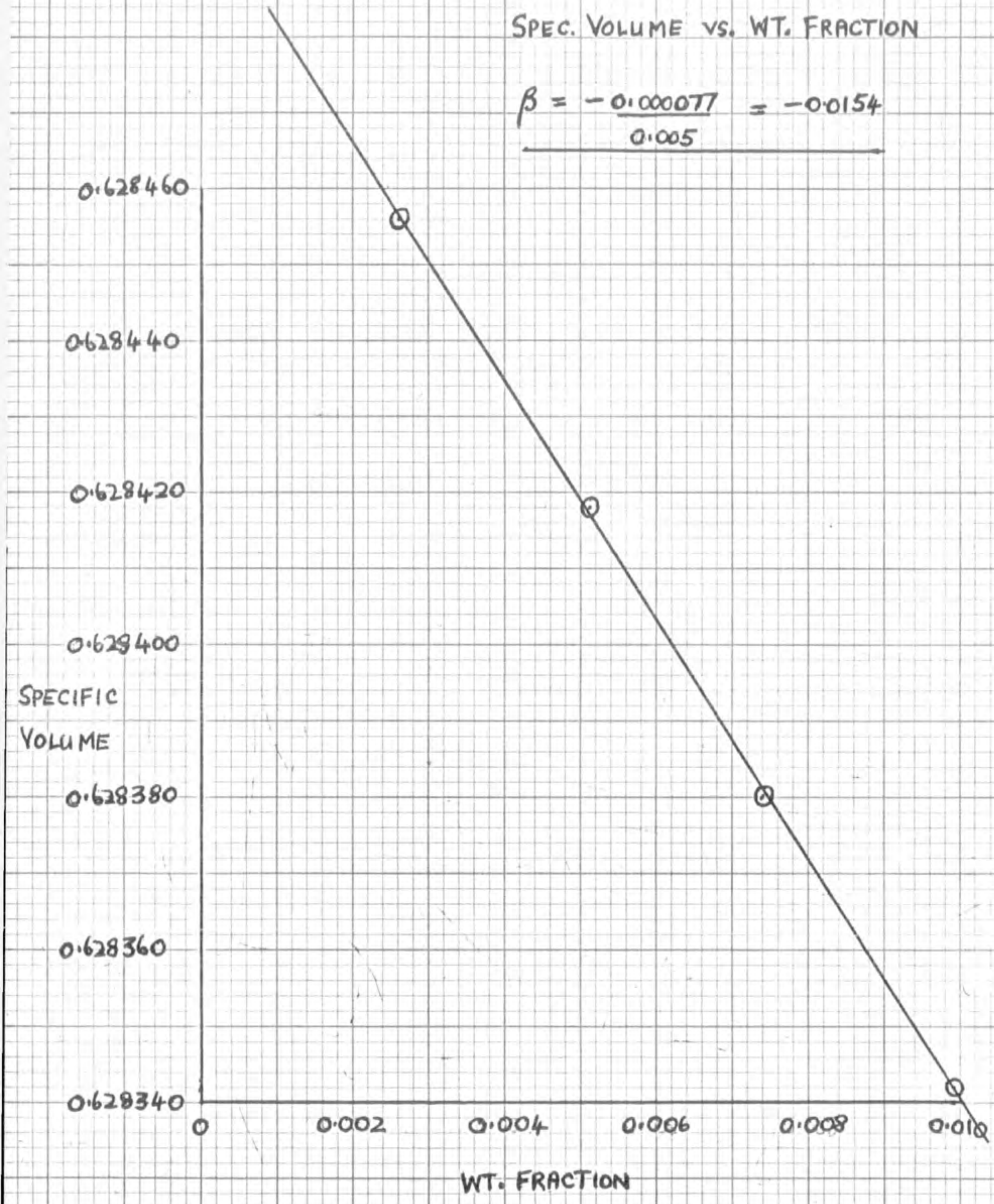
$$\alpha = 23.35 \times 0.14711 = 3.4350$$



$C_6F_5NO_2$ in CCl_4 at 25°C

SPEC. VOLUME VS. WT. FRACTION

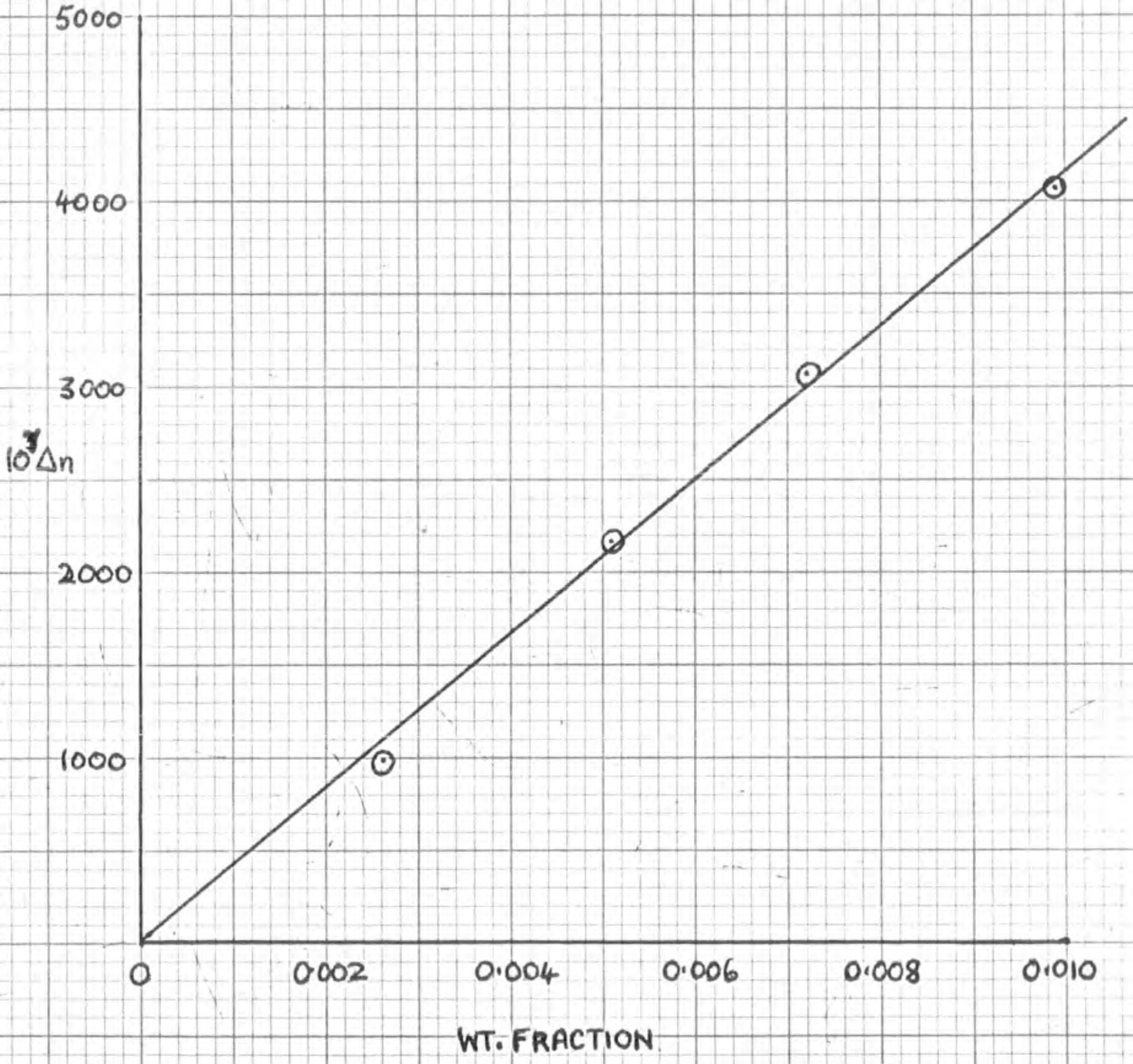
$$\beta = -\frac{0.000077}{0.005} = -0.0154$$



$C_6F_5NO_2$ in CCl_4 at 25°C.

REFRACTIVITY VS. WT. FRACTION

$\gamma = 4167 \times 10^{-5} = 0.04167$



$C_6F_5NH_2$.

10^6 W	V	$10^7 \Delta$ n
2826	0·628504	725
4601	0·628523	1268
8087	0·628561	2174
10481	0·628590	2899

$\frac{d\epsilon}{dw}$ = 8·4691 $\frac{dv}{dw}$ = 0·011 $\frac{dn}{dw}$ = 0·02718

TP_2 = 198·41 ml. EP_2 = 33·67 ml. μ = 2·85D.

C_6F_5NO

10^6 W	V	$10^7 \Delta$ n
2382	0·628504	815
4724	0·628513	1721
7096	0·628532	2536
9445	0·628552	3352

$\frac{d\epsilon}{dw}$ = 1·8904 $\frac{dv}{dw}$ = 0·6071 $\frac{dn}{dw}$ = 0·03533

TP_2 = 76·00 ml. EP_2 = 36·56 ml. μ = 1·39D.

$\underline{C_6F_5H}$

10^6 W	V	$10^7 \Delta n$
2152	0·628647	-1449
5505	0·628799	-3261
8161	0·628914	-4620
9675	0·62900	-5797

$\frac{d\epsilon}{dw}$ = 1·7653 $\frac{dv}{dw}$ = 0·0436 $\frac{dn}{dw}$ = - 0·05975

TP_2 = 64·37 ml. EP_2 = 27·66 ml. μ = 1·34D.

$\underline{C_6F_5OCH_3}$

10^6W	V	$10^7 \Delta n$
2475	0·628647	1631
5749	0·628865	3714
7686	0·629009	4892
10045	0·629172	6431

$\frac{d\epsilon}{dw}$ = 4·4280 $\frac{dv}{dw}$ = 0·068 $\frac{dn}{dw}$ = 0·06431

TP_2 = 133·15 ml. EP_2 = 41·90 ml. μ = 2·11D

C_6F_5NHMe

$10^6 w$	v	$10^7 \Delta n$
2865	0·628656	634
4615	0·628761	1087
7498	0·628914	1721
9412	0·629028	2265

$\frac{d\epsilon}{dw}$ = 8·8634 $\frac{dv}{dw}$ = 0·0484 $\frac{dn}{dw}$ = 0·02355

TP_2 = 223·98 ml. EP_2 = 38·03 ml. μ = 3·02D.

$C_6F_5.CH_3$

$10^6 w$	v	$10^7 \Delta n$
2730	0·628742	1993
4847	0·628904	3533
7662	0·629124	5707
9862	0·629286	7337

$\frac{d\epsilon}{dw}$ = 3·6438 $\frac{dv}{dw}$ = 0·0778 $\frac{dn}{dw}$ = 0·07428

TP_2 = 107·87 ml. EP_2 = 39·59 ml. μ = 1·83D.

C_6F_5OH

10^6W	V	$10^7\Delta n$
2537	0·628494	1268
4060	0·628494	2174
7513	0·628494	3805
9774	0·628494	5073

$\frac{d\epsilon}{dw} = 4{\cdot}7222$ $\frac{dv}{dw} = 0$ $\frac{dn}{dw} = 0{\cdot}05163$

$TP_2 = 125{\cdot}82$ ml. $EP_2 = 34{\cdot}76$ ml. $\mu = 2{\cdot}11D.$

C_6F_5CN

10^6W	V	$10^7\Delta n$
2660	0·628590	1268
5015	0·628685	2355
7451	0·628785	3442
9877	0·628876	4620

$\frac{d\epsilon}{dw} = 5{\cdot}5166$ $\frac{dv}{dw} = 0{\cdot}0384$ $\frac{dn}{dw} = 0{\cdot}04710$

$TP_2 = 150{\cdot}39$ ml. $EP_2 = 38{\cdot}20$ ml. $\mu = 2{\cdot}34D.$

$C_6F_5NMe_2$

10^6W	V	$10^7\Delta n$
2578	0·628761	815
4827	0·629018	1449
7571	0·629277	2174
9735	0·629487	2808

$\frac{d\epsilon}{dw} = 5{\cdot}7667$ $\frac{dv}{dw} = 0{\cdot}1026$ $\frac{dn}{dw} = 0{\cdot}02899$

$TP_2 = 173{\cdot}98$ ml. $EP_2 = 44{\cdot}23$ ml. $\mu = 2{\cdot}52D$

C_6F_5SH

10^6W	V	$10^7\Delta n$
2176	0·628513	181
4332	-	272
7174	0·628523	453
9907	0·628542	544
5366	0·628523	-

$\frac{d\epsilon}{dw} = 1{\cdot}9235$ $\frac{dv}{dw} = 0{\cdot}0045$ $\frac{dn}{dw} = 0.00616$

$TP_2 = 77{\cdot}71$ ml. $EP_2 = 35{\cdot}08$ ml. $\mu = 1{\cdot}44D$

C_6F_5CHO

$10^6 w$	v	$10^7 \Delta n$
1199	0·628494	453
3002	0·628494	906
4435	0·628475	1268
5093	0·628475	1449

$\frac{d\epsilon}{dw} = 2{\cdot}4567$ $\frac{dv}{dw} = 0{\cdot}003$ $\frac{dn}{dw} = 0{\cdot}02898$

$TP_2 = 87{\cdot}15$ ml. $EP_2 = 35{\cdot}75$ ml. $\mu = 1{\cdot}59$D

$2,3,5,6\text{-}H.C_6F_4.NH_2$

$10^6 w$	v	$10^7 \Delta n$
2716	0·628761	181
5682	0·628761	362
7301	0·628895	453
9313	0·628981	634

$\frac{d\epsilon}{dw} = 3{\cdot}3982$ $\frac{dv}{dw} = 0{\cdot}0518$ $\frac{dn}{dw} = 0{\cdot}00652$

$TP_2 = 92{\cdot}19$ ml. $EP_2 = 31{\cdot}10$ ml. $\mu = 1.74$D

$2,3,5,6\text{-}H.C_6F_4.NO_2$

10^6w	v	$10^7\Delta n$
2318	0·628552	815
5074	0·628590	1540
7379	0·628628	2174
9427	0·628666	2718

$\frac{d\epsilon}{dw} = 10{\cdot}640 \quad \frac{dv}{dw} = 0{\cdot}0183 \quad \frac{dn}{dw} = 0{\cdot}02971$

TP_2 = 256·67 ml. EP_2 = 36·43 ml. μ = 3·28D

$2,3,5,6\text{-}H.C_6F_4NMe_2$

10^6w	v	$10^7\Delta n$
1331	0·628694	91
2893	0·628933	181
7652	0·629621	362
9341	0·629860	453

$\frac{d\epsilon}{dw} = 2{\cdot}2361 \quad \frac{dv}{dw} = 0{\cdot}145 \quad \frac{dn}{dw} = 0{\cdot}00481$

TP_2 = 89·30 ml. EP_2 = 41·18 ml. μ = 1·54D

2,3,5,6-H.C_6F_4.NHMe.

10^6W	V	$10^7\Delta n$
1171	0·628599	0
2147	0·628685	0
4347	0·628904	91
6057	0·629152	181

$\frac{d\epsilon}{dw} = 4{\cdot}0308$ $\frac{dv}{dw} = 0{\cdot}095$ $\frac{dn}{dw} = 0{\cdot}00272$

$TP_2 = 114{\cdot}27$ ml. $EP_2 = 35{\cdot}63$ ml. $\mu = 1{\cdot}96D$

4-F.C_6H_4.OMe

10^6W	V	$10^7\Delta n$
3072	0·629324	- 997
5896	0·630128	-2084
7507	0·630550	-2536
10678	0·631452	-3714

$\frac{d\epsilon}{dw} = 6{\cdot}7229$ $\frac{dv}{dw} = 0{\cdot}2756$ $\frac{dn}{dw} = -\ 0{\cdot}03442$

$TP_2 = 123{\cdot}03$ ml. $EP_2 = 29{\cdot}77$ ml. $\mu = 2.14D$

4-F.C_6H_4.Me

$10^6 w$	v	$10^7 \Delta n$
2549	0·629439	- 272
5292	0·630473	- 544
7421	0·631298	- 815
9575	0·632097	-1087

$\frac{d\epsilon}{dw} = 5{\cdot}4136$ $\frac{dv}{dw} = 0{\cdot}3756$ $\frac{dn}{dw} = -\ 0{\cdot}01087$

$TP_2 = 95{\cdot}34$ ml. $EP_2 = 29{\cdot}84$ ml. $\mu = 1{\cdot}79D$

4-F.C_6H_4.OH.

$10^6 w$	v	$10^7 \Delta n$
2877	0·628940	1540
5840	0·629550	3352
8251	-	4710
9704	0·630415	5435
7527	0·629932	-
10044	0·630391	-

$\frac{d\epsilon}{dw} = 6{\cdot}5170$ $\frac{dv}{dw} = 0{\cdot}208$ $\frac{dn}{dw} = -0{\cdot}05652$

$TP_2 = 104{\cdot}72$ ml. $EP_2 = 23{\cdot}60$ ml. $\mu = 1{\cdot}99D$

2,3,5,6-H.C_6F_4.CN

10^6W	V	$10^7\Delta n$
2713	0·628607	997
4148	0·628911	1449
6872	0·629035	2355
9792	0·629302	3080

$\frac{d\epsilon}{dw} = 14\cdot373$ $\frac{dv}{dw} = 0\cdot100$ $\frac{dn}{dw} = 0\cdot03261$

$TP_2 = 303\cdot77$ ml. $EP_2 = 36\cdot76$ ml. $\mu = 3\cdot62D$

2,3,5,6-H.C_6F_4.OMe.

10^6 W	V	$10^7\Delta n$
2650	0·629575	1178
5255	0·628797	2265
8001	0·629092	3442
8666	0·629140	3805

$\frac{d\epsilon}{dw} = 2\cdot3390$ $\frac{dv}{dw} = 0\cdot0935$ $\frac{dn}{dw} = 0\cdot04348$

$TP_2 = 82\cdot54$ ml. $EP_2 = 38\cdot13$ ml. $\mu = 1\cdot47D$

C_6H_5F

$10^6 w$	v	$10^7 \Delta n$
2940	0·629515	- 181
5428	0·630387	- 362
7635	0·631202	- 634
10137	0·632078	- 815

$\frac{d\epsilon}{dw} = 4\cdot1706$ $\frac{dv}{dw} = 0\cdot357$ $\frac{dn}{dw} = -\ 0\cdot00725$

$TP_2 = 70\cdot04$ ml. $EP_2 = 25\cdot67$ ml. $\mu = 1\cdot47$D.

$4.F.C_6H_4.NO_2$

$10^6 w$	v	$10^7 \Delta n$
2694	0.628626	1812
4712	0·629964	3352
7452	0·629216	5345
9212	0·629407	6613

$\frac{d\epsilon}{dw} = 9\cdot5622$ $\frac{dv}{dw} = 0\cdot1164$ $\frac{dn}{dw} = -\ 0\cdot07156$

$TP_2 = 173\cdot57$ ml. $EP_2 = 25\cdot49$ ml. $\mu = 2.69$D

$4.F.C_6H_4.CHO$

$10^6 w$	v	$10^7 \Delta n$
2162	0·628712	1540
5480	0·629474	3714
8485	0·630132	5888
9619	0·630391	6884

$\frac{d\epsilon}{dw} = 6{\cdot}7082$ $\frac{dv}{dw} = 0{\cdot}224$ $\frac{dn}{dw} = -\ 0{\cdot}07029$

$TP_2 = 119{\cdot}03$ ml. $EP_2 = 26{\cdot}11$ ml. $\mu = 2{\cdot}13D$

$4.F.C_6H_4.NH_2$

$10^6 w$	v	$10^7 \Delta n$
2582	0·628902	2899
5424	0·629655	5797
8013	0·630305	8424
9310	0·630620	9874

$\frac{d\epsilon}{dw} = 12{\cdot}063$ $\frac{dv}{dw} = 0{\cdot}256$ $\frac{dn}{dw} = -\ 0{\cdot}1027$

$TP_2 = 170{\cdot}63$ ml. $EP_2 = 23{\cdot}18$ ml. $\mu = 2{\cdot}69D$

4-F.C_6H_4.NMe_2

10^6w	v	$10^7\Delta n$
2062	0·628997	-1993
4683	0·629903	-4348
8446	0·631032	-8153
8862	0·631176	-8424

$\frac{d\epsilon}{dw} = 11{\cdot}298$ $\frac{dv}{dw} = 0{\cdot}302$ $\frac{dn}{dw} = -\ 0{\cdot}09511$

$TP_2 = 204{\cdot}29$ ml. $EP_2 = 31{\cdot}12$ ml. $\mu = 2{\cdot}91D$

4-F.C_6H_4.SH.

10^6w	v	$10^7\Delta n$
2904	0·628965	-3171
5848	0·629531	-6069
7570	0·629874	-7881
9555	0·630333	-9693

$\frac{d\epsilon}{dw} = 1{\cdot}7065$ $\frac{dv}{dw} = 0{\cdot}2064$ $\frac{dn}{dw} = -\ 0{\cdot}10327$

$TP_2 = 54{\cdot}33$ ml. $EP_2 = 24{\cdot}97$ ml. $\mu = 1{\cdot}20D$

$4\text{-F.C}_6\text{H}_4\text{.NHMe}$

$10^6 w$	v	$10^7 \Delta n$
2218	0·628883	-2265
4518	0·629540	-4710
5666	0·629865	-5888
7042	0·630295	-7247

$\frac{d\epsilon}{dw} = 12{\cdot}754$ $\frac{dv}{dw} = 0{\cdot}293$ $\frac{dn}{dw} = -\ 0{\cdot}10327$

$TP_2 = 202{\cdot}68$ ml. $EP_2 = 27{\cdot}34$ ml. $\mu = 2{\cdot}93D$

$4\text{-F.C}_6\text{H}_4\text{.CN}$

$10^6 w$	v	$10^7 \Delta n$
2395	0·629105	1449
4430	0·629563	2174
8304	0·630530	4348
9868	0·630933	5435

$\frac{d\epsilon}{dw} = 11{\cdot}0038$ $\frac{dv}{dw} = 0{\cdot}2445$ $\frac{dn}{dw} = -\ 0{\cdot}05344$

$TP_2 = 171{\cdot}98$ ml. $EP_2 = 26{\cdot}82$ ml. $\mu = 2{\cdot}67D$

III.6. Preparation and Purification of Materials.

Spectroscopic grade carbon tetrachloride was used as the solvent in all determinations. It was stored over molecular sieve and blown out of the storage flask with dry nitrogen.

The infra-red spectrum of each compound was determined and agreed with published data where available as did their melting points and boiling points where applicable. The infra-red spectra of new compounds and 4-fluorobenzonitrile are reproduced in the thesis. Nuclear magnetic resonance spectra of some new compounds were determined and interpreted by Mr. J. Dyson, B.Sc.

The following compounds were available in this laboratory:- $C_6F_5NO_2$, $C_6F_5NH_2$, C_6F_5H, 2,3,5,6-$H.C_6F_4.NH_2$, C_6H_5F. Other C_6F_5X compounds (except X = NHMe, NMe_2, NO) were obtained from the Imperial Smelting Corporation. All $4F.C_6H_4.X$ compounds (except X = NHMe, CN) were obtained from Koch-Light.

The following compounds were purified by crystallisation to constant melting point:- $C_6F_5NH_2$ [33] m.p. 33-34°; 2,3,5,6-$H.C_6F_4.NH_2$ [33] m.p. 30·5-32·5°; $4.F.C_6H_4.NMe_2$ [37] m.p. 34-35·5°.

The following compounds were tested for purity by analytical-scale gas-liquid chromatography, followed by purification, where necessary, by preparative-scale gas-liquid chromatography, and distillation from phosphorus pentoxide of those compounds which do not react with phosphorus pentoxide:- $C_6F_5NO_2$,[34] b.p.159-161°; C_6F_5OMe,[48] b.p. 138-140°; C_6F_5Me,[49] b.p. 116-118°; C_6F_5CN,[50] b.p. 190-192°; C_6F_5SH,[51] b.p. 144°; C_6F_5CHO,[49] b.p. 168-170°; C_6F_5OH,[48] b.p. 143°; $4\text{-}F.C_6H_4.NH_2$,[52] b.p. 186-188°; $4\text{-}F.C_6H_4.CHO$,[52] b.p. 179-180°; $4\text{-}F.C_6H_4.NO_2$,[52] b.p. 206°; $4\text{-}F.C_6H_4.SH$,[52] b.p. 166-168°; $4\text{-}F.C_6H_4.OMe$,[52] b.p. 154°; $4\text{-}F.C_6H_4.Me$,[52] b.p. 116-118°; C_6H_5F,[52] b.p. 86-88°.

Pentafluoronitrosobenzene. This was prepared by the method of Brooke et.al.[53] and recrystallised from 40-60 petroleum ether to constant m.p. 43·5-44°.

Pentafluoro-N-methyl aniline. This was prepared by the method of Brooke et.al.[33] and shown to be pure by analytical-scale gas-liquid chromatography (b.p. 168-170°).

Pentafluoro-N-dimethyl aniline. This was prepared by the method of Allen et.al.[37] and purified by preparative-scale gas-liquid chromatography (b.p. 161-3°).

4-fluoro-benzonitrile.[52] A method previously used to convert pentafluoro bromobenzene to pentafluorobenzonitrile was employed. 4-fluorobromobenzene (12·4 g.), cuprous cyanide (64·6 g.) and dimethyl formamide (150 ml.) were heated under reflux for 15 hr. The solution was cooled, ferric chloride (375 g.) in water (400 ml.) and conc. hydrochloric acid (80 ml.) added. This mixture was extracted with ether, the extracts dried ($MgSO_4$), and the ether distilled off to give a white solid, 4-fluorobenzonitrile, which was recrystallised to constant m.p. 33-35°.

2,3,5,6-tetrafluoro anisole,[54] was prepared and purified by Dr. G.M. Brooke. The following new compounds were prepared and purified. All gave correct analyses:-

2,3,5,6-tetrafluoro-N-methyl aniline. Pentafluorobenzene (9·0 g.) and methylamine [distilled from methylamine hydrochloride (22 g.) and dilute alkali] were heated in a sealed tube at 95° for 18 hr. The mixture was then diluted with water and extracted with ether. Distillation of the dried ($MgSO_4$) extracts afforded 2,3,5,6-tetrafluoro-N-methyl aniline (7·9 g.) b.p. 172-174° which was purified by gas-liquid chromatography. The F^{19} nuclear magnetic resonance spectrum was consistent with the 2,3,5,6-tetrafluoro structure.

2,3,5,6-tetrafluoro-N-dimethyl aniline. Treated as in the previous experiment but at 85° for 16 hr., pentafluorobenzene (5·5 g.) and dimethylamine [from dimethylamine hydrochloride (16·5 g.)] gave 2,3,5,6-tetrafluoro-N-dimethyl aniline (4·0 g.) b.p. 167-70°, which was purified by gas-liquid chromatography. The F^{19} nuclear magnetic resonance spectrum was consistent with the 2,3,5,6-tetrafluoro structure.

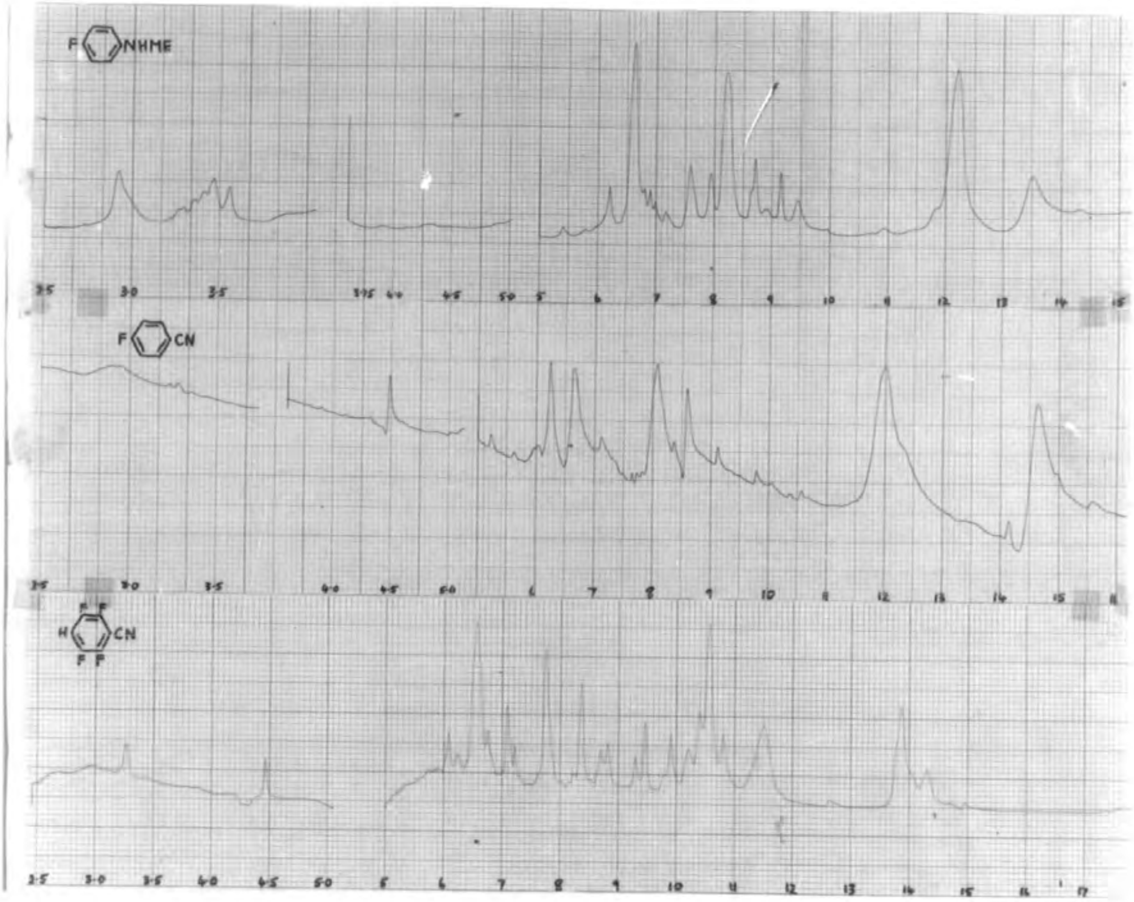
<u>4-fluoro-N-methyl aniline.</u> (a) 4-fluoroaniline (25 g.) and p-toluene sulphonyl chloride (42·9 g.) in pyridine, were heated on a steam-bath for 4 hr. The mixture was poured into water and the p-toluene sulphonate of 4-fluoro aniline separated out and was crystallised once from carbon tetrachloride (34·4 g.) m.p. 74-77°.

(b) The product from (a) (16·7 g.) was suspended in 2N. sodium hydroxide (20 ml.) and dimethyl sulphate (6 ml.). The mixture was boiled gently and a moderate reaction set in. Alkalinity to phenolpthalein was maintained by addition as required of N/10 sodium hydroxide. More dimethyl sulphate (6 ml.) was added after the disappearance of the first instalment. On cooling, a solid separated, and was crystallised once from absolute alcohol to give the p-toluene sulphonate of N-methyl aniline (16·0 g.) m.p.91-95°.

(c) The product from (b) (12 g.) was hydrolysed by heating for 1 hr. on a steam-bath with a mixture of glacial acetic acid (8 ml.) and conc.sulphuric acid (20 ml.). Onpouring into water, p-fluoro-N-methyl aniline separated. The amine was purified by crystallisation to constant m.p. (119-121°) of the hydrochloride formed by passing dry hydrogen chloride into a solution of the amine in dry ether. Addition of sodium hydroxide, followed by ether extraction gave the p-fluoro-N-methyl aniline (4·5 g.) b.p. 196-198°.

2,3,5,6-tetrafluorobenzonitrile, was prepared and purified by Mr. L. Chadwick of these laboratories.

2,3,5,6-tetrafluoronitrobenzene. We followed Brooke et. al.'s [34] method for the preparation of pentafluoronitrobenzene. Pure 2,3,5,6-tetrafluoroaniline (8·5 g.), trifluoroacetic anhydride (25 ml.) and hydrogen peroxide (10 ml.) in methylene chloride (25 ml.) were heated under reflux for 18 hr. The reaction mixture was neutralised (Na_2CO_3), and the methylene chloride layer was separated, dried ($MgSO_4$), and distilled, to give a yellow oil, 2,3,5,6-tetrafluoronitrobenzene (7·6 g.).


F⟨⟩NHME
2·5
3·0
3·5
3·75
4·0
4·5
5·0
5
6
7
8
9
10
11
12
13
14
15
F⟨⟩CN
2·5
3·0
3·5
4·0
4·5
5·0
6
7
8
9
10
11
12
13
14
15
16
F F
H⟨⟩CN
F F
2·5
3·0
3·5
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17

NHME
2·5 3 3·5 4 4·5 5 5 6 7 8 9 10 11 12 13 14
N(ME)₂
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16
NO₂
·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16

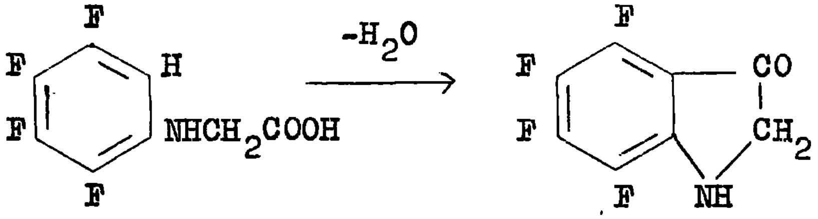
PART II

CHAPTER IV: A ROUTE TO PARTIALLY FLUORINATED HETEROCYCLES.

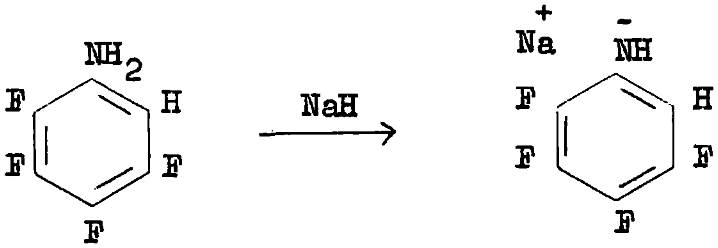
IV.1. Introduction and Discussion.

As part of a programme concerning the preparation and properties of partially fluorinated heterocyclic compounds,[55] the preparation of 4,5,6,7-tetrafluoro-indoxyl and hence the provision of a route to 4,5,6,7-tetrafluoro-indole, was attempted.

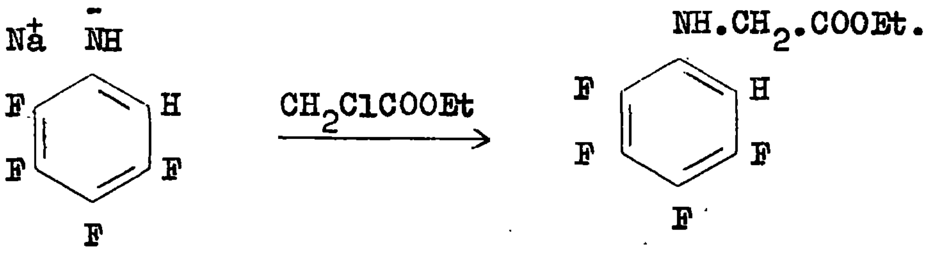
By analogy with the hydrocarbon analogue, it was hoped that elimination of water from N(2,3,4,5-tetrafluoro phenyl)-glycine followed by cyclisation would give the 4,5,6,7-tetrafluoro-indoxyl:-



The suggested route to the substituted glycine was as follows:- Treatment of 2,3,4,5-tetrafluoro-aniline with equimolar sodium hydride should give the sodium anilide:-

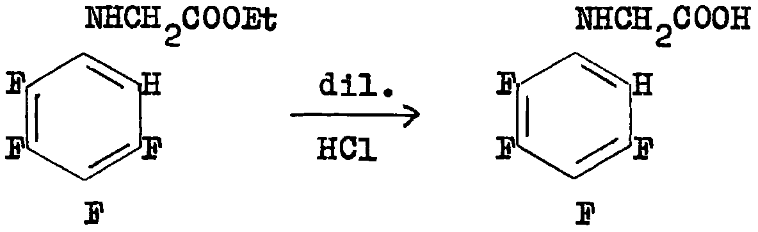


Treatment of this with chloracetic ester should give the glycine ethyl ester:-



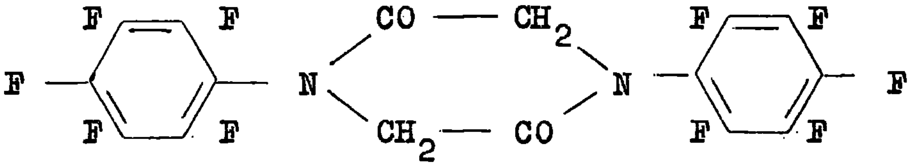
These two stages were based on Tamborski's[56] preparation of polyfluorodiphenylamines in which, for example, he treated pentafluoroaniline with sodium hydride to form the anion, which displaced F^- in hexafluorobenzene to give the diphenylamine.

Hydrolysis of the glycine ethyl ester should then give the acid:-



Only small quantities of 2,3,4,5-tetrafluoroaniline were available and optimum reaction conditions were discovered by using pentafluoroaniline and 2,3,56-tetrafluoroaniline.

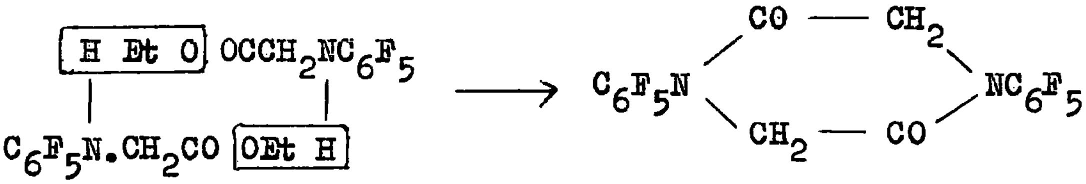
Treatment of pentafluoroaniline in tetrahydrofuran with sodium hydride at -20° C followed by addition of choracetic ester and heat under reflux gave a white solid which was shown by analysis and infra-red spectrum to be:-



N,N'-(bis pentafluorophenyl)-2,5-diketopiperazine.

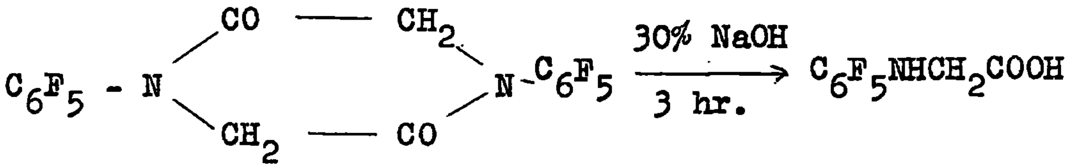
The 2,3,5,6- and 2,3,4,5-tetrafluoro-analogues were obtained under similar reaction conditions.

Presumably the glycine ethyl ester forms as an intermediate in this reaction and intermolecular elimination of two molecules of ethanol then occurs as follows:-

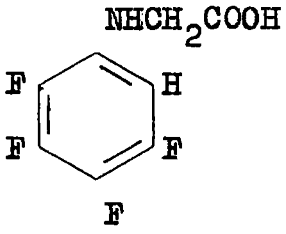


N.N' diphenyl-2,5-diketopiperazine is prepared by a similar elimination of ethanol from two molecules of glycine ethyl ester.[57]

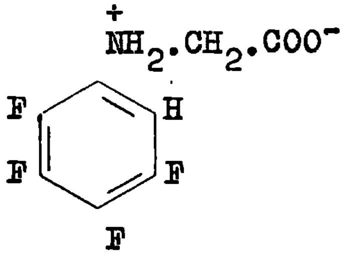
Alkaline hydrolysis of the diketopiperazines gave the required N-(polyfluorophenyl)-glycines, e.g.



The infra-red spectra of these amino-acids were surprising in that, unlike other amino-acids, they were shown to be un-ionised. All show a single N - H band in the region 3325-3375 cm^{-1} and a carbonyl band at 1724 $cm.^{-1}$ Ionic carboxyl in amino-acids absorbs [58] in the region 1600-1560 cm^{-1} and unionised carbonyl, as in amino-acid hydrochlorides, absorbs [58] in the region 1754-1720 $cm.^{-1}$ Presumably electron withdrawl by the ring fluorine atoms causes the delocalisation of the nitrogen lone pair, thus reducing the basicity of the amine and preventing the formation of a salt with the acid. The author has observed a similar low base strength in pentafluoroaniline due to the same effect. The structure of N-(2,3,4,5-tetrafluorophenyl)-glycine is therefore [1] rather than [2]



[1]



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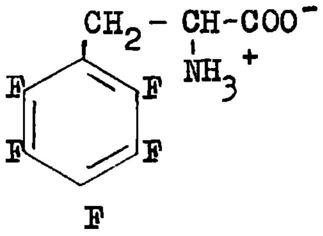


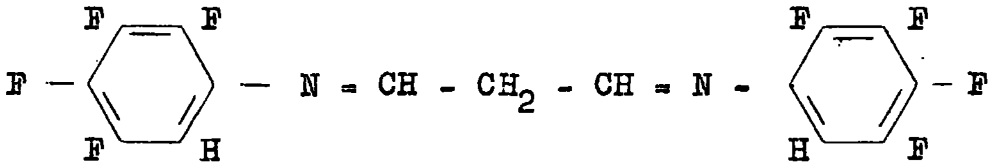
[3]

The only other polyfluorophenyl amino acid known is pentafluorophenylaniline.[59] [3] This molecule does exist in an ionised form, but the amino group has a weakly basic character, reflected in the rapid loss of HCl from its hydrochloride, and its low base strength has been attributed to an interaction between an ortho fluorine atom and the NH_3^+ group across intramolecular space.

A large number of mono, di and tri-halogen derivatives of N-phenylglycine have been prepared by Finger[60] as part of a programme on the synthesis of fluorinated herbicides and medicinals. His method of preparation was to condense the appropriately substituted primary aniline with ethyl chloroacetate in the presence of sodium acetate. An investigation into the herbicidal properties of our N-(polyfluorophenyl)-glycines may be of interest.

Treatment of N(2,3,4,5-tetrafluorophenyl)-glycine with polyphosphoric acid, a milder dehydrating agent than phosphorus pentoxide, gave a compound which showed C = N unsaturation in its infra-red spectrum, and was shown, by its nuclear magnetic resonance spectrum, to be symmetrical.

On the basis of this evidence, and the analysis figures, we tentatively suggest the following di-imino structure:-



IV.2. Experimental.

(a) N N'-(bis pentafluorophenyl)-2,5-diketopiperazine.

A 150 ml. two-necked flask was fitted with a dropping funnel, a magnetic stirrer, and a condenser leading to a gas burette through a calcium chloride tube. The dropping funnel was fitted with a 'T' piece so that nitrogen could be passed through the apparatus or provide an atmosphere of nitrogen in the dropping funnel. Pentafluoroaniline (5 g, 0·0273 M) and tetrahydro furan (T.H.F., 50 ml.) were placed in the flask, the apparatus was flushed with nitrogen and allowed to equilibrate. Sodium hydride 65% oil suspension (0·964 g., 0·0273 M) was placed in the dropping funnel and washed with T.H.F. (25 ml.) to remove the oil by hand-stirring the suspension with a glass rod, allowing the suspension to settle, and pipetting off the T.H.F./oil solution. A stream of nitrogen was passed through the dropping funnel during this and the next stage, in order to keep an atmosphere of nitrogen above the sodium hydride. More T.H.F. (25 ml.) was then added to the sodium hydride, and, stirring the suspension before each addition, this was added slowly with stirring to the flask over 2-3 hrs. The flask was kept at -30° C to -20° C by an acetone/drikold bath. The reaction could be followed by noting the rate of evolution of hydrogen on the gas burette. After 3 hrs. the reaction mixture was allowed to equilibrate at room temperature and a grey suspension in a dark green solution obtained. The amount of hydrogen evolved during the reaction was 560 ml. (calc. 610 ml.) Ethyl chloroacetate (3·37 g., 0·0273M) in T.H.F. (25 ml.) was then added dropwise over ½ hr. with stirring at room temperature and an exothermic reaction took place. The reaction mixture was then heated under reflux for 1 hr., allowed to cool, poured into water (500 ml.), and extracted with ether (2 x 75 ml.). The ethereal extract was dried ($MgSO_4$), filtered, and evaporated. The solid residue was vacuum-distilled at 0·001 mm/140° C - 160° C to give N,N'-(bis-pentafluorophenyl)-2,5-diketopiperazine. (3·3 g. 53·6%). This was recrystallised from 60-80 petroleum ether/benzene to constant m.p. 171-173·5° C. (Found: C, 43·3; H, 1·00; F, 43·3. Calc. for $C_{16}H_4F_{10}N_2O_2$: C, 43·1; H, 0·94; F, 42·6%).

(b) N,N'-(bis 2,3,5,6-tetrafluorophenyl)-2,5-diketopiperaazine.

2,3,5,6-tetrafluoroaniline (5·0 g., 0·0303 M), sodium hydride (1·11 g., 0·03 M, 65% suspension), and ethyl chloroacetate (3·71 g., 0·33 M) were caused to react, using the same apparatus and under the same reaction conditions as in (a) except that the flask was kept at -10° C during the addition of sodium hydride. The solid residue from the ether extraction was vacuum-distilled at 0•001 mm/ 160-180° C to give N,N'-(bis-2,3,5,6-tetrafluorophenyl)-2,5-diketopiperazine (3•0 g., 48•3%). This was recrystallised from benzene to constant m.p. 219-225° C. (Found: C, 46•9; H, 1•54; F, 36•8; Calc. for $C_{16}H_6F_8N_2O_2$: C, 46•8; H, 1•46; F, 37•1%).

(c) N,N'-(bis-2,3,4,5-tetrafluorophenyl)-2,5-diketopiperazine.

2,3,4,5-tetrafluoroaniline (5•0 g., 0•0303 M), sodium hydride (1 g., 0•03 M, 65% suspension), and ethyl chloroacetate (3•71 g., 0•33M) were caused to react, using the same apparatus, and under the same reaction conditions as in (a), except that the flask was kept -10° C to 0° C during the addition of the sodium hydride. The product was only slightly soluble in ether/benzene and was filtered from the ether/benzene layer (1•5 g.). The ether/benzene layer was dried ($MgSO_4$), filtered, and evaporated. Vacuum sublimation of the residue at 0•001 mm/200-210° C gave more product (0•3 g.). The product was N,N'-(bis-2,3,4,5-tetrafluorophenyl)-2,5-diketopiperazine (1•8 g., 29•0%). This was recrystallised from T.H.F./60-80 petroleum ether to constant m.p. 259-263° C. (Found: C, 47•1; H, 1•75; F, 36•8; Calc. for $C_{16}H_6F_8N_2O_2$: C, 46•8; H, 1•46;

F, 37·1%).

(d) Hydrolysis of N,N'-(bis pentafluorophenyl)2,5-diketopiperazine with N sodium hydroxide.

N,N'-bis-pentafluorophenyl-2,5-diketopiperazine (0·25 g.) was added to N sodium hydroxide (50 ml.) and the mixture was refluxed for ½ hr. The reaction mixture was then neutralised (HCl), ether extracted, and the extracts dried (MgSO$_4$), and evaporated. The solid residue was vacuum-sublimed at 0·001 mm/70-80° to give N-(pentafluorophenyl)-glycine (0·2 g., 72·1%). This was recrystallised from warm water(80-90° maximum temperature) to constant m.p. 120-122·5°. (Found: C, 39·6; H, 1·81; F, 39·2. Calc. for $C_8H_4F_5NO_2$: C, 39·2; H, 1·66; F, 39·4%).

(e) Hydrolysis of N,N'-(bis-2,3,5,6-tetrafluorophenyl)-2,5-diketopiperazine with 30% sodium hydroxide.

N,N'-2,3,5,6-tetrafluorophenyl-2,5-diketopiperazine (0·3 g.) was added to 30% sodium hydroxide (25 ml.) and the mixture was refluxed for 3 hr. The solution was worked up as in (d) and vacuum sublimation of the solid thus obtained at 0·001 mm/60-70° gave N-(2,3,5,6-tetrafluorophenyl)-glycine (0·22 g., 67·4%). This was recrystallised from warm water (80°. Higher temperatures cause decomposition) to constant m.p. 105-107·5°. (Found: C, 43·5; H, 2·29; F, 33·6; Calc. for $C_8H_5F_4NO_2$: C, 43·1; H, 2·24; F, 34·1%).

(f) Hydrolysis of N,N'-(bis-2,3,4,5-tetrafluorophenyl)-2,5-diketopiperazine with 2N sodium hydroxide.

N,N'-(bis-2,3,4,5-tetrafluorophenyl)-2,5-diketopiperazine (0·82 g.) was added to 2N sodium hydroxide (50 ml.) and the mixture was refluxed for ¼ hr. only. The solution was worked up as in (d) and vacuum sublimation of the solid thus obtained at 0·001 mm/120° gave N-(2,3,4,5,-tetrafluorophenyl)-glycine (0·8 g., 94 %). This was recrystallised from boiling water to constant m.p. 175-178·5°. (Red spots begin to appear at 170°). (Found: C, 43·0; H, 2·29; F, 33·8. Calc. for $C_8H_5F_4NO_2$: C, 43·1; H, 2·24; F, 34·1%). All three N-(polyfluorophenyl)-glycines decompose at their melting points.

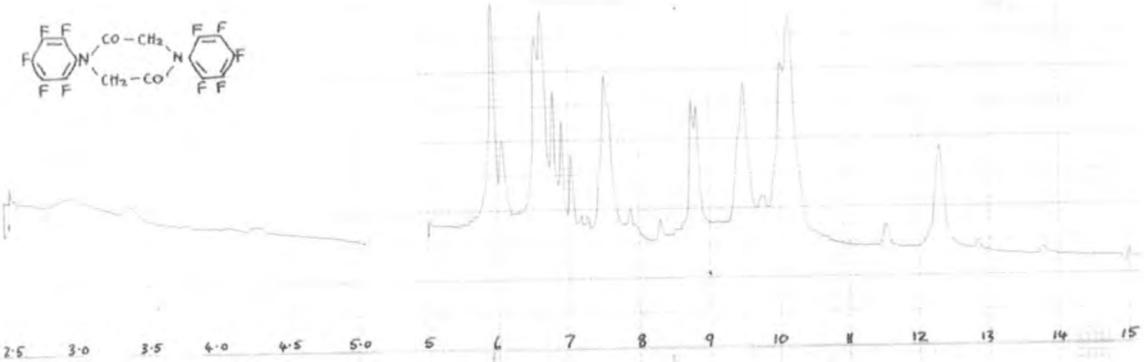
Reaction of N-(2,3,4,5-tetrafluorophenyl)-glycine with Polyphosphoric Acid. Polyphosphoric acid (20 ml.) was heated to 130° and N-(2,3,4,5-tetrafluorophenyl)-glycine (0·6g.) added in small quantities. After 20 min. water was added to the brown reaction mixture, the resulting mixture neutralised (Na_2CO_3), ether extracted, and the extracts dried ($MgSO_4$). Evaporation of the ether, followed by sublimation at 0·003 mm/130° of the residue obtained, gave a white solid (0·2 g.) which was recrystallised from 40-60 petroleum ether to constant m.p. 187-189°. We suggest the following di-imino structure for this compound (2,3,4,5-C_6F_4.H)-N=CH-CH_2-CH=N-(2,3,4,5-C_6F_4.H). (Found: C, 49·1%; H, 1·8%; F, 41·3%. Calc. for $C_{15}H_6F_8N_2$: C, 49·18%; H, 1·64%; F, 41·53%). The F^{19} nuclear magnetic resonance spectrum indicated the presence of four different fluorine environments, therefore the molecule is symmetrical. The infra-red spectrum has a band at 1650 cm^{-1} (C = N).

Infra-red Spectroscopy. All spectra were obtained on potassium bromide discs of the solid. The N,N' disubstituted 2,5-diketopiperazines gave bands at the following frequencies:-

$(C_6F_5.NCOCH_2)_2$	1694 cm^{-1} (C = O)
$(2,3,5,6\text{-}C_6F_4H.NCOCH_2)_2$	1694 cm^{-1} (C = O)
$(2,3,4,5\text{-}C_6F_4H.NCOCH_2)_2$	1681 cm^{-1} (C = O)

Each of the N-substituted glycines gave a band at 1724 cm^{-1} (C = O), and also as follows:-

$C_6F_5.NH.CH_2.COOH$	3400 cm^{-1} (N - H)
2,3,5,6-$C_6F_4H.NH.CH_2.COOH$	3413 cm^{-1} (N - H)
2,3,4,5-$C_6F_4H.NH.CH_2.COOH$	3367 cm^{-1} (N - H)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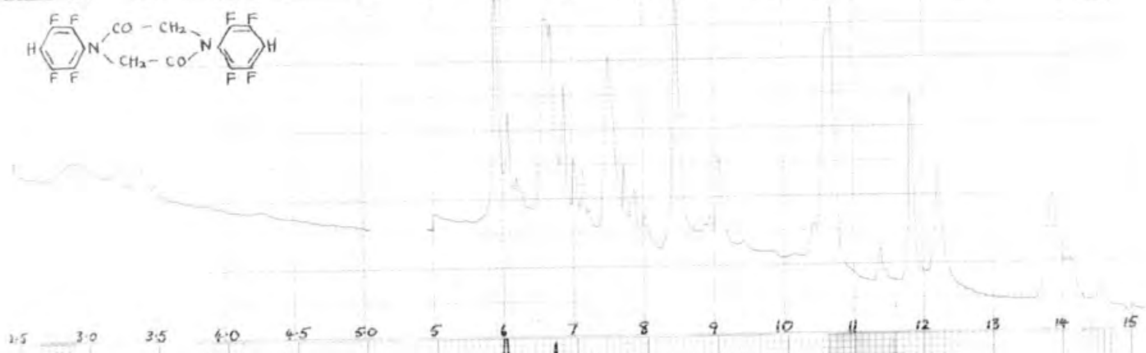
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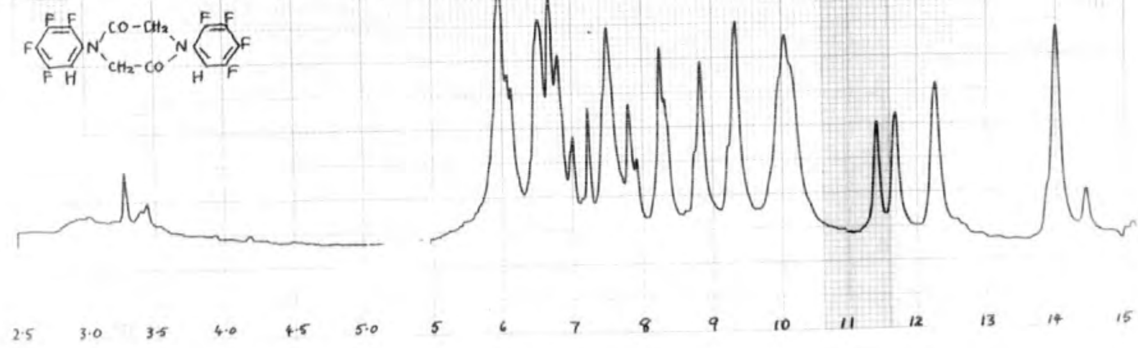
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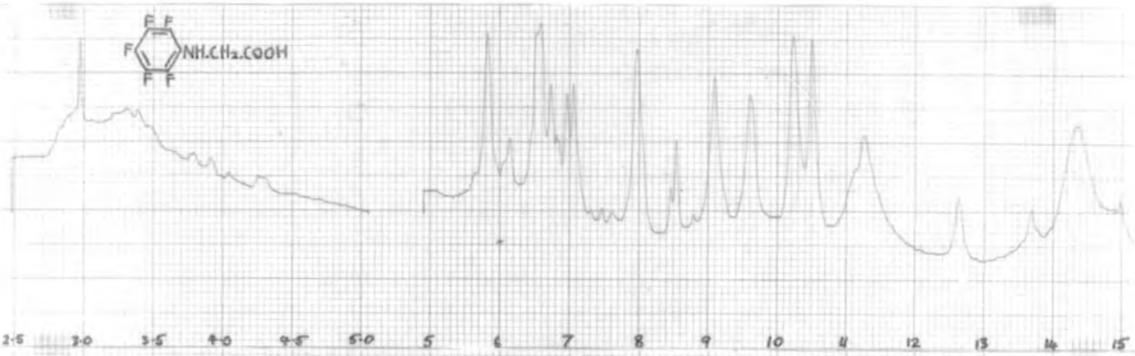
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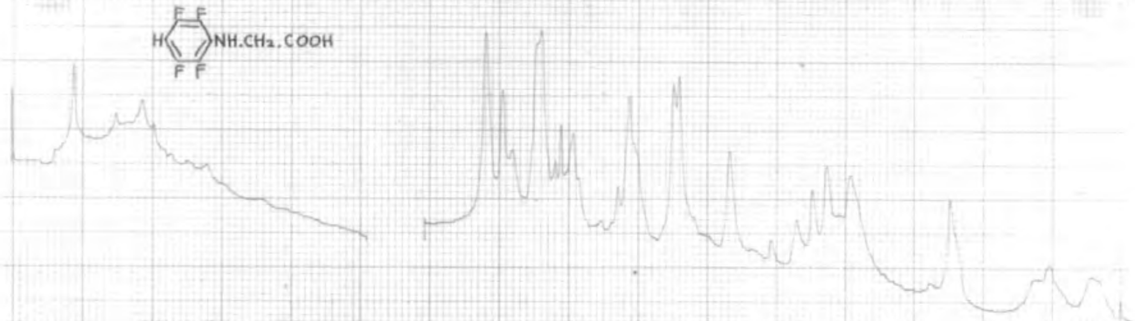
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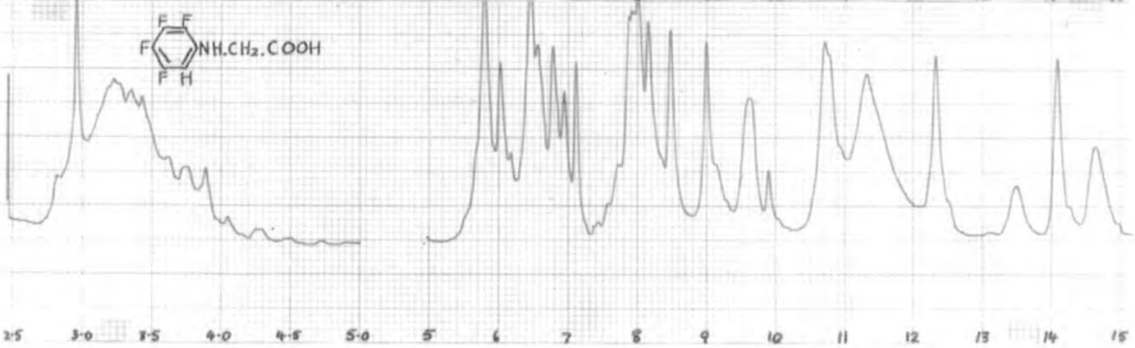
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