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Lavender, Ian (1992) *Some reactions of dithianitronium hexafluroarsenate (v) with Mono-and multi-nitriles*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/5729/

SOME REACTIONS OF DITHIANITRONIUM HEXAFLUOROARSENATE(V) WITH MONO- AND MULTI- NITRILES

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A thesis submitted in partial fulfillment for the degree of PhD
to the University of Durham
November 1992

to mom and dad
for much love and encouragement

to Lisa
for being so special

"...The Race is not to the swift,
or the battle to the strong,
nor does food come to the wise,
or wealth to the brilliant
or favour to the learned
but time and chance happen to them all."
Eccl. 9 v 11

Acknowledgements

Firstly, I would like to thank my family and friends who have provided much needed help, support and advice during the past, often traumatic, thirty seven months.

Special thanks go to Dr Arthur Banister for his guidance on all aspects of life and chemistry and not least for his boundless enthusiasm and steady hand in times of trouble.

Thanks also to Dr Jeremy Rawson for providing a role model for all in our lab. with his patience, ideas, drive and a sound epicurean taste. All of this would have been much more difficult without you, Jeremy.

It has been a privilege for me to work with Dr Zdenek Hauptman, who still continues to amaze with his breadth of knowledge in every aspect of science and technology and his skill in the design and crafting of first rate equipment.

The members of lab. 100 other, both past and present, have provided sterling support (by way of laughs, beers, encouragement, sarcasm and sometimes even chemicals) and deserve praise for providing a very productive, easy-going atmosphere in which to work. So, in no particular order, thanks to: Ant Luke, Phil Coates, Chris Aherne, Simon Lawrence, Tom Hibbert and Iain May.

Mention must be made of the infamous lab. 101 (or is it 19?) boyz, especially; Phil 'how did you survive my cooking and personal hygiene' Dyer, Ed 'we could've if we'd wanted to' Marshal, Andy 'wibble' Poole, Matt 'how many pizzas?' Jolly and Jon 'L.A. 1992' Mitchell.

The technical staff at Durham have provided a consistently excellent service with special mention to Gordon and Ray for their 'grand' glassware, and to Julia Say, Dr Alan Kenwright and Dr Ray Matthews for listening to me gabble on about nmr. Also thanks to Dr Roger Whitehead and Dr David Lambrick for magnetisation data, to Dr Jeremy Cockcroft and Jason Cole for providing some excellent diagrams.

Without the hard work of Dr William Clegg of Newcastle University in solving the solid state structures that make up a large proportion of this thesis there would have been little point in doing the synthesis, thank you Bill.

On a more personal note, I would like to thank my friend and tutor Euan Ross for encouragement and practical support during the past months and for showing me the great joys of climbing up barren mountainsides in the pouring rain. Also love and hugs to Jenny, Ewan, Hayley, Steve, Ness, Claire, Lucy, Jon, Paul, Mark, Nicky, Andrew, Ian, Harry, Jules, Emma and all my friends from Grey - we had a great time, didn't we ?

Memorandum

The work described in this thesis was carried out by me, in the Department of Chemistry at the University of Durham between October 1989 and August 1992. I declare that this work has not been submitted previously for a degree at this or any other University. This thesis is a report of my own original work, except where acknowledged by reference. The copyright of this thesis rests with the author. No quotation should be published without his written consent, and information derived from it should be acknowledged. Material from this thesis has been or will be included in the following publications:

1. " Cycloaddition Reactions of $[SNS][AsF_6]$ with Potassium Tricyanomethanide; Preparation and X-Ray Structures of $(NC)_2C{=}CNSNS$ and $[C(CNSNS)_3][AsF_6]_2.\ SO_2$.". A.J. Banister, I. Lavender, J.M. Rawson and W. Clegg; *J. Chem. Soc., Dalton Trans.*, **1992**, 859.
2. " Convenient Preparations of the Mixed 1,3,2,4/1,2,3,5-Dithiadiazolium Salt *p*-$[SNSNC.C_6H_4.CNSSN][AsF_6]_2$ and the First Mixed Free Radical *p*-$[SNSNC.C_6H_4.CNSSN]$.". A.J. Banister, I. Lavender, J.M. Rawson and R.J. Whitehead; *J. Chem. Soc., Dalton Commun.*, **1992**, 1449.
3. " Preparation and Characterisation of the Mixed 1,3,2,4-/1,2,3,5-Dithiadiazolylium Salts and Related Free Radicals; *m*- and *p*-$[SNSNC.C_6H_4.CNSSN]^x$ (x=2+, $+^\bullet$ and $2^\bullet$) ", A.J. Banister, I. Lavender, J.M. Rawson, W. Clegg, B.K. Tanner and R.J. Whitehead, *J. Chem. Soc., Dalton Trans.*, **1993**, accepted for publication.
4. " Preparation and Characterisation of the First Dithiadiazolylium / Diselenadiazolylium Dications; $[SNSNC.C_6H_4.CNSeSeN][AsF_6]_2$, $[NSSNC.C_6H_4.CNSeSeN][AsF_6]_2$ and Related Radicals ", A.J. Banister, I. Lavender, J.M. Rawson and D.B. Lambrick, *J. Chem. Soc., Dalton Trans.*, in preparation.
5. " Dithiadiazolium Fluoride: Fact or Fiction? ", A.J. Banister, I.B. Gorrell, I. Lavender, J.M. Rawson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, in preparation.
6. " Reactions of $[SNS][AsF_6]$ with Metal Cyanides: Preparation and Crystal Structure of $[PhSNSNSNSPh][AsF_6]$ ", A.J. Banister, I. Lavender, J.M. Rawson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, in preparation

Abstract

This work primarily concerns the compound dithianitronium hexafluoroarsenate(V), $[SNS][AsF_6]$, and its use in the synthesis of 1,3,2,4-dithiadiazolylium salts.

Chapter one provides a short review of the dithianitronium cation, the physical and chemical properties of its salts and outlines various synthetic methods and reaction types.

General details of experimental methodology are outlined in chapter two.

The third chapter covers the reactions of $[SNS][AsF_6]$ with $K[C(CN)_3]$, the first example of a reaction of the former species with a delocalised anionic system. Sequential reactions with one, two and three equivalents of $[SNS][AsF_6]$ gave $(NC)_2.C{=}CNSNS$ (**1**), $[(NC).C(CNSNS)_2][AsF_6]$ (**2**) and $[C(CNSNS)_3][AsF_6]_2$ (**3**), respectively. Compounds **1** and **3** were characterised by single crystal X-ray diffraction.

Chapter four outlines the preparation of mixed 1,2,3,5- / 1,3,2,4-phenylene - bridged dithiadiazolyliums, in high yield, from $[SNS][AsF_6]$ and $[(NC).C_6H_4.CNSSN][AsF_6]$. Both the *meta* and *para* isomers were prepared, *p*-$[NSNSC.C_6H_4.CNSSN][AsF_6]_2.MeCN$ was characterised by single crystal X-ray diffraction, the magnetic and electronic properties of the radical cations and diradicals were studied. The radical cation salt, *p*-$[NSNSC.C_6H_4.CNSSN]Cl$ was shown to be a spin = $^1/_2$ paramagnet.

In the fifth chapter a similar methodology was applied in order to prepare and study the *p*-$[NSNSC.C_6H_4.CNSeSeN]$ dication and its corresponding diradical and radical cation. Preliminary magnetisation data indicate the latter chloride salt to be paramagnetic.

The sixth chapter outlines the reaction of $[SNS][AsF_6]$ with metal cyanides and rationalises the unexpected reaction with $PhHgC{\equiv}N$, where a cationic linear thiazene, $[PhSNSNSNSPh]^+$ (4), is formed. The hexafluoroarsenate(V) salt of **4** was characterised by single crystal X-ray diffraction. Thiazyl chloride, $(NSCl)_3$, was utilised in the synthesis of the analogous compounds, $[Ar_2S_4N_3]Cl$ (where Ar=*o* and *p*-$(O_2N).C_6H_4$), from the corresponding shorter, neutral, acyclic thiazenes ($Ar_2S_3N_2$).

An attempt to prepare the first dithiadiazolylium fluoride is described in chapter 7. The unexpected product of the reaction of [*p*-$Cl.C_6H_4.CNSSN][AsF_6]$ with $[Me_4N]F$ is the radical, [*p*-$Cl.C_6H_4.CNSSN]$, which was shown, by X-ray structure determination, to contain unusual $S{\cdots}N$ interactions which give rise to the formation of tetramers in the solid state.

Abbreviations

The following abbreviations are used in this thesis:

Ar	aryl
Bu	butyl
C_6H_4	phenylene
C.I.	chemical ionisation
-CNSNS	the 1,3,2,4-dithiadiazolyl/ium ring system
-CNSSN	the 1,2,3,5-dithiadiazolyl/ium ring system
-CNSeSeN	the 1,2,3,5-diselenadiazolyl/ium ring system
CV	cyclic voltammetry
Dsc	differential scanning calorimetry
E.I.	electron impact
esr	electron spin resonance
HOMO	highest occupied molecular orbital
IR	infra-red
LUMO	lowest unoccupied molecular orbital
Me	methyl
MeCN	acetonitrile
MNDO	modified neglect of diatomic overlap
mnt	maleonitriledithiolate [cis-1,2-dicyano-1,2-ethylenedithiolate]
nmr	nuclear magnetic resonance
Ph	phenyl
Pr	propyl
R	alkyl substuent
SOMO	singly occupied molecular orbital
thf	tetrahydrofuran

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Some aspects of the chemistry of the dithianitronium cation

"An expert is one who knows more and more about less and less"

Nicholas M. Butler

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"Give us the tools and we'll finish the job"

Winston L.S. Churchill

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"Cast thy bread upon the waters for thou shalt find it after many days"

Ecc. 11v1

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> *"Life is the art of drawing sufficient conclusions from insufficient premises"*
>
> Samuel Butler

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"The rankest compound of villainous smell that ever offended nostril"
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> *"The ropy drivel of rheumatic brains"*
>
> William Gifford

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> *"Under the budgeonings of chance my head is bloody but unbowed"*
>
> William Ernest Henley

Appendices

"If life had a second edition, how I would correct the proofs"

John Clare

1: The Reactions of $[SNS][AsF_6]$ with $(NC)_2CH_2$ and $Na[(NC)_2CH]$

2: The preparation of some dithiazolium salts

Chapter 1

Introduction:

Some aspects of the chemistry of the dithianitronium cation

1.1 Historical background to sulphur-nitrogen chemistry

Inorganic chemistry has been for many years the poor relation of both organic and physical chemistry, certainly if we consider the degree to which it is widely understood (for example in terms of the mechanistics of reactions, and on a broader scale, by the average person). This inequality has arisen for several reasons, not least the greater efforts devoted to the study of organic systems (for example there is a whole Chemical Society journal devoted to physical organic chemistry, whereas there are comparatively few publications in the area of physical inorganic chemistry) and the ease with which those compounds are characterised.

Furthermore, as living systems (and their products which surround us) contain more organic materials than bio-inorganic or inorganic then research devoted to the synthesis and study of so-called organic compounds has continued to have far more impetus (both financial and cultural). Furthermore, the stability of many of these compounds towards both air and moisture aids their synthesis and characterisation, which together with the development of powerful, modern techniques such as high-field ^{1}H and ^{13}C nmr has hastened research into organic synthesis, mechanistics and structures. This has resulted in a far deeper understanding of how organic compounds react and consequently insight into how other derivatives may be best prepared.

In contrast, sulphur-nitrogen chemistry is just over 150 years old. S_4N_4[1]was first reported in the 1830s, but its stoichiometry was not established until 1851, in the year that S_3N_2Cl was first prepared[2]. At least until the 1950s most sulphur-nitrogen compounds were only of academic interest rather than being directly applicable in industrial or commercial fields. However, with the continued drive to develop materials that exhibit unusual optical and electronic properties, for use in the burgeoning high technology industries much effort was expended in the study of a wide variety of delocalised and polymeric systems including those containing SN groups. There emerged a whole range of new and potential applications for instance organic conductors[3a,b], components for molecular computers[4] or in non-linear optics[5].

The turning point was probably the discovery in 1975 of the superconducting properties of $(SN)_x$ [T_c=0.26 K], by Street and co-workers[6], which led to increased research interest in $(SN)_x$[7] itself and also SN compounds in general, particularly delocalised[8] and linear[9] materials. This has been coupled with great advances in the equipment and methods used in the field. For example:

(i) Inert-gas techniques have developed employing modern glove boxes and double-manifold lines based on those developed by Stock[10]

(ii) Aprotic solvents are used regularly, particularly liquid SO_2 - widely employed in the work described herein and elsewhere[11]

(iii) High field multinuclear nmr has been developed - notably ^{15}N labelling[12a,b], ^{14}N nmr[12a] and ^{13}C nmr[13].

(iv) Modern methods for structural characterisation of solids, liquids and gases are now much improved. In addition to single crystal X-ray diffraction there are newer methods such as determination of solid-state structures from X-ray powder diffraction data[14], potentially a very powerful tool. Several of the compounds described in this work required a solid state structure to establish their identity unambiguously, as other methods could not differentiate absolutely between isomers or reveal structural information adequately.

(v) Accurate and fast molecular orbital calculations[15] (e.g. *ab initio* calculations at the PM3 level such as those employed during this work) can be used to probe the bonding and reactivity of these systems.

So we have seen a revival in interest in sulphur-nitrogen based systems over the past twenty years and some of the most recent work could hardly have been envisioned in the early 1970s (e.g. the use of ^{15}N labelling techniques in nmr-based kinetic and mechanistic studies [16]). However, there still remain many unsolved puzzles in this area of chemistry and perhaps a higher ratio of unanswered questions to answers gained than in any significant area of chemistry - certainly in any with a 150 year history.

The problems begin with sulphur itself having multiple valencies (up to 6 and formal oxidation states between -2 and +6). Investigations are complicated further by the dearth of available nmr nuclides, the high sensitivity of the reagents and products to both air and moisture, and the specialised techniques required to handle and even store many of the reagents. It is not suprising that only a handful of research groups worldwide are active in this field.

These factors seem to suggest that progress may well continue at about the present rate (albeit with some unusual and sometimes perplexing chemistry being carried out on the way) for the foreseeable future.

In order to understand the breadth of study in this diverse area (and that of related main-group chemistries) the reader should consult the following books and articles:

(a) "The Chemistry of Inorganic Ring Systems", Editor : R. Steudel (1992)[17] (especially chapters 16 to 18)

(b) “Dithiadiazoles : Members of a New Family of Free Radicals”, A.J. Banister and J.M. Rawson (1991)[18]

(c) "Non-metal Rings Clusters and Cages", J.D. Woollins (1988)[19]

(d) " Chemistry of Inorganic Homo- and Heterocycles", 2 Volumes, I. Haiduc and D.B. Sowerby (1987)[20]

(e) finally the classic text, "The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorous", H.G. Heal (1972)[21]

In the following pages I hope to outline the chemistry of a small area of this field with a short treatise on the preparation, properties and chemistry of the various salts of the dithianitronium cation. One particular dithianitronium salt, the hexafluoroarsenate(V), proved highly versatile during the course of my studies.

1.2 A short review of the chemistry of the dithianitronium cation

The dithianitronium cation is a versatile, high yielding reagent useful in the synthesis of carbon-sulphur-nitrogen heterocycles. It provides a convenient route to 1,3,2,4-dithiadiazolylium salts and hence, their related free radicals. However, as its chemistry has not been catalogued exhaustively since the extensive work of M.J. Schriver[22] in 1988, a short account of the chemistry of $[SNS]^+$ follows.

1.2.1 Preparative routes to various dithianitronium salts

The first $[SNS]^+$ compound to be prepared was the hexachloroantimonate (V) salt, $[SNS][SbCl_6]$, which was isolated in 1978 by Gillespie and co-workers[23] from the reaction of $SbCl_5$ with a variety of SN reagents in liquid SO_2 (see equations 1.1 to 1.3).

$$S_7NH + SbCl_5 \xrightarrow{SO_2} [SNS][SbCl_6] + HCl + S_8 + SbCl_3 \qquad [Eq.\ 1.1]$$

$$1{,}4\text{-}S_6N_2H_2 + SbCl_5 \xrightarrow{SO_2} [SNS][SbCl_6] + HCl + S_8 + SbCl_3 \qquad [Eq.\ 1.2]$$

$$S_7NBCl_3 + SbCl_5 \xrightarrow{SO_2} [SNS][SbCl_6] + S_8 \qquad [Eq.\ 1.3]$$

The stoichiometries of all three reactions were not fully established, although HCl, S_8 and $SbCl_3$ were isolated from the reaction mixture in the first two reactions and S_8 observed as a product from the third reaction. In all three cases the yield of $[SNS][SbCl_6]$ was not specified (so may be presumed to be less than 50%). Furthermore, several synthetic steps are required in order to prepare the starting materials (e.g. S_7NH and derivatives).

The corresponding hexafluoroarsenate(V) salt, $[SNS][AsF_6]$, had also been prepared, at approximately the same time[24] by the low-yield (~20%) reaction of $S_8[AsF_6]_2$ with sodium azide in liquid SO_2 (see equation 1.4). This route was further developed into a higher-yield synthesis[16,25,26] (>75%) utilising sulphur, AsF_5, S_4N_4 and a trace of bromine in liquid SO_2 (see equation 1.5).

$$S_8[AsF_6]_2 + NaN_3 \xrightarrow{SO_2} [SNS][AsF_6] + NaAsF_6 + {}^3/_4\, S_8 + N_2 \qquad \text{[Eq. 1.4]}$$

$$S_8 + 2\,S_4N_4 + 12AsF_5 \xrightarrow{SO_2} 8\,[SNS][AsF_6] + 4\,AsF_3 \qquad \text{[Eq. 1.5]}$$

Recent ^{14}N nmr studies by Passmore and Awere[16] have revealed the energetics and mechanistics of the second of these routes to $[SNS][AsF_6]$ (see section 1.2.4 for further details). This method remains the most convenient, high-yield preparation of that highly versatile reagent. The only subsequent amendments to this synthesis concern the final purification and isolation of $[SNS][AsF_6]$ with yields increased to 84% (on a 13 g scale) by washing with SO_2 / CCl_3F at -78°C [16] and to 95% (on a 6 g scale) by washing with CH_2Cl_2[26]. The quality of the products has also been improved by vacuum thermolysis[27] at 250°C, which removes S_8 and other volatiles. The direct reaction of $AlCl_3$ with S_4N_4 in CH_2Cl_2 gives $[SNS][AlCl_4]$ of unreported yield and stoichiometry[28].

All of the syntheses outlined above give products of reasonable quality (all three $[SNS]^+$ salts prepared by these routes have been characterised in the solid state as single crystals - see section 1.2.2). However, each requires either several steps of complex synthesis and / or the use of hazardous reagents (e.g. S_4N_4 and AsF_5) so a more general method involving fewer, high yield, steps and more convenient reagents was sought.

The first progress toward a more facile general route was made when $[SNS][AsF_6]$ was synthesised in almost quantitative yield from elemental sulphur and the unstable salt, $[SN][AsF_6]$[25].

$${}^1/_8\, S_8 + [SN][AsF_6] \xrightarrow{SO_2} [SNS][AsF_6] \qquad \text{[Eq. 1.6]}$$

Isolation of the product, however, proved difficult and the recovered yield was only 50%.

Considering this route and that $[SNS][SbCl_6]$ could be prepared in a similar fashion[29], a readily available source of $[SN]^+$ was sought. As a result of this $(NSCl)_3$ was found[30] to react with $SbCl_5$ (either in CH_2Cl_2 or $SOCl_2$ solution) and then further with S_8 to give the desired product in 35% yield.

$$(NSCl)_3 + 3\,SbCl_5 + {}^{3}/_{8}\,S_8 \xrightarrow[\text{or } SOCl_2]{CH_2Cl_2} 3\,[SNS][SbCl_6] \qquad \text{[Eq. 1.7]}$$

However, significant side reactions between $[SNS]^+$, $(NSCl)_3$ and $SOCl_2$ generate several contaminants, viz. $[S_3N_2Cl]^+$ and $[N(SCl)_2]^+$.

The latter side-product is also readily prepared (in yields > 80%) from $(NSCl)_3$, SCl_2 and the appropriate Lewis acid[31] (e.g. $AlCl_3$, $FeCl_3$ or $SbCl_5$, which give the $[AlCl_4]^-$, $[FeCl_4]^-$ or $[SbCl_6]^-$ salts respectively). Both $[SNS][AlCl_4]$ and $[SNS][SbCl_6]$ have been prepared in high yield (86 and 70% respectively from the appropriate $[N(SCl)_2]^+$ salt) by reductive dechlorination using $SnCl_2$[32].

$$^{1}/_{3}(NSCl)_3 + SCl_2 + AlCl_3 \xrightarrow{SO_2} [N(SCl)_2][AlCl_4] \qquad \text{[Eq. 1.8a]}$$

$$[N(SCl)_2][AlCl_4] + SnCl_2 \xrightarrow{CH_2Cl_2} [SNS][AlCl_4] + SnCl_4 \qquad \text{[Eq. 1.8b]}$$

$$^{1}/_{3}(NSCl)_3 + SCl_2 + SbCl_5 \xrightarrow{SO_2} [N(SCl)_2][SbCl_6] \qquad \text{[Eq. 1.9a]}$$

$$[N(SCl)_2][SbCl_6] + SnCl_2 \xrightarrow{SO_2} [SNS][SbCl_6] + SnCl_4 \qquad \text{[Eq. 1.9b]}$$

Again side-reactions between $[SNS]^+$ and $(NSCl)_3$ or $[N(SCl)_2]^+$ give rise to complex reaction mixtures if the appropriate solvent or reaction conditions are not used[33].

Also both of these $[SNS]^+$ salts suffer from being insoluble or unreactive and so do not readily take part in all of the usual cycloaddition reactions of compounds such as $[SNS][AsF_6]$ (e.g. with nitriles, olefins, and alkynes)[31]. Consequently they are not of great synthetic utility. The salt $[SNS][CF_3SO_3]$, prepared by M. Hansford[34] using sulphur, $(NSCl)_3$ and $Ag[CF_3SO_3]$ (see equation 1.10), is also of little synthetic utility, mainly because it is highly sensitive to air and moisture and is obtainable only in 37% yield.

$$(NSCl)_3 + {}^3/_8\, S_8 + 3\, Ag[CF_3SO_3] \xrightarrow{SO_2} 3[SNS][CF_3SO_3] \qquad [Eq.\ 1.10]$$

A similar approach has been adopted by Banister *et.al.*[31] in developing a systematic, generalised route to $[SNS]^+$ salts. This involves the *in situ* generation of the appropriate [SN][X] salt from the corresponding silver salt and $(NSCl)_3$, followed by the addition of a slight molar excess of SCl_2 to yield the $[N(SCl)_2]^+[X]^-$ salt in high yield (>75% - see table 1.1). For X = AsF_6, $SbCl_6$, $AlCl_4$, $FeCl_4$, SbF_6 and CF_3SO_3. (See equation 1.11). These crystalline solids can then be dechlorinated (as outlined above) by addition of an equivalent of $SnCl_2$ to yield the appropriate $[SNS]^+$ salts.

$$AgX + {}^1/_3(NSCl)_3 \xrightarrow{SO_2} [SN][X] \xrightarrow[-AgCl_{(s)}]{SCl_2} [N(SCl)_2][X] \qquad [Eq.\ 1.11]$$

$$[N(SCl)_2][X] + SnCl_2 \xrightarrow{SO_2} [SNS][X] + SnCl_4 \qquad [Eq.\ 1.12]$$

The only disadvantage of this route is in the high cost of the silver salts. Several attempts using alkali metal salts of $[AsF_6]^-$ have so far only given uncharacterisable products[35]. This is counterbalanced through the facility of bulk scale (>10 g) preparations in which no toxic (AsF_5) or potentially explosive (S_4N_4) reagents are used. Furthermore, the only specialised equipment required in this method is that for the handling of liquid SO_2 (see chapter 2), rather than that required for AsF_5.

Table 1.1. Preparation of $[N(SCl)_2]X$ and [SNS]X (taken from ref. 31)

Anion [X]	Recovered Yield $[N(SCl)_2]X$	Recovered Yield [SNS]X	Total Yield of [SNS]X based on $(NSCl)_3$
AsF_6	96%[a]	94%	90%
$SbCl_6$	90%[b]	90%	81%
$AlCl_4$	82%[b]	86%	71%
$FeCl_4$	85%[b]	72%	61%
SbF_6	80%[a]	75%	60%
CF_3SO_3	75%[a]	70%	53%
$SeCl_6$	84%[b]	0%[c]	0%

Notes a: prepared from the silver salt, b: prepared from $(NSCl)_3$ and the corresponding Lewis acid, c: formed $[S_3N_2Cl]_2SeCl_6$

1.2.2 Solid state structures of various dithianitronium salts

Single crystal X-ray structures have been reported for salts of $[SNS]^+$ with $[SbCl_6]^-$ [23], $[AlCl_4]^-$ [28] and $[AsF_6]^-$ [36]. A summary of the structural data is given in table 1.2

Table 1.2 Bond lengths (in Å) and angles (in degrees) of various $[SNS]^+$ salts

Anion	SNS Angle	S(1)-N distance	S(2)-N distance	Corrected SN distance	Ref.
$SbCl_6$	'linear'	1.463(4)	1.463(4)	1.490	23
$AlCl_4$	179.5(3)	1.464(5)	1.472(5)	1.494, 1.517	28
AsF_6	'linear'	1.480(3)	1.480(3)	1.510	36

After applying the 'riding model' of Busing and Levy[37], Johnson *et.al.*[36] concluded that the bond distances in each $[SNS]^+$ cation were within 0.02Å of 1.50Å and are not significantly different from one another. This bond distance indicates a significant contribution by the valence-bond structure $[S=N=S]^+$ as this bond distance corresponds to a bond order of 2.10 (calculated[22] using Nyberg's equation[38]).

However, it has been argued[23] that there is some degree of S≡N character. Also the bond length is significantly shorter than that in the isoelectronic species CS_2 (1.55Å)[39], c.f. N=O bond in NO_2^+ at 1.10Å [40] vs. C=O bond in CO_2 (1.16Å)[41] - which is expected from simple considerations of the covalent radii of nitrogen and carbon.

The $[SNS]^+$ cation is essentially linear, the only a slight variation in the tetrachloroaluminate(III) salt probably arising from the more significant cation-anion interactions observed in that structure. Hexafluoroarsenate (V) is a 'harder' anion and a weaker Lewis base than $[SbCl_6]^-$, which is in turn 'harder' and less interacting (certainly with a 'soft' electrophilic cation such as $[SNS]^+$) than $[AlCl_4]^-$. The S···Cl interactions[28] in $[SNS][AlCl_4]$ are at 3.26(1), 3.36(1)Å and the N···Cl at 3.37(1)Å. The interactions are less than the van der Waals contacts[42] of ~3.5Å and 3.46Å respectively (for 'head on' contacts see table 1.3). These are more significant structurally than the anion-cation interactions in $[SNS][AsF_6]$ and $[SNS][SbCl_6]$ (which are also less than the sum of the van der Waals radii).

Packing diagrams for the $[SbCl_6]^-$ [23], $[AlCl_4]^-$ [28] and $[AsF_6]^-$ [36] salts are shown in figures 1.1, 1.2 and 1.3 respectively.

Figure 1.1 The solid state structure of [SNS][SbCl$_6$]

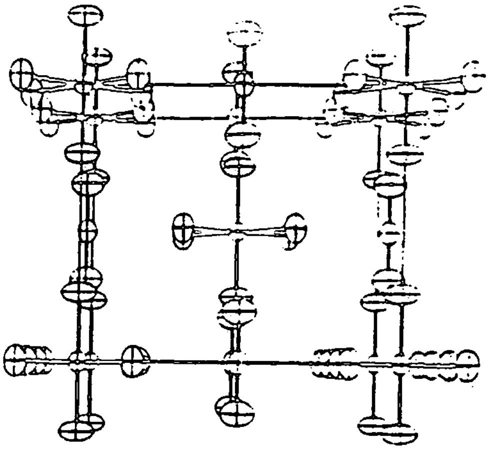


Figure 1.2 The solid state structure of [SNS][AlCl$_4$]

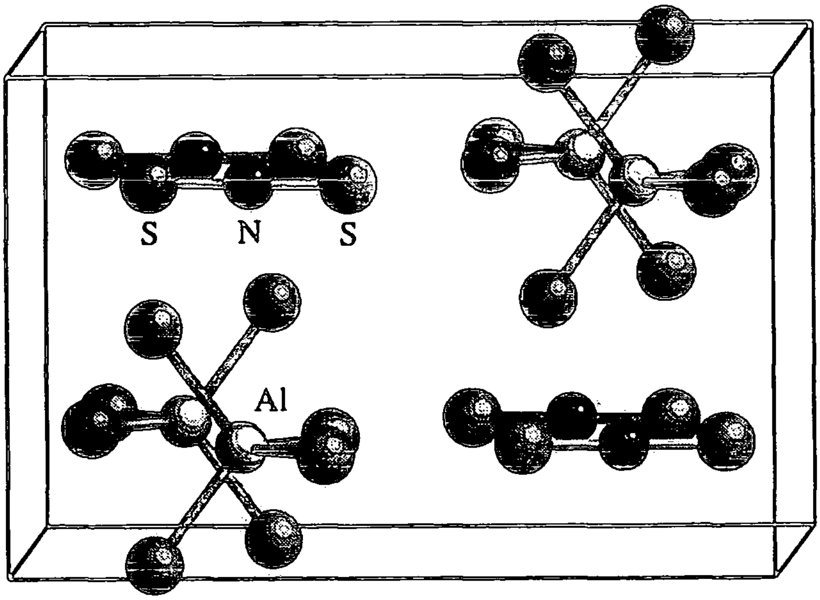


Figure 1.3 The solid state structure of [SNS][AsF$_6$] indicating anion-cation contacts

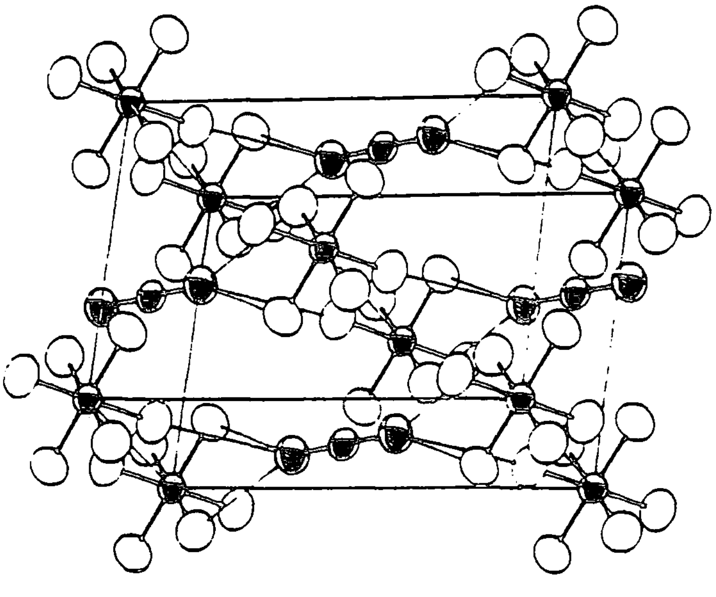


Table 1.3 Effective radii (Å) of selected atoms

	Spherical Radius[a]	Major Radius[b]	Minor Radius[b]
sulphur	1.74	2.03	1.60
nitrogen	1.70	1.60	1.60
chlorine	1.76	1.78	1.58

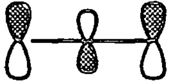
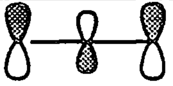
Notes. a:taken from ref 42, b:taken from refs. 43,44.

1.2.3 Molecular orbital studies

During the course of his extensive work[22] on the reactivity of $[SNS]^+$, M.J. Schriver undertook a significant number of molecular orbital calculations (CNDO/2 and *ab initio*) on the $[SNS]^+$ cation, using the crystal data from the $[AsF_6]^-$ salt (i.e. linear, corrected S–N bond distance of 1.510Å).

A summary of the frontier orbitals that he determined is given in table 1.4. The present author repeated some of these calculations using the MOPAC package[15] at the PM3 level (with the S-N bond length initially set at 1.480Å) and allowing the structural parameters to minimise. The results of these are summarised in table 1.4 (see chapter 3 also). Here, the calculations minimised the S-N bond length to 1.53Å and the SNS bond angle to 179.9°.

Table 1.4 Molecular orbital studies on the $[SNS]^+$ cation

	HOMO	LUMO	Ref.	Package
			22	CNDO/2
Orbital Coefs (p_z)	+0.67 (S1) -0.67(S2)	+0.51(S1) +0.51(S2) -0.38(N)		
Eigenvalue	-0.71 aU	-0.39 aU		
			This work	MNDO PM3 level
Orbital Coefs (p_z)	+0.71(S1) -0.71(S2)	+0.55(S1) +0.55(S2) -0.64(N)		
Eigenvalue	-15.69 eV	-8.56 eV		

The results obtained for these calculations are similar to those of Haiduc *et.al.*[45], but the PM3 data set assigns more electron density to the nitrogen atom in the LUMO. This contrasts with the earlier results of Schriver[22] and also with the observed reactivity of $[SNS]^+$ (*vide infra*), which seems to be mainly at the sulphur atoms. This would be expected from considerations of electronegativity (and thus charge distribution) alone - with the sulphur atoms carrying the positive charge. Furthermore, the MO calculations of Schriver[22] suggest the LUMO of the cation to be mainly centred on the sulphur atoms, accounting for their greater reactivity and for the observed retention of the SNS unit in many of the reactions of $[SNS]^+$.

1.2.4 Physical properties of salts of the dithianitronium cation (including the mechanism for the formation of $[SNS][AsF_6]$ from S_8, S_4N_4 and AsF_5, and from S_8 and $SNAsF_6$)

Generally $[SNS]^+$ salts, when pure, are pale yellow in colour; although in the crude state the $[AsF_6]^-$ salt varies from being a deep green or black powder to a yellow microcrystalline solid. Each of these forms does have almost identical elemental analyses and IR spectra - the deep colour is probably due to the presence of relatively small quantities of intensely coloured side-products, either poly-sulphur cations[16], $S_x[AsF_6]_2$ $x=16\text{-}22$, or possibly some type of complex SN based radical. Deeply discoloured samples of $[SNS][AsF_6]$ can be easily rendered pale yellow by repeated recrystallisation from SO_2[24], washing with CH_2Cl_2[26] or $CFCl_3$[16], or by thermolysis at >200°C[27].

Every known $[SNS]^+$ salt is moisture sensitive, usually decomposing to a sticky, deep brown material (shown to contain O-H and N-H groups by IR[34]) within minutes of exposure to moist air. The salts containing harder counterions, e.g. the $[SbCl_6]^-$ and $[AsF_6]^-$ salts, are much more hydrolytically stable than $[AlCl_4]^-$ (but $[SO_3CF_3]^-$ is very sensitive[34]). This stabilityis is probably due to a higher lattice energy component, which has to be overcome before hydrolys occurs. Such hydrolysis can be considered to arise through the nucleophilic attack at the positively charged sulphur atoms - it should be noted that the tetra-methyl derivative, $[Me_2SNSMe_2][AsF_6]$, is hydrolytically stable[35,46]. Alternatively, the stability may be due to packing differences - the large $[SbCl_6]^-$ anions pack well leaving small gaps for the $[SNS]^+$ cations to fill and so not allowing space for water molecules to diffuse into the structure. Even so, a pure sample of $[SNS][AsF_6]$will decompose on the bench within three or four minutes. Pure samples, however, may be stored indefinitely if sealed under dry nitrogen (or in a stoppered flask in the glove box) and may be handled easily in the glove box. Pure samples of $[SNS][AsF_6]$ are photolytically[27] and thermally[27] stable up to 275°C, hence thermolytic purification[27].

Further characterisation of the $[SNS]^+$ salts has been achieved using vibrational spectroscopy[24](see table 1.5) and ^{14}N nmr spectroscopy (δ=-91ppm, referenced to an external nitromethane standard[16]).

The standard molar enthalpy of formation of $[SNS][AsF_6]$ has been determined at 298.15 K using fluorine combustion calorimetery[47] and this datum has been utilised in subsequent mechanistic studies concerning the reactions leading to $[SN][AsF_6]$ and $[SNS][AsF_6]$ [16].

Table 1.5 Vibrational spectra (cm^{-1}) of selected dithianitronium salts (taken from ref. 24)

$[SNS][AsF_6]$		$[SNS][SbCl_6]$		Assignment
IR	Raman	IR	Raman	
1494(m)		1498(m)		$\nu_3(SNS^+)$
1088(w)				$\nu_1+\nu_2(SNS^+)$
818(w)				$[AsF_6]^-$
	798(18,br)		766(17)	$2\nu_2(SNS^+)$
	779(3)		747(2)	$2\nu_2(^{32}SN^{34}S^+)$
	696(100)		688(44)	$\nu_1(SNS^+)$
		374(m)		$\nu_2(SNS^+)$
	682(30)		333(100)	$\nu_1((A_1g)[AsF_6]^-, [SbCl_6]^-)$
697(vs)		320(s)		$\nu_3((T_1u)[AsF_6]^-, [SbCl_6]^-)$
391(s)				$\nu_4((T_1u)[AsF_6]^-)$
	573(8)		293(12)	$\nu_2((Eg)[AsF_6]^-, [SbCl_6]^-)$
			283(8)	
			180(26)	
	368(10)		175(48)	$\nu_5((T_2g)[AsF_6]^-, [SbCl_6]^-)$
			78(100)	Lattice Modes
			62(76)	

Note : IR spectra recorded as nujol mulls, raman spectra of solid samples.

These studies have revealed a rather complex reaction mechanism in which several intermediate sulphur-nitrogen cationic species as well as poly-sulphur cations undergo reactions with S_4N_4 and AsF_5. The overall stoichiometry remains as outlined in equation 1.5, but the need for a trace of Br_2 (or I_2, Cl_2, or $AsCl_4AsF_5$)[48,16] has been clearly substantiated, and the reaction mechanism is now much more clearly understood.

This work serves as a good example of how the techniques outlined in section 1.1 are now allowing for a deeper understanding of the inorganic pathways in SN chemistry. These can often be very complex. A summary of the proposed reaction scheme and the mechanism of the reaction of S_8 with $[SN]^+$ (taken from ref. 16) are given in scheme 1.1 and scheme 1.2 respectively.

Integrated ^{14}N nmr spectra of small SN species were utilised together with observation of the colour changes and the yields of $[SNS][AsF_6]$ with various reaction mixtures and times in this study. The addition of Br_2 was shown to aid the rapid oxidation of S_8 by AsF_5 to give $S_4[AsF_6]_2$, rather than $S_8[AsF_6]_2$ which reacts much more slowly with AsF_5 or $[SN][AsF_6]$ and so allows some AsF_5 to react directly with S_4N_4 to produce the observed side-products, $[S_4N_4]AsF_6$ and $[S_3N_2]_2[AsF_6]_2$. The presence of a trace of bromine also allows any sulphur produced at an intermediate stage in the reaction (e.g. by equation 1.13b) to be oxidised rapidly by any unreacted AsF_5 to give $S_4[AsF_6]_2$ (equation 1.13a'). Any further sulphur generated towards the end of the reaction is converted to $[SNS][AsF_6]$ by reaction with $[SN][AsF_6]$ (equation 1.13e).

Scheme 1.1 Proposed mechanism for the formation of $[SNS][AsF_6]$ in the presence of Br_2 (taken from ref. 16)

Overall:

$$S_8 + 2S_4N_4 + 12AsF_5 \xrightarrow{SO_2 \text{ trace } Br_2} 8[SNS][AsF_6] + 4AsF_3 \quad \text{[Eq.1.13]}$$

By:

$$S_8 + 6\,AsF_5 \xrightarrow[\text{Trace } Br_2]{\le 5 \text{ min}} 2\,S_4[AsF_6]_2 + 2\,AsF_3 \quad \text{[Eq. 1.13a]}$$

$$2\,S_4[AsF_6]_2 + 2\,S_4N_4 \xrightarrow{\le 1 \text{ h}} 2\,[S_3N_2]_2[AsF_6]_2 + \tfrac{1}{2}\,S_8 \quad \text{[Eq. 1.13b]}$$

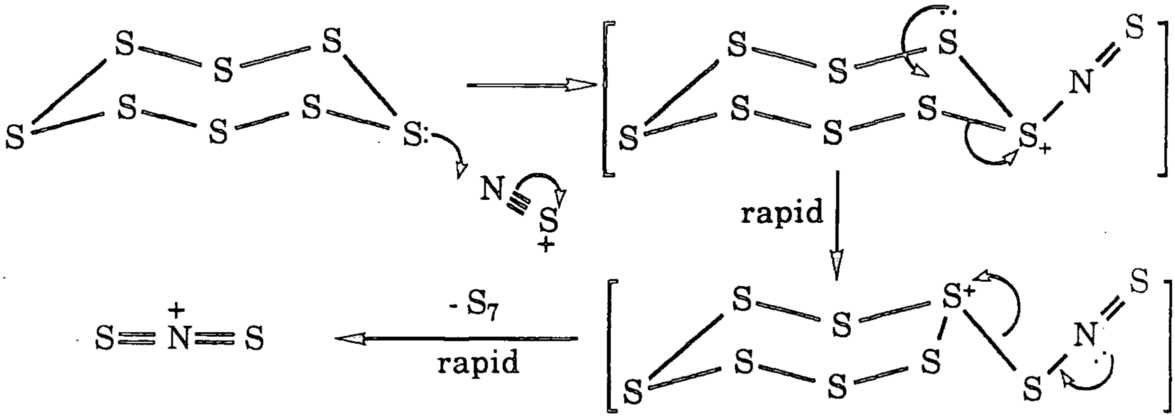
$$\tfrac{1}{2}S_8 + 3AsF_5 \xrightarrow[\text{Trace } Br_2]{\le 5 \text{ min}} S_4[AsF_6]_2 + AsF_3 \quad \text{[Eq. 1.13a']}$$

$$[S_3N_2]_2[AsF_6]_2 + 3AsF_5 \xrightarrow[\text{Trace } Br_2]{\le 1 \text{ h}} 2\,[SNS][AsF_6] + 2SNAsF_6 + AsF_3 \quad \text{[Eq. 1.13c]}$$

$$S_4[AsF_6]_2 + [S_3N_2]_2[AsF_6]_2 \xrightarrow{\le 1 \text{ h}} 4[SNS][AsF_6] + \tfrac{1}{4}S_8 \quad \text{[Eq. 1.13d]}$$

$$\tfrac{1}{4}\,S_8 + 2\,[SN][AsF_6] \xrightarrow{\le 5 \text{ min}} 2\,[SNS][AsF_6] \quad \text{[Eq. 1.13e]}$$

In the absence of bromine most of the reaction steps are far slower (all reactions to give [SNS][AsF_6] were still incomplete after 3 weeks, compared with a reaction time of less than 2 days) and some of the AsF_5 is used up in oxidation of S_4N_4, therefore resulting in incomplete oxidation and contamination of the final product.



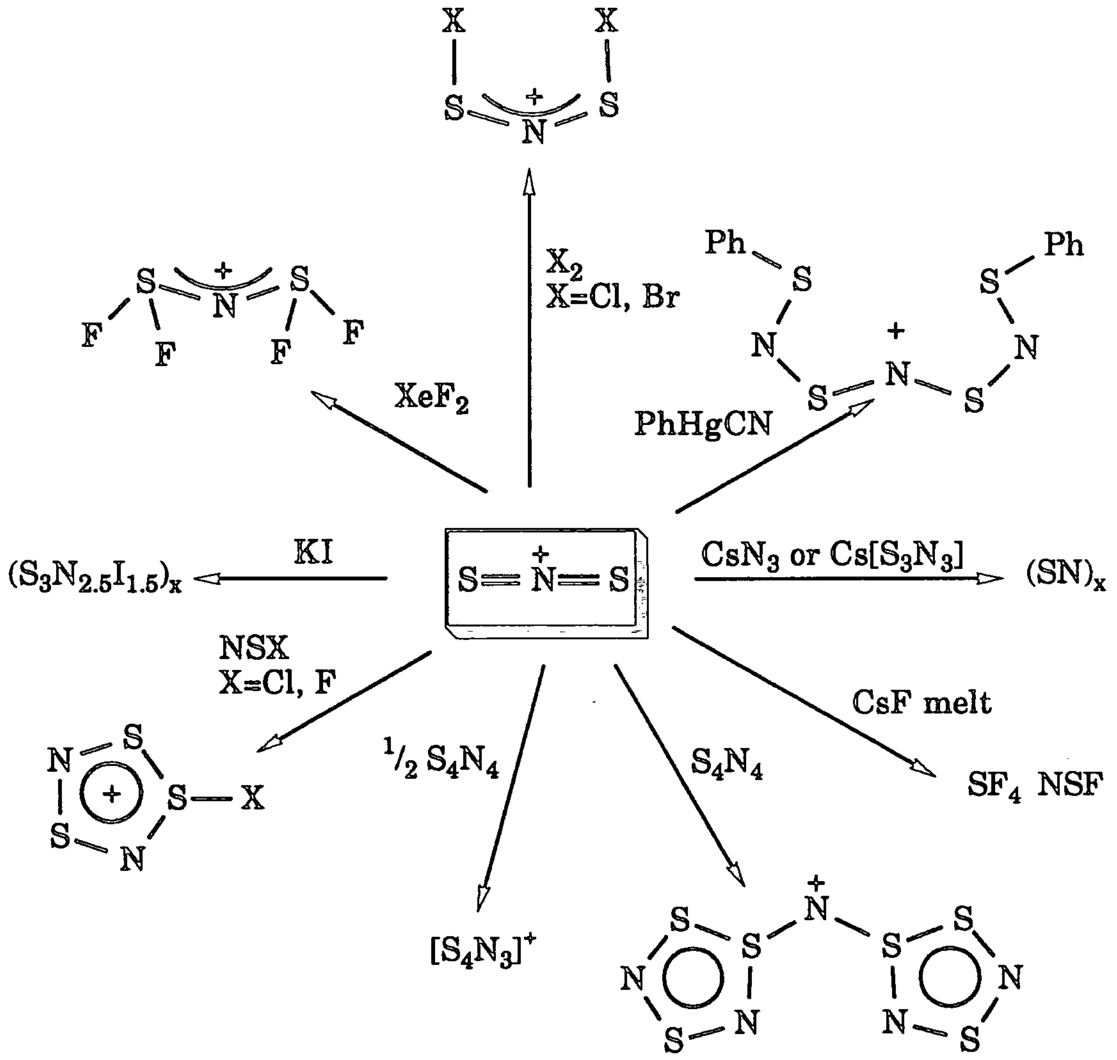
Scheme 1.2 Proposed mechanism for the reaction of [SN][AsF_6] with S_8 to generate [SNS][AsF_6] (taken from ref. 16)

Neither of the two reaction intermediates in this proposed scheme was observed by ^{14}N nmr, so it is assumed that their interconversion and decomposition to give S_7 (which may itself undergo further reaction with other SN^+ cations) is very rapid.

1.2.5 Reactions of dithianitronium salts with inorganic materials (summarised in scheme 1.3)

The [SNS]$^+$ cation is an unsaturated, electrophilic species with low-lying LUMOs and terminal sulphur atoms that can adopt valencies of 2, 4 or 6, so therefore it should be extremely reactive towards both unsaturated organics (*vide infra*) and electron-rich, nucleophilic inorganics. MacLean *et.al.*[49] reported the reactions of [SNS][AsF_6] with halogens and halogenating agents, and Passmore *et.al.* also investigated[50] its reactions with halides, azides and S_4N_4. A.G. Kendrick[51] studied the reaction of [SNS][AsF_6] with NSF in liquid SO_2 and this reaction is also reported, together with the reaction with $(NSCl)_3$ and a rationale for the addition of [SNS]$^+$ to unsaturated organics, in a subsequent publication[52]. In all of these cases the SNS fragment is preserved and the sulphur atoms are attacked. This is expected from the MO data which locates the positive charge in [SNS]$^+$ on the more electropositive sulphur atoms and shows them to be the site of greatest orbital density in the LUMO.

However, the reactions with metal cyanides, e.g. PhHgCN (see chapter 6) and $[M(CN)_4]^{2-}$ (M= Pt, Pd and Ni)[53], are more complex, with the SNS unit not being preserved.



Scheme 1.3 Reactions of $[SNS][AsF_6]$ with inorganic reagents

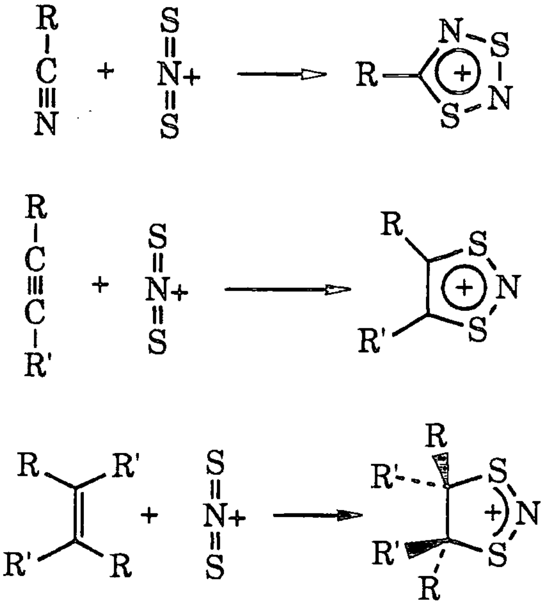
1.2.6 Reactions of the dithianitronium cation with organic materials (summarised in scheme 1.4)

The first reactions of $[SNS]^+$ reported[54] in the literature were those of $[SNS][AsF_6]$ with neat acetonitrile, acetylene and propyne to yield 5-methyl-1,3,2,4-dithiadiazolylium hexafluoroarsenate and the corresponding 1,3,2-dithiazolium hexafluoroarsenate salts respectively. These novel compounds were isolated in almost quantitative yield and further illustrate the general synthetic utility of $[SNS][AsF_6]$ as a source of the $[SNS]^+$ moiety. This work was extended by the addition of $[SNS]^+$ to the alkenes[55] trans-but-2-ene and norbornene (in either 1:1 or 1:2

stoichiometries). These reactions of [SNS][AsF$_6$] with organics illustrate the unique nature of [SNS][AsF$_6$] in SN chemistry, i.e. it is

(i) a general reagent - reacting with all organic nitriles, alkynes and alkenes (except nucleophilic or deactivated ones)

(ii) a high yielding reagent - nearly all cycloadditions occur with quantitative or semi-quantitative yields.



Scheme 1.4 Reactions of [SNS][AsF$_6$] with unsaturated organic reagents

1.2.6.1 General reactivity towards organic compounds

The frontier molecular orbitals for [SNS]$^+$ and the various unsaturated systems (viz. C≡N, >C=C< and -C≡C-) are shown in figure 1.4. In general these cycloadditions have been rationalised[55] by a reverse-electron demand cycloaddition (first proposed by Oakley[56] and then illustrated more quantitatively by Passmore *et.al*[57, 52]), where electron density is transferred predominantly from the HOMO of the unsaturated species to the LUMO of [SNS]$^+$ (which is at a very low energy compared to the dienes encountered in organic synthesis).

This occurs readily for [SNS]$^+$ (as opposed to neutral SN heterocycles[58]) as it is cationic and can accept electron density into its low-lying LUMO from the HOMO of the unsaturated organic. Passmore and co-workers[57] have recently correlated kinetic data for the cycloadditions of [SNS]$^+$ with various alkynes and nitriles and have found, by the use of ^{19}F nmr and ^{14}N nmr techniques, that these cycloadditions have overall second-order kinetics (being first order in both reagents). They noted, also, that the reaction rates increased with a decrease in HOMO-LUMO energy gap (as expected if we consider the matching of frontier orbitals).

In the same publication the reactions of [SNS][AsF$_6$] with dicyanogen and N≡C-C≡C-H were studied (see scheme 1.5).Isolation of a 1:1 addition compound with dicyanogen, rather than the expected 2:1, was predicted on the basis that the HOMO-LUMO energy gap (13.36eV) would give a slow reaction rate. It is significant that dicyanobenzene does not form a 1:1 adduct (see chapter 3).

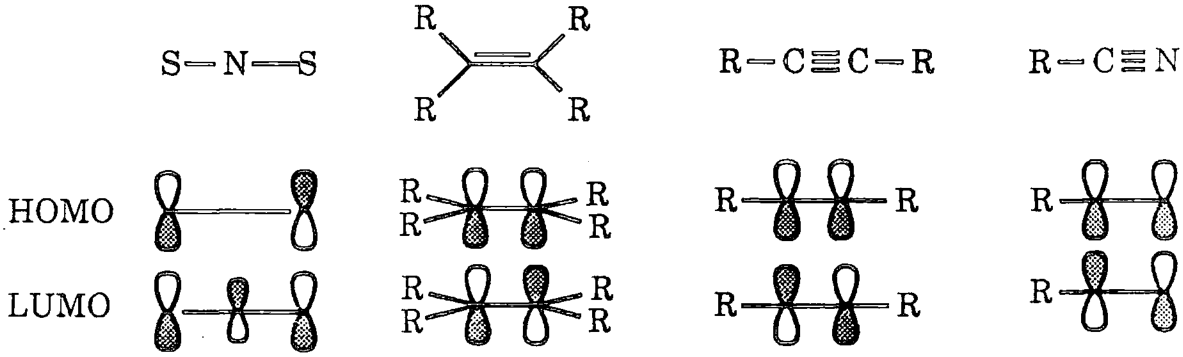
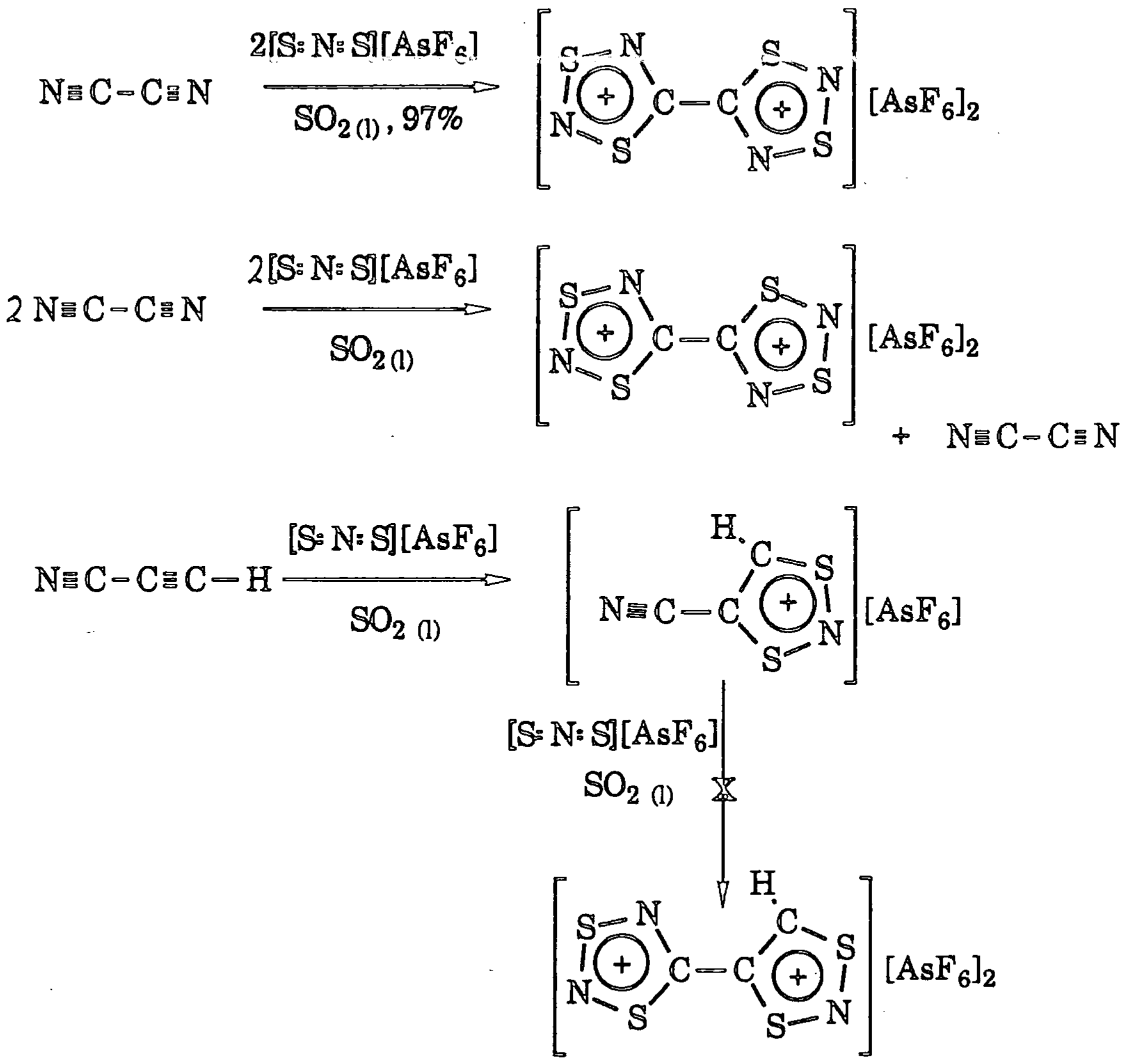


Figure 1.4 Frontier molecular orbitals for [SNS]$^+$, olefins, alkynes and nitriles.

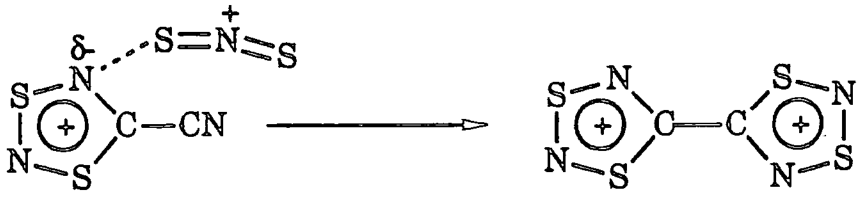
Furthermore, the quantitative reaction of [SNS][AsF$_6$] with N≡C-C≡C-H occurs in 1:1 stoichiometry only. This is as expected, because the lowering of energy of the HOMO in the 1:1 mono-adduct, increases the HOMO-LUMO energy gap and so deactivates the intermediate with respect to further [SNS]$^+$ addition. This reaction occurs at the alkyne moiety only (as expected from considerations of ionisation energies: 11.60 eV for C≡C and 14.03 eV for N≡C).

Such specificity of [SNS]$^+$ towards a particular functional group is of great synthetic importance and side reactions are minimised. For example, the addition of further [SNS][AsF$_6$] to the 1:1 adduct of [SNS][AsF$_6$] with potassium tricyanomethanide^{26} occurs at the C≡N groups only, and not at the C=C functionality. However, with N≡C-C≡N the 2:1 adduct is produced in all cases and the 1:1 adduct could not be isolated even with excess dicyanogen.



Scheme 1.5 Reactions of [SNS][AsF$_6$] with dicyanogen and N≡C-C≡C-H

These apparent anomalies are explained by the rapid addition of the second equivalent of [SNS]$^+$ being facilitated by complexation to the N4 atom on the dithiadiazolylium ring (which has a slight negative charge associated with it) thus allowing the [SNS]$^+$ unit to swing round to the adjacent C≡N unit and also for the HOMO-LUMO energy gap to be reduced (see scheme 1.6).



Scheme 1.6 Transoid directing effect of dithiadiazolylium nitrogen in [SNS]$^+$ addition to alkyl multi-nitriles.

This explanation accords with the 1:1 addition with the alkyne substituent (there is no N4 atom to complex the second $[SNS]^+$ unit and so no further reaction occurs) and it has been used in conjunction with further MO calculations on the proposed intermediates to rationalise the reactivity of $[SNS][AsF_6]$ with $K[C(CN)_3]$ (see chapter 3) and the stereo-specificity of these reactions with multi-nitriles (figure 1.5).

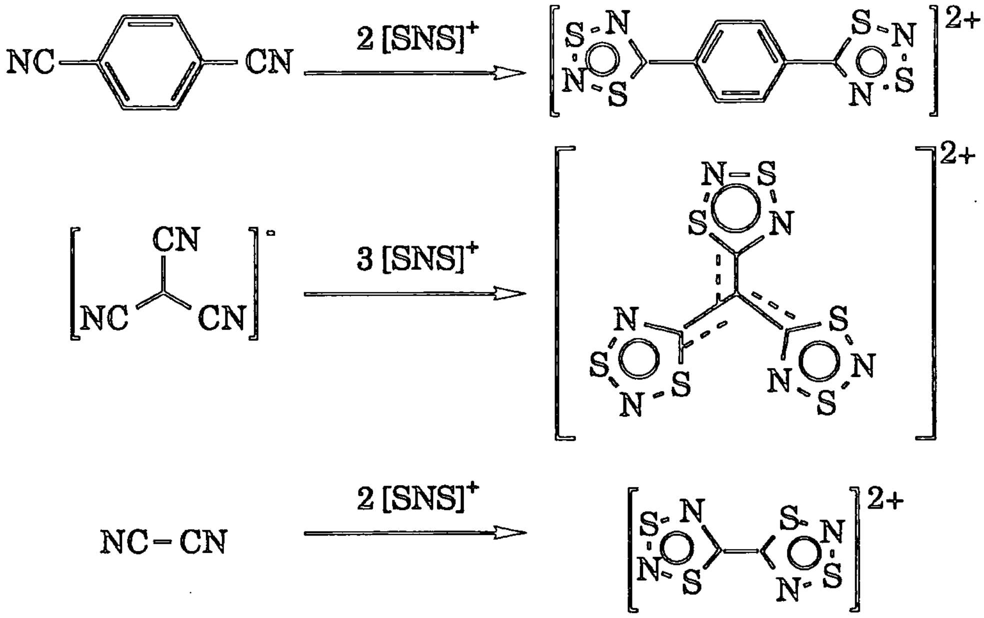


Figure 1.5 Examples of the stereo-specificy of reactions of $[SNS]^+$ with multi-nitriles; addition occurs in a 'transoid' fashion in all cases

1.2.6.2 Reactions with nitriles

Recently, $[SNS]^+$ additions to a wide range of para-substituted benzonitrile derivatives[60] (see table 1.6) and multi-nitriles (see tables 3.2 to 3.3) have been utilised in order to prepare a wide variety of substituted 1,3,2,4-dithiadiazolyliums. They can be readily reduced to give the corresponding dithiadiazolyls[61], free-radical species, which although photolytically stable in the solid state are thermally unstable solids[62] and photolytically rearrange in solution to give the corresponding 1,2,3,5-isomer[61].

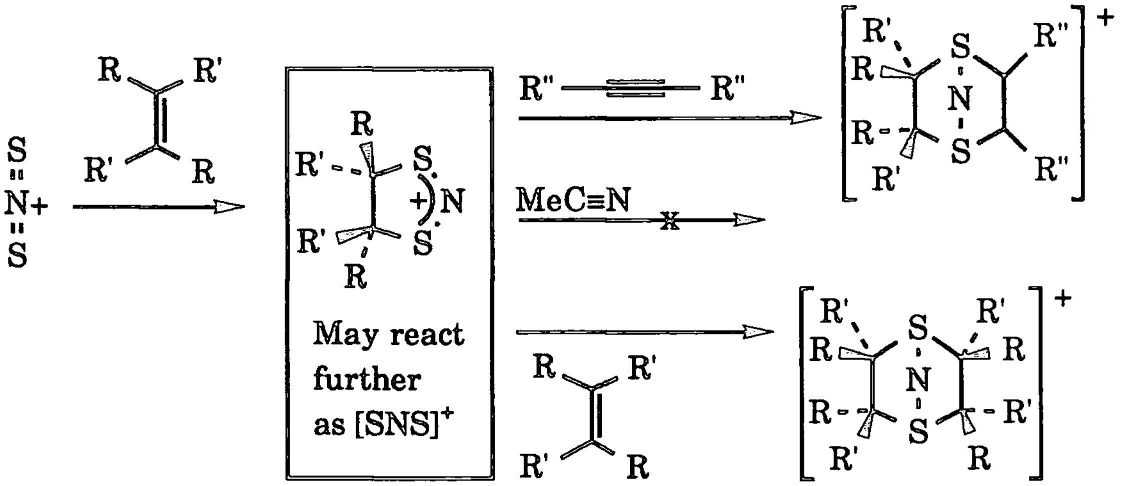
Table 1.6 Preparation of some p-[X-C_6H_4-CN_2S_2]$^+$[AsF_6] -salts.

X	Yield (%)
CF_3	83.3%
Br	79.5%
MeS	86.3%
MeO	70.0%
CH_3	86.7%

These materials and their selenium derivatives are the subject of recent interest as potential molecular magnets[63] and conductors[64-66] (see chapters 3, 4 and 5).

1.2.6.3 Reactions with alkenes

[SNS][AsF_6] can react with one or two equivalents of a wide range of alkenes (e.g. norbornene, ethene, $H_2C=C(H)CH_3$) in quantitative yield in liquid SO_2[55]. The intermediate 1:1 compound, [RR'CSNSCRR']$^+$ (**1**), has been shown to react with alkynes[22] in a similar way to [SNS]$^+$ itself, but it does not form addition compounds with the less reactive nitrile moiety (e.g. acetonitrile[22]). The LUMO of **1** is of similar energy and geometry to [SNS]$^+$ itself (see scheme 1.7) and so may undergo the usual reverse-demand 4+2 cycloaddition reactions with alkynes but not with the less reactive nitriles.



Scheme 1.7 Reactions of the [$(RR')_2C_2$.SNS]$^+$ intermediate with unsaturated organics

More recently[67] this chemistry has been extended to the chlorinated derivative, [ClSNSCl]$^+$, which also undergoes symmetry-allowed, reverse-electron demand, concerted cycloadditions with alkynes as well as alkenes. However, only the reaction with ethene is quantitative. Figure 1.6 compares the HOMOs and LUMOs in $[SNS]^+$, $[N(SCl)_2]^+$, $[(CH_2)_2S_2N]^+$ and ethyne.

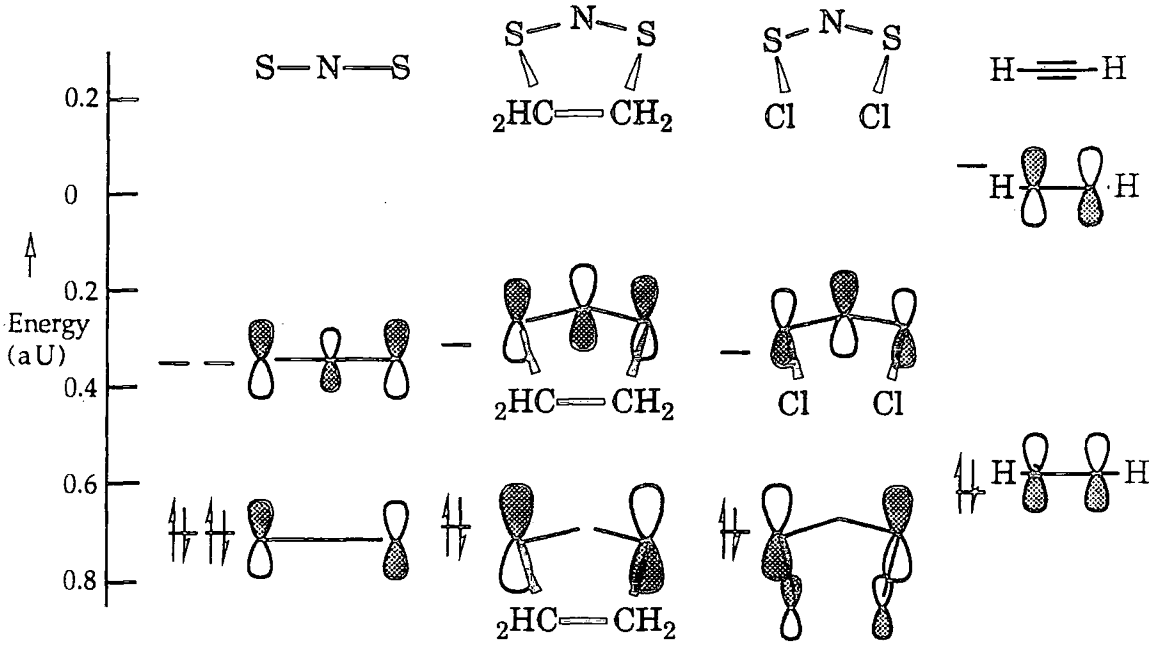


Figure 1.6 A Comparison of the HOMOs and LUMOs in $[SNS]^+$, $[N(SCl)_2]^+$, $[(CH_2)_2S_2N]^+$ and Ethyne (taken from ref 67)

1.2.6.4 Reactions with alkynes

Many quantitative reactions of $[SNS][AsF_6]$ with alkynes have been studied. They further illustrate its synthetic utility and are summarised in table 1.7

Table 1.7 The reactions of $[SNS][AsF_6]$ with alkynes

R	R'	Yield (%)	Ref
H	H	100	68
CF_3	CF_3	95	69
Me	Me	---	22
$SiMe_3$	$SiMe_3$	100	52
CO_2Me	CO_2Me	95	22
H	CH_3	94	68
H	CF_3	100	22
H	CN	96	57

1.2.6.5 Reactions with other multiple bonds

In principle, $[SNS]^+$ can react with a wide range of multiple bonds, provided the LUMO - HOMO energy gap is not too high and the orbitals are of the correct symmetry.

Recent work has suggested that $[SNS]^+$ may react with Ar-N=S=O[34,70] and R-N≡C[35]. The reactions of $[SNS][AsF_6]$ with R-C≡P[71] have very recently been established.

1.2.7 Derivatives of the dithianitronium cation

As outlined in section 1.2.5, $[SNS]^+$ may be halogenated[49] using Br_2, Cl_2 and XeF_2 to give $[ClSNSCl]^+$, $[BrSNSBr]^+$ and $[F_2SNSF_2]^+$ respectively. The corresponding iodine derivative is unstable (probably due to the weaker S-I bond). The structure of $[F_2SNSF_2]^+$ has been determined[49] (see figure 1.7) and the cation[59] is similar to that of $[Me_2SNSMe_2]^+$, with C_{2v} symmetry. This contrasts[72] with the conformation of $[XSNSX]^+$, in which the S-Cl bonds point away from the N atom (see fig 1.8).

The chemistry of the chlorinated derivatives has been studied[67], and it is similar to that of $[SNS]^+$ itself (see section 1.2.6.3).

The tetra methyl derivative has been prepared,as the chloride salt, from the reaction[46] of dimethylsulphoxide with $(NSCl)_3$ in CH_2Cl_2 (see equation 1.14), or by the reaction[73] of Cl-C≡N with dimethylsulphoxide (see equation 1.15). The $[AsF_6]^-$salt has been prepared (by metathesis with $AgAsF_6$) and its chemistry is currently under investigation[35].

$$(NSCl)_3 + Me_2S{=}O \xrightarrow{CH_2Cl_2} [Me_2SNSMe_2]Cl + SO_{2(g)} \qquad [Eq. 1.14]$$

$$N{\equiv}C\text{-}Cl + Me_2S{=}O \xrightarrow{DMSO} [Me_2SNSMe_2]Cl + CO_{2(g)} \qquad [Eq. 1.15]$$

1.2.8 Conclusions and general remarks

The salts of the $[SNS]^+$ cation have been shown to be of broad use in the preparation of CSN heterocycles. The $[AsF_6]^-$ salt, in particular, has the following convenient properties as a reagent for the insertion of an SNS unit :

1. *General* - The salt can be used to prepare a whole range of derivatives; for example a range of para-substituted 1,3,2,5-dithiadiazolyliums has been prepared[60] by reactions of $[SNS][AsF_6]$ with the corresponding nitriles in SO_2 solutions - see table 1.8.

Figure 1.7 The solid state structure of the $[F_2SNSF_2]^+$ cation

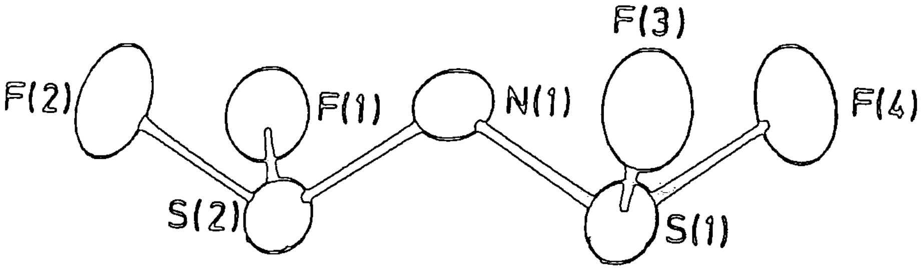
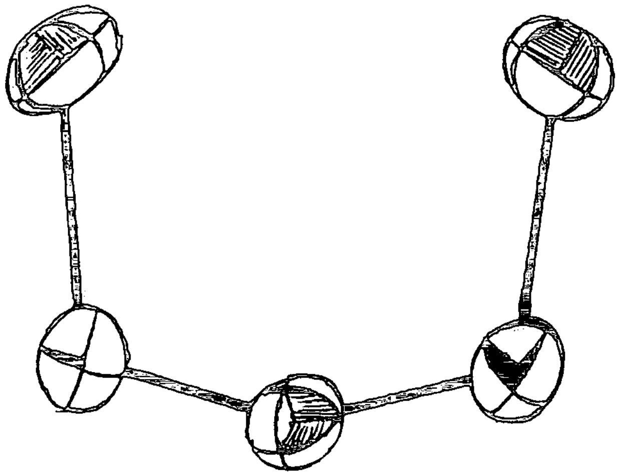


Figure 1.8 The solid state structure of the $[ClSNSCl]^+$ cation



2.*High Yielding* - Most of the addition reactions are quantitative, or near quantitative.

3. *Specific* - There are very few side-reactions and the reactivity of a particular functionality can be generally predicted.

4. *Versatile* - The salt reacts with olefins, alkynes, nitriles and several inorganic compounds to give novel products.

Furthermore, recent developments[31] in the synthesis of [SNS][AsF_6] have made it more generally available.

[A final comment on the reactivity of these salts - by far the most versatile is [SNS][AsF_6]. Other salts, especially [SNS][$AlCl_4$], undergo competing reactions, (e.g. to form $S_3N_2^+$) and in some cases, even SNSAsF_6 will be affected by other reagents. For example, *p*-[NC.C_6H_4.CNSSN] does not form the expected salt , *p*-[SNSNC.C_6H_4.CNSSN[AsF_6], but it is reduced to give $S_3N_2^+$ and sulphur - see chapter 4.

A general overview of reactivities can be seen from the details in table 1.8 - showing the reactions[31] of various [SNS]$^+$ salts with benzonitrile in a variety of solvents.

Perhaps the only disadvantage of these reagents is that reactions require polar, aprotic solvents which do not attack the electrophilic cation, so acetonitrile[54], thf[53] and alcohols[53] cannot be used.

Table 1.8 Reactions of [SNS]X with PhCN (taken from ref. 31)

SNS Reagent	Conditions	Time	Temp./ °C	Yield
[SNS]AsF_6	neat	5 min	20	90%
	l. SO_2	1 h	20	95%
[SNS]$SbCl_6$	neat	7 d	20	0%^{a}
	neat	3 h	110	75%
	CH_2Cl_2	1 d	40	0%^{a}
	l. SO_2	7 d	20	0%^{a}
[SNS][CF_3SO_3]	neat	1 h	20	70%
	l. SO_2	2 h	20	74%
	CH_2Cl_2	2 h	40	30%
[SNS]SbF_6	neat	1 h	20	35%
	l. SO_2	3 h	20	50%
[SNS]$AlCl_4$	neat	1 h	20	0%^{b}
	CH_2Cl_2	2 h	20	0%^{b}
	l. SO_2	1 h	20	0%^{b}

Notes a: Did not react ; b: Decomposed.

1.3 General rationale and summary of this thesis

There has been continued recent interest in the potential use of dithiadiazolyls and their selenium derivatives as organic magnets[63] and conductors[64-66]. The addition of [SNS][AsF_6] to a variety of multi-nitriles has been explored and is a high yielding route into this type of system (it is also the only method of introducing a 1,3,2,4-dithiadiazolylium moiety).

Of particular interest are the radical cations of the multi-dithia / diselenadiazolyliums (where the free electron on each molecule may well line up and so give rise to para or ferro-magnetic behaviour). In these cases the cationic part of the radical cation is held firmly by coulombic attraction to the counterion and this may prevent spin-pairing of radical centres (which gives rise to diamagnetic behaviour).

Also greater inter-molecular interactions have been observed for the selenium analogues of these materials[74] (as expected - selenium has larger d-orbitals and a lower ionisation potential, thereby facilitating greater intermolecular interactions in the solid state).

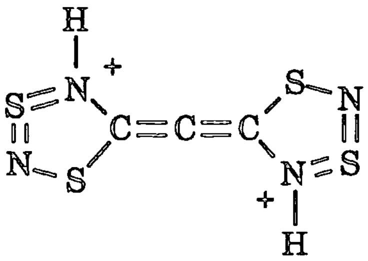
Therefore, the so-called 'mixed' dithiadiazolylium and diselenadiazolylium salts were prepared (with both 1,2,3,5- and 1,3,2,4-dithiadiazolylium isomers present in each cation) and subsequently reduced to the corresponding radical cations and diradicals (see chapters 4 and 5). The reactions of [SNS][AsF_6] with potassium tricyanomethanide (chapter 3) resulted in materials with isolable radical cations, but these were highly moisture sensitive and so could not be fully characterised.

Also considered were the reactions of $[SNS]^+$ with cyanides bound to metal or metalloid centres. Very little work has been done in this area and the resulting dithiadiazolyliums could well be useful as transfer reagents (c.f. organometallic transfer reagents) for the dithiadiazolylium moiety.

The result of the addition of [SNS][AsF_6] to PhHgCN was not a dithiadiazolylium salt but [$Ph_2S_4N_3$][AsF_6] (see chapter 6) and this led to an attempt to synthesise other SN chains by more general routes. As a result $(NSCl)_3$ was found to extend the $Ar_2S_3N_2$ chain to give [$Ar_2S_4N_3$]Cl.

The derivative chemistry of the dithiadiazolyliums was explored in an attempt to prepare a fluoride salt However, an unexpected product of the reaction of *p*-[Cl.C_6H_4.CNSSN][AsF_6] with Me_4NF was the crystalline [Cl.C_6H_4.CNSSN] radical, the X-ray crystal structure of which was determined and compared to some recent[74] cyano-substituted analogues (chapter 7).

Malononitrile was used (appendix 1) as a model compound for the study of reactions of [SNS][AsF_6] with K[C(CN)$_3$] and the 2:1 product, although initially considered to be extensively hydrolysed, appears to contain an allene carbon:



It is of the correct formulation and no CH_2 groups are observed in either the ^1H nmr or ^{13}C nmr, although N-H coupling is seen.

Finally, considering the charge-transfer nature of the $[S_3N_3]^-$ salts of the dithiadiazolyliums [75] and the charge transfer complexes of benzo-1,3,2-dithiazol-2-yls[76], then attempts were made to prepare $[S_3N_3]^-$ salts of aryl dithiazoliums (see appendix 2).

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Chapter 2

General Experimental

2.1 General experimental techniques

Many of the compounds prepared during the course of this work are sensitive to moisture, although moderately stable in dry air. Thus, inert atmosphere techniques are required and have been carefully employed throughout this work.

All air- and moisture- sensitive materials were handled under dry nitrogen in a Vacuum Atmospheres HE43-2 glove box fitted with a HE493 Dri-Train. All glassware was pre-dried overnight at ca. 130°C prior to use. For most reactions standard vacuum-line methods were used in conjunction with oxygen free nitrogen (BOC white spot) as inert gas (further dried by passing through a P_2O_5 column). Liquid sulphur dioxide, elemental bromine and arsenic pentafluoride were handled on a Monel vacuum line (fitted with stainless steel and monel 'Whitey' taps (IKS4) fitted with teflon compression ferrules) - designed and built by Dr Z.V. Hauptman of Durham University, Chemistry Department. Arsenic pentafluoride, being a highly moisture sensitive gas was transferred from the original cylinder to a pressure vessel only after the line had been thoroughly dried, usually by purging it with sulphur tetrafluoride.

2.2 More specialised apparatus

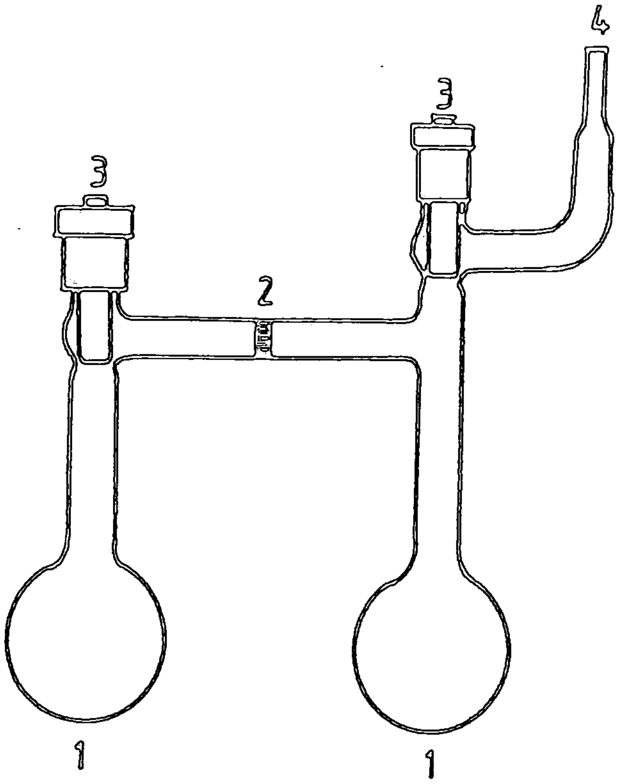
2.2.1 The "Dog"

This is a twin-bulbed reaction vessel incorporating a glass sinter in the horizontal tube connecting the two legs. Teflon vacuum taps (J. Young Co.) enable this apparatus (shown in Fig. 2.1) to be used for all reactions incorporating liquified gases *eg* SO_2, AsF_5. The $^1/_4$ - inch tubing facilitates connection to the metal vacuum line via Swagelok Teflon compression fittings or alternatively to the double-manifold line via a suitable glass adapter and Swagelok fitting.

2.2.2 The closed extractor

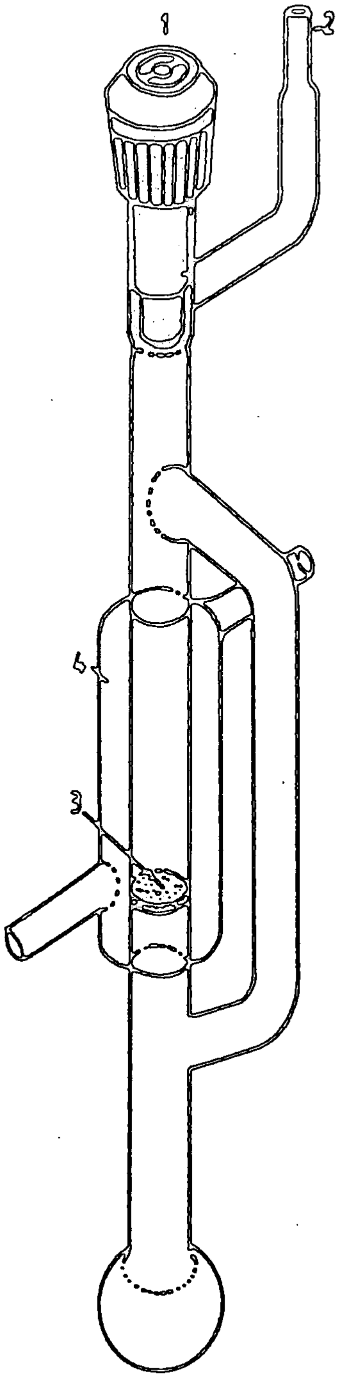
This apparatus was designed by Dr Hauptman and is based on the common Soxhlet extractor. The closed design and the Teflon vacuum tap enable the apparatus (shown in figure 2.2) to be used for extractions involving liquid sulphur dioxide as well as with less volatile solvents (a partial vacuum may be applied in order to facilitate low temperature operation). The bulb is usually warmed and the solvent condenses onto the extractant in the cooling jacket.

Figure 2.1 The twin-bulbed reaction vessel or 'dog'



1. Reaction bulb.
2. Glass sinter (usually porosity grade 3).
3. J. Young teflon tap.
4. $\frac{1}{4}$" ground glass.

Figure 2.2 The closed extractor



1. J. Young teflon tap.
2. ¼" Ground glass.
3. Glass sinter (usually porosity grade 3).
4. Cooling jacket.

In both this and the 'dog' apparatus solid material could be recovered from the bulbs by scoring with a glass knife and then breaking them off (in the glove box) - the apparatus being readily cleaned and re-assembled. Thorough annealing of the apparatus is required in order for it to remain suitable for use with SO_2 / AsF_5 where pressures in excess of 4 atm. are developed.

2.2.3 High vacuum apparatus

When pressures less than 10^{-4} torr were required, for example in high vacuum sublimation for crystal growth, then a high vacuum apparatus (assembled and maintained by Dr Hauptman) was used. This comprised an Edwards oil diffusion pump backed by an Edwards No.5 two-stage rotary pump. The vacuum was measured using Edwards No.8 Penning and Pirani gagues. A vacuum in excess of 10^{-7} torr was obtained routinely with this system.

2.3 Temperature control

Reactions were conducted at room temperature unless otherwise stated. For controlled cooling and warming, between ca. -40°C and +40°C, for example for use in cyclic voltammetry, a Haake F2 circulator with methylated spirit coolant was employed. A Haake PG10 programmer was utilised in addition to the normal apparatus for temperature programming (e.g. for slow heating and cooling of a solution - usually employed in the 'ripple' technique of crystal growth[1]). Silicone oil or water baths were used, where necessary, to heat reactions and dri-ice / acetone slush baths employed for low temperature work.

2.4 **Physical methods** [Operator(s) in brackets]

2.4.1 Infrared spectroscopy

Infrared spectra were recorded as Nujol mulls between KBr or CsI plates using either a Perkin-Elmer 577 or 457 grating infrared spectrophotometer or a Perkin-Elmer FT 1720X spectrophotometer. For all moisture-sensitive samples mulls were made up in the glove box and the plates sealed in a brass holder. Nujol was stored in the glove box over sodium.

2.4.2 **Electron spin resonance spectroscopy (esr)** [Dr J.M. Rawson and Dr R. Whitehead]

Esr spectra were obtained on a Varian Associates V-4502 EPR spectrometer. In a typical experiment an oven-dried quartz esr tube was loaded with a dithiadiazolylium salt, tetrabutylammonium chloride (omitted if using the chloride salt) and triphenylantimony. Addition of a suitable solvent (commonly toluene or acetonitrile) via a syringe followed by sonication in an ultrasonic cleaning bath generated the radical, and spectra were obtained generally within 10 minutes of radical generation.

2.4.3 **Nuclear magnetic resonance spectrometry (nmr)** [Dr R.S. Matthews, Mrs J.M. Say]

Nmr spectra were recorded on Varian Gemini 200 (^{1}H and ^{13}C), Bruker VXR400S (^{1}H, ^{19}F and ^{13}C), Bruker AC250 MHz (^{19}F and ^{13}C) and AMX 500 MHz (^{14}N and ^{13}C) spectrometers.

2.4.4 **Differential scanning calorimetry (dsc)**

Dsc measurements were carried out using a Mettler FP80 control unit linked to a Mettler FP85 thermal analysis cell and a Fisons y-t chart recorder. The whole apparatus was interfaced with an Opus PC III computer running a dsc analysis program written by Dr Rawson. Samples were cold - sealed in aluminium sample pans in the glove box.

2.4.5 **Ultraviolet - visible spectroscopy**

Solutions in acetonitrile were recorded on a Perkin Elmer Lambda 3 spectrophotometer using a specially constructed cell comprising a quartz cuvette summounted by a J. Young Teflon tap and $^1/_4$-inch o.d. glass tube.

2.4.6 **Mass spectrometry** [Dr M. Jones, Miss L.M. Turner]

Spectra were recorded on a VG Analytical 7070E spectrometer using electron-impact (EI), chemical-ionisation (CI) or fast atom bombardment (FAB) techniques.

2.4.7 **Elemental analyses.**

Carbon, hydrogen and nitrogen analyses were performed by Mrs M. Cocks, Mrs J. Dostal and Miss J. Magee on a Carlo Erba 1106 Elemental Analyser. All other analyses were performed by Miss Magee or Mrs Dostal.

2.4.8 **Electrochemical techniques**

General procedures

A constant potential difference was maintained by a Ministat precision potentiostat, supplied by H.G. Thompson Associates, Newcastle upon Tyne.

The cyclic voltammograms were recorded using a Bioanalytical Systems type CV-1B potential wave generator and a Linseis type LY1710Q x-y chart recorder.

The reference electrode was checked against the saturated standard calomel electrode before use. Connection was via a salt bridge (of 0.1M $[Bu_4N][BF_4]$ solution in acetonitrile) and the potential difference measured with a Thandar TM351 digital multimeter.

A Solatron LM1240 Multimeter was used to measure current flow in the electrocrystallisation experiments and a Coulomb meter (designed and built by Dr. A. Royston, Department of Chemistry, University of Durham) to determine the quantity of material deposited.

A galvanostat (also designed and built by Dr. Royston) was employed in several of the electrocrystallisations.

As a high degree of purity and cleanliness of operation is required for electrochemical work, acetonitrile (which was the only solvent used for the electrochemistry undertaken here) was specially purified (HPLC grade, distilled off CaH_2 and further dried by passing through an alumina column) before use.

The platinum electrodes (e.g. auxiliary platinum coil and working platinum sheet electrodes) were cleaned by immersing in concentrated hydrochloric acid (to remove any heavy metals from the surface and so prevent destructive alloying of the platinum) and then heated to redness in a moderate flame (care was needed to prevent the fine metal from melting, however, it was a simple process to weld the platinum coil back together).

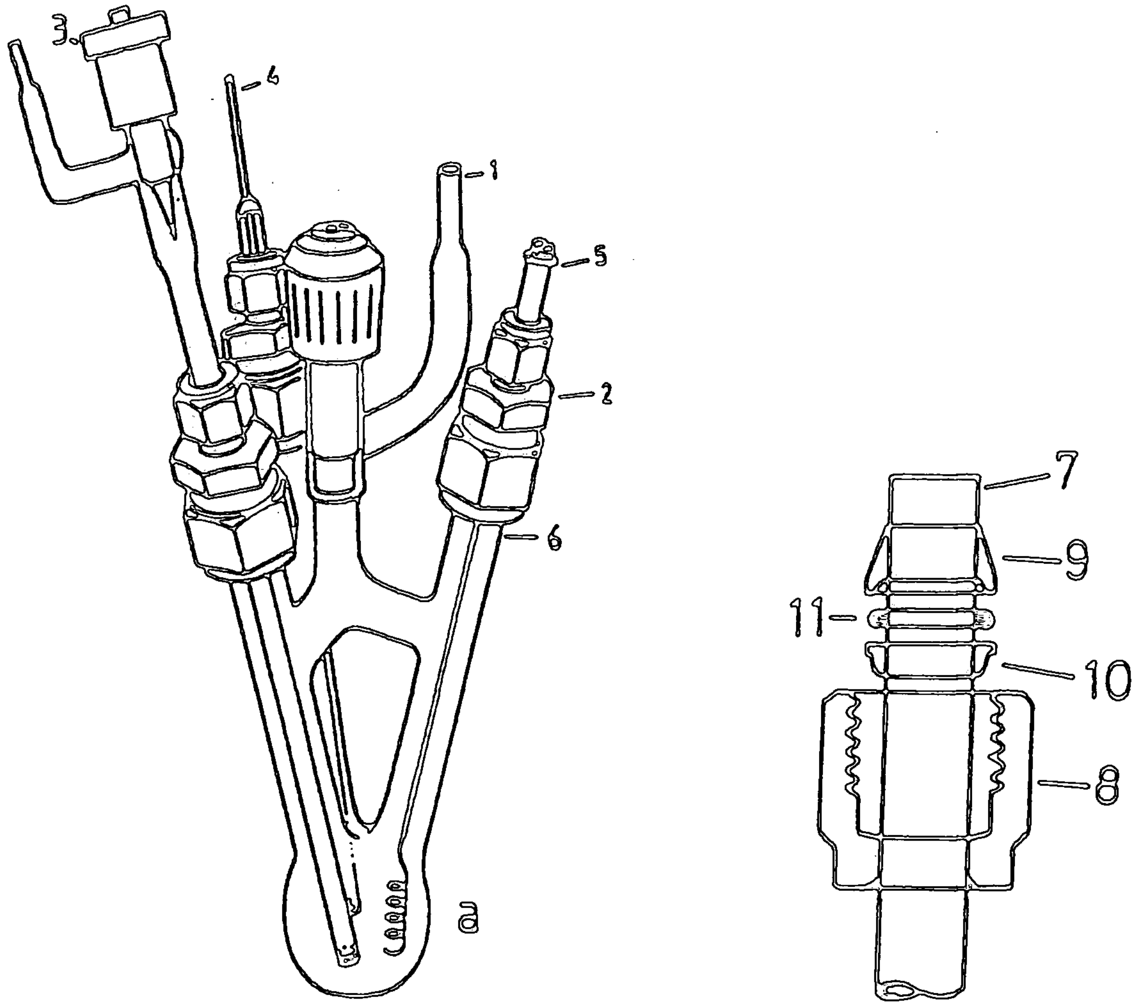
2.4.8.1 Cyclic voltammetry

This was carried out in a 3-limbed undivided cell[2] with a bulb volume of approximately 15 ml, designed by Dr. Hauptman. Each limb allowed the use of an electrode via modified "Swagelok" connectors which also provided an air-tight system. The apparatus used a reference electrode, a working electrode and an auxiliary electrode. The cell is shown in figure 2.3.

The reference electrode

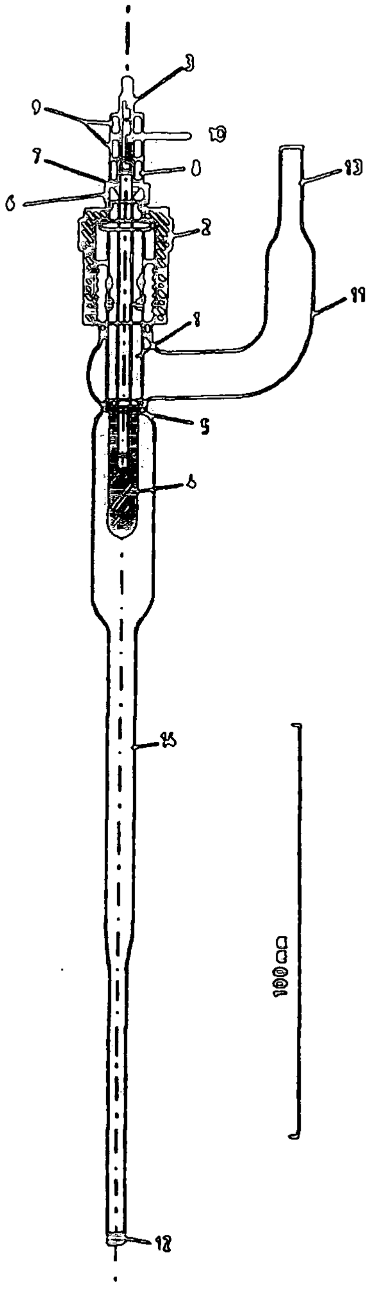
This was designed by Dr. Hauptman and is of the Ag / Ag^+ type previously reported[3] (see figure 2.4). This electrode maintains a constant potential for a prolonged period (several months) and is dependent on room temperature, and not on the temperature of the solution it is in.

Figure 2.3 The cyclic voltammetry cell illustrating the modified Swagelok glass to metal connector (insert).



1. $\frac{1}{4}$" Ground glass.
2. Swagelock $\frac{1}{2}$" to $\frac{1}{4}$" reducing union.
3. Reference electrode.
4. Micro electrode (usually platinum).
5. Auxiliary electrode (platinum).
6. $\frac{1}{2}$" Ground glass.
7. Same as 6.
8. Compression nut.
9. Front ferrule.
10. Back ferrule (reversed).
11. PTFE "O" ring.

Figure 2.4 The Ag / Ag$^+$ reference electrode



1. PTFE stem of Young's greaseless tap.
2. Turning knob of Young's greaseless tap.
3. Stainless steel (or monel) rod, eigth inch diameter, with 5BA thread on both ends tightly fitting into the central bore in the PTFE stem.
4. Metal electrode (e.g. silver) screwed onto the central rod.
5. Knife edge machined on the flat end of 4 (to achieve a tight seal).
6. Brass ring around PTFE stem (to prevent yielding through axial compression).
7. "O" ring in conical groove machined in the top of the PTFE stem.
8. Washer.
9. 5BA nuts.
10. Soldering eyelet.
11. Side arm of Young's greaseless tap ended with a ¼ O.D. tube for swagelock connection.
12. Pyrex sinter porosity grade 4.
13. See 11.
14. ¼" O.D. section for air-tight mounting (using the swagelock connector).

The design incorporates a J. Young tap at the apex of the electrode which confers several major advantages over previous designs. Any gas bubbles which build up in the electolyte solution (over a period of months) may be vented by simply opening the tap and allowing the solution in the reservoir to fill the gap. The tap may be completely unscrewed to allow for cleaning and polishing of the silver metal of the electrode (which is attacked by sulphur-containing electrolytes that happen to diffuse into the electrode from the bulk solution). It may also be used under pressure, e.g. in conjunction with liquid SO_2.

The working electrode

This was also designed by Dr Hauptman and consists of a polished platinum disc mounted in FEP tubing and connected to a $^1/_4$-inch steel bar.

The auxiliary electrode

This was again designed by Dr Hauptman and consists of a platinum coil connected to a monel bar by means of two holes which allow the bar to be slotted through a connecting sheet.

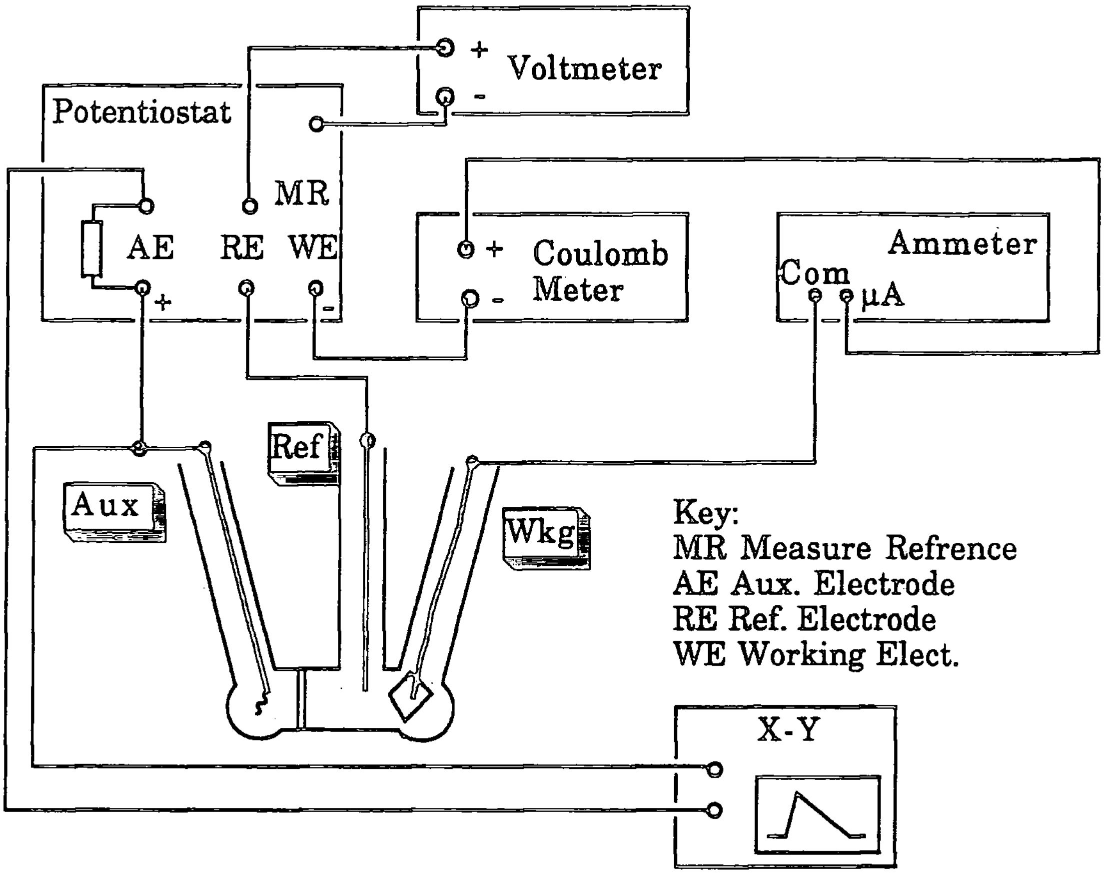
2.4.8.2 Electrocrystallisation

For all electrocrystallisations the reference electrode and auxiliary electrode utilised were of the type described in section 2.4.8.1. Electrocrystallisations were conducted by one of three methods:

Potentiostatic electrocrystallisations: utilising the reference electrode, auxiliary electrode, coulomb meter, ammeter, x-y chart recorder (to record any decay in the current), with the potential (measured using a multimeter) vs. the reference electrode held constant by the precision potentiostat. The working electrodes were either a polished platinum sheet held in platinum jaws (designed and made by Dr Hauptman), a platinum wire or a glass sheet (with one face coated in zinc oxide conducting film). See figure 2.5 for a schematic of this method.

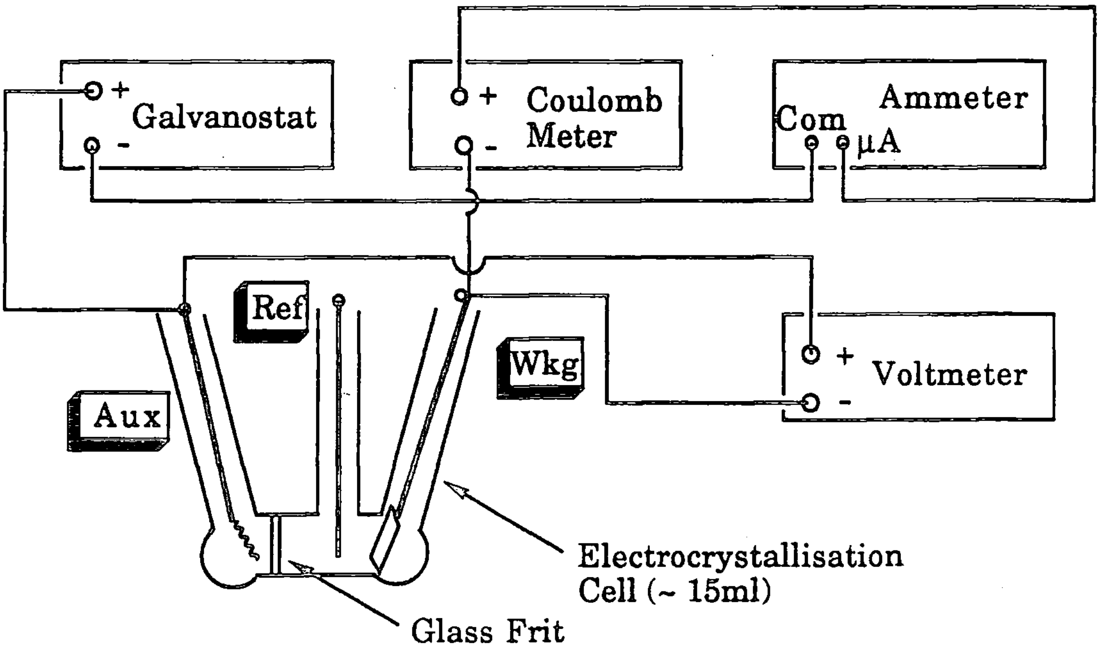
Potentiostatic electrocrystallisations utilising the CV apparatus: these utilised the potential wave generator as used in CV determinations as a potentiostatic source (with the cycle stopped at approximately the half wave potential of the reductions).

Figure 2.5 Schematic of the apparatus used in potentiostatic electrocrystallisations



Key:
MR Measure Refrence
AE Aux. Electrode
RE Ref. Electrode
WE Working Elect.

Figure 2.6 Schematic of the apparatus used in galvanostatic electrocrystallisations



Galvanostatic electrocrystallisations - here a constant current was maintained by use of the galvanostat, with higher current "spikes" used in an attempt to induce nucleation. See figure 2.6 for a schematic of this method.

2.4.9 X-ray structure determinations

2.4.9.1 Single crystal X-ray structure determination.

Crystals were mounted in glass or quartz Lindemann tubes and X-ray oscillation photographs were taken on a Nonius integrating Weissenburg goniometer with a Philips X-ray generator (type PW1009 130) fitted with an X-ray tube (Cu anode, Ni filter) at 42 kV and 16 mA.

Providing the image (recorded on Agfa-Gevaert Osray X-ray film) indicated that the crystal was single then it was submitted for a full X-ray structure determination. This was carried out at the University of Newcastle-Upon-Tyne by Dr W. Clegg on a Siemens AED2 diffractometer with a graphite monochromator using MoK_α radiation ($\lambda = 0.71073Å$). A $\omega-\theta$ scan mode was used for data collection with appropriately chosen scan width and time. Programs (SHELTXL, SHELXS[4] and local software[5]) were run on a Data General model 30 computer.

2.4.9.2 X-ray powder diffraction

X-ray powder data was obtained using a Debye-Scherrer camera and the simulation of data was run using commercially available software[6].

2.5 Chemicals and solvents

2.5.1 Purification of solvents

Acetonitrile (Aldrich HPLC Grade) was dried by refluxing over CaH_2 under an atmosphere of dry nitrogen, followed by distillation (with filtration through a glass column packed with pre-dried Al_2O_3) into clean dry flasks, where it was degassed and then stored under dry nitrogen.

Dichloromethane was dried by distillation from CaH_2 into clean, dry flasks under an atmosphere of dry nitrogen.

Diethyl ether (anhydrous) was stored over sodium wire and used directly from the bottle.

Toluene was dried by refluxing over lump sodium, followed by distillation under an atmosphere of dry nitrogen onto fresh sodium wire in clean dry flasks.

Hexane was dried by refluxing over P_2O_5, followed by distillation under an atmosphere of dry nitrogen and degassing by freeze-thaw cycles.

Tetrahydrofuran (thf) was purified by fractional distillation from sodium under an atmosphere of dry nitrogen, and stored over sodium wire, by Mr B. Hall in the Department of Chemistry.

Sulphur dioxide (BDH GPR Grade) was dried by standing over P_4O_{10} for one week, followed by distillation onto CaH_2 at least 24 hrs before use. It was vacuum transfered onto the solutes at -78°C and used as a liquified gas in either a 'dog' or closed extractor (see section 2.2).

1,2-Dichlorobenzene (Aldrich) was dried over $CaCl_2$ chips and distilled into a dry bulb under nitrogen.

Deuterated solvents (Aldrich): CD_3CN, CD_2Cl_2, and toluene-d_8 were all used without further purification under an atmosphere of dry nitrogen - CD_3CN was stored over pre-dried (ca. 130°C for 48 hours) magnesium sulphate.

2.5.2 Purification of solid reagents

Ammonium Chloride (Aldrich ACS Grade) was oven-dried at ca. 130°C for at least 24 hrs prior to use.

Bu_4NCl, Bu_4NBr, Et_4NI and Bu_4NI (Lancaster Synthesis) were purified twice by precipitation from acetone solution with anhydrous diethyl ether, followed by filtration. The purified materials were then heated *in vacuo* at >50°C for several hours, and transferred into the glove box in sealed vessels for storage.

Triphenylantimony (Aldrich) was recrystallised twice from dry acetonitrile and stored in the glove box. (Purification by A.W. Luke.)

4-Chlorobenzonitrile, 1,2-Dicyanobenzene and 1,3-Dicyanobenzene (Aldrich), were purified by sublimation *in vacuo* prior to use. (Purification by A.W. Luke.)

Malononitrile (Fluka) was purified by sublimation at room temperature and stored in a sealed tube at -10°C.

Potassium Tricyanomethanide (Strem) was washed with liquid SO_2 and thf (to remove an oily orange impurity) and then dried at 40°C *in vacuo* .

Sodium Hydride (Aldrich) was obtained as an 80% suspension in mineral oil. Petroleum ether was used to wash any remaining mineral oil free of the rquired material before use.

Caesium Iodide (Aldrich) was precipitated from a saturated solution in acetone by addition of diethyl ether and then was dried *in vacuo*.

2.5.3 Gaseous reagents

Chlorine (BOC) was dried by passing through a drying column packed with P_4O_{10}.

Arsenic Pentafluoride (Fluorochem) was vacuum transferred into a steel pressure vessel specially designed by Dr ZV Hauptman: measured quantities (determined by pressure reading on a Bundenberg gauge) were transfered to the required vessel via the monel vacuum line.

2.5.4 Liquids

Bromine (BDH "ARISTAR") was dried by repeated distillation *in vacuo* prior to use and stored under vacuum in a tube equipped with a J. Youngs tap and $^1/_4$ - inch glass adapter.

Antimony Pentachloride (Aldrich) was distilled and stored under nitrogen prior to use.

Trimethylsilyl Azide was kindly supplied, distilled, by Dr Hauptman.

2.5.5 Preparation of starting materials

Dithianitronium Hexaflurorarsenate(V) was prepared according to the literature route[7], with slight modifications[8]. The crude product was washed with dry dichloromethane to render it a pale yellow powder and remove any residual AsF_3. Quantities of this material were also kindly donated by Dr Hauptman and Dr Rawson.

4-(4-Chloro-phenyl)-1,2,3,5-dithiadiazolylium Chloride was prepared from $Cl.C_6H_4.CN$, SCl_2 and NH_4Cl according to the literature route[9].

4-(4-Chloro-phenyl)-1,2,3,5-dithiadiazolyl Dimer was prepared by reduction of 4-(4-chloro-phenyl)-1,2,3,5-dithiadiazolylium chloride according to the literature route[9], and was purified by sublimation *in vacuo* prior to use.

4-(4-Chloro-phenyl)-1,2,3,5-dithiadiazolylium Hexafluoroarsenate (V) was prepared by metathesis of the chloride salt using one equivalent of silver hexafluoroarsenate in liquid SO_2.

Silver Hexafluoroarsenate(V) was prepared by reaction of powdered silver with AsF_5 in liquid SO_2 (kindly provided by Drs Hauptman and Rawson). Subsequent samples were obtained from Aldrich.

Tetramethylammonium Fluoride was kindly supplied anhydrous by Dr C.J. Ludman (University of Durham)

Caesium Azide was kindly supplied anhydrous by Dr Hauptman.

Tetra-alkylylammonium Metal (mnt)$_2$ salts were prepared by Dr Rawson and A.W. Luke.

Tetrasulphur Tetranitride was prepared by the reaction of S_2Cl_2 and NH_3 according to the literature method[10]. Samples prepared by Dr S.T. Wait were readily available.

$S_4N_4H_4$ was prepared[11] by the reduction of S_4N_4 with aqueous $SnCl_2$.

(NSCl)$_3$ was prepared according to the method of Jolly and Maguire[12], by the direct chlorination of $S_3N_2Cl_2$. Samples were kindly donated by Mr S.E. Lawrence, Dr Rawson and Dr Hauptman.

$[N(SCl)_2][AsF_6]$ was prepared[3] by the reaction of $(NSCl)_3$, SCl_2 and $AgAsF_6$ in liquid SO_2 followed by washing with CH_2Cl_2

$[Pr_4N]N_3$ was prepared by the method devised by Dr Ludman [13].

$[Pr_4N][S_3N_3]$ was prepared according to the literature method[14] with slight modifications[13].

2.5.6 Materials used without further purification

2.5.6.1 Solids

Sulphur [Aldrich, Gold Label, 99.9999%], *Lithium bis(trimethylsily)amide* [Aldrich, Tech.], *4-nitro-benzenesulphenyl chloride* [Aldrich, Tech. 90%], *2-nitro-benzenesulphenyl chloride* [Aldrich, 97%], *Lithium iodide* [Fluka, Purum], *1,2-Benzene-dithiol* [Aldrich, 96%], *3,4-Toluene-dithiol*, *t-Butyl lithium* [Aldrich, ca. 1.6 M solution in Hexane], *Silver triflate* [Fluka, Purum], *Tetrabutylammonium tetrafluoroborate* [Fluka, Electrochemical Grade], *Silver cyanide* [Aldrich, 99%], *Triphenyltin chloride* [Aldrich, 95%], *Phenylmercuric chloride* [Aldrich, purity not specified].

2.5.6.2 Liquids and gases

Sulphur tetrafluoride [Fluorochem], *Sulphur dichloride* [Fluka, Tech.]

2.6 References

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11. N.R.M. Smith, Ph.D. Thesis, University of Durham, 1982.

12. W.L. Jolly and K.D. Maguire, *Inorg. Synth.*, 1977, **9**, 102.

13. S.T. Wait, Ph.D. Thesis, University of Durham, 1989.

14. J. Bojes and T. Chivers, *Inorg. Chem.*, 1978, **17**, 188.

Chapter 3

The reactions of [SNS][AsF$_6$] with potassium tricyanomethanide.

3.1 Introduction

There has been much interest in the development of free radical materials in the preparation of organic magnets[1]. Of particular interest have been multi-radicals with trigonal or higher symmetries, e.g. multicyano-hydrocarbons[2] and dithiolylidines[3]. Oakley *et.al.*[4] have also prepared low-dimensional molecular conductors based on the use of thiazyl radicals as molecular building blocks for polymeric arrays of radicals.

It has been proposed that the higher symmetry of these systems may stabilise the triplet/multiplet ground state required for possible ferro- or ferri-magnetism to occur[5]. Some research groups[6] have concentrated on nitroxide radicals but, these require bulky substituents to protect the =N-O° functionality which, by necessity, limits the degree of secondary interaction between adjacent molecules. Consequently the possibility of cooperative magnetic interaction is greatly reduced. In dithiadiazolyls, however, delocalisation helps to stabilise the radicals without the need for steric-protecting groups, thus enhancing the possibility and extent of secondary interaction.

Other workers have used radicals as molecular building blocks for the formation of low-dimensional materials with novel electronic properties; Haddon[7] proposed that stacked, polymeric arrays of radical units may combine to form a conduction band. Work by Banister *et.al.*[8,9] and Oakley *et.al.*[10] has recently concentrated on the synthesis and characterisation of multi-dithia / diselenadiazolyl radicals; the higher symmetry of these materials facilitates more highly ordered packing in the solid state.

For example, p-$C_6H_4(CNSNS)_2$[8] was prepared by reduction of the corresponding dichloride, [p-$C_6H_4(CNSNS)_2]Cl_2$), 5',5'-phenylene bis (1,3,2,4-dithiadiazolylium) dichloride. The solid, which is an insulator, contains a polymeric array of neutral molecules interacting through secondary S···N contacts and is the first extended system based on the thiazyl radical. Unlike most dithiadiazolyl radicals this material is only slightly air-sensitive (surviving for days in the atmosphere) and does not readily rearrange photochemically. It is indefinitely stable in the solid state (under normal illumination).

Tables 3.1 to 3.3 list the multi-dithia/diselenadiazolylium cations prepared to date.

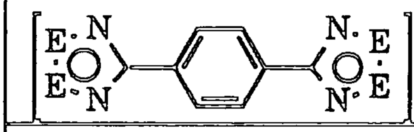
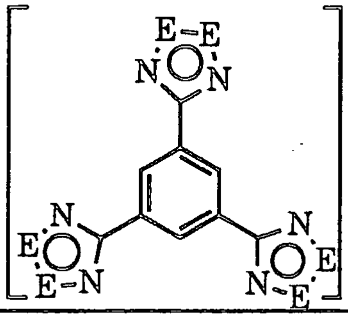
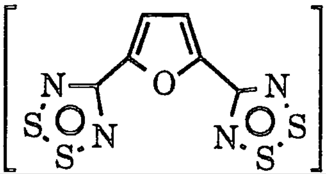
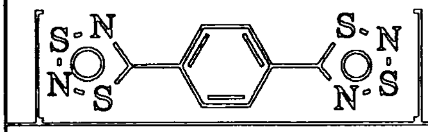
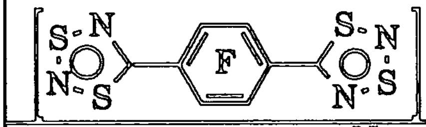
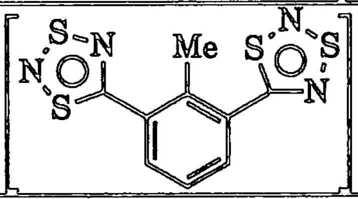
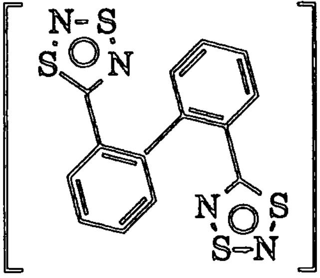
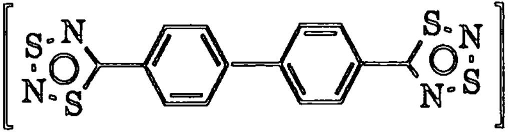
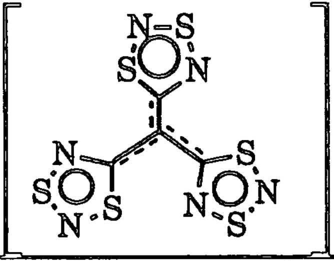
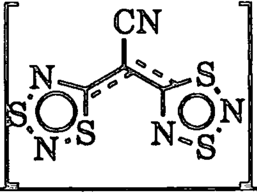
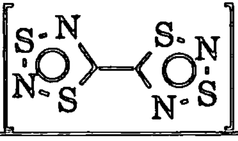
Compound	Route	Yield	Reference
 ++, +. or .. E = S, Se (also *meta*)	Via silylated amidine	*p* 65% *m* --	4a 4b
 +++ or . . . E = S or Se	Via silylated amidine	40% (as tri-radical)	10
 ++ or ..	Via silylated amidine	44% (as di-radical)	11

Table 3.1 Multi-1,2,3,5-dithiadiazolyliums (and their diselena diazolylium analogues; yields quoted are for the [multi]cations)

The various 1,2,3,5- isomers have been prepared by Oakley and co-workers (see above), whilst in this laboratory the 1,3,2,4- dithiadiazolyl salts, their corresponding free radicals (see table 3.2) and mixed 1,3,2,4- / 1,2,3,5- dithiadiazolyl salts and their selenyl analogues have been synthesised (see table 3.3, chapter 4 and chapter 5).

Reductions of the bis and tris 1,3,2,4-dithiadiazolylium salts yield the analogous free-radical dithiadiazolyls[8,12,13]. The lower solubility of these bis and tris 1,3,2,4- dithiadiazolyls (relative to the 1,2,3,5- isomers) has allowed their isolation in high yield.

Table 3.2 Multi-1,3,2,4-dithiadiazolyliums (yields for the cations)

Compound		Route	Yield	Reference
	++ or .. (also *meta* and *ortho*)	Ar(CN)$_2$ (*o*, *m*, *p*) + 2 [SNS][AsF$_6$]	*p* 95% *m* 85% *o* 75%	8 14
	++ or .. (also *meta* and *ortho*)	*o, m, p*-C$_6$F$_4$(CN)$_2$+ 2 [SNS][AsF$_6$]	*p* 96% *m* 95% *o* 94%	15
	++ or ..	1,3-(CN)$_2$-2-Me-C$_6$H$_3$ + 2 [SNS][AsF$_6$]	92%	15
	++	Appropriate biphenyl dicyanobenzene with two equivalents of [SNS][AsF$_6$]	84%	15
	++	Appropriate biphenyl dicyanobenzene with two equivalents of [SNS][AsF$_6$]	79%	16
	++, +. or ..	K[C(CN)$_3$] + 3 [SNS][AsF$_6$]	85%	this work
	+ or .	K[C(CN)$_3$] + 2 [SNS][AsF$_6$]	65%	this work
	++, .. or +.	NC-CN + 2 [SNS][AsF$_6$]	97%	12

The photochemical rearrangement of the 1,3,2,4-dithiadiazolyls to the 1,2,3,5-isomer is readily monitored by esr spectroscopy[13] and their thermal rearrangement by differential scanning calorimetery[16].

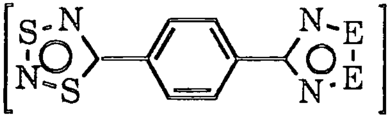
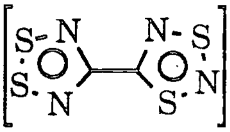
Compound	Route	Yield	Reference
 ++, +. or .. E = S, Se	[ArCNEEN][AsF_6] + [SNS][AsF_6]	97%	9
 ++ , .. or +.	via reduction and rearrangement of corresponding bis 1,3,2,4-diradical (See table 3.2)	39%	12

Table 3.3 Mixed 1,2,3,5 and 1,3,2,4-dithiadiazolyliums (and their diselena diazolylium analogues) (yields are for the [multi]cations)

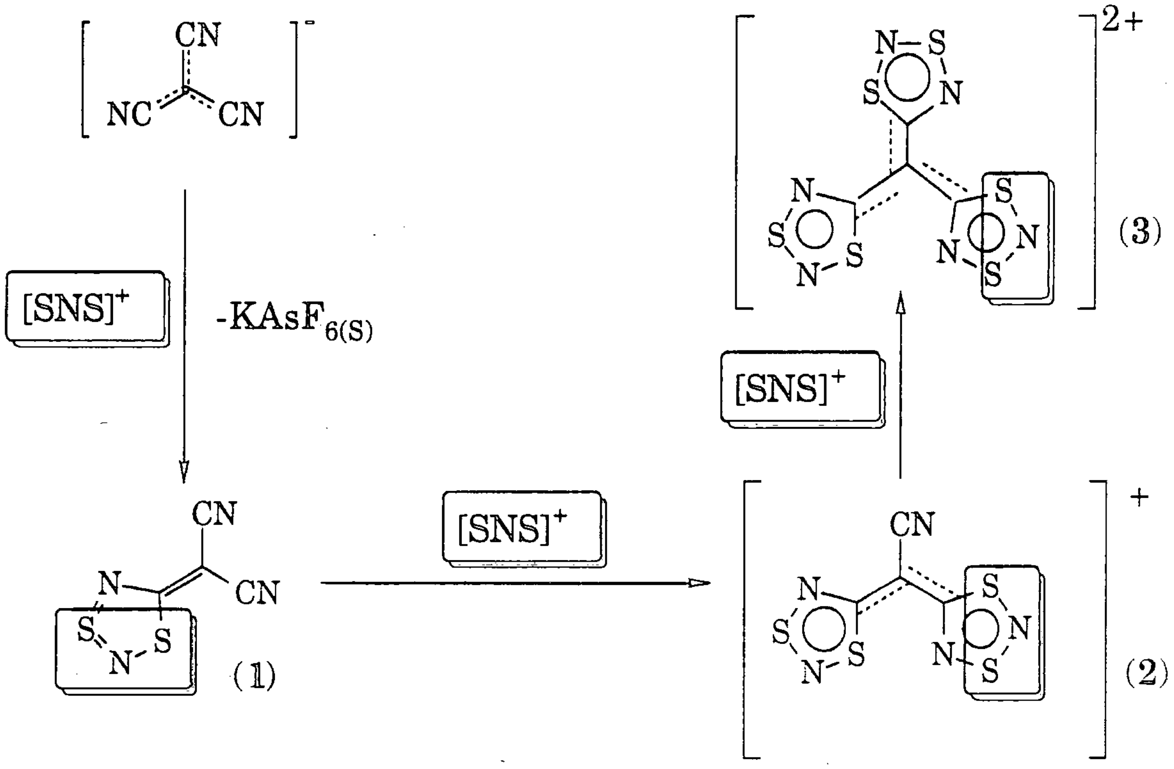
However, there has been relatively little work done on the more simple alkyl-multi-dithiadiazolyl systems (except work on dicyanogen and $[SNS]^+$ which was conducted by Passmore *et. al.* [12] at approximately the same time as this study), and none involving the reactions of $[SNS]^+$ with an unsaturated anionic species such as $[C(CN)_3]^-$.

Therefore the sequential reactions of [SNS][AsF_6] with the D_{3h} species, $[C(CN)_3]^-$, were studied as a route to possible precursors to such organic materials; with the $[C(CN)_3]^-$ anion providing a template for a tris-dithiadiazolyl diradical with trigonal symmetry.

3.2 Results and discussion

Upon condensation of SO_2 onto the various stoichiometric mixtures of [SNS][AsF_6] and K[$C(CN)_3$] (1:1, 2:1 and 3:1), at liquid nitrogen temperatures, an immediate deep purple colour was observed - later found to be indicative of the formation of the neutral 1:1 cycloaddition compound ($(NC)_2C$=CNSNS, **1**) (see scheme 3.1). (For experimental details see section 3.4.1.)

The 1:1 reaction (formation of **1**) was complete within minutes. Yields of **1**, **2** and **3** (60-80%) were similar to those found for the reactions of $[SNS]^+$ with $C_6H_4(CN)_2$ and $C_6H_3(CN)_3$[8,16]. After overnight reaction, the corresponding 2:1 and 3:1 mixtures gave the red powders **2** and **3**, respectively, the latter crystallising as an SO_2 solvate from liquid SO_2 (see section 3.2.2.2 for structure).



Scheme 3.1 The stepwise reaction of $[SNS][AsF_6]$ with $K[C(CN)_3]$

Although these reactions appeared to be very promising, even at the first (trial-scale) attempts; the potassium tricyanomethanide (as supplied by Strem Chemical Co.) was contaminated with a brown impurity which rendered it slightly pale brown instead of the expected white powder. This also gave rise to poor quality products with variable elemental analyses: sometimes if the reagents were left together in the reaction vessel for several minutes then the $[SNS][AsF_6]$ itself began to turn brown - indicative of hydrolysis.

The work of Trofimeiko *et.al.*[17] on the preparation of $K[C(CN)_3]$ describes the use of ether to remove reaction side products. However, diethyl ether is reactive towards $[SNS]^+$ salts and so thf was utilised instead (as it is less nucleophilic, although it is polymerised by the dithiadiazolylium cations[14]). A simple wash with thf removed the brown impurity and the potassium tricyanomethanide work was resumed with improved products and higher yields; both the 1:1 and 3:1 adducts (**1** and **3** respectively) were then crystallised. Analyses were poor in the case of compounds **2** and **3** in spite of repeated recrystallisation. This was tentatively attributed to volatile SO_2 of solvation (*vide infra*).

All three addition products appeared to be stable to the atmosphere for several hours (as shown by their appearance and relatively unchanged IR spectra - no broad N-H stretches at > 3000cm^{-1}) although **3** slowly gave up SO_2 of solvation upon standing. Single crystals of **1** and **3**, suitable for X-ray diffraction, were picked in the air over a period of an hour or so.

3.2.1 Molecular orbital calculations and mechanistic rationale

[Author's Note: Although I ran the initial PM3 calculations on the compounds **1**, **2** and **3** and on $[C(CN)_3]^-$, the mechanistic rationale and calculations on the various postulated intermediates - such as those illustrated in fig. 3.2 - were provided by Dr J. M. Rawson, to whom much credit is due.]

M.O. Calculations (at the PM3 level)[18] were carried out on the tricyanomethanide anion and on its products with $[SNS][AsF_6]$. These calculations indicated a somewhat more complex reaction mechanism than the usual HOMO-LUMO interaction seen in most $[SNS]^+$ reactions (see chapter 1). The reaction of tricyanomethanide with $[SNS]^+$ does not appear to proceed through this HOMO-LUMO cycloaddition process, since the HOMO of $[C(CN)_3]^-$ does not retain the correct orbital symmetry to interact with the SNS^+ LUMO (see figure 3.1).

Instead the reaction would appear to be electrostatically induced through $[SNS]^+$ / $[C(CN)_3]^-$ attraction, followed by an electron donation process from lower-lying, filled molecular orbitals of $[C(CN)_3]^-$ (10 and/or 11 at -8.66 and -8.65 eV respectively), of the correct symmetry, into the $[SNS]^+$ LUMO (-8.42 eV).

A second cycloaddition process, between the first product, $[(NC)_2C{=}CNSNS]^+$, and $[SNS]^+$, would also appear to be hindered, on symmetry and energetic grounds, from undergoing a conventional [4+2] cycloaddition. However, J. Passmore *et al.*[13] have recently proposed that for a similar reaction ($[NC.CNSNS]^+$ with $[SNS]^+$) a second cycloaddition reaction may be induced by the approach of $[SNS]^+$ on the most electronegative ring nitrogen, 4-N in the usual nomenclature (the nitrogen α to the dithiadiazolyl carbon), allowing a further cyclisation through a second molecular orbital, of similar energy to the HOMO, on the dieneophile. This is an in-plane π-MO which is almost entirely located on the cyano group.

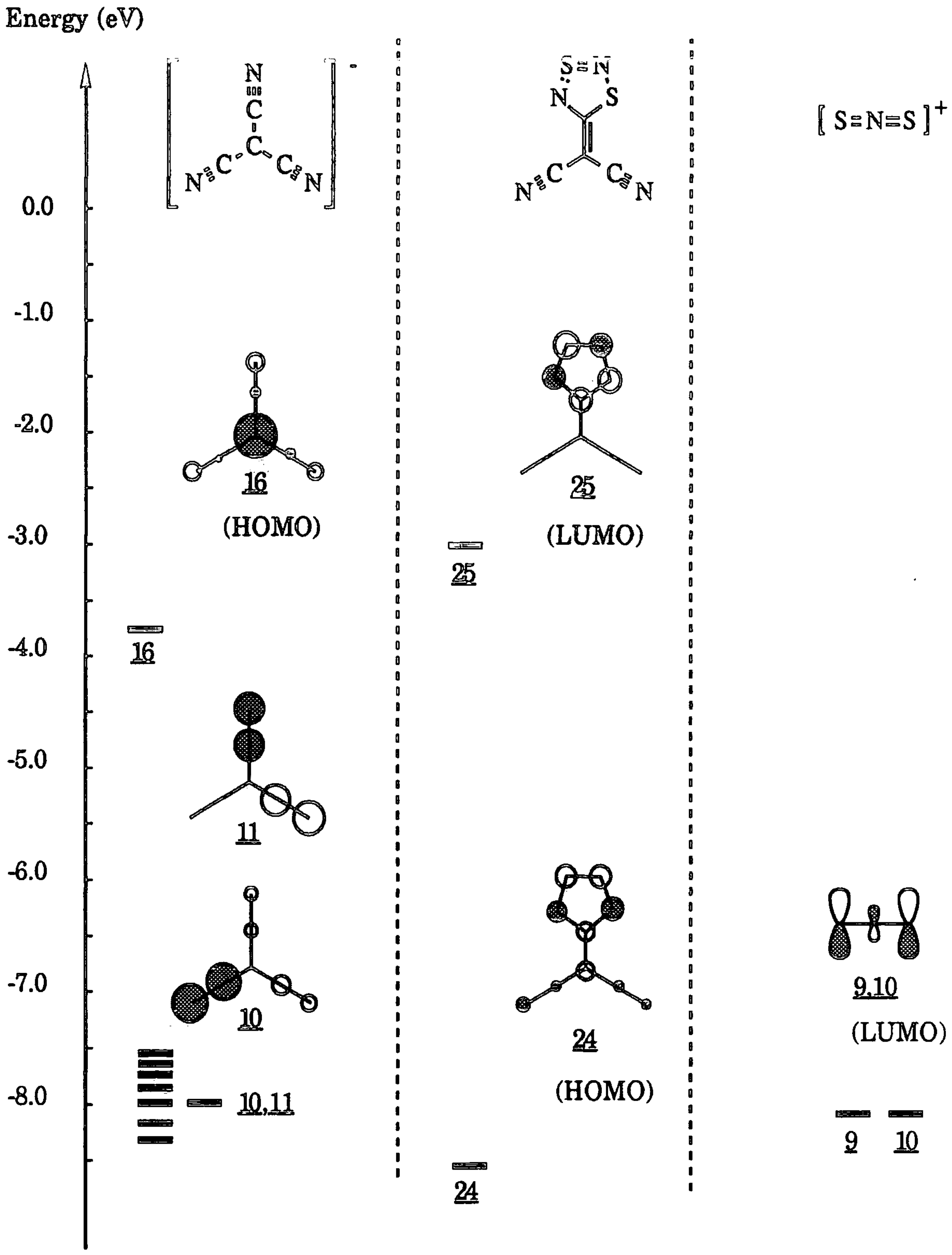


Figure 3.1 Frontier molecular orbitals for $[C(CN)_3]^-$, 1 and $[SNS]^+$

In the case of $(NC)_2C$=CNSNS, there is, indeed, a lower lying orbital with strong in-plane C≡N characteristics (19) but this appears some 3.5 eV lower in energy than the HOMO. It is proposed, therefore, on the basis of MO calculations, that an intermediate complex, [(NC)$_2$C=CNSNS.SNS]$^+$(see fig 3.2) exists, in which the [SNS]$^+$ cation is bonded to the ring nitrogen (4-N).

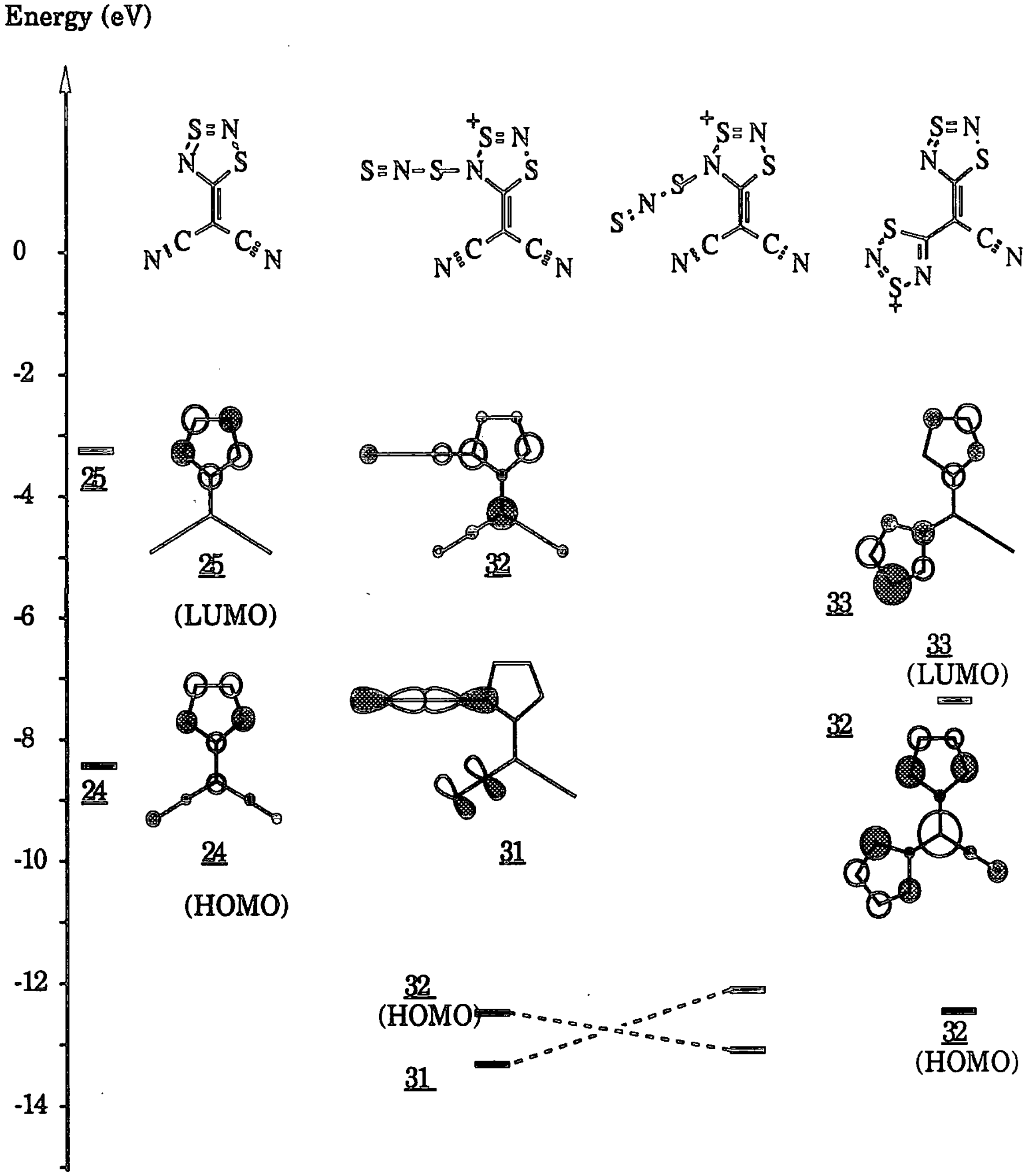
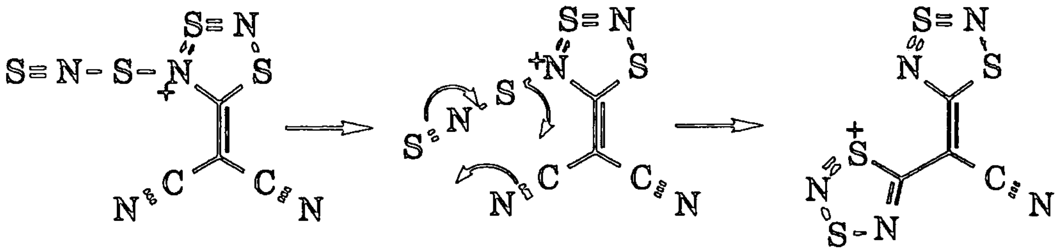
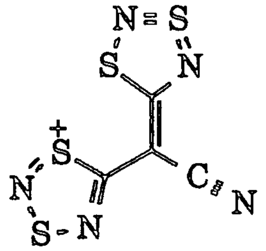


Figure 3.2 Frontier molecular orbitals for 1 and 2 and the proposed intermediate complex, [(NC)$_2$C(CNSNS).SNS]$^+$

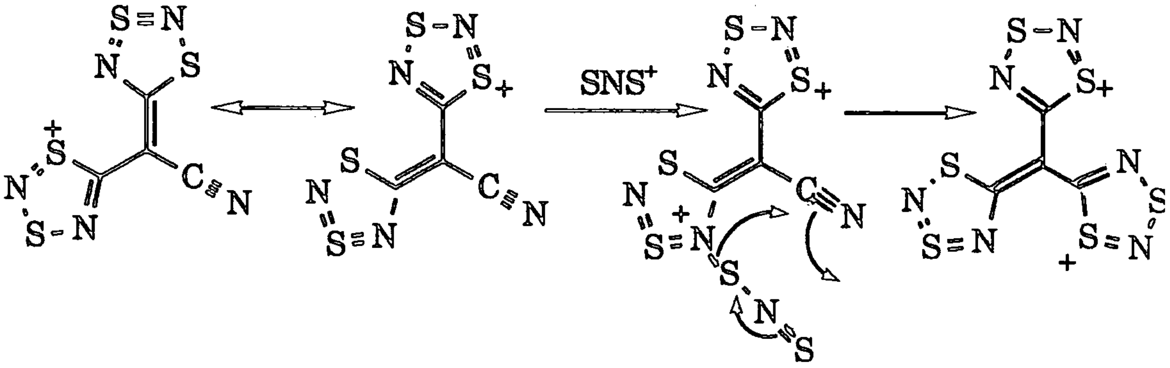
The MO diagram of this complex shows a HOMO with strong contributions on both the $C\equiv N$ and SNS functionalities, allowing in-plane cyclisation to give $[(NC)C(CNSNS)_2]^+$ as shown below:



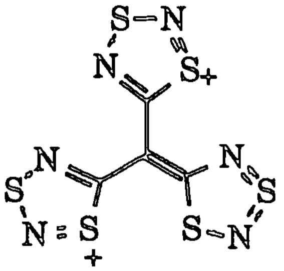
rather than the other possible, transoid isomer:



In the final stage of the reaction, i.e. the formation of the 3:1 product, we again see an intermediate $[SNS]^+$ complex undergoing intramolecular cyclisation to give the dication of salt **3** :



This gives the observed isomer rather than the other possible transoid one:



An important consequence of this mode of attachment of $[SNS]^+$ to the ring nitrogen is the stereochemical specificity induced in the final product(s). Due to the formation of these complex intermediates, attack of the $[SNS]^+$ cation occurs only on one face of the cyano functionality (i.e. the face on the same side as the CNSNS ring nitrogen, 4-N, with which the $[SNS]^+$ unit is interacting) and hence leads to only one isomer for the cations of **2** and **3**. This specificity is seen in all *bis*- and *tris*-1,3,2,4-dithiadiazolyl/iums so far examined[8,13], viz $C(CNSNS)_3{}^{2+}$, $[SNSNC.CNSNS]^{2+}$ and p-$C_6H_4(CNSNS)_2$. For the aryl substituted systems the intermediate mono-cation may exert only a moderate effect on the stereo-selectivity as is it much further away from the remaining cyano group.

This is borne out by the powder diffraction data obtained from the bulk sample (see table 3.4). They show that the crystals obtained correspond to the vast majority of product in the bulk of **3**, as the powder diffraction lines predicted from the crystal parameters for **3** (from single crystal data) are the only significant bands present in a powder photograph of the bulk sample. No further lines were observed so no other isomers were present as micro-crystalline solids. However, it is possible that another, amorphous, isomer may have been present (this would not diffract concertedly and so not give any bands in the powder photograph).

Furthermore, $[SNS]^+$ reacts with **1** at the C≡N functionality only, rather than at the C=C bond. This is explained by the higher activity of the triple bond towards cycloadditons (as outlined in the extensive work conducted by Schriver[19]). Also this system differs from the aryl multi-nitriles in that it is possible to isolate all three cycloaddition products. In the aryl case the addition of $[SNS]^+$ is reported to occur at all C≡N groups of the nitrile at once. This phenomenon is thought to occur because of the activating effect of the dithiadiazolylium cation in the aryl systems.

In order to expand this work and examine the addition of $[SNS]^+$ to other nitriles a further set of PM3 calculations was run. When $[SNS][AsF_6]$ reacts with $NC.C_6H_4.CN$ in a 1:1 stoichiometry then the 1:1 addition product, $[SNSNC.C_6H_4.CN][AsF_6]$, is not isolated but the IR data indicate the presence of unreacted $NC.C_6H_4.CN$ and $[SNSNC.C_6H_4.CNSNS][AsF_6]_2$.

This suggests that either there is a thermodynamic effect causing the intermediate cation to be more reactive towards $[SNS]^+$ than $NC.C_6H_4.CN$ (in spite of both reagents being positively charged) or that perhaps some concerted reaction is occuring, with both $[SNS]^+$ cations being added at the same time. Therefore, the use of PM3 calculations to determine the energies and symmetries of the HOMOs in $NC.C_6H_4.CN$

and [SNSNC.C_6H_4.CN][AsF_6] should indicate whether or not there is an activating effect that causes the 1:1 addition compound not to be isolated.

Table 3.4 X-Ray powder diffraction data for a powdered sample of 3

Diffrac'n Line No.	d_{hkl} (obs.)	d_{hkl} (calc.)	h	k	l	I / I_0 (obs.)	I / I_0 (calc.)
1	6.752	6.664	0	1	2	m	16
2	4.469	4.450	0	4	0	vs	81
3	4.247	4.350	1	3	1	vs	62
4	3.987	3.979	2	0	0	vs	100
		3.976	-2	1	1		
5	3.376	3.405	-2	1	3	m, br	37
		3.363	-2	3	1		
		3.332	0	2	4		
		3.307	2	3	4		
6	3.209	3.233	-2	2	3	m, br	14
		3.197	-1	4	3		
		3.195	0	5	2		
7	2.988	2.984	-2	1	4	m, br	10
		2.985	1	1	4		
		2.996	-2	3	3		
8	2.704	2.698	1	3	4	w	10
		2.689	-3	1	1		
9	2.612	2.602	-3	2	1	w	9
10	2.132	2.129	3	5	0	w	4
		2.122	1	6	4		
11	2.064	2.068	3	2	3	vw	2
		2.062	1	5	5		
		2.061	3	4	2		
12	2.022	2.024	1	8	2	w	3
		2.018	-3	0	6		
		2.007	-3	6	1		
13	1.920	1.923	1	9	0	vw	3
14	1.691	1.687	-3	8	3	vw	5
		1.684	2	9	2		
		1.682	-4	6	2		
		1.681	4	4	2		
15	1.598	1.597	-4	2	7	vw	1

The results of the PM3[18] calculations on $[SNS]^+$, $NC.C_6H_4.CN$ and $[SNSNC.C_6H_4.CN]^+$ are summarised in figure 3.3. There is an obvious HOMO-LUMO interaction of correctly matched orbitals. These are reasonably well matched in terms of symmetry and energy (but not as good as for $[C(CN)_3]^-$, compare with figure 3.1). Level 23 (HOMO) of $NC.C_6H_4.CN$ and the degenerate LUMOs of $[SNS]^+$ (levels 9 and 10) may well interact although the HOMO of dicyanobenzene is higher in energy than the LUMO of $[SNS]^+$. Therefore, the electron flow is uphill in terms of energy. This may help to explain the (observed) relative rates of reaction of $[SNS][AsF_6]$ with dicyanobenzene and potassium tricyanomethanide - the former reacts much more slowly.

The HOMO of the proposed intermediate cation, $[SNSNC.C_6H_4.CN]^+$, (level 31) does not have the correct symmetry (there is no orbital density on the -C≡N functionality at all), and neither do levels 30 (again no electron density on the -C≡N functionality) or 29 (where the -C≡N based part of the orbital is of incorrect symmetry for good overlap). In contrast level 28 has the correct orbital symmetry at the -C≡N group to allow for interaction with the $[SNS]^+$ LUMO. But there is a much greater energy difference (the occupied orbital on $[SNSNC.C_6H_4.CN]^+$ is ca. 7 eV lower in energy than the LUMOs in $[SNS]^+$) between the interacting orbitals, which suggests that the intermediate cation could well be de-activated with respect to $[SNS]^+$ addition (not to mention the positive charge on both reagents giving rise to coulombic repulsion).

This would result in a large energy barrier to reaction, tempered by an increased thermodynamic driving force (as two electrons from the lower energy HOMO of $[NC.C_6H_4.CNSNS]^+$ are being transfered to a higher energy LUMO). Furthermore, the reverse in relative energies of the HOMO and LUMO in the dicyanobenzene case (relative to tricyanomethanide) causes electron drift to the LUMO to be uphill and so the rate of reaction of $[SNS][AsF_6]$ with $NC.C_6H_4.CN$ is lower than that with $[C(CN)_3]^-$ (as observed).

It is possible that electron density could be transfered from the HOMO (level 31) of $[SNS]^+$ to higher energy orbitals (e.g. the LUMO, level 32) and that this could then interact with the LUMO (level 32 at -7.80 eV) of $[SNSNC.C_6H_4.CN]^+$. However, in spite of the favourable energy matching of these reagents there is no orbital of correct symmetry located on the cyano species before level 40. This possibility seems, therefore, very unlikely.

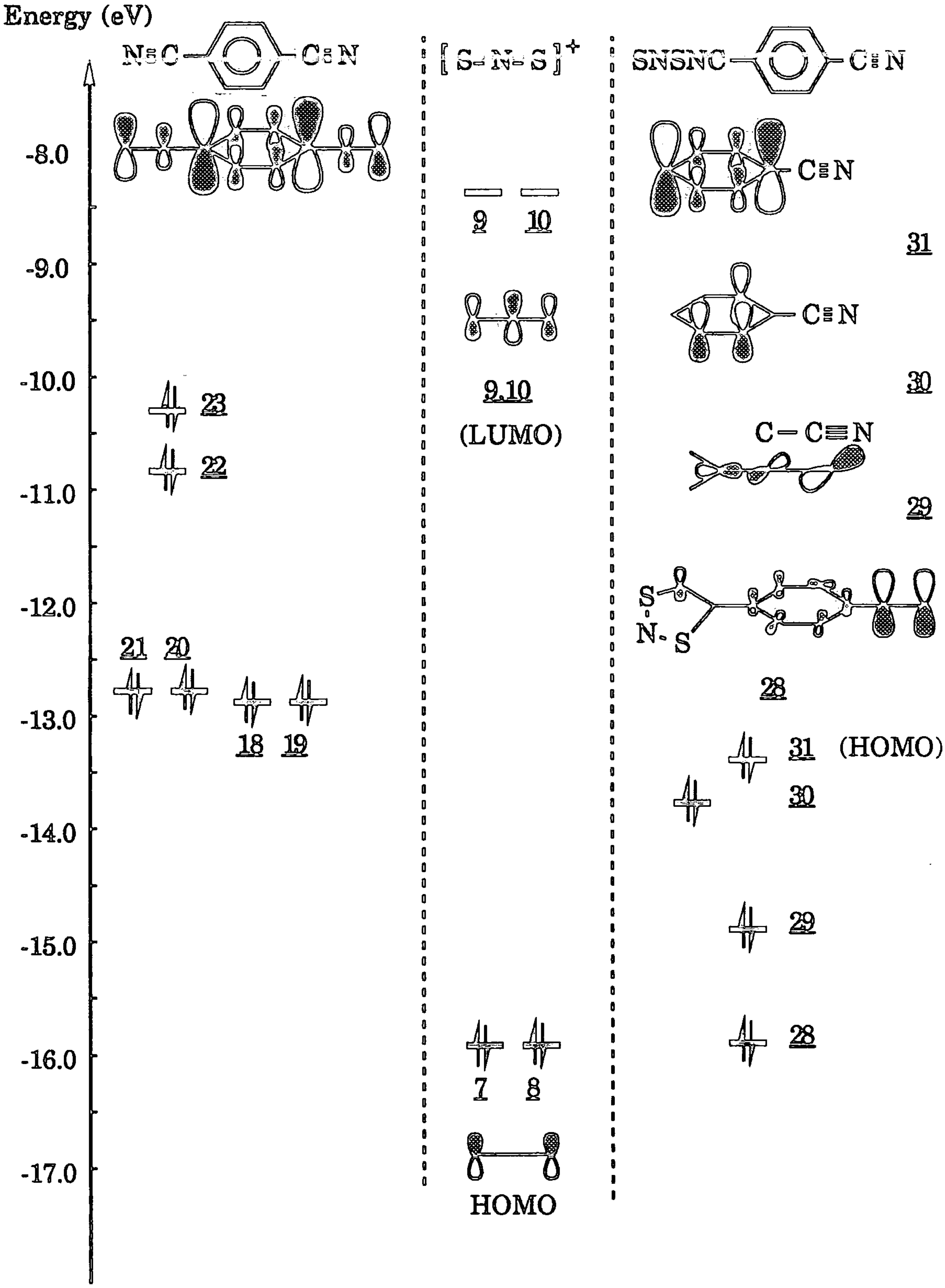


Figure 3.3 The frontier molecular orbitals for NC.C_6H_4.CN, $[SNS]^+$ and $[SNSNC.C_6H_4.CN]^+$.

A further significant contribution to this reaction system may well be the high lattice energy (and low solubility in liquid SO_2) of the product, $[SNSNC.C_6H_4.CNSNS][AsF_6]_2$, which precipitates out from the reaction mixture. This lattice energy component could provide a 'driving force' for the second addition of $[SNS]^+$ and so make the second step considerably faster.

The molecular orbital data suggest that the intermediate cation, $[SNSNC.C_6H_4.CN]^+$, should be isolable and so further experimental work (utilising different solvent systems and reaction conditions) should be undertaken, together with further MO studies, in order to confirm or refute these conclusions.

In order to examine this reaction still further, attempts were made to study the effects on the frontier molecular orbitals of $[SNSNC.C_6H_4.CN]^+$ of bringing the $[SNS]^+$ cation close in (in a similar manner to that in $[C(CN)_3]^-$ with complexation of $[SNS]^+$ to the 4-N nitrogen, so allowing for a rapid second cycloaddition). PM3 calculations with the $[SNS]^+$ being moved sequentially closer to the cyano substituted cation were attempted but these took very long periods to compute (e.g. > 36 hours c.p.u. time per intermediate) and so these were abandoned.

3.2.2 Solid state structures

The solid state structures of **1** and **3** were determined by single-crystal X-ray diffraction.

Crystal parameters, refined coordinates, bond lengths, bond angles and thermal anisotropic parameters for **1** are given in tables 3.5, 3.6, 3.7, 3.8 and 3.9 respectively. Crystal parameters, refined coordinates, bond lengths, bond angles and thermal anisotropic parameters for **3** are given in tables 3.11, 3.12, 3.13, 3.14 and 3.15 respectively.

3.2.2.1 Solid state structure of 1

There are two independent neutral molecules of **1** in the crystallographic asymmetric unit (figure 3.4) and each is essentially planar. The root mean-square deviations from mean planes are 0.039 and 0.042 Å.

Figure 3.4 The crystallographic asymmetric unit of $(NC)_2C{=}CNSNS$ (1) - showing the two planar neutral molecules and atom numbering scheme

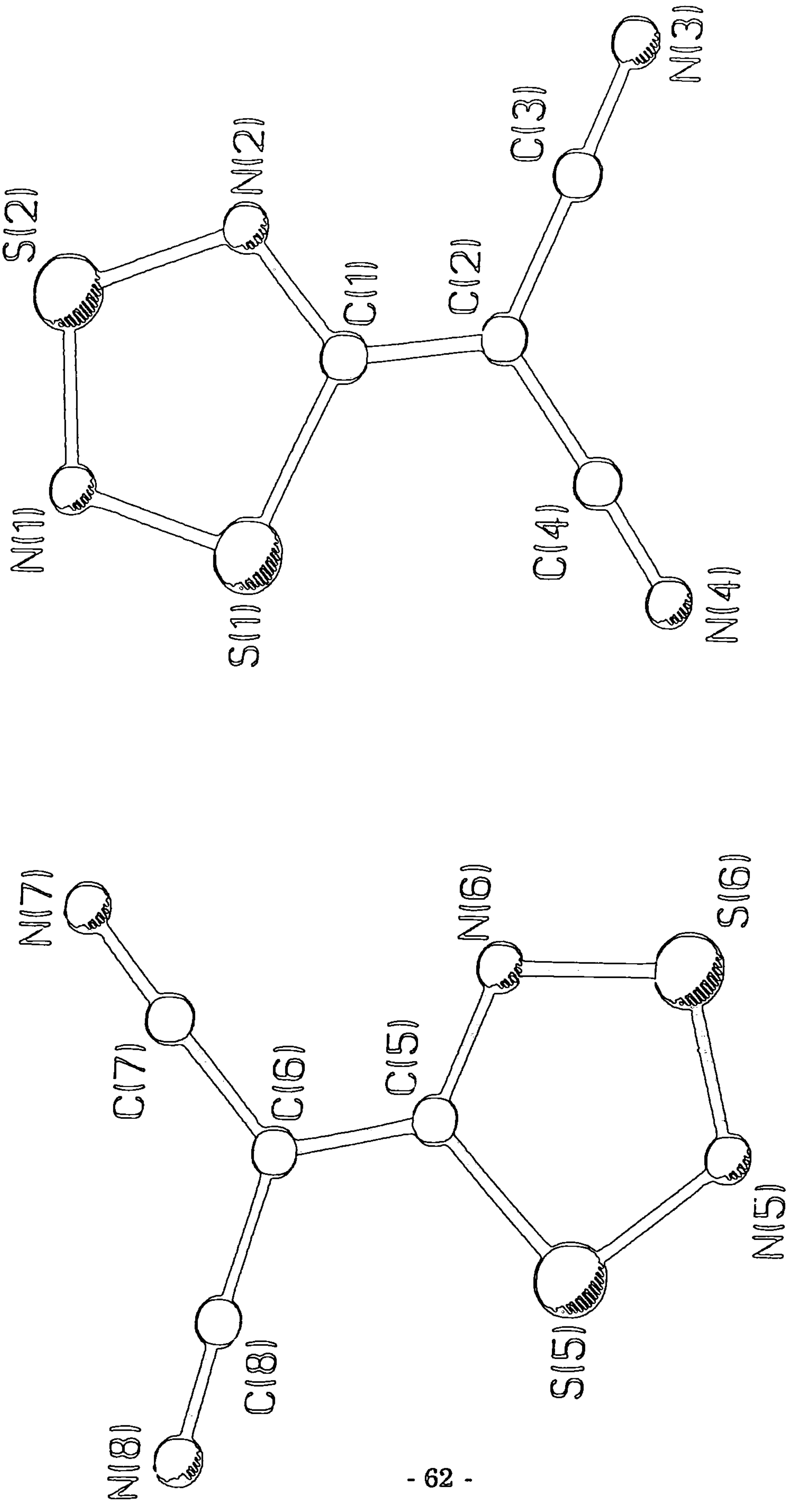


Figure 3.5 Intermolecular S···N interactions within and between sheets of molecules in the structure of compound 1. The view direction is the same as for figure 3.4

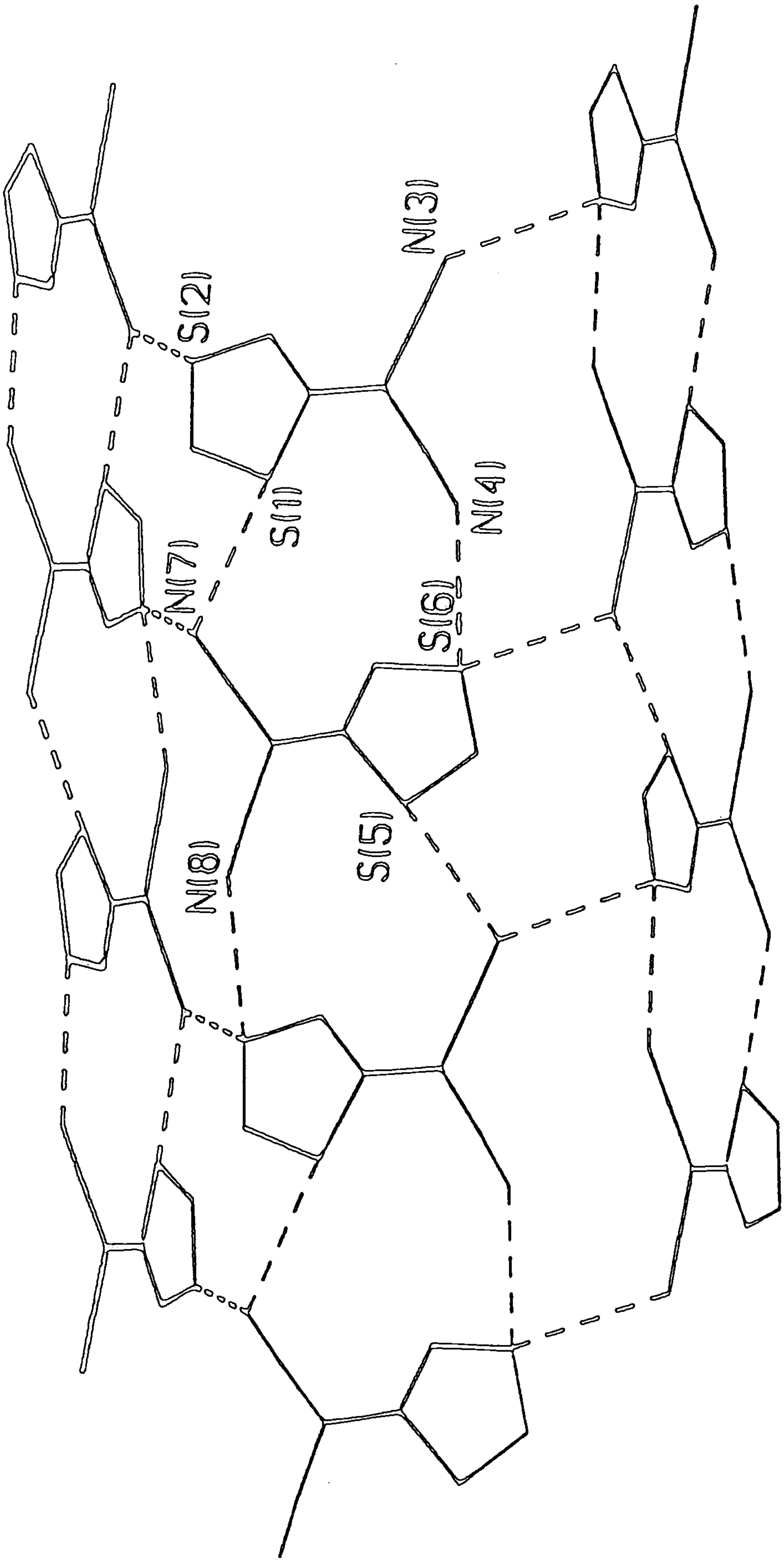


Figure 3.6a The 'herringbone' structure of compound 1.

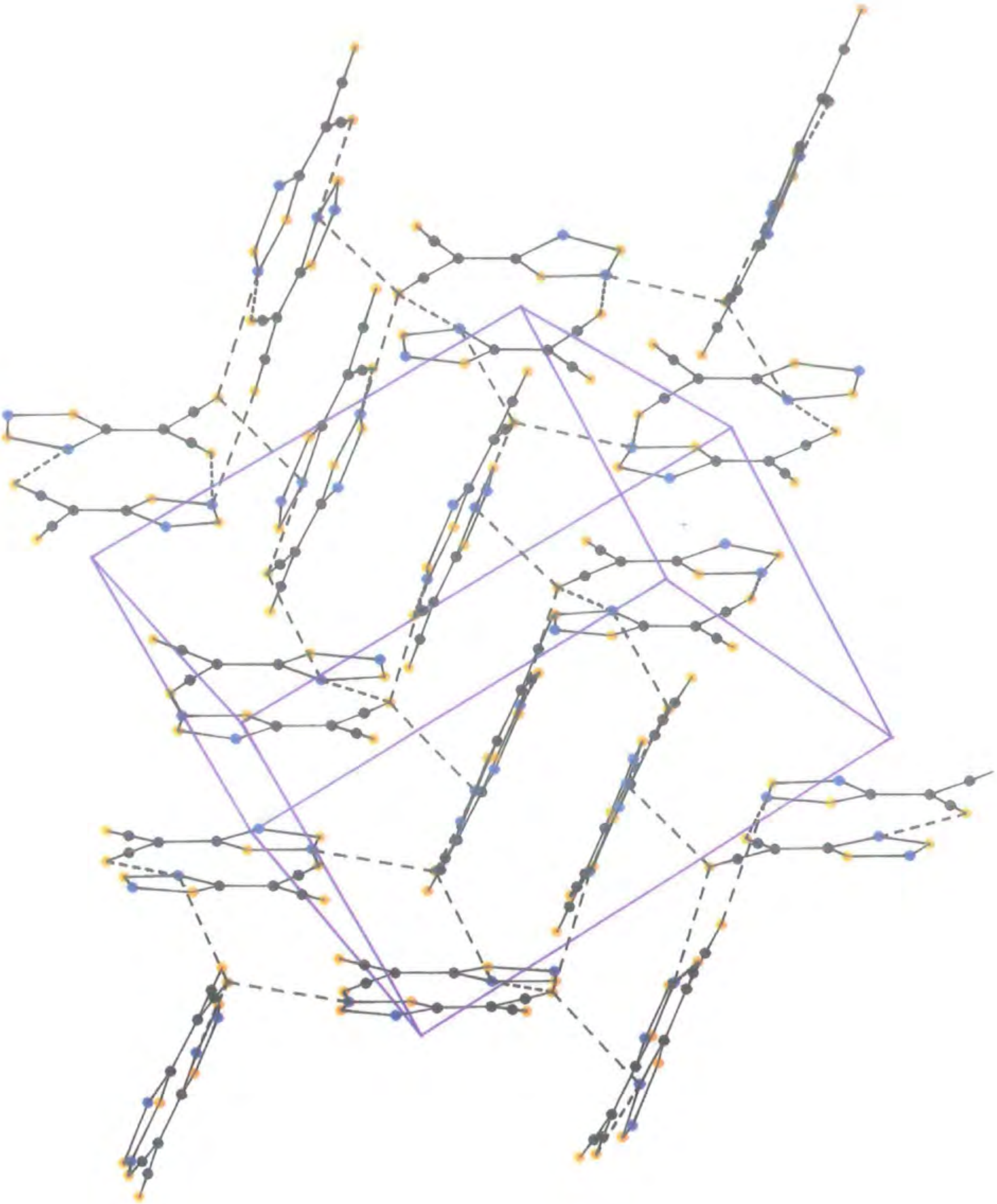
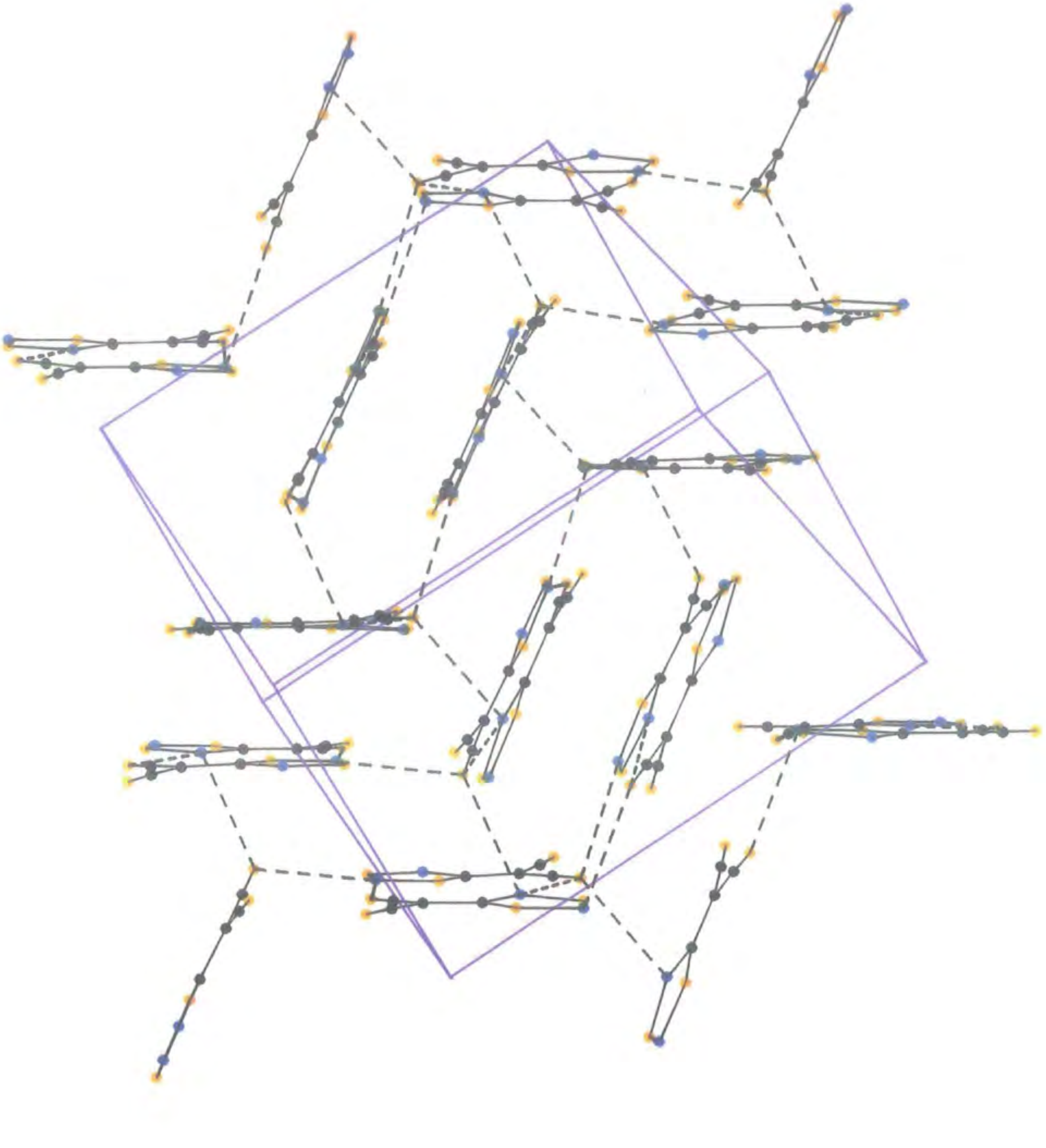


Figure 3.6b An alternative view of he 'herringbone' structure of compound **1**.



In-plane intermolecular CN···S interactions link the molecules together into planar sheets (Fig. 3.5 and 3.6: S(1)···N(7) 3.103, S(5)···N(3') 3.103, S(2')···N(8) 3.051, S(6)···N(4) 2.971 Å, the prime denoting an atom in a symmetry-related molecule); the dihedral angle between the mean planes of two adjacent molecules is 2.9°. These sheets are also linked to each other by further CN···S out-of-plane intermolecular interactions to give a 'herring-bone' like three-dimensional network (Fig. 3.5 and 3.6, S(2)···N(3') 3.163, S(6)···N(7') 3.127 Å); the dihedral angle between molecular planes is 117.3°. Each molecule thus engages in six CN···S secondary interactions involving its two dithiadiazolyl sulphur atoms and both nitrile nitrogen atoms, whilst the dithiadiazolyl nitrogen atoms are not involved.

Table 3.5 Crystal parameters and data collection/refinement for $(NC)_2C{=}CNSNS$ (1)

Formula	$C_4N_4S_2$	2θ range for unit cell / °	20-25 °
M.W.	168.19	Space Group	$P2_1/c$
Crystal Size (mm)	0.16x0.20x0.52	Z	8
Crystal Form	Black Prisms	D_c (gcm^{-3})	1.748
Instrument	Stoe-Siemens	F(000)	672
Radiation	Mo(Kα)	μ/mm^{-1}	0.71
λ(Å)	0.71073	T/K	240
Scan Type	ω/θ	2θ range for data	0-50 °
Crystal System	Monoclinic	Total Data Measured	2252
a/Å	11.8595(10)	Total Unique	2252
b/Å	13.2788(10)	Total Observed	1555
c/Å	8.4688(6)	Significance Test	$F_o>4\sigma(F_o)$
α/°	90	No. of Parameters	181
β/°	106.558(5)	ρ_{min}- ρ_{max}/eÅ^{-3}	(-0.24)-(0.28)
γ/°	90	Weighting Scheme	$\sigma(F_o)^{-2}$
V/Å^3	1278.4	R	0.0321
		R_w	0.0409

Table 3.6 Atomic coordinates ($\times 10^4$) for $(NC)_2C{=}CNSNS$ (1)

Atom	x	y	z
S(1)	2136(1)	1784(1)	1602(1)
N(1)	1230(2)	2662(2)	1796(3)
S(2)	-7(1)	2572(1)	475(1)
N(2)	80(2)	1604(2)	-585(3)
C(1)	1147(2)	1151(2)	-56(3)
C(2)	1447(2)	273(2)	-721(3)
C(3)	621(3)	-201(2)	-2069(4)
N(3)	-61(2)	-583(2)	-3141(3)
C(4)	2556(3)	-173(2)	-7(4)
N(4)	3468(3)	-517(2)	619(4)
S(5)	7508(1)	447(1)	5478(1)
N(5)	7158(2)	-455(2)	4107(3)
S(6)	5868(1)	-340(1)	2939(1)
N(6)	5366(2)	646(2)	3553(3)
C(5)	6154(2)	1097(2)	4822(4)
C(6)	5956(2)	1994(2)	5532(4)
C(7)	4858(3)	2502(2)	4939(4)
N(7)	3963(2)	2894(2)	4426(4)
C(8)	6882(3)	2436(2)	6785(4)
N(8)	7666(3)	2764(2)	7777(4)

Table 3.7 Bond lengths (Å) in $(NC)_2C{=}CNSNS$ (1)

S(1)-N(1)	1.624(3)	S(1)-C(1)	1.765(3)
N(1)-S(2)	1.576(3)	S(2)-N(2)	1.589(3)
N(2)-C(1)	1.356(4)	C(1)-C(2)	1.385(4)
C(2)-C(3)	1.423(4)	C(2)-C(4)	1.411(4)
C(3)-N(3)	1.148(4)	C(4)-N(4)	1.154(4)
5(5)-N(5)	1.637(3)	S(5)-C(5)	1.767(3)
N(5)-5(6)	1.575(3)	S(6)-N(6)	1.586(3)
N(6)-C(5)	1.347(4)	C(5)-C(6)	1.384(4)
C(6)-C(7)	1.424(4)	C(6)-C(8)	1.419(4)
C(7)-N(7)	1.151(4)	C(8)-N(8)	1.146(4)

Table 3.8 Bond angles (degrees) in $(NC)_2C{=}CNSNS$ (1)

N(1)-S(1)-C(1)	96.6(1)	S(1)-N(1)-S(2)	112.5(2)
N(1)-S(2)-N(2)	105.3(1)	S(2)-N(2)-C(1)	112.1(2)
S(1)-C(1)-N(2)	113.4(2)	S(1)-C(1)-C(2)	122.3(2)
N(2)-C(1)-C(2)	124.3(2)	C(1)-C(2)-C(3)	120.0(3)
C(1)-C(2)-C(4)	119.7(2)	C(3)-C(2)-C(4)	120.2(3)
C(2)-C(3)-N(3)	178.8(4)	C(2)-C(4)-N(4)	177.8(4)
N(5)-S(5)-C(5)	96.4(1)	S(5)-N(5)-S(6)	112.3(2)
N(5)-S(6)-N(6)	105.2(1)	S(6)-N(6)-C(5)	112.9(2)
S(5)-C(5)-N(6)	113.3(2)	S(5)-C(5)-C(6)	122.4(2)
N(6)-C(5)-C(6)	124.3(3)	C(5)-C(6)-C(7)	120.4(2)
C(5)-C(6)-C(8)	119.3(3)	C(7)-C(6)-C(8)	120.2(3)
C(6)-C(7)-N(7)	178.1(3)	C(6)-C(8)-N(8)	176.9(4)

Table 3.9 Anisotropic thermal parameters ($Å^2 x10^3$) for $(NC)_2C{=}CNSNS$, 1

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	32(1)	45(1)	41(1)	-8(1)	7(1)	-4(1)
N(1)	45(2)	42(2)	42(2)	-9(1)	14(1)	-6(1)
S(2)	39(1)	40(1)	42(1)	-4(1)	12(1)	4(1)
N(2)	32(1)	36(1)	33(1)	1(1)	9(1)	2(1)
C(1)	30(1)	36(2)	28(1)	3(1)	8(1)	-3(1)
C(2)	30(2)	34(2)	33(2)	1(1)	7(1)	0(1)
C(3)	31(2)	33(2)	37(2)	4(1)	9(1)	6(1)
N(3)	42(2)	52(2)	43(2)	-7(1)	2(1)	4(1)
C(4)	32(2)	35(2)	42(2)	-5(1)	5(1)	-2(1)
N(4)	43(2)	50(2)	69(2)	-8(2)	-3(2)	9(1)
S(5)	30(1)	39(1)	47(1)	0(1)	2(1)	5(1)
N(5)	40(2)	41(2)	49(2)	-4(1)	10(1)	7(1)
S(6)	37(1)	42(1)	47(1)	-11(1)	7(1)	3(1)
N(6)	30(1)	38(2)	38(1)	-3(1)	6(1)	0(1)
C(5)	25(1)	34(2)	36(2)	5(1)	6(1)	-3(1)
C(6)	28(2)	34(2)	38(2)	-2(1)	4(1)	-1(1)
C(7)	35(2)	29(2)	39(2)	-3(1)	9(1)	-3(1)
N(7)	34(2)	44(2)	56(2)	2(1)	7(1)	3(1)
C(8)	32(2)	38(2)	45(2)	-3(2)	8(1)	2(1)
N(8)	40(2)	58(2)	56(2)	-13(2)	2(1)	1(1)

The carbon-carbon double bond length in **1** compares well[20] with a similar compound, $MeS(Me_2N)C=C(CN)_2$, (**4**) (see Table 3.10), but it is longer than that observed in cubic TCNE[21]. The CN bond lengths in **1** are also similar to those in **4** (1.148 Å and 1.154 Å, compared with 1.130 Å and 1.132 Å, respectively) but shorter than those in cubic TCNE.

Table 3.10 Selected bond lengths (Å) in $(NC)_2C=CNSNS$ and comparable systems

	p-$C_6H_4(CNSNS)_2$	$(NC)_2C=CNSNS$	$(NC)_2C=CNSNS$	SNSNC=O
C1-N2	1.276(4)	1.356(4)	1.347(4)	1.374(7)
N2-S2	1.646(4)	1.589(3)	1.586(3)	1.584(4)
S2-N1	1.695(4)	1.576(3)	1.575(3)	1.572(5)
N1-S1	1.632(4)	1.624(3)	1.637(3)	1.630(4)
S1-C1	1.775(4)	1.765(3)	1.767(3)	1.813(5)
ref	8	**This work**	**This work**	22
	$(NC)_2C=CNSNS$	TCNE (cubic)	$MeS(Me_2N)C=C(CN)_2$	$(Me_2N)_2C=C(CN)_2$
C=C	1.385(4) 1.384(4)	1.353(3)	1.397(8)	1.407(4)
C-C=C	1.411(4) 1.423(4) 1.424(4) 1.419(4)	1.432(2)	1.430(8)	1.410(5)
C≡N	1.148(4) 1.154(4) 1.151(4) 1.146(4)	1.166(2)	1.130(9) 1.132(10)	1.143(5) 1.151(6)
ref	**This work**	21	20	20

The dithiadiazolyl bond lengths in **1** correspond better to those in NSNSC=O[22] than those in *p*-$C_6H_4(CNSNS)_2$[8]. This is probably due to a combination of (i) the greater exocyclic double bond character in **1** (see below) and in O=CNSNS, and (ii) the electron withdrawing effect of the dicyanomethyne group (cf O=CNSNS) which is greater than that of para - phenylene(dithiadiazolyl) -C_6H_4(CNSNS).

3.2.2.2 Solid state structure of 3

The dication of **3** is essentially planar with C_{3h} symmetry (Fig.3.5), the $[SNS]^+$ cations being added in a *cis* fashion as described above for **2**. R.M.S. deviations for the three CNSNS rings are 0.005, 0.008 and 0.011 Å, and for the central C_4 unit 0.005 Å; the three rings have dihedral angles of 1.3°, 5.6° and 2.2° to the C_4 mean plane.

As expected, PM3 calculations on the parent dication indicate an even distribution of charge around the three CNSNS heterocyclic rings

(+0.73), which is also in accord with the equivalent geometries of the three CNSNS rings.

Table 3.11 Crystal parameters and data collection/refinement for $[C(CNSNS)_3][AsF_6]_2.SO_2$ (**3**)

Formula	$C_4As_2F_{12}N_6O_2S_7$	2θ range for unit cell / °	20-25 °
M.W.	766.3	Space Group	$P2_1/c$
Crystal Size (mm)	0.25x0.30x0.80	Z	4
Crystal Form	Red Blocks	D_c (gcm^{-3})	2.432
Instrument	Stoe-Siemens	F(000)	1472
Radiation	Mo(Kα)	μ/mm^{-1}	3.98
λ(Å)	0.71073	T/K	240
Scan Type	ω/θ	2θ range for data	0-50 °
Crystal System	Monoclinic	Total Data Measured	6078
a/Å	8.168(3)	Total Unique	3705
b/Å	17.839(6)	Total Observed	2892
c/Å	14.747(5)	Significance Test	$F_o>4\sigma(F_o)$
α/°		No. of Parameters	181
β/°	103.12(3)	ρ_{min}- ρ_{max}/eÅ^{-3}	(-1.13)-(1.29)
γ/°		Weighting Scheme	$\sigma(F_o)^{-2}$
V/Å^3	2092.7	R	0.0550
		R_w	0.0318

All three rings are thus chemically equivalent, with no significant differences in their geometries. There are, however, small differences among the three C-C bonds; these minor distortions of the cation from ideal C_{3h} symmetry may be due to weak interactions with the anions and solvent molecules in the structure. Within the crystal, anions and solvent molecules lie above and below each of the rings of the cations, and there are numerous S···F and S···O contacts between 2.90 and 3.25 Å involving the more electropositive dithiadiazolylium sulphur atoms S-3 (see fig 3.8 and 3.9). The cations lie in parallel planes with anions and solvent molecules lying over the dithiadiazolylium rings (see fig 3.8 and 3.9).

Figure 3.7 The dication of compound 3 showing the atom numbering scheme

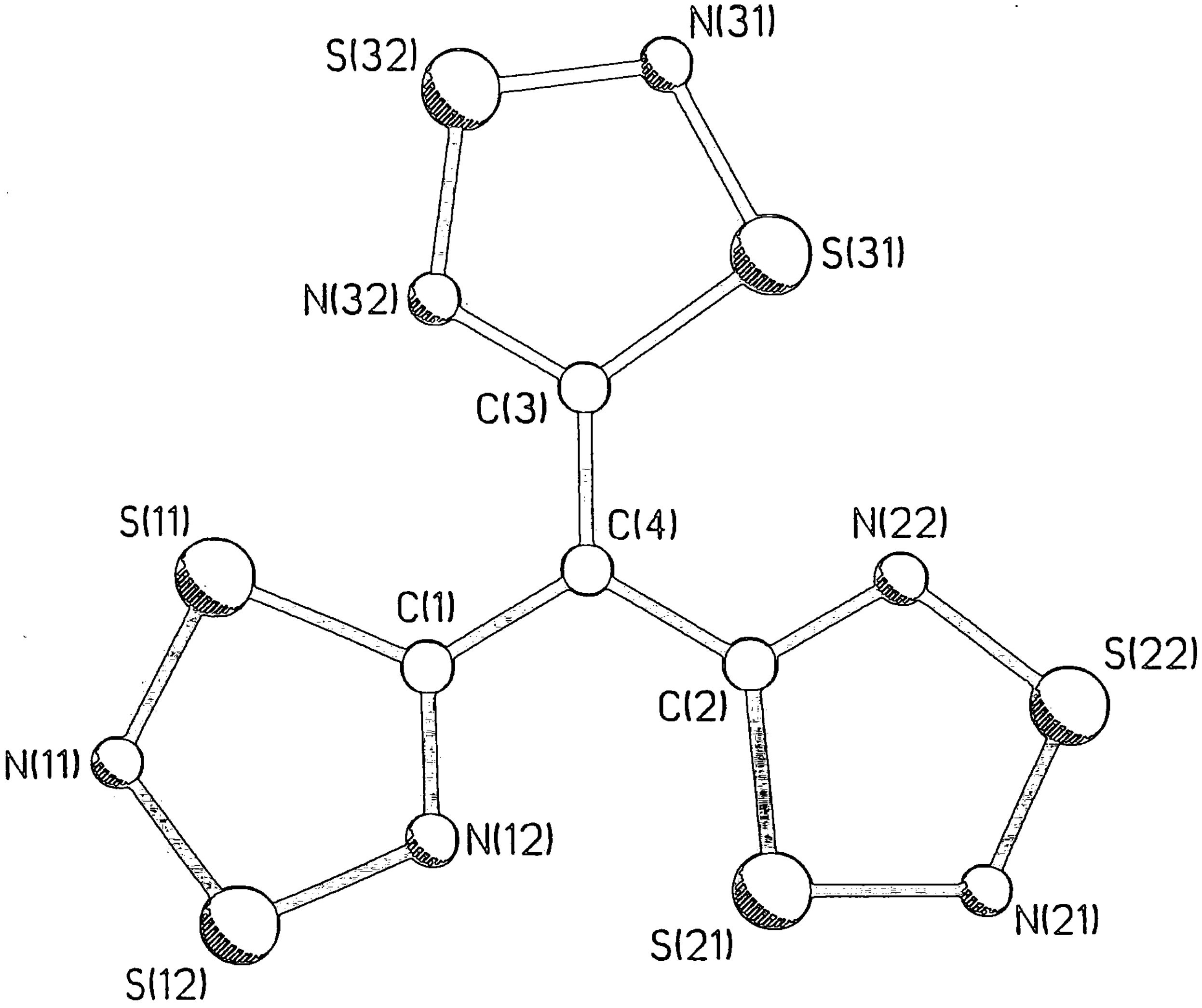


Figure 3.8 Packing of cations, anions and solvent molecules in the solid state structure of compound 3, showing the cations lying in parallel with associated anions and solvent molecules above the dithiadiazolylium rings

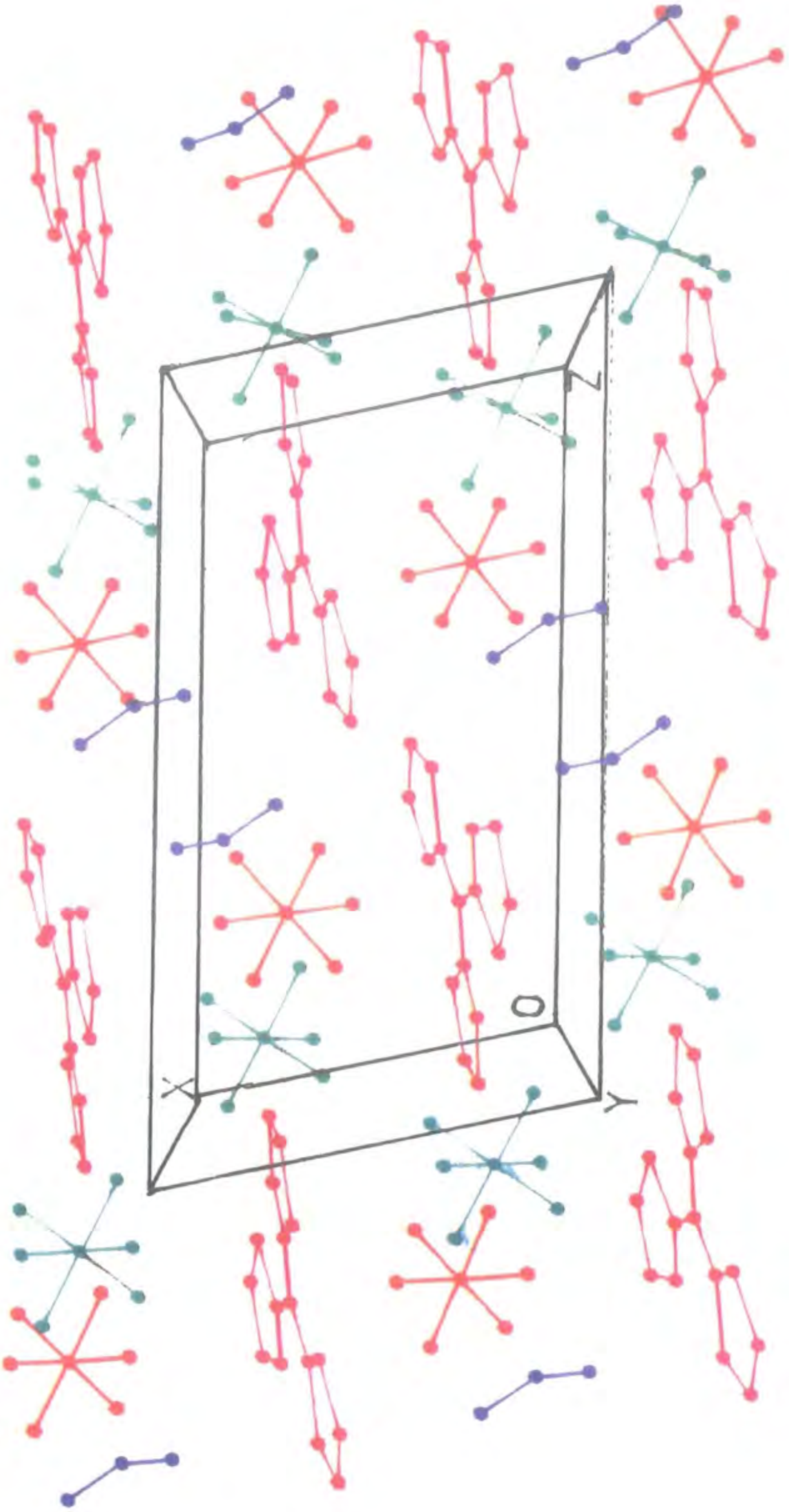


Figure 3.9 View down onto the plane of the cations showing packing of cations, anions and solvent molecules

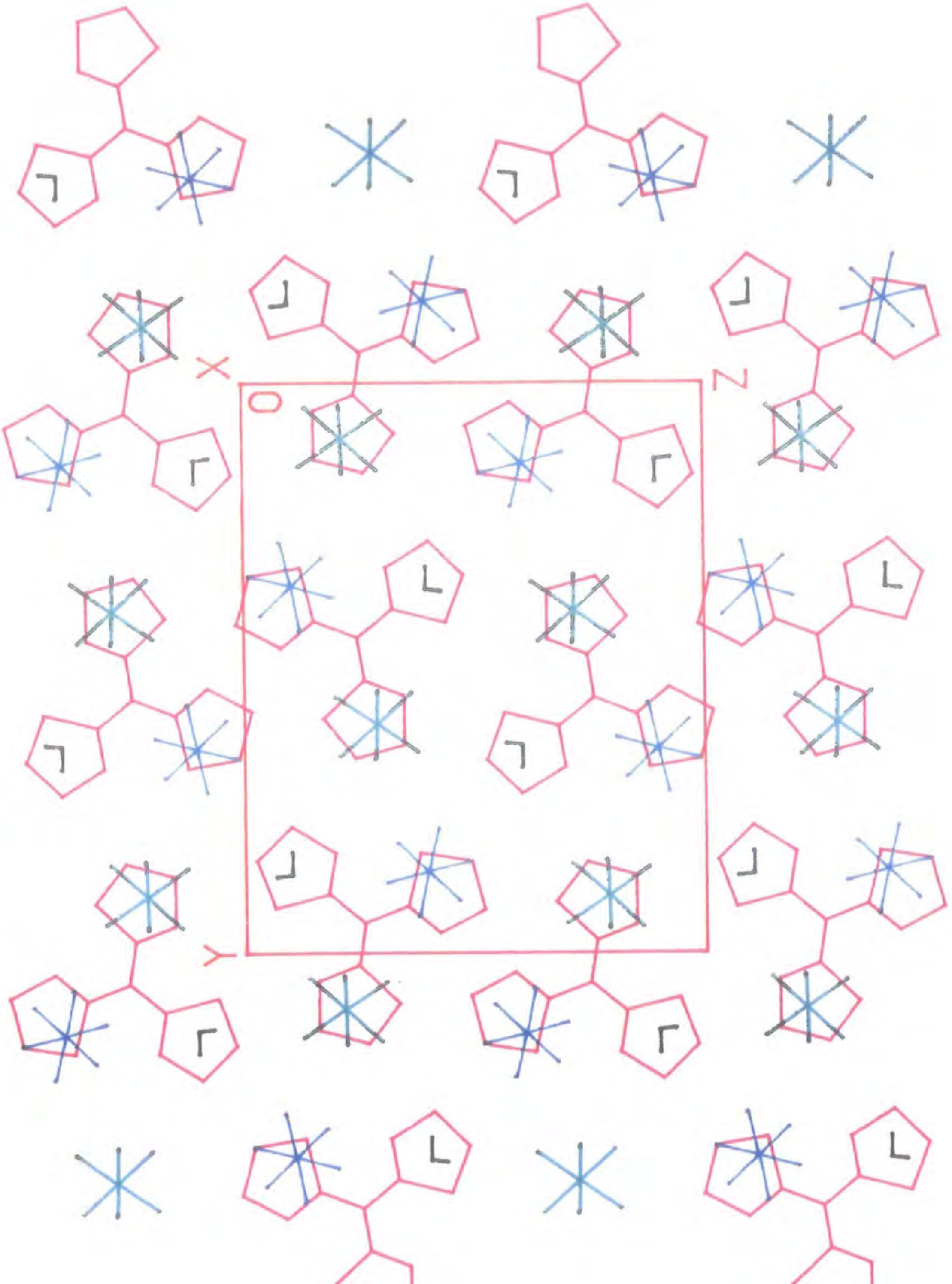


Table 3.12 Atomic coordinates for $[C(CNSNS)_3][AsF_6]_2.SO_2$ (3)

Atom	x	y	z
C(1)	3459(6)	3973(3)	3204(3)
S(11)	3729(2)	4204(1)	4378(1)
N(11)	4262(6)	3378(3)	4765(3)
S(12)	4278(2)	2783(1)	3996(1)
N(12)	3730(5)	3254(2)	3054(2)
C(2)	2809(5)	4190(3)	1518(3)
S(21)	3051(2)	3249(1)	1223(1)
N(21)	2710(5)	3400(3)	109(3)
S(22)	2397(2)	4247(1)	-169(1)
N(22)	2488(5)	4653(2)	804(2)
C(3)	2618(5)	5216(3)	2593(3)
S(31)	2046(2)	5891(1)	1712(1)
N(31)	1847(5)	6587(2)	2394(3)
S(32)	2217(2)	6350(1)	3452(1)
N(32)	2719(5)	5488(3)	3442(3)
C(4)	2972(6)	4474(3)	2443(3)
As(1)	2753(1)	4004(1)	7135(1)
F(11)	3960(4)	4490(2)	8031(2)
F(12)	1101(4)	4584(2)	7113(2)
F(13)	2035(4)	3444(2)	7911(2)
F(14)	4374(4)	3388(2)	7165(2)
F(15)	3499(4)	4557(2)	6376(2)
F(16)	1557(4)	3511(2)	6240(2)
As(2)	2111(1)	6421(1)	8966(1)
F(21)	915(5)	5632(3)	8759(4)
F(22)	3657(5)	5913(2)	9633(3)
F(23)	2997(5)	6232(3)	8059(3)
F(24)	585(4)	6924(3)	8288(3)
F(25)	1201(6)	6583(4)	9844(3)
F(26)	3345(5)	7186(2)	9195(3)
S(4)	998(5)	8636(3)	1046(2)
O(41)	2323(6)	8671(4)	693(4)
O(42)	-266(8)	8239(5)	1038(4)

Table 3.13 Bond lengths (Å) in $[C(CNSNS)_3][AsF_6]_2.SO_2$ (3)

C(1)-S(11)	1.746(5)	C(1)-N(12)	1.329(7)
C(1)-C(4)	1.418(7)	S(11)-N(11)	1.602(5)
N(11)-S(12)	1.557(5)	S(12)-N(12)	1.599(4)
C(2)-S(21)	1.756(6)	C(2)-N(22)	1.316(6)
C(2)-C(4)	1.433(7)	S(21)-N(21)	1.626(4)
N(21)-S(22)	1.571(5)	S(22)-N(22)	1.594(4)
C(3)-S(31)	1.755(5)	C(3)-N(32)	1.328(6)
C(3)-C(4)	1.384(8)	S(31)-N(31)	1.629(5)
N(31)-S(32)	1.578(5)	S(32)-N(32)	1.592(5)
As(1)-F(11)	1.695(3)	As(1)-F(12)	1.694(4)
As(1)-F(13)	1.719(4)	As(1)-F(14)	1.714(4)
As(1)-F(15)	1.706(4)	As(1)-F(16)	1.699(3)
As(2)-F(21)	1.700(5)	As(2)-F(22)	1.679(4)
As(2)-F(23)	1.692(5)	As(2)-F(24)	1.671(4)
As(2)-F(25)	1.659(5)	As(2)-F(26)	1.685(4)
S(4)-O(41)	1.305(7)	S(4)-O(42)	1.250(9)

The bond lengths in the CNSNS rings of the dication of 3 compare well with previously reported dithiadiazolylium cations (e.g. phenyl, methyl - see table 3.16), although here the cations have only a charge of + 0.67 on them. This effect could be due to increased stabilisation of the trigonal system deriving from an effect similar to “Y-delocalisation” or cross-conjugation, as observed in species such as the methylenecycloheptatrienyl dianion[25], trimethylenemethane[26] and $[C(CN)_3]^-$ itself, which allows for a type of aromatic stabilisation in acyclic compounds[25].

Table 3.14 Bond angles (degrees) in $[C(CNSNS)_3][AsF_6]_2.SO_2$ (3)

S(11)-C(1)-N(12)	113.9(3)	S(11)-C(1)-C(4)	125.9(4)
N(12)-C(1)-C(4)	120.2(4)	C(1)-S(11)-N(11)	95.7(2)
S(11)-N(11)-S(12)	114.5(3)	N(11)-S(12)-N(12)	103.1(2)
C(1)-N(12)-S(12)	112.7(3)	S(21)-C(2)-N(22)	114.5(4)
S(21)-C(2)-C(4)	125.6(4)	N(22)-C(2)-C(4)	119.9(5)
C(2)-S(21)-N(21)	95.1(2)	S(21)-N(21)-S(22)	113.7(3)
N(21)-S(22)-N(22)	103.4(2)	C(2)-N(22)-S(22)	113.2(4)
S(31)-C(3)-N(32)	113.4(4)	S(31)-C(3)-C(4)	124.7(4)
N(32)-C(3)-C(4)	121.9(5)	C(3)-S(31)-N(31)	96.5(2)
S(31)-N(31)-S(32)	112.5(3)	N(31)-S(32)-N(32)	104.0(2)
C(3)-N(32)-S(32)	113.6(4)	C(1)-C(4)-C(2)	118.7(5)
C(1)-C(4)-C(3)	120.5(4)	C(2)-C(4)-C(3)	120.8(4)
F(11)-As(1)-F(12)	91.3(2)	F(11)-As(1)-F(13)	90.3(2)
F(12)-As(1)-F(13)	88.7(2)	F(11)-As(1)-F(14)	89.9(2)
F(12)-As(1)-F(14)	177.7(2)	F(13)-As(1)-F(14)	89.3(2)
F(11)-As(1)-F(15)	89.1(2)	F(12)-As(1)-F(15)	92.1(2)
F(13)-As(1)-F(15)	179.0(2)	F(14)-As(1)-F(15)	89.9(2)
F(11)-As(1)-F(16)	179.5(2)	F(12)-As(1)-F(16)	89.2(2)
F(13)-As(1)-F(16)	89.6(2)	F(14)-As(1)-F(16)	89.6(2)
F(15)-As(1)-F(16)	91.0(2)	F(21)-As(2)-F(22)	89.1(2)
F(21)-As(2)-F(23)	91.4(3)	F(22)-As(2)-F(23)	87.4(2)
F(21)-As(2)-F(24)	91.0(2)	F(22)-As(2)-F(24)	179.1(2)
F(23)-As(2)-F(24)	91.7(2)	F(21)-As(2)-F(25)	86.7(3)
F(22)-As(2)-F(25)	92.7(2)	F(23)-As(2)-F(25)	178.1(3)
F(24)-As(2)-F(25)	88.2(2)	F(21)-As(2)-F(26)	178.1(2)
F(22)-As(2)-F(26)	89.1(2)	F(23)-As(2)-F(26)	88.6(2)
F(24)-As(2)-F(26)	90.9(2)	F(25)-As(2)-F(26)	93.2(3)
0(41)-S(4)-0(42)	141.4(6)		

Table 3.15 Anisotropic thermal parameters ($\AA^2 \times 10^3$) for $[C(CNSNS)_3][AsF_6]_2.SO_2$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	30(3)	41(3)	37(3)	-1(3)	10(2)	-10(3)
S(11)	51(1)	52(1)	31(1)	0(1)	6(1)	-3(1)
N(11)	-65(3)	60(4)	34(3)	8(2)	9(2)	-8(3)
S(12)	69(1)	51(1)	40(1)	12(1)	13(1)	1(1)
N(12)	48(3)	35(3)	34(3)	-2(2)	11(2)	-5(2)
C(2)	7(2)	48(4)	38(3)	3(3)	1(2)	1(2)
S(21)	51(1)	37(1)	39(1)	-4(1)	11(1)	0(1)
N(21)	42(3)	55(3)	33(2)	1(2)	8(2)	3(3)
S(22)	55(1)	50(1)	32(1)	0(1)	12(1)	3(1)
N(22)	28(2)	45(3)	33(2)	1(2)	6(2)	1(2)
C(3)	18(3)	67(4)	27(3)	0(3)	7(2)	-10(3)
S(31)	45(1)	38(1)	41(1)	2(1)	6(1)	5(1)
N(31)	45(3)	35(3)	55(3)	-1(2)	0(2)	3(3)
S(32)	50(1)	46(1)	48(1)	-11(1)	10(1)	3(1)
N(32)	26(2)	50(3)	35(2)	-2(2)	1(2)	-3(2)
C(4)	27(3)	43(3)	30(3)	-5(3)	10(2)	-6(3)
As(1)	39(1)	54(1)	43(1)	-6(1)	13(1)	-5(1)
F(11)	47(2)	94(3)	63(2)	-30(2)	14(2)	-10(2)
F(12)	38(2)	84(3)	117(3)	-8(2)	23(2)	7(2)
F(13)	84(3)	97(3)	81(3)	28(2)	37(2)	-17(3)
F(14)	50(2)	73(3)	96(3)	-20(2)	18(2)	10(2)
F(15)	70(3)	96(3)	63(2)	23(2)	25(2)	-17(2)
F(16)	56(2)	121(4)	69(2)	-36(2)	3(2)	-18(3)
As(2)	44(1)	47(1)	67(1)	17(1)	19(1)	5(1)
F(21)	64(3)	86(4)	351(7)	37(5)	48(4)	-20(3)
F(22)	59(3)	92(4)	166(4)	64(3)	12(3)	11(3)
F(23)	91(3)	195(6)	103(4)	-33(3)	46(3)	-1(4)
F(24)	66(3)	123(4)	108(3)	66(3)	10(2)	20(3)
F(25)	156(4)	250(8)	83(3)	80(4)	77(3)	99(5)
F(26)	91(3)	66(3)	166(4)	-6(3)	13(3)	-8(3)
S(4)	119(3)	485(9)	128(3)	-127(3)	68(2)	-116(4)
O(41)	76(4)	166(7)	133(5)	-46(5)	46(4)	-1(4)
O(42)	81(5)	272(11)	110(5)	37(5)	6(4)	2(6)

Table 3.16 Selected bond lengths (Å) in $[C(CNSNS)_3][AsF_6]_2.SO_2$ and comparable systems.

			$[C(CNSNS)_3]^{2+}$		
	$PhCNSNS^+$	$MeCNSNS^+$	C1 ring	C2 ring	C3 ring
N2-S2	1.576(7)	1.57(2)	1.599(4)	1.594(4)	1.592(5)
S2-N1	1.561(8)	1.59(2)	1.557(5)	1.571(5)	1.578(5)
N1-S1	1.596(8)	1.63(2)	1.602(5)	1.626(4)	1.629(5)
S1-C1	1.732(8)	1.77(2)	1.745(5)	1.756(6)	1.755(5)
C1-N2	1.336(9)	1.32(3)	1.329(7)	1.316(6)	1.328(6)
ref	23	24	This work	This work	This work

3.2.3 Reduction properties of the addition compounds

Reduction of dithiadiazolylium cations has been shown[27] to yield the corresponding dithiadiazolyl neutral free-radical species; the 1,3,2,4-dithiadiazolyls have been found to be photochemically and thermally unstable with respect to rearrangement to their 1,2,3,5-dithiadiazolyl analogues[28,16]. The rearrangement process takes between a few minutes and several weeks, depending upon the organic substituent and is more rapid in solution - see chapter 4.

For example, the diradicals *m* and *p*-$[(SNSNC).C_6H_4.(CNSNS)]^{\circ\circ}$ or the triradical *sym*-$[C_6H_4(CNSNS)_3]^{\circ\circ\circ}$ undergo thermal rearrangement[16] in the solid state at elevated temperatures (110°C, 145°C and 290°C respectively) to the corresponding 1,2,3,5-isomers. Such a rearrangement in the solid state has been proposed to occur through a dimeric head-to-tail arrangement of dithiadiazolyl rings (see figure 3.10) and is similar to that proposed[28] for the photolytically induced rearrangement that occurs in solution (see figure 3.11). For $[Ph.CNSNS]^{\circ}$, the rearrangement occurs over a period of hours and may be monitored by esr spectroscopy.

Earlier cyclic voltammogram studies[8,29] on a variety of dithiadiazolylium cations have shown that they can be reduced readily to their neutral free-radical analogues and that, in some cases, the reduction to the dithiadiazolide anion is partially reversible (the reversibility being dependent upon the sweep rate).

Figure 3.10 Mechanism of the solid state rearrangement of 1,3,2,4-dithiadiazolyl radicals (taken from ref. 16)

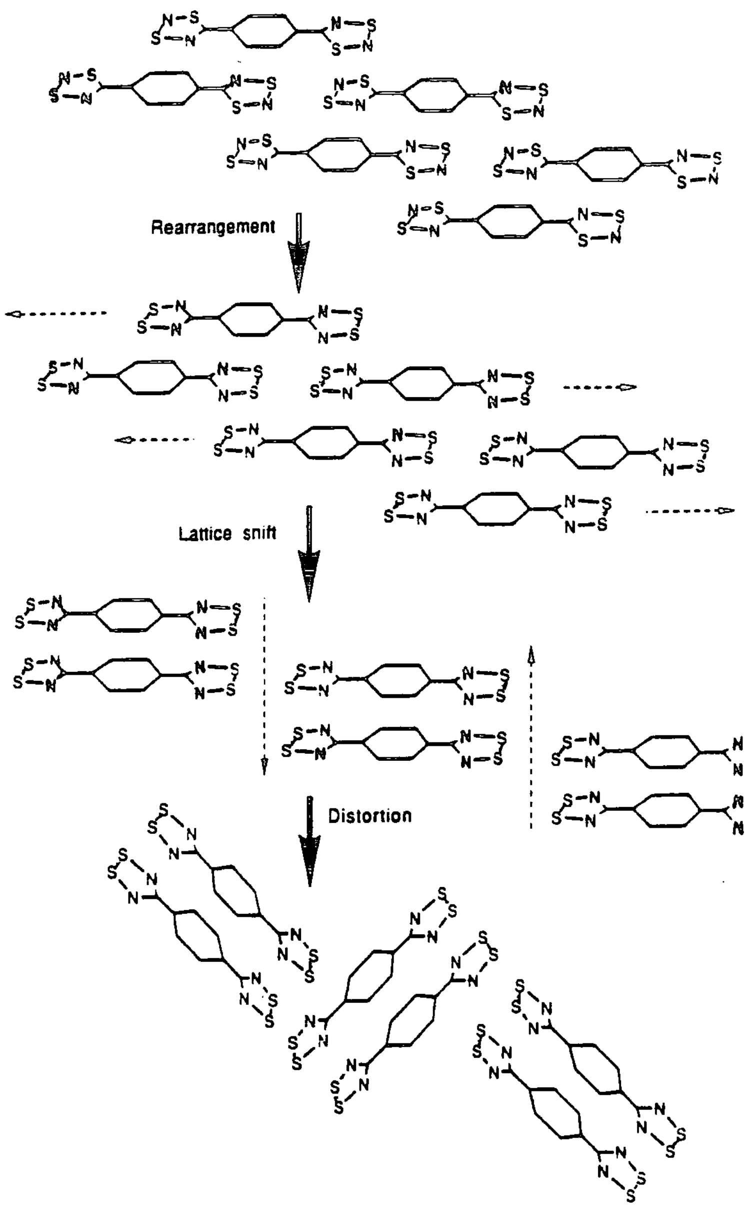
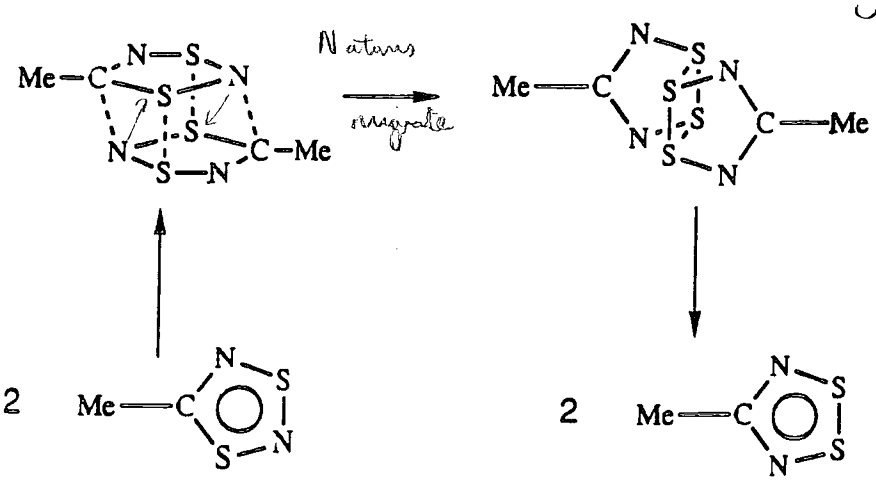


Figure 3.11 Mechanism of the solution state rearrangement of 1,3,2,4-dithiadiazolyl radicals (also from ref. 16) really ref ㉘



Reduction of 1

A cyclic voltammogram of $(NC)_2CCNSNS$,1, (fig.3.12) showed that it may be reduced ($E_{p/2}$=0.41 V) to the radical anion (peak 1) in acetonitrile and this process to be reversible.

No solution esr spectrum was obtained for the neutral species (also it does not appear to rearrange in the solid state, as shown by differential scanning calorimetry). This is not surprising as the S···S interactions observed in the solid state structure of 1 do not allow for the head-to-tail arrangement of the molecules. Furthermore this compound is electron paired as there is a carbon-carbon double bond present (to satisfy the valency of the dicyanomethyne carbon) as is Roesky's ketone[22], SNSNC=O.

The solution state esr spectrum in the presence of lithium iodide (figure 3.13) confirmed it as a suitable reducing agent - a 1:1:1 triplet was observed (indicative of the radical anion, with the electron sited on one nitrogen atom). However, isolation of a characterisable, solid product from the reactions of 1 with either CsI, Bu_4NI or Et_4NI proved impossible as the oily solids obtained were intractable. It did appear that iodine was generated in each of these reactions, though.

The reaction with lithium iodide on a preprative scale did allow for isolation of a solid product, a grey powder. This material showed a favourable infra red spectrum, with the peaks for compound **1** observed but shifted by a few wavenumbers. Bands assignable to SO_2 (at 525 cm^{-1}) were observed. This material was recrystallised from acetonitrile and large gold crystals which were obtained by slow solvent removal did not provide sufficiently strong diffraction data for a solid state structure to be determined.

Consequently, only circumstantial evidence can be offered for the isolation of the radical anion, namely the apparent loss of iodine (colour change to deep red-brown), its infra-red data (showing bands for compound **1** shifted slightly, together with SO_2 bands), esr data (a 1:1:1 triplet indicative of a dithiadiazolyl radical) and the elemental analyses (indicating a formulation consistent with $[Li]^+[\mathbf{1}]^- .3SO_2$).

Perhaps a larger counterion could aid diffraction and allow for unambiguous identification of the product. Caesium iodide was used but it too gave only intractable products.

Figure 3.12 Cyclic voltammogram of compound 1 (vs. Ag-Ag$^+$ reference electrode / calibrated to saturated SCE); as a ca. 1×10^{-3} mol dm^{-3} solution in acetonitrile with $[Bu_4N]BF_4$ as supporting electrolyte (ca. 0.1 mol dm^{-3}) at -13°C

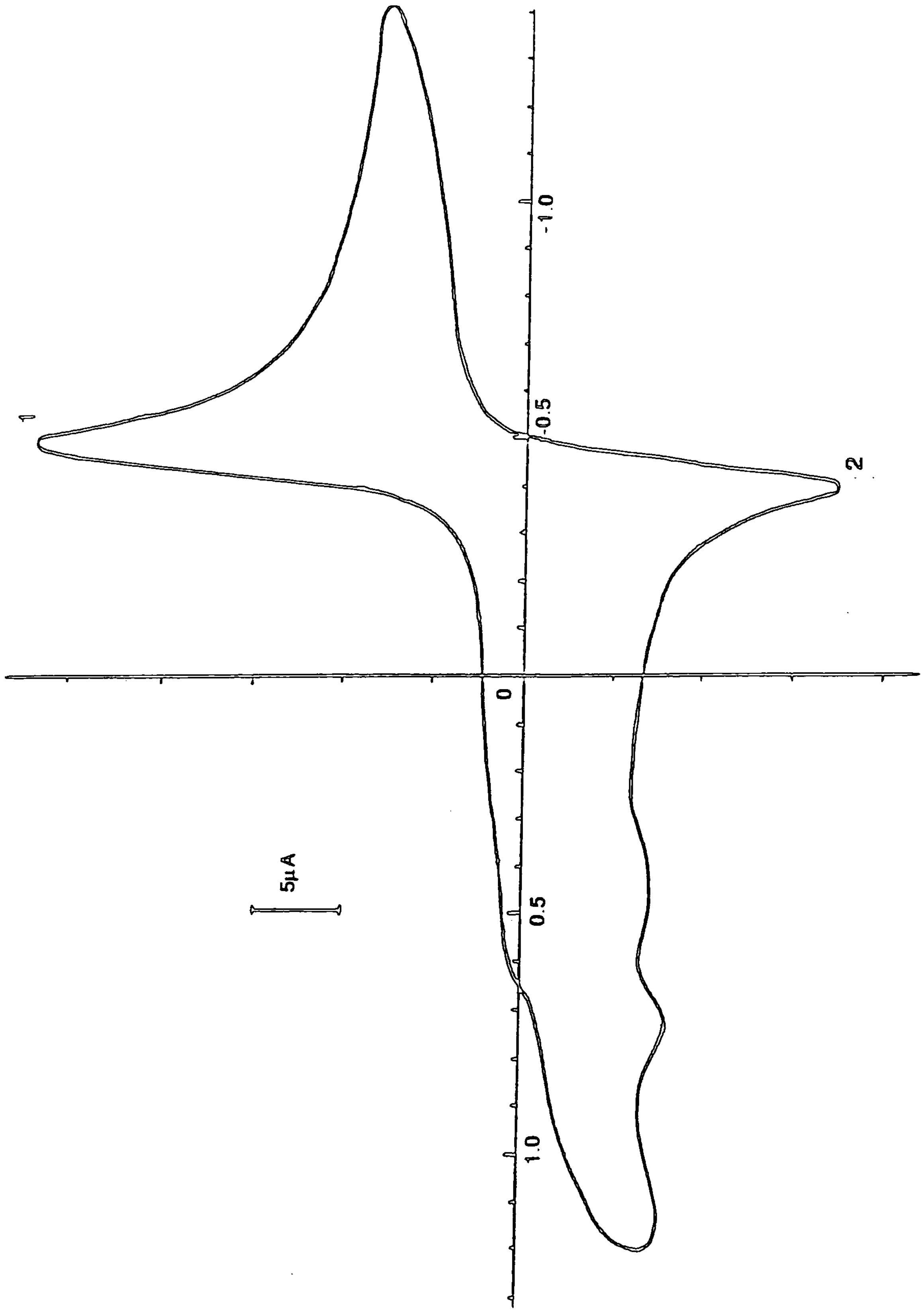
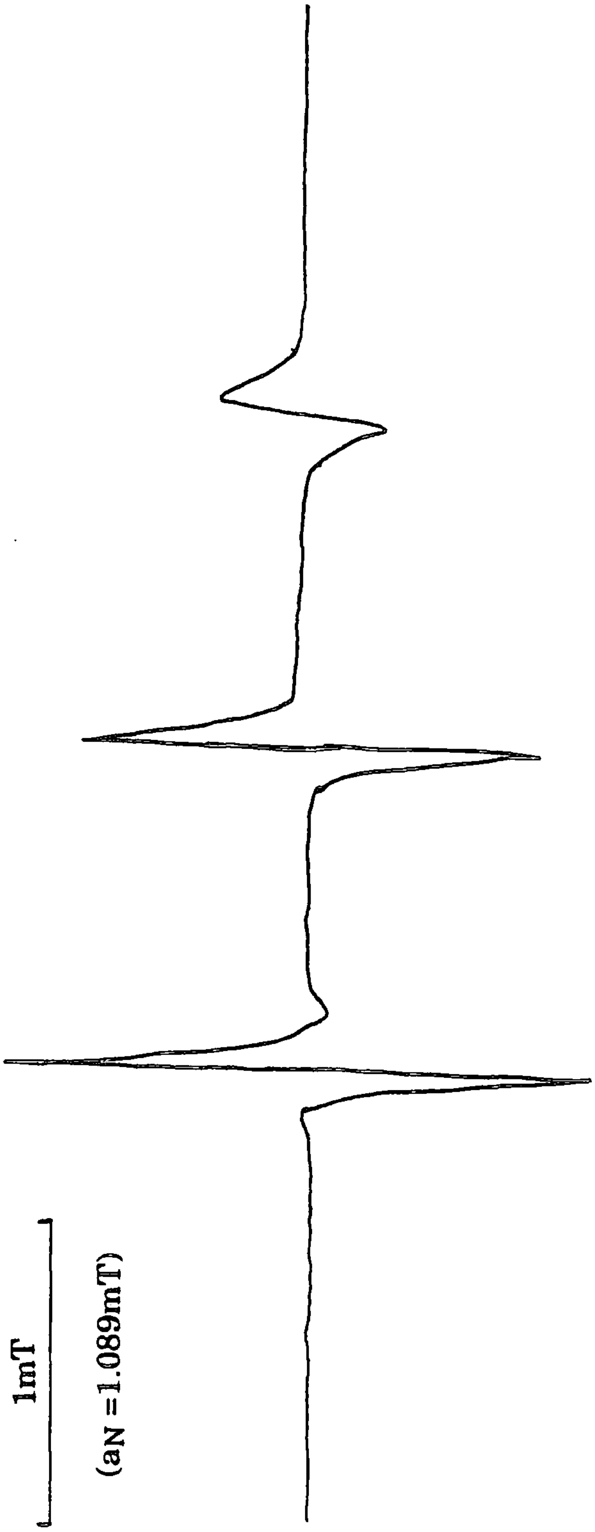


Figure 3.13 Solution state esr spectrum of 1 in the presence of LiI showing the 1:1:1 triplet indicative of the formation of the dithiadiazolide radical anion



Reduction of 2

Compound **2**, $[(NC)C(CSNSN)_2][AsF_6]$, was less readily reduced to the corresponding anion ($E_{p/2}$=0.525 V) or to the dianion ($E_{p/2}$=0.675 V) (fig.3.14, peaks 2 and 3), but it rapidly and reversibly accepted one electron to form the neutral species (peak 1, $E_{p/2}$=0.030 V). The solution state esr spectrum of the radical (in acetonitrile) shows a 1:1:1 triplet indicative of formation of the dithiadiazolyl radical (see figure 3.15). No spin-spin exchange bands were observed, so no through-space or through-bond coupling occurs. Isomerisation of the radical was not observed in solution: there was no emergence of the characteristic 1:2:3:2:1 pentet, produced by coupling to two equivalent nitrogens in the 1,2,3,5-dithiadiazolyl, either on heating or by photolysis. However, heating did give rise to the emergence of fine structure (figure 3.16). Although the resolution of this spectrum is poor (possibly due to low solubility of the radicals in acetonitrile) it can be seen that there are four triplets superimposed in the spectrum. These could arise from the four different possible chemical environments of the N-2 atom (this is the nitrogen atom coupled to the free electron in a 1,3,2,4-dithiadiazolyl radical). These isomers arise from rotation of one of the dithiadiazolyl rings about the carbon-carbon bond (see figure 3.17). The four signals would be expected to be close together in g-value and almost identical in coupling.

The solid radical prepared by reduction of the chloride salt of **2** was isolated on a milligramme scale as a brown-black powder which proved to be highly moisture sensitive.The analytical data obtained for it, although indicative of the formation of $[(NC).C(CNSNS)_2]^\bullet$, were ambiguous.

In order to substantiate this proposition further work needs to be conducted on these reduction products.

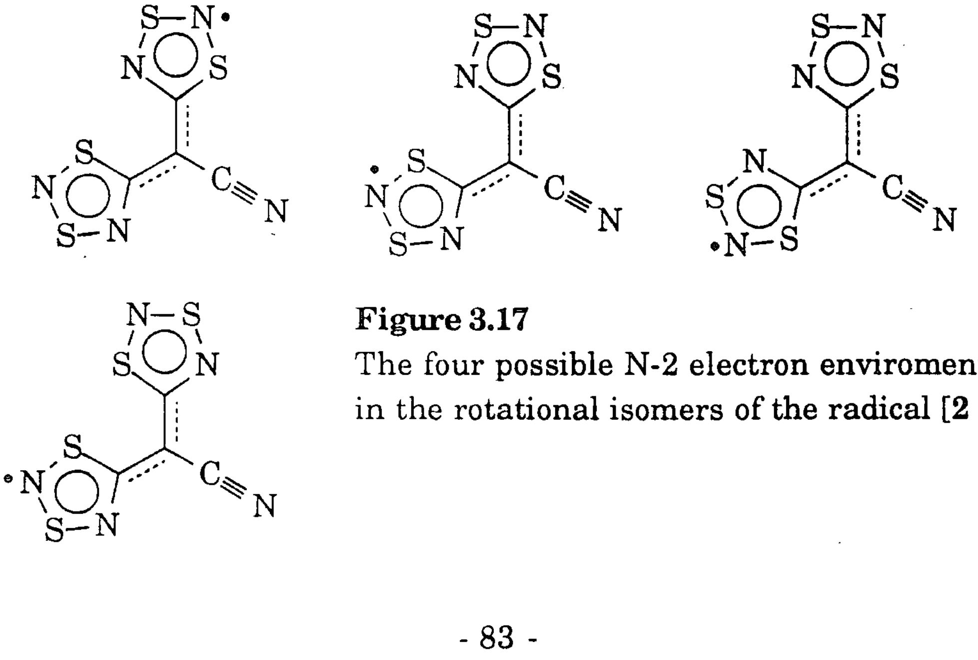


Figure 3.17
The four possible N-2 electron enviroments in the rotational isomers of the radical [**2**]$^{\circ}$

Figure 3.14 Cyclic voltammogram of compound 2 (vs. Ag-Ag$^+$ reference electrode / calibrated to saturated SCE); as a ca. 1×10^{-3} mol dm^{-3} solution in acetonitrile with $[Bu_4N]BF_4$ as supporting electrolyte (ca. 0.1 mol dm^{-3}) at -13°C

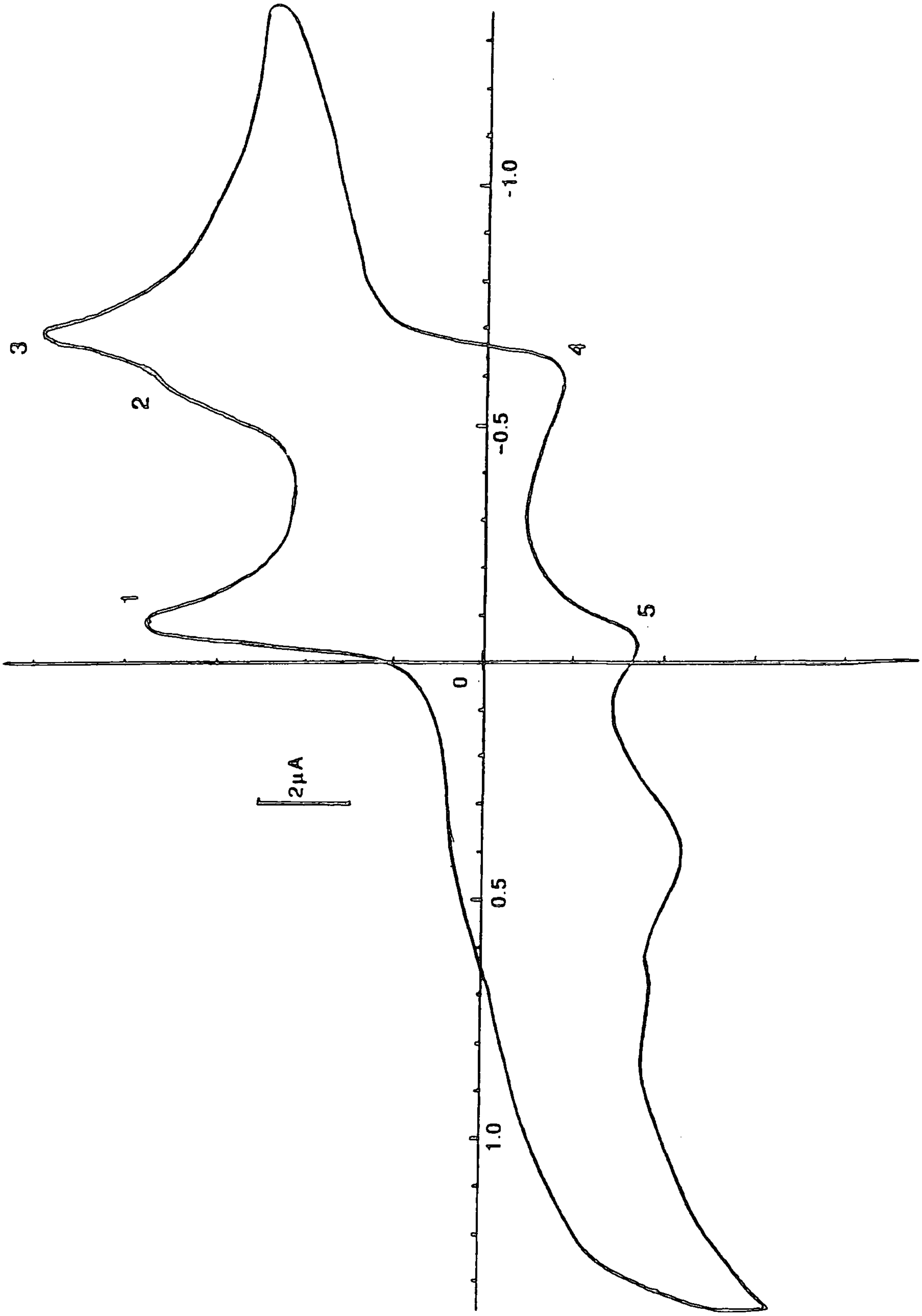


Figure 3.15 Solution state esr spectrum of the reduction product of the cation in 2 showing the 1:1:1 triplet indicative of the formation of the dithiadiazolyl radical

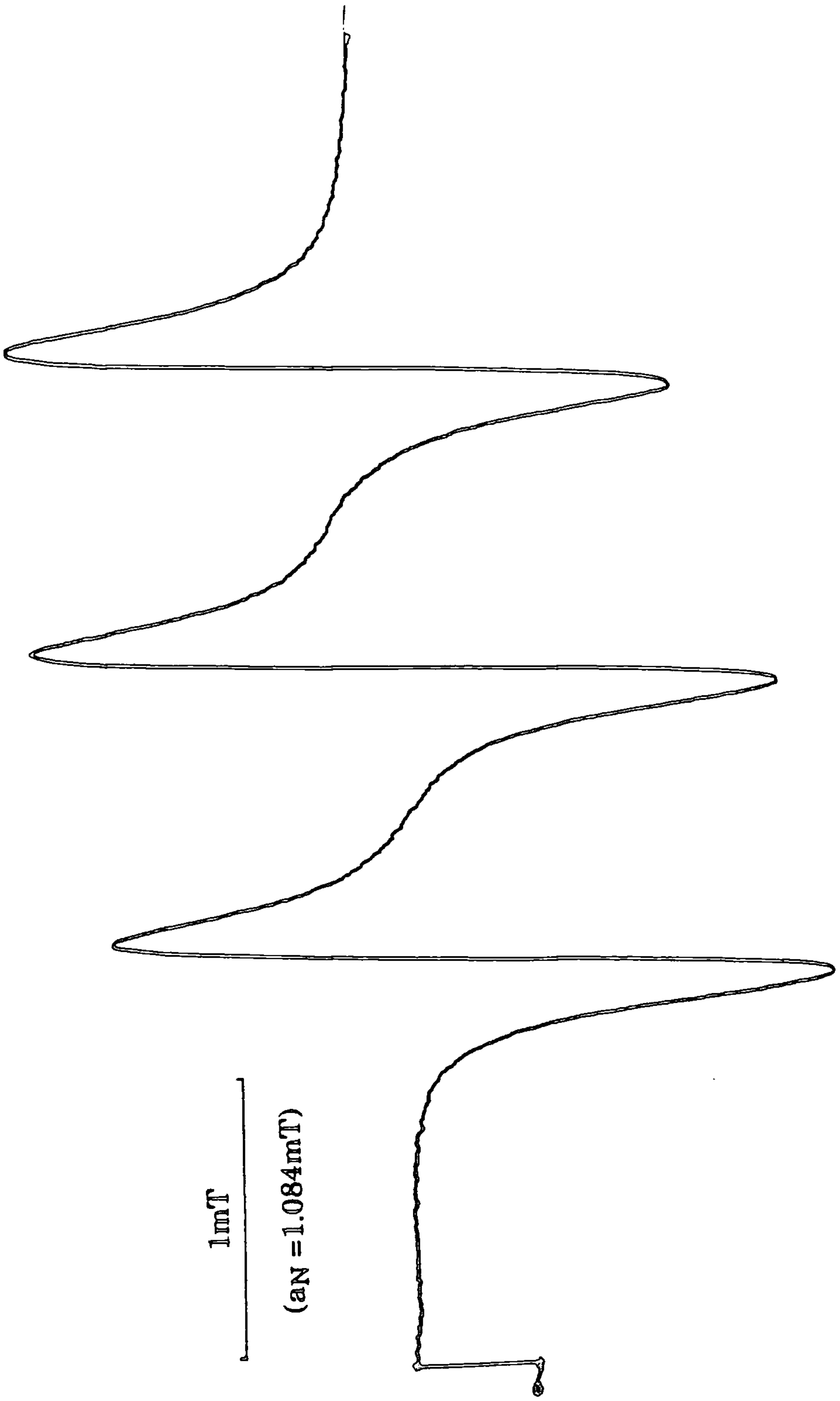
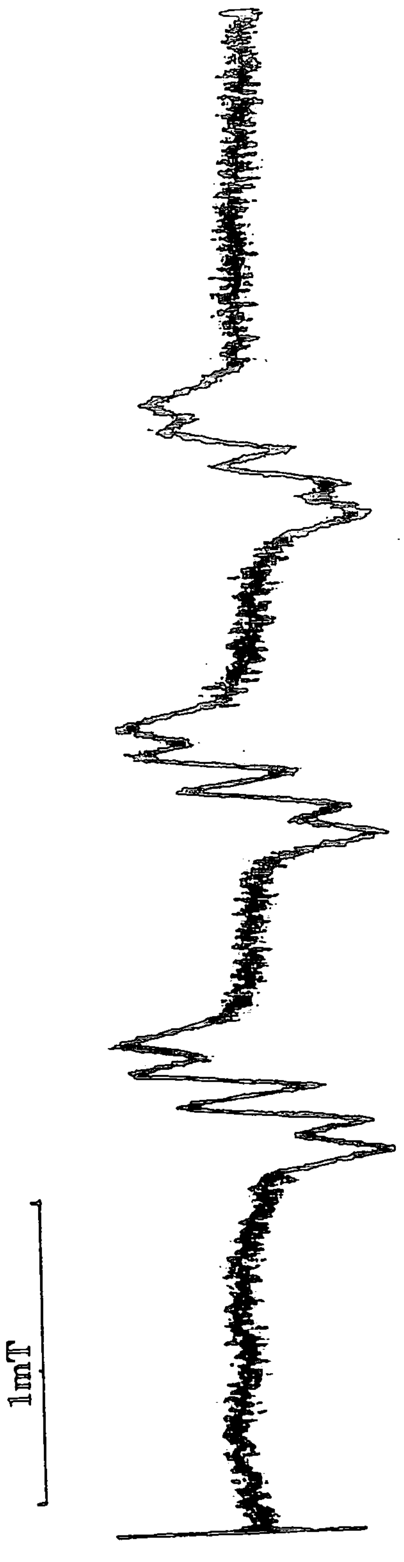


Figure 3.16 Solution state esr spectrum of the reduction product of the cation in **2** after heating to ca. 60°C showing the fine structure deriving from isomerisation of the radical



Reduction of 3

Compound 3, $[C(CSNSN)_3][AsF_6]_2$, was even more readily reduced, (fig.3.18), to the mono-cation ($E_{p/2}$=0.03 V) and further to the neutral species ($E_{p/2}$=-0.1 V) (both peaks 1 and 2 were reversible).

The esr spectrum obtained from the complete reduction of this dication showed, again, the expected 1:1:1 triplet. In addition there were peaks at half field indicative of spin-spin exchange (these appear between the peaks in the triplet) and also some fine structure revealed in both the main triplet and the spin-spin exchange bands. Again this may be due to isomerisation in solution (see figure 3.19).

Both the radical cation (as the chloride salt) and diradical were isolated on the preparative scale. Satisfactory analyses were obtained although both of these materials are highly moisture sensitive (as shown by their IR spectra).

The isolation of a radical cation is in sharp contrast to the aryl multi-dithiadiazolylium system (e.g. $[p\text{-}C_6H_4.(CNSNS)_2]^{2+}$) where the dithiadiazolylium rings undergo simultaneous reduction and hence no radical cation is isolated. However, Passmore and co-workers[12] have isolated the radical cation systems from the reaction of $[SNS][AsF_6]$ with dicyanogen (see chapter 1) - this dication is probably more closely related to the tricyanomethanide adducts. Such a marked contrast between aryl and alkyl systems can be considered to arise through the relative separation (both physical and chemical) of the dithiadiazolylium rings. In the aryl case there is much less possibility for communication between the radical centres, either through space (as the radicals are distant from each other) or via bonds (as the phenylene group acts like an electronic insulator or 'earth' for charge). Therefore both rings act independently and are reduced as isolated cations would be (i.e. at or very close to the reduction potential of the mono-cation).

In the alkyl case (as in tricyanomethanide and dicyanogen adducts) the first reduction influences the environment of the second cation. Thus the reduction potential is changed and a radical cation may be observed in the CV and furthermore it may be isolated as a characterisable product (as observed for both $[C(CNSNS)_3]^{2+}$ and $[(SNSNC).(CNSNS)]^{2+}$).

Figure 3.18 Cyclic voltammogram of compound 3 (vs. Ag-Ag$^+$ reference electrode / calibrated to saturated SCE); as a ca. 1x10^{-3} mol dm^{-3} solution in acetonitrile with [Bu$_4$N]BF$_4$ as supporting electrolyte (ca. 0.1 mol dm^{-3}) at -11°C

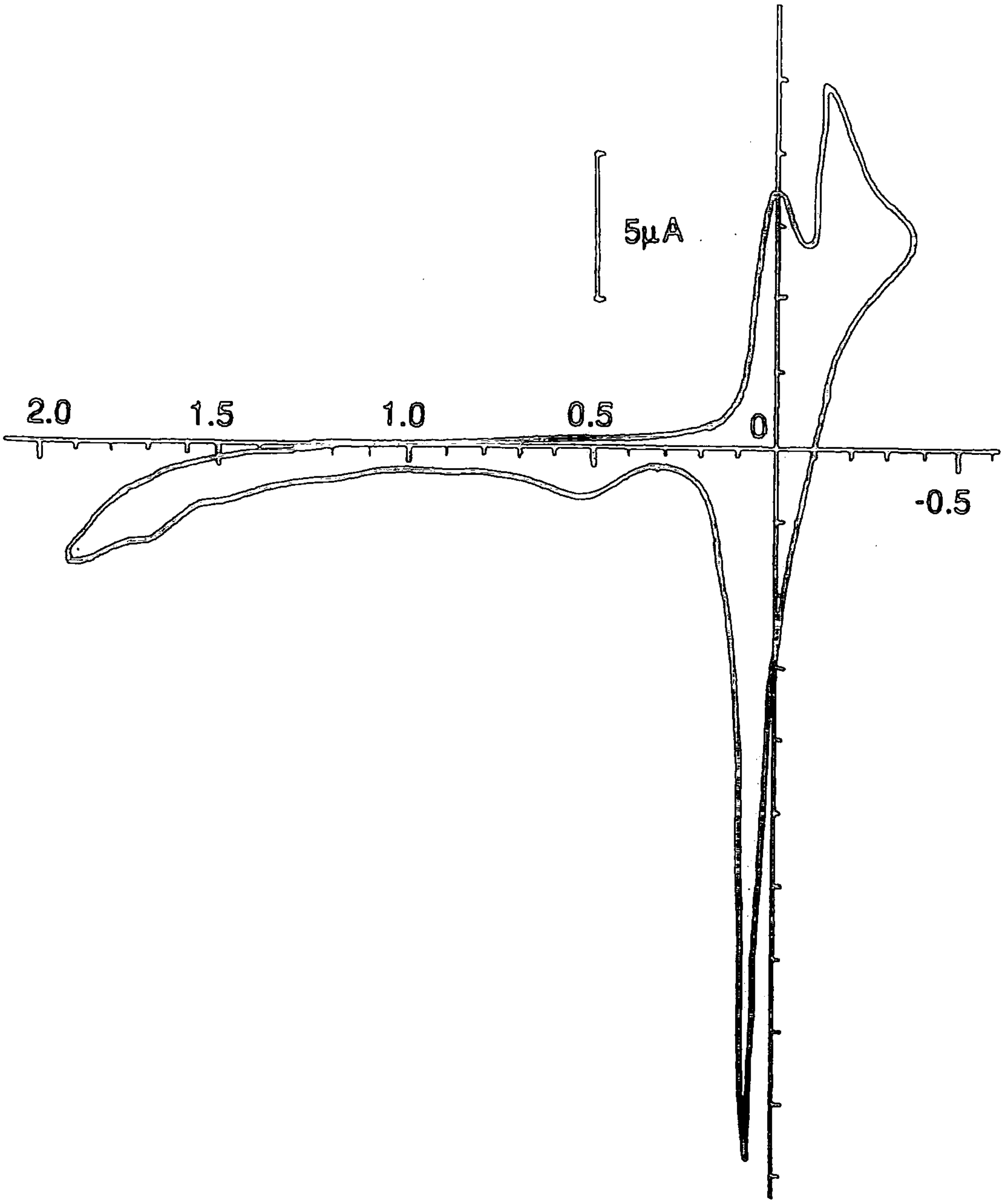
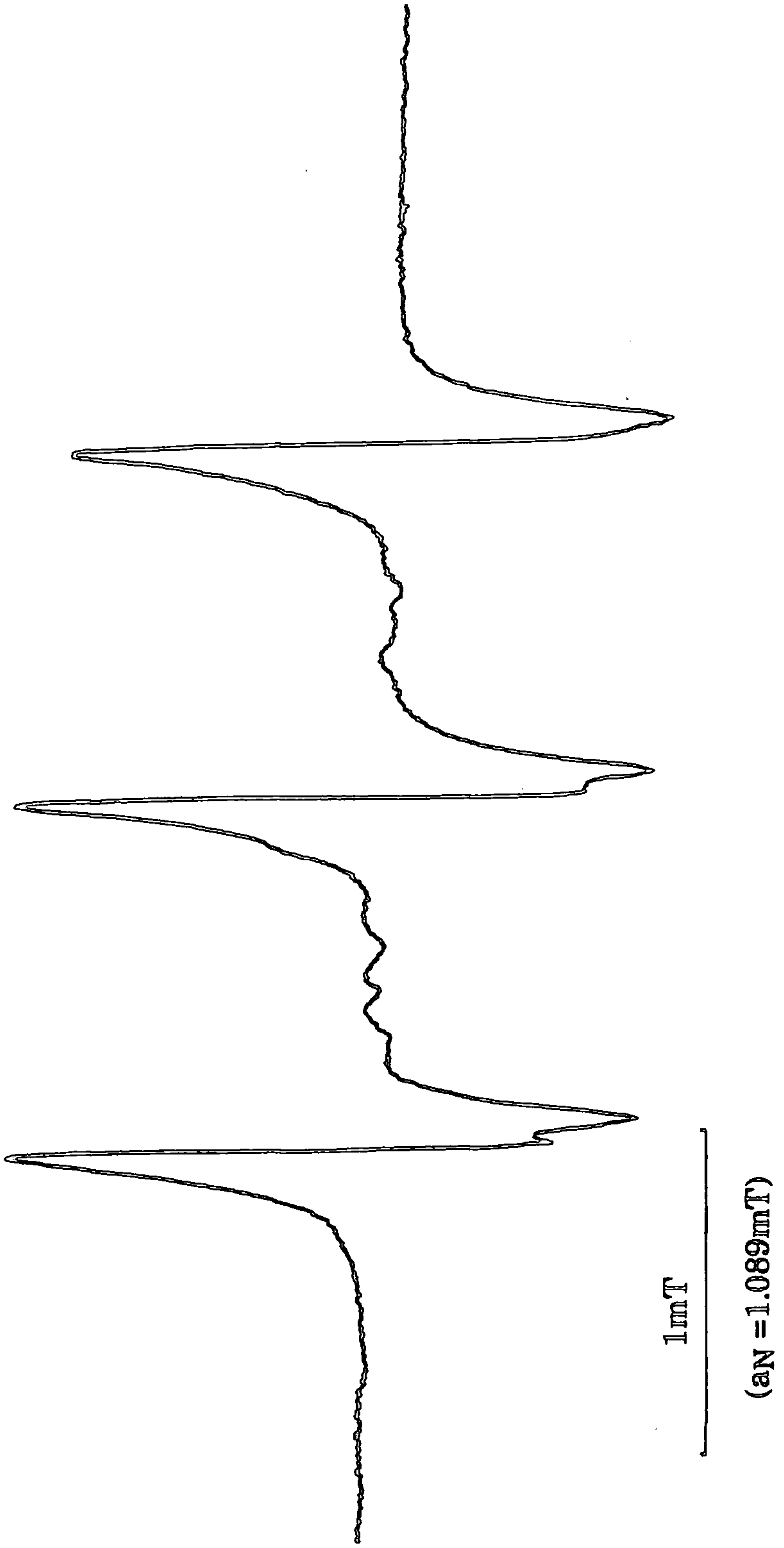


Figure 3.19 Solution state esr. spectrum of the reduction product of the cation in **3** showing the 1:1:1 triplet indicative of the formation of the dithiadiazolyl di-radical and peaks at half field (arising from spin-spin exchange between radical centres) together with some fine structure (possibly due to some degree of isomerisation in solution)



3.3 Conclusions and suggestions for further work

The reactions of $[SNS][AsF_6]$ with $K[C(CN)_3]$ have provided the first examples of $[SNS]^+$ reacting with an anion containing an unsaturated centre. These cycloaddition processes do not appear to proceed through conventional frontier orbital HOMO-LUMO interactions. Instead a stepwise reaction, mediated by the attachment of an $[SNS]^+$ cation to a dithiadiazolylium nitrogen atom, followed by its addition across the adjacent CN bond, leads to stereochemically pure products. The geometries of the reaction products have been rationalised, together with a possible reaction mechanism.

$(NC)_2CCSNSN$, **1**, the product of the 1:1 reaction between $[C(CN)_3]^-$ and $[SNS]^+$ shows the tendency of these 1,3,2,4-dithiadiazolyls to form polymeric arrays rather than the dimeric solid state structures favoured by the 1,2,3,5- dithiadiazolyls with numerous secondary S···N interactions holding the neutral molecules together in a pseudo-2-dimensional network. **1** may be reduced using various iodide salts to yield $[(NC)_2C{=}CNSNS]^{\circ -}$ salts (as indicated by IR and esr), but these have not as yet been crystallised or fully characterised.

Reactions of two or three equivalents of $[SNS][AsF_6]$ with $K[C(CN)_3]$ leads to the mono- and bis-dithiadiazolylium salts (**2** and **3**; see scheme 3.1); the dication in the latter species possesses C_{3h} symmetry and crystallises as an SO_2 solvate.

The reduction products of all three compounds warrant further investigation together with preparation of possible charge-transfer salts of the multications; for example the preparation of metal maleonitriledithiolato (mnt) and tricyanomethanide salts.

Reactions of $[SNS][AsF_6]$ with other unusual multi-nitriles, for example $[Cu(CN)_3]^-$, $P(CN)_3$, $S(CN)_x$, appear worthy of study also.

3.4 Experimental

3.4.1 Reactions of various stoichiometries of $[SNS][AsF_6]$ with $KC(CN)_3$

3.4.1.1 Preparation of $(NC)_2C(CNSNS)$ (**1**)

Potassium tricyanomethanide (218 mg, 1.7 mmol) was stirred with a slight excess of $[SNS][AsF_6]$ (450 mg, 1.7 mmol) in liquid SO_2 in a two-limbed reaction vessel for 1½ h to yield a deep purple-black solid under a dichroic red-purple solution. Filtration and repeated back-extraction gave a deep purple-black solid upon solvent removal from the filtrate. Extraction with CH_2Cl_2 for 2 days in a closed extractor followed by solvent removal gave a purple filtrate (205 mg, 72%) and brown residue. IR ν_{max} (cm^{-1}): 422sh, 635w, 656w, 692vw, 722m, 750sh, 758s, 760m, 935sh, 940m, 953m, 966m, 1020w, 1150vw, 1205s, 1275w, 1305w, 2210s, 2225s. Mass spectroscopy (electron impact): (m/z) 246 (51.77), 168 (100), 78 (100), 46(15.79). ^{14}N nmr -29.2, -88.3, -112.9ppm (1:1:2). ^{13}C nmr: only CN seen at 126.1ppm. UV/Vis : 248 (.84), 251 (.84), 330 (.82), 418 (.11), 556 (1.3) and 577nm (1.3). In order to obtain single crystals of **1** for X-ray crystallography, a sample was sublimed at 10^{-7} Torr / 85°C for 5 days and the small, black, lustrous prisms collected at a constriction in the sublimer. This material analysed well as **1** (found 33.28%N, 28.26%C; calculated 33.31%N, 28.56%C).

3.4.1.2 Preparation of $[(NC)C(CNSNS)_2][AsF_6]$ (**2**)

Potassium tricyanomethanide (59 mg, 0.46 mmol) was stirred with a slight excess of $[SNS][AsF_6]$ (247 mg, 0.92 mmol) in liquid SO_2 in a two-limbed reaction vessel for 16 h to yield a deep red-purple solution. Filtration and repeated back extraction with SO_2 followed by continuous extraction of the filtrate with CH_2Cl_2 in a closed extractor for 16 h yielded a residual reddish brown solid (120 mg, 59% recovered yield). The IR spectrum of this material suggested that the expected product had been formed; elemental analysis was in agreement with the expected C:N ratio for **2** but volatile SO_2 of solvation caused inconsistent carbon and nitrogen analyses (both values were lower than expected). IR ν_{max} (cm^{-1}): 400s, 440m, 455w, 588w, 638m, 650m, 668m, 698s,br, 720sh, 780m, 798m, 904m, 930m,br, 960sh, 965m, 980m, 1017w, 1034w, 1160w,br, 1225m, 1237sh, 1275sh, 1280m, 1310m, 1350sh, 1370sh, 1415s, 2220m.

3.4.1.3 Preparation of $[C(CNSNS)_3][AsF_6]_2.SO_2$(**3**)

Potassium tricyanomethanide (130 mg, 1 mmol) was stirred with a slight excess of $[SNS][AsF_6]$ (820 mg, 3 mmol) in liquid SO_2 in a two-limbed reaction vessel for 16 h to yield a deep orange-red solid under a red solution. Filtration and repeated back-extraction gave a red solid and solution (from filtrate), and a residual heterogeneous, brown-pink solid (shown by IR spectroscopy to be $K[AsF_6]$). Solvent removal yielded a crude red solid which was extracted with CH_2Cl_2 in a closed extractor for 3 days (to remove soluble impurities) before being recrystallised from liquid SO_2. Slow solvent removal yielded red crystals and a red microcrystaline powder (655 mg, 84%). Crystals suitable for X-ray analysis were picked from the solid mass. UV/Vis 485 (1.2), 339 (1.3), 304 (1.0) and 242 nm (1.3). IR spectra showed no C≡N stretch (at 2200 cm^{-1}) and the presence of $[AsF_6]^-$ (strong, broad bands at 398 and 692 cm^{-1}) as well as SO_2 of solvation (528 and 1150 cm^{-1}); ν_{max}/ cm^{-1}: 1500m, 1440sh, 1335m, 1310w, 1265m, 1150w, 1090w, 1030w, 980sh, 974m, 945sh, 937m, 800m, 773w, 738m, 720sh, 692s,br, 650sh, 647m, 570w, 528vw, 452m, 398vs. Elemental analysis was, again, in agreement with the expected C:N ratio for **3**, but inconsistent results were obtained (due to volatile SO_2 of crystallisation being present).

3.4.2 Further chemistry of the addition compounds

3.4.2.1 Preparation of $[C(CNSNS)_3]Cl_2$

Tetrabutylammonium chloride (420 mg, 1.4 mmol) was stirred with $[C(CNSNS)_3][AsF_6]_2$ (500 mg, 0.7 mmol) in acetonitrile in a two limbed reaction vessel for 1 h to yield a brick-red ppt under a purple-red liquor. Filtration and repeated back-extraction followed by solvent removal gave a brownish-white crystalline filtrate and a pale brick-red solid which was washed for 16h in a closed extractor with acetonitrile. The residual, highly air and moisture sensitive, brick-red solid (200 mg, 73%) analysed well as the dichloride: Found 21.35 %N, 13.22%C, 0.55%H; calc. 21.92 %N, 12.53%C. IR showed no $[AsF_6]^-$ to be present, $\nu_{max}/\ cm^{-1}$: 438m, 565w, 590vw, 642m, 685vw, 725m, 790m, 845w, 917m br, 968s br, 1020m, 1110m br, 1260m, 1292m, 1430sh.

3.4.2.2 Preparation of $[(NC)C(CNSNS)_2]Cl$

Tetrabutylammonium chloride (102 mg, 0.34 mmol) was stirred with $[(NC)C(CNSNS)_2][AsF_6]$ (150 mg, 0.34 mmol) in acetonitrile in a two limbed reaction vessel for 16 h to yield a deep red ppt under a purple-red liquor. Filtration and repeated back-extraction followed by solvent removal gave a brownish-white crystalline filtrate and a residual maroon solid which was washed for 16h in a closed extractor with acetonitrile. The residual, highly air and moisture sensitive, red solid (65 mg, 68%) analysed well as the dichloride: Found 25.04 %N, 17.54%C, 0.42%H; calc. 24.88%N, 17.06%C. IR showed no $[AsF_6]^-$ to be present, $\nu_{max}/\ cm^{-1}$: 2204s, 1631w, 1552w, 1519w sh, 1430vs br, 1272m, 1255s, 1237m, 1170m, 1029m, 1011vs, 956m, 926m, 918m, 877m, 824w, 793s, 775m, 733m, 704w, 674m, 659m, 646m, 631m, 588w, 573m, 568m, 568m, 509w, 462m, 437m, 417m, 406w.

3.4.3 Reductions of the chloride salts

3.4.3.1 Preparation of $[C(CNSNS)_3]^{\circ\circ}$

Triphenylantimony (70 mg, 0.2 mmol) and $[C(CNSNS)_3]Cl_2$ (76 mg, 0.2 mmol) were stirred together in acetonitrile in one bulb of a two-limbed reaction vessel for 3 h and the resultant red-purple solution filtered off a black solid residue which was recovered after solvent removal. Yield 45mg (74%). Analysis was poor - found 21.23%N, 13.65%C, 0.79%H, calc. 25.91%N, 14.82%C. This did not improve after washing with acetonitrile - 18.37%N, 12.05%C, 0.81%H - suggesting that the compound was highly moisture sensitive.

3.4.3.2 Preparation of $[C(CNSNS)_3]^{+\circ}[Cl]$

Triphenylantimony (23 mg, 7×10^{-5}mol) and $[C(CNSNS)_3]Cl_2$ (50 mg, 0.13 mmol) were stirred together in acetonitrile in one bulb of a two-limbed reaction vessel for 2 days and the resultant red-purple solution filtered off a brown solid residue which was recovered after solvent removal. Yield 30mg (66%). Analysis was consistent with the formation of the radical cation: found 22.54%N, 14.59%C, 0.84%H, calc. 23.37%N, 13.35%C.

3.4.3.2 Preparation of $[(NC)C(CNSNS)_2]^{\circ}$

Triphenylantimony (25 mg, 0.07 mmol) and $[(NC)C(CNSNS)_2]Cl$ (40 mg, 0.14 mmol) were stirred together in acetonitrile in one bulb of a two-limbed reaction vessel for 5 h and the resultant red solution filtered off a black-brown solid residue which was recovered after solvent removal. Yield 24mg (55%). Analysis was poor but indicated formation of the radical: found 25.13%N, 18.45%C, 1.01%H, calc. 26.91%N, 18.45%C.

3.4.4 Attempted reduction of 1 using a variety of iodides

3.4.4.1 Reduction of 1 with LiI

Lithium iodide (80 mg, 0.6 mmol) was stirred with 1 (100 mg, 0.6 mmol) in liquid SO_2 in a two limbed reaction vessel for 18 h to yield a red solution over a golden-grey powder. Filtration and repeated back-extraction followed by solvent removal gave a grey residual powder (100mg) and an oily red filtrate. A sample (50mg) of the grey solid was recrystallised (by slow removal of solvent from a saturated acetonitrile solution over 18 h) to yield some black needles and golden blocks which were washed with liquid SO_2 and CCl_4. Crystals of approx. 0.5mm diameter were picked but these gave reflections of insufficient intensity to yield an X-ray crystal structure. IR data suggested a shift in bands (as expected for the radical anion of 1) and the presence of SO_2 of crystallisation (525 cm^{-1}). ν_{max}: 398s, 445m, 498m, 525w sh, 530w, 625m, 662m, 695w, 722m, 730w sh, 768m, 800w, 945m, 970m, 1030m br, 1160w br, 1210m, 1280m br, 1305w, 1465vs, 2220s, 2245s. Elemental analysis also suggested a solvated product. Found 14.99%N, 12.63%C 1.63%Li. Calculated for $Li[(NC)_2C(CNSNS)].3SO_2$ 15.26%N, 13.08%C, 1.90%Li.

3.4.4.2 Reduction of 1 with [Et_4N]I or [Bu_4N]I

Both tetrabutylammonium and tetraethylammonium iodide reacted rapidly with a stoichiometric quantity of 1 to give red-brown solutions in liquid SO_2. However, only intractable oils were obtained in spite of attempts to clean these up using a variety of solvents e.g. CH_2Cl_2, toluene, acetonitrile, CCl_4

3.4.4.3 Reduction of 1 with CsI

Caesium iodide (31 mg, 0.1 mmol) was stirred with 1 (20 mg, 0.1 mmol) in liquid SO_2 in a two limbed reaction vessel for 18 h to yield a red solution over a sticky brown solid. The SO_2 was removed to give an oily brown-red solid. CCl_4 (5ml) was added and after sonication there remained a black solid and pale blue solution. Repeated washing and back extraction yielded a black residual solid which was soluble in SO_2, a solution of which gave up a golden material upon solvent removal.

3.4.5 Attempted syntheses of $(NC)_2C{=}CNSSN$

3.4.5.1 Reaction of $KC(CN)_3$ with NSCl and S_8

$(NSCl)_3$ (245 mg, 3 mmol), $K[C(CN)_3]$ (390 mg, 3 mmol) and sulphur (100 mg, 30 mmol) were stirred together in CH_2Cl_2 (10ml) for 3 days to give a deep red-purple solution over a white solid (possibly KCl). Filtration and back extraction, followed by solvent removal, gave a purple-white residual solid (280mg) and oily red filtrate (310mg). Extraction of this red product with liquid SO_2 gave a red glassy filtrate with a very complex IR (with one ν_{CN} - as expected for the 1,2 isomer of 1) - would expect a less complex IR than for 1 as this isomer is more symmetrical.

3.4.5.2 Reaction of $KC(CN)_3$ with $LiN(SiMe_3)_2$ and SCl_2

$K[C(CN)_3]$ (3.0g, 0.02mol) and $Li[N(SiMe_3)_2$ (3.0g, 0.02mol) were stirred together in Et_2O (15ml) for 18 h after which the solvent was removed *in vacuo* and the resulting whitish-yellow solid scraped out into an ice cooled, stirred solution of SCl_2 (3ml, 4.89g, 0.05mol) in CH_2Cl_2 (30ml). An immediate exothermic reaction occured inducing boiling in the solvent. After stirring for a further 15 h a deep red-purple powder was obtained from which no solid product could be isolated from the LiCl tarry.

3.6 References

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Chapter 4

Some mixed 1,2,3,5- / 1,3,2,4- dithiadiazolylium salts and their derivatives

4.1 Introduction

In the recent work conducted in this laboratory[1] and by Oakley *et.al.*[2] several multi-dithiadiazolyliums and related free-radicals have been prepared so that their solid state properties could be studied and their potential as organic magnets and metals could be judged. Figure 4.1 shows some examples of the solid state structures of the multi- 1,3,2,4 and 1,2,3,5-dithiadiazolyls.

Wide-ranging physical methods (e.g. single crystal conductivity, magnetisation and esr) have shown the multi-radicals to be variously:

(i) insulators, for example *m*-(NSSNC).C_6H_4.(CNSSN)[2b];

(ii) semiconductors, for example *m*-(NSeSeN).C_6H_4.(CNSeSeN)[2b] with a conductivity of 10^{-6} Scm^{-1} at 200 K and up to 2 x 10^{-3} S cm^{-1} at 470 K);

(iii) diamagnetic, for example, *p*-(SNSNC).C_6H_4.(CNSNS)[1a,3]

The 1,2,3,5-dithiadiazolyls (and their selenium derivatives, see chapter 5) have been a more productive area for structural data, because their greater photolytic[4] and thermal[1c] stability allow for crystals of the multi-radical species to be grown by sublimation at elevated temperatures[2].

There are several mono- and multi-1,2,3,5-dithiadiazolyl / ium solid state structures known, with cations[5], diradicals[2d] and even a triradical[2e] characterised by X-ray structure determination.

The only known multi-1,3,2,4-dithiadiazolyl to have been characterised by single crystal X-ray crystallography is 5',5'-phenylene bis (1,3,2,4-dithiadiazolyl)[1a], [(SNSNC).C_6H_4.(CNSNS)], although several structures of the mono-dithiadiazolyls are known; for example, $(NC)_2C$=CNSNS (chapter 3), O=CNSNS[6] and 4-Me-C_6H_4.N(C=O).CNSNS[7].

The packing of the two previously prepared isomers of *p*-(S_2N_2C).C_6H_4.(CN_2S_2) are considerably different (as shown in figure 4.2).

The difference in packing can be rationalised as resulting from different modes of association of the diradicals. The 1,2-isomer employs an eclipsed structure[2a] (see figure 4.3) with S···S contacts between each diradical (which, at 3.121 Å, are longer than the sum of the van der Waals radii[8]), holding the molecules together in pairs. In contrast, the 1,3-isomer oligomerises in a head-to-tail fashion[1a] (see figure 4.4). Here, the dithiadiazolyl rings cannot overlap as they do in the 1,2-case, so they form infinite 'wavy sheets'.

Figure 4.1 Examples of solid state structures of multi- 1,2,3,5 and 1,3,2,4-dithiadiazolyls

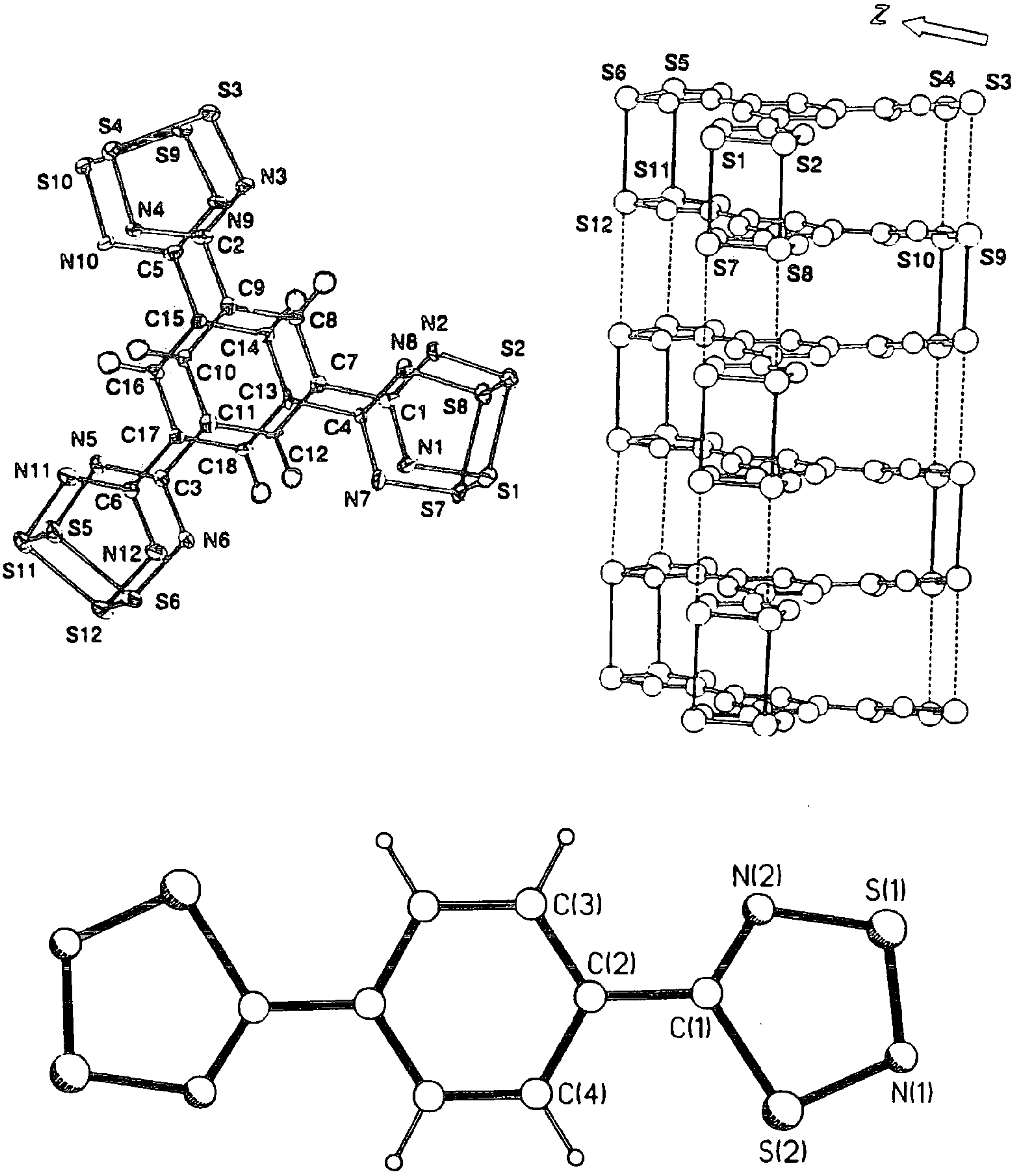
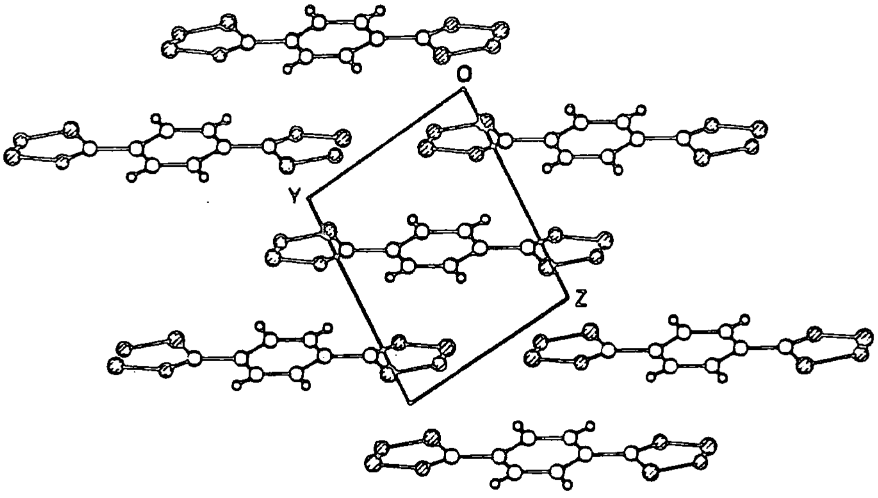
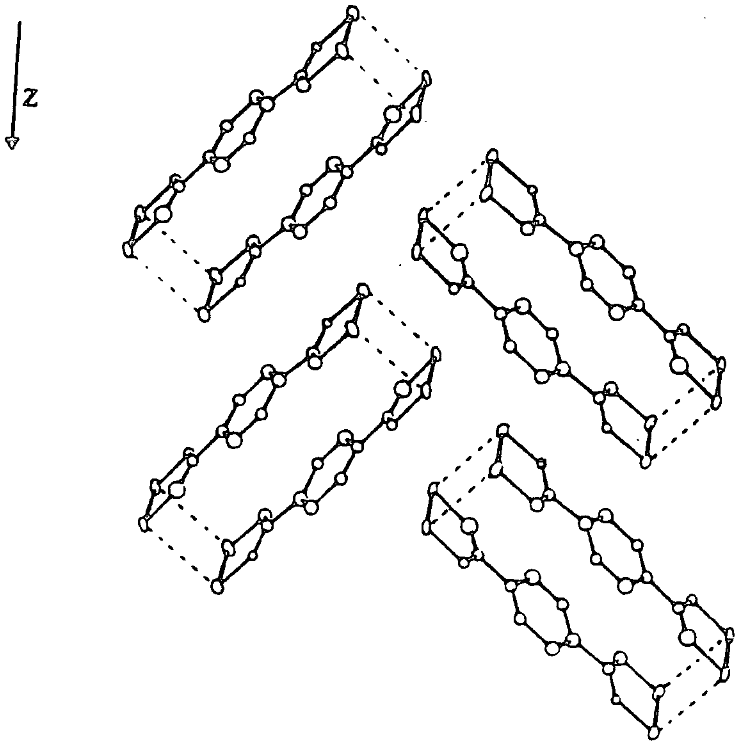


Figure 4.2 Solid state packing in the isomers of the *p*-[$S_2N_2C.C_6H_4.CN_2S_2$] diradical



Structure of *p*-[$C_6H_4(\overline{CNSNS})_2$]

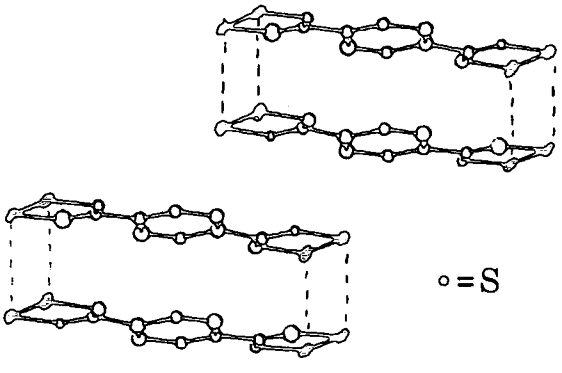


Structure of *p*-[$C_6H_4(\overline{CNSSN})_2$]

In order to extend the chemistry of these multi-radicals it was envisioned that the so called 'mixed' 1,2,3,5- / 1,3,2,4- dithiadiazolylium salts (containing 1,2,3,5 and 1,3,2,4 isomers in one dication unit) could be prepared from the corresponding cyano-substituted phenyl dithiadiazolylium salts and [SNS][AsF$_6$], which themselves are prepared by addition of [SNS]$^+$ to the cyano-substituted dithiadiazolylium[9]. These cyano-substituted dithiadiazolyliums had been prepared concurrently by Oakley and co-workers[2f]. Reduction sequentially to the radical cation (isolable because of the different reduction potentials of the two rings) and finally to the diradical was considered feasible.

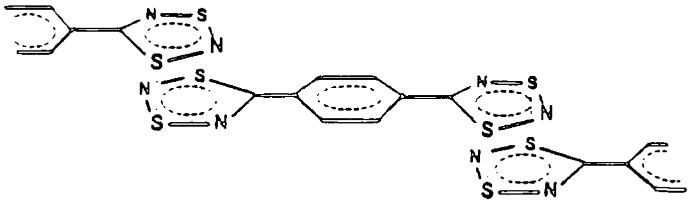
A comparison of the magnetic, electronic and structural properties of these mixed radicals with those of the earlier multi-dithiadiazolyls should provide us with information about the mechanism of magnetic behaviour and conductivity in dithia / diselenadiazolyl based systems. Of particular interest are the radical cations, in which the coulombic energy gained by association of the cationic end of the molecule with its attendant counterions (of the order of hundreds of kJ mol^{-1}) should far outweigh the dimerisation energy of the radical end (ca. 35-45 kJ mol^{-1} [10]). This should give rise to unassociated radical centres in the solid state and perhaps to strong paramagnetic (or ferromagnetic) couplings .

Figure 4.3 Dimerisation of the *p*-[NSSNC.C$_6$H$_4$.CNSSN] diradical in the solid state



A further reason for studying this type of compound is that characterisation and purification should be more facile than for the 1,3,2,4-dithiadiazolyls, as the former materials should not have a centre of symmetry and so will have an overall dipole. Therefore, the cations and radicals should be more soluble in polar solvents, so aiding purification and crystallisation, which has been difficult for the aryl- 1,3,2,4-dithiadiazolyls prepared so far.

Figure 4.4 Oligomerisation of the *p*-[SNSNC.C_6H_4.CNSNS] diradical in the solid state



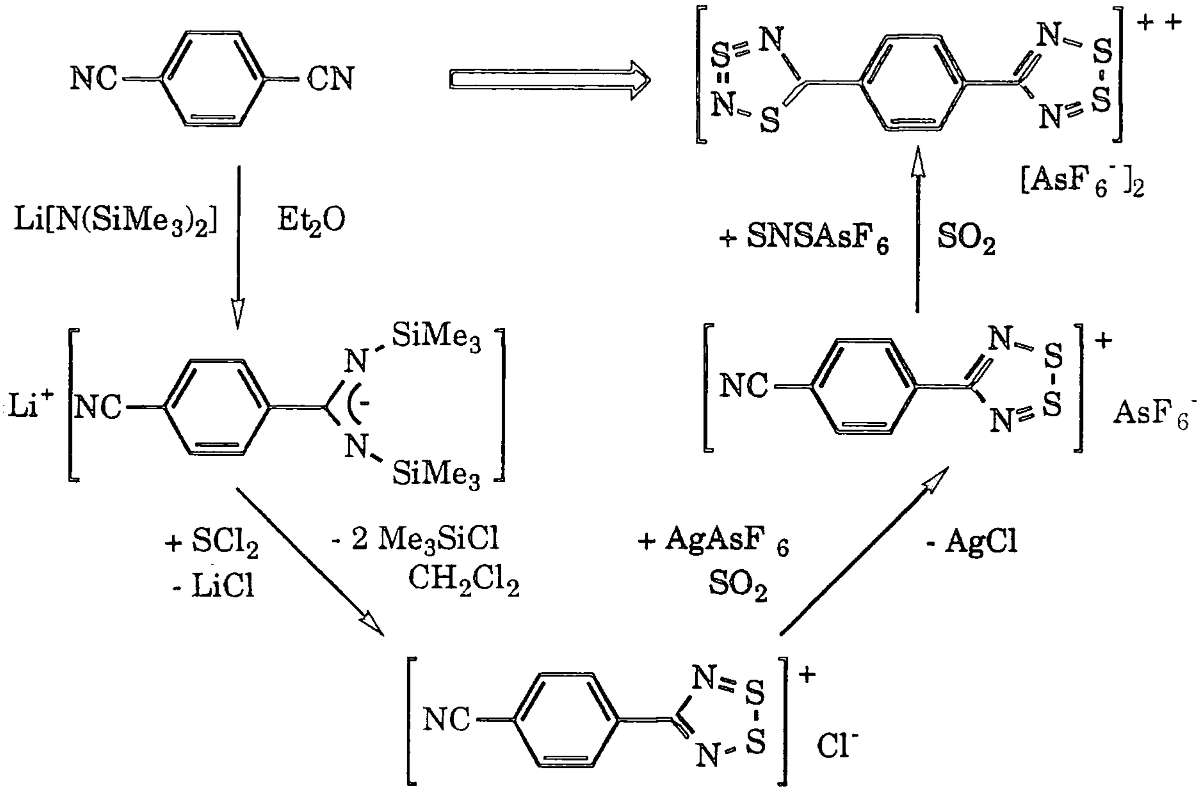
4.2 Results and discussion

4.2.1 General reactivity

Oakley and co-workers have previously shown[2] that the reaction of persilylated amidines, RC(=$NSiMe_3$)$N(SiMe_3)_2$, with either SCl_2 or $SeCl_2$ (formed *in situ* from $SeCl_4$ / Se or $SeCl_4$ / Ph_3Sb) provides a convenient, high-yield route to aryl 1,2,3,5-dithiadiazolylium and diselenadiazolylium salts. In some cases (R= *p*-NO_2.C_6H_4 or *p*-NC.C_6H_4) preparation of the silylated amidine was not possible, despite the apparently quantitative formation of the precursor N-lithio compound (as shown by ^{1}H n.m.r.), e.g. Li[NC.C_6H_4.C($NSiMe_3$)$_2$][11]. This work has shown that reaction of these N-lithio intermediates with a slight excess of SCl_2 provided the dithiadiazolylium chloride in high yield (typically >70%). In the case of the mono-dithiadiazolylium derivatives, the dithiadiazolylium chlorides obtained were readily recovered from LiCl by extraction with liquid SO_2 and then washed with CH_2Cl_2,to remove any unreacted SCl_2[12]. In the case of *m*- and *p*- [NC.C_6H_4CNSSN]Cl, recovered yields were in excess of 70%. See scheme 4.1 for an overview of the synthesis of the dications.

Metathesis of these chloride salts with $AgAsF_6$, in liquid SO_2, provided the hexafluoroarsenate(V) salts *m*- and *p*-[NC.C_6H_4CNSSN][AsF_6]. An important contribution to the driving force for these reactions is the loss of insoluble silver chloride. For example, in the preparation of [SNS][AsF_6] from $(NSCl)_3$, SCl_2 and the hexafluoroarsenate salt (see section 1.2.1) silver hexafluoroarsenate(V) will give the desired product, whereas lithium hexafluoroarsenate(V) will not[9].

Reduction of the chlorides with Ph_3Sb led to the corresponding dithiadiazolyl radicals *m* - and *p*- (NC.C_6H_4.CNSSN)$_2$ in high yield. (A full structural characterisation of these radicals by Oakley and co-workers has been published recently[2f] - see chapter 7.) The subsequent reactions of these materials (i.e. [NC.C_6H_4.CNSSN]Cl, [NC.C_6H_4.CNSSN][AsF_6] and [NC.C_6H_4.CNSSN]$_2$) with [SNS][AsF_6] were then studied, in order to prepare the corresponding mixed 1,3,2,4-/1,2,3,5-dithiadiazolylium cations and radical cations respectively.



Scheme 4.1 Synthesis of the mixed 1,2,3,5 / 1,3,2,4 - dithiadiazolylium salts.

The reaction of $[SNS][AsF_6]$ with p-$[NC.C_6H_4.CNSSN]Cl$ did not result in the expected chloride / hexafluoroarsenate(V) salt, p-$[SNSNC.C_6H_4.CNSSN][AsF_6]Cl$, which would have then given the desired radical cation when reduced with half an equivalent of $SbPh_3$, according to equation 4.1.

$$[SNS][AsF_6] + [p\text{-}NC.C_6H_4.CNSSN][Cl] \longrightarrow [NSNSC.C_6H_4.CNSSN][AsF_6][Cl]$$

$$\downarrow \text{reduction}$$

$$[NSNSC.C_6H_4.CNSSN][AsF_6]$$

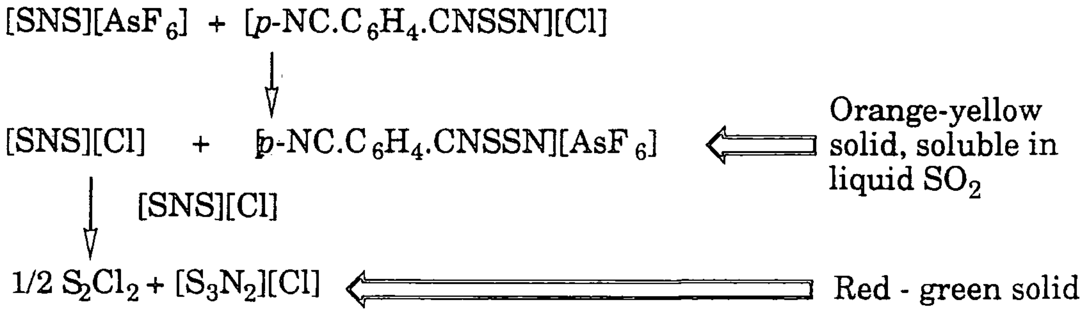
[Eq. 4.1]

However, $[NC.C_6H_4.CNSSN][AsF_6]$ (which was positively identified by its characteristic IR spectrum and elemental analysis) was observed in the reaction products, together with a red-green insoluble material (shown to be $[S_3N_2]Cl$ by IR) and a red, soluble, volatile component.

The reaction products can be considered to arise through an initial metathesis step, driven by the size-matching of one of the products of metathesis relative to the reactants. The $[AsF_6]^-$ anion is larger than $[Cl]^-$

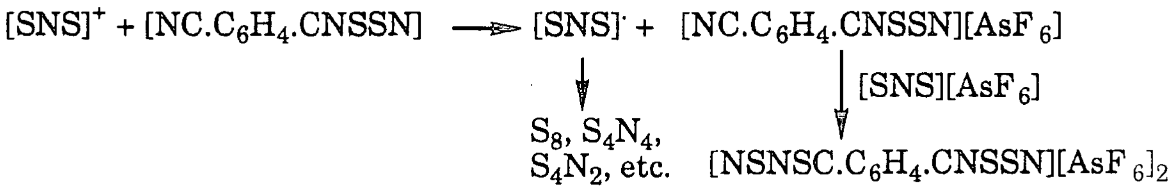
and $[NC.C_6H_4.CNSSN]^+$ is larger than $[SNS]^+$; furthermore, as lattice energy increases exponentially when ions are brought closer together then salts containing small ions have relatively large lattice energies, with the lattice energy gained by the formation of {[SNS][Cl]} driving the metathesis to form the observed product, $[NC.C_6H_4.CNSSN][AsF_6]$, and the highly thermodynamically unstable species, {[SNS][Cl]}.

The dithianitronium chloride formed immediately disproportionates to give the red volatile solute, S_2Cl_2 and the red-green dichroic solid, $[S_3N_2]Cl$ (equation 4.2).



[Eq. 4.2]

The analogous reaction of $[SNS][AsF_6]$ with p- $[NC.C_6H_4.CNSSN]_2$ (equation 4.3) was attempted, in order to prepare the radical cation directly, but this provided only a yellow solid p- $[NC.C_6H_4.CNSSN][AsF_6]$ (as shown by IR and elemental analysis), unreacted p- $[NC.C_6H_4.CNSSN]_2$ and a red oil (presumably S_4N_2) which on standing yielded small red-orange crystals (identified by IR as mainly S_4N_4) and amorphous sulphur.



[Eq. 4.3]

In contrast, reaction of m- and p-$[NC.C_6H_4.CNSSN][AsF_6]$ with $[SNS][AsF_6]$ in liquid SO_2 yielded the desired mixed- 1,3,2,4- / 1,2,3,5-dithiadiazolylium salts in greater than 90% yield.

The hexafluoroarsenate(V) salts were then metathesised with the corresponding tetra-alkyl ammonium salt to give the dichlorides (which were used in the preparation of the radical cation chlorides and diradicals) or dibromide. Metathesis of the dichloride with two equivalents of $Ag[F_3CSO_3]$ gave the 'triflate' salt. These derivatives were originally prepared in order to find a more readily crystallised salt and hence a solid state structure.

However, in the event, the hexafluoroarsenates were obtained crystalline as acetonitrile solvates and were used for structural investigations.

Recrystallisation of *m*- and *p*- [SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ from *o*-$C_6H_4Cl_2$/MeCN by slow removal of MeCN under a temperature gradient yielded long, thin crystals of the hexafluoroarsenate(V) salts as MeCN solvates. However only the structure of the para isomer could be solved. This gave a high R_w value, which was mainly due to the morphology of the crystals: they were very long, fine needles which had to be picked and mounted in air and so suffered from surface tarnishing, which caused the poor diffraction effects.

4.2.2 Reduction products

4.2.2.1 Cyclic voltammetry

Both the para- and meta- isomers showed the expected behaviour, with two discrete, reversible reductions observed for each system, (see figures 4.5 and 4.6), indicating the formation of the radical cation and diradical. This contrasts with the single reduction peaks observed for the corresponding bis-1,3,2,4[1a] and for the bis-1,2,3,5[2c] dithiadiazolylium salts, where no radical cation can be isolated, and in which there is no interaction between the dithiadiazolylium rings. The resulting two-electron reduction is concerted or takes place over a very small potential (<0.01 V) compared to 0.29 V for the mixed para dication and 0.26 V for the meta isomer.

Here we see that the 1,2,3,5 - dithiadiazolylium ring is reduced first (E1: +0.595 V for *p*, +0.647 V for *m*) followed by the 1,3,2,4 ring (E2: +0.303 V for *p*, +0.387 V for *m*). The first reduction peak has a long reverse (oxidation) tail, which may be due to adsorption of the product at the working electrode. The adsorption implies a very rapid electrode process and may affect the validity of the quantitative data obtained in that particular c.v. experiment.

Figure 4.5 Cyclic voltammogram of p-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ in MeCN at -10°C with [NBu_4][BF_4] supporting electrolyte. $E_{red}(1)$= +0.595 V, $E_{red}(2)$= +0.303 V, *vs.* standard saturated calomel electrode

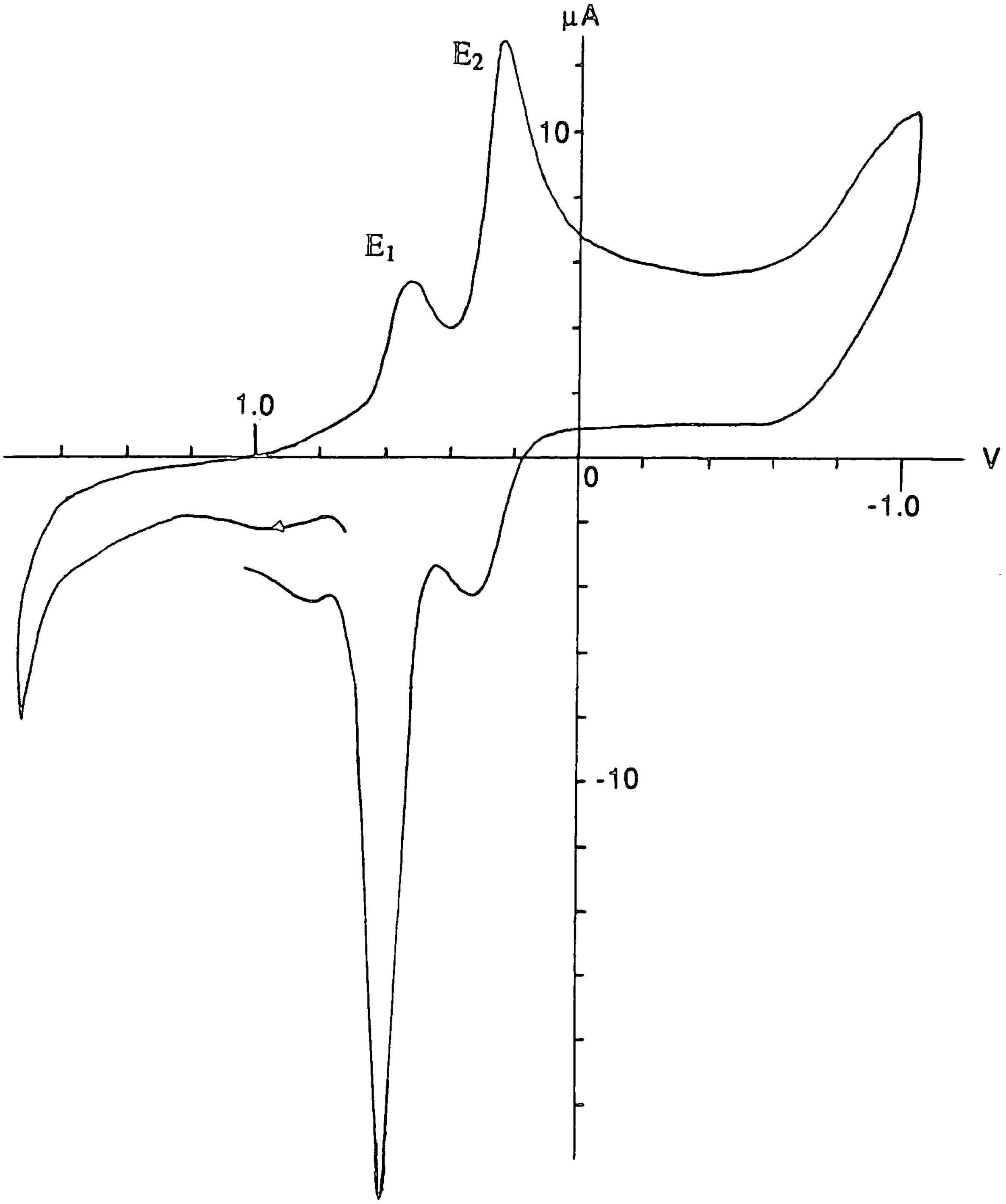
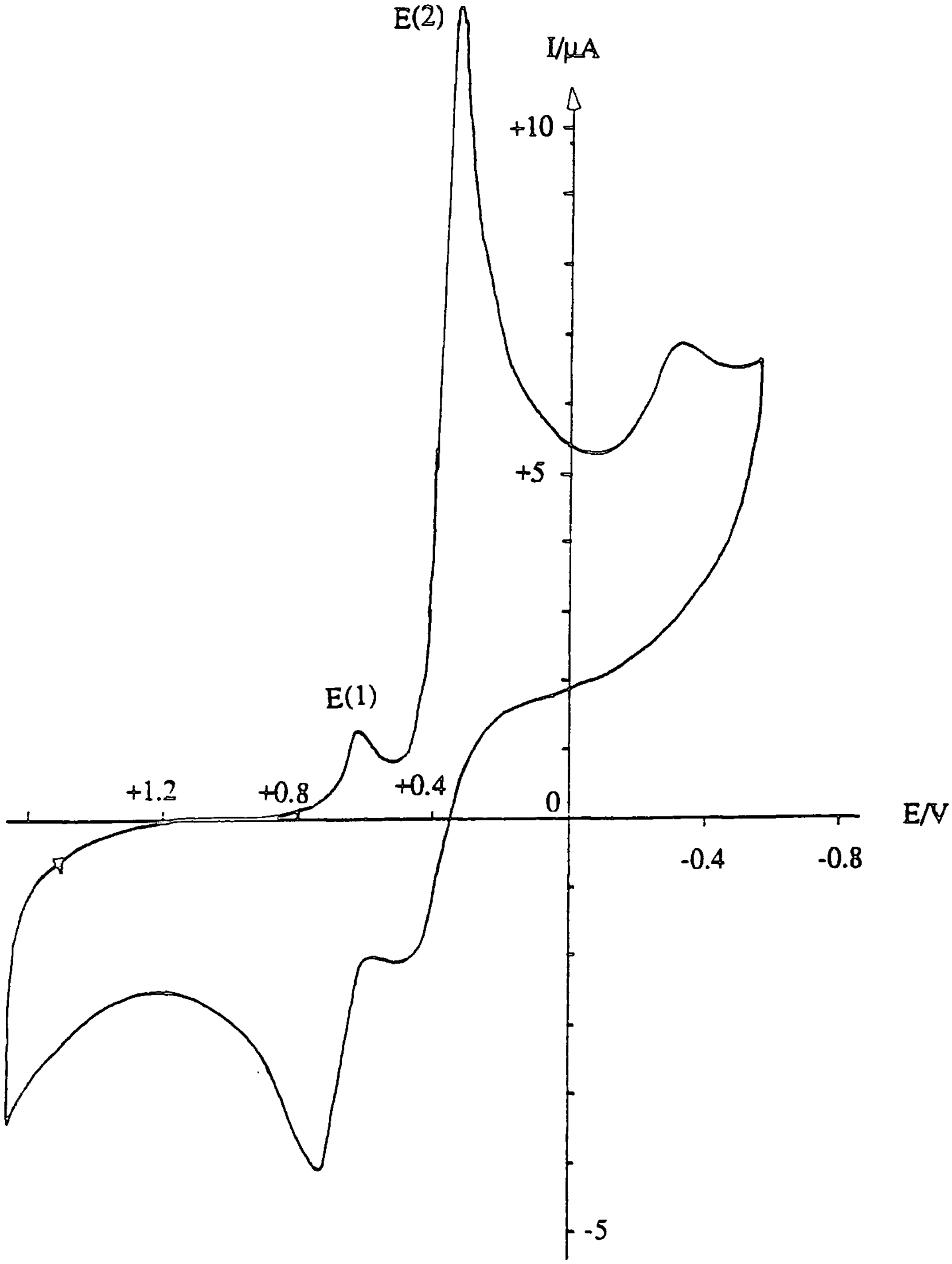


Figure 4.6 Cyclic voltammogram of *m*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ in MeCN at -10°C with [NBu_4][BF_4] supporting electrolyte. $E_{red}(1)$= +0.647 V, $E_{red}(2)$= +0.387 V, *vs.* standard saturated calomel electrode



4.2.2.2 Electron spin resonance studies

Partial reduction (using an excess of salt and a deficit of $SbPh_3$ in toluene solution) of the dications *m*- or *p*- $[SNSNC.C_6H_4.CNSSN]Cl_2$ gave the expected 1:2:3:2:1 pentet associated with formation of the 1,2,3,5-dithiadiazolyl radical (see figure 4.7)[13]. Such a spectrum is indicative of the formation of $[SNSNC.C_6H_4.CNSSN]^{+\circ}$. There was no observable indication of spin-leakage* from the 1,2,3,5-ring to the isomeric 1,3,2,4-ring on either warming or cooling as shown by unchanged spectra. Indeed the simple pentet spectrum had esr parameters comparable to other aryl mono-1,2,3,5-dithiadiazolyl radicals ($g= 2.01$, $a_N= 0.5$ mT)[10].

Complete reduction of these radical cations (with an excess of $SbPh_3$) showed a 1:2:3:2:1 pentet overlapping the 1:1:1 triplet, indicative of the diradical $[SNSNC.C_6H_4.CNSSN]^{\circ\circ}$ (see figure 4.8) . On warming, there was no evidence for the spin-spin exchange bands observed in other multi-dithiadiazolyl radicals[14,2a,2b] but rearrangement was observed on stronger heating to give the previously reported $[NSSNC.C_6H_4.CNSSN]$ systems[2a,b] ($g=2.011$, $a_N=0.51$ mT) - see figure 4.9. Such a process has previously been described in terms of a thermal[1c] or photochemical[4] bimolecular rearrangement.

Note: there were no significant differences between the spectra of *para* and *meta* isomers either in the form of the spectra or coupling constants.

**Spin leakage* or intra-molecular, through-bond, electron delocalisation occurs in aryl 1,3,2,4-dithiadiazolyl radicals and is mediated by the SOMO of such radicals. In this isomer the SOMO has some orbital density residing on the carbon atom of the dithiadiazolyl and this allows for through bond coupling onto the phenylene ring and any substituents. In comparison, 1,2,3,5-dithiadiazolyl radicals should not exhibit spin leakage since the SOMO possesses a nodal plane through carbon. However, molecular interactions or perturbations may facilitate some second order delocalisation.

SOMOs of the 1,2,3,5- and the 1,3,2,4-dithiadiazolyl respectively

Figure 4.7 Esr spectrum of *p*-[SNSNC.C_6H_4.CNSSN]Cl_2 in acetonitrile with a deficit of Ph_3Sb

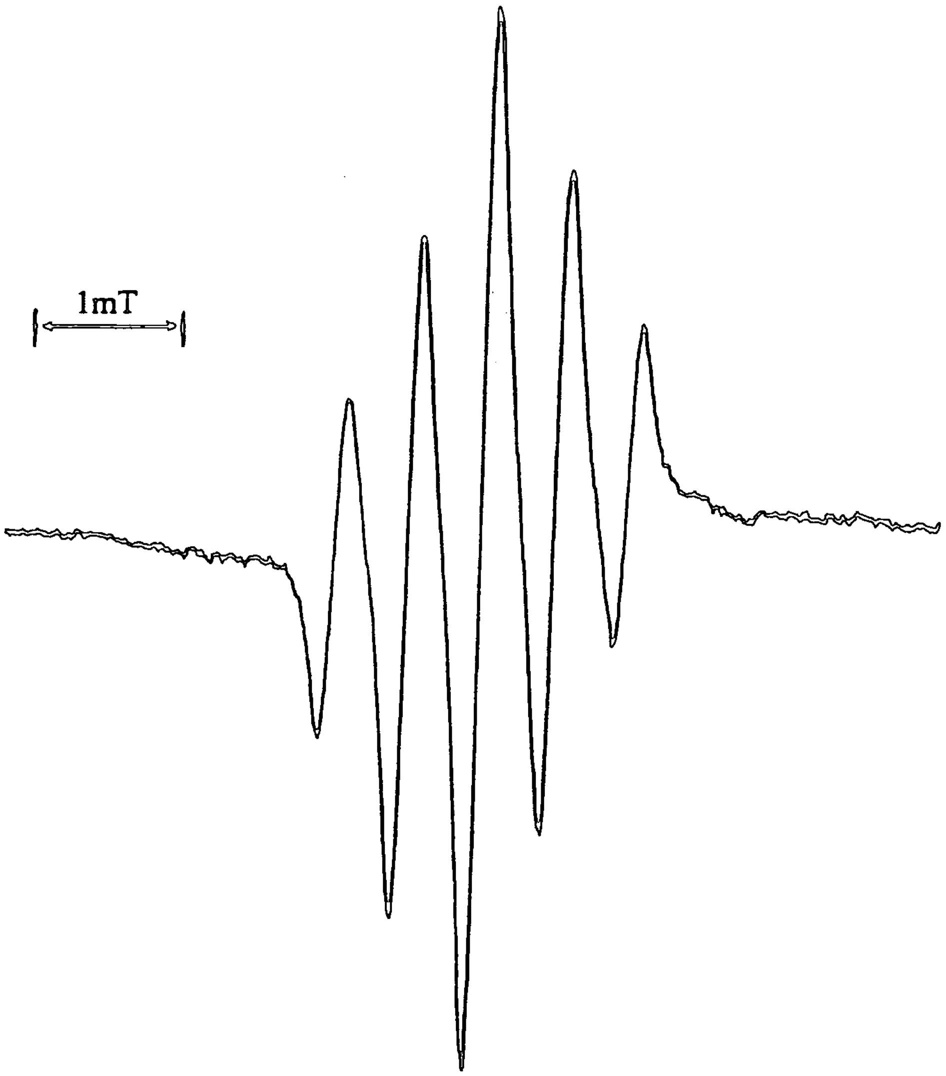


Figure 4.8 Esr spectrum of *p*-[SNSNC.C_6H_4.CNSSN]Cl_2 in acetonitrile with an excess of Ph_3Sb

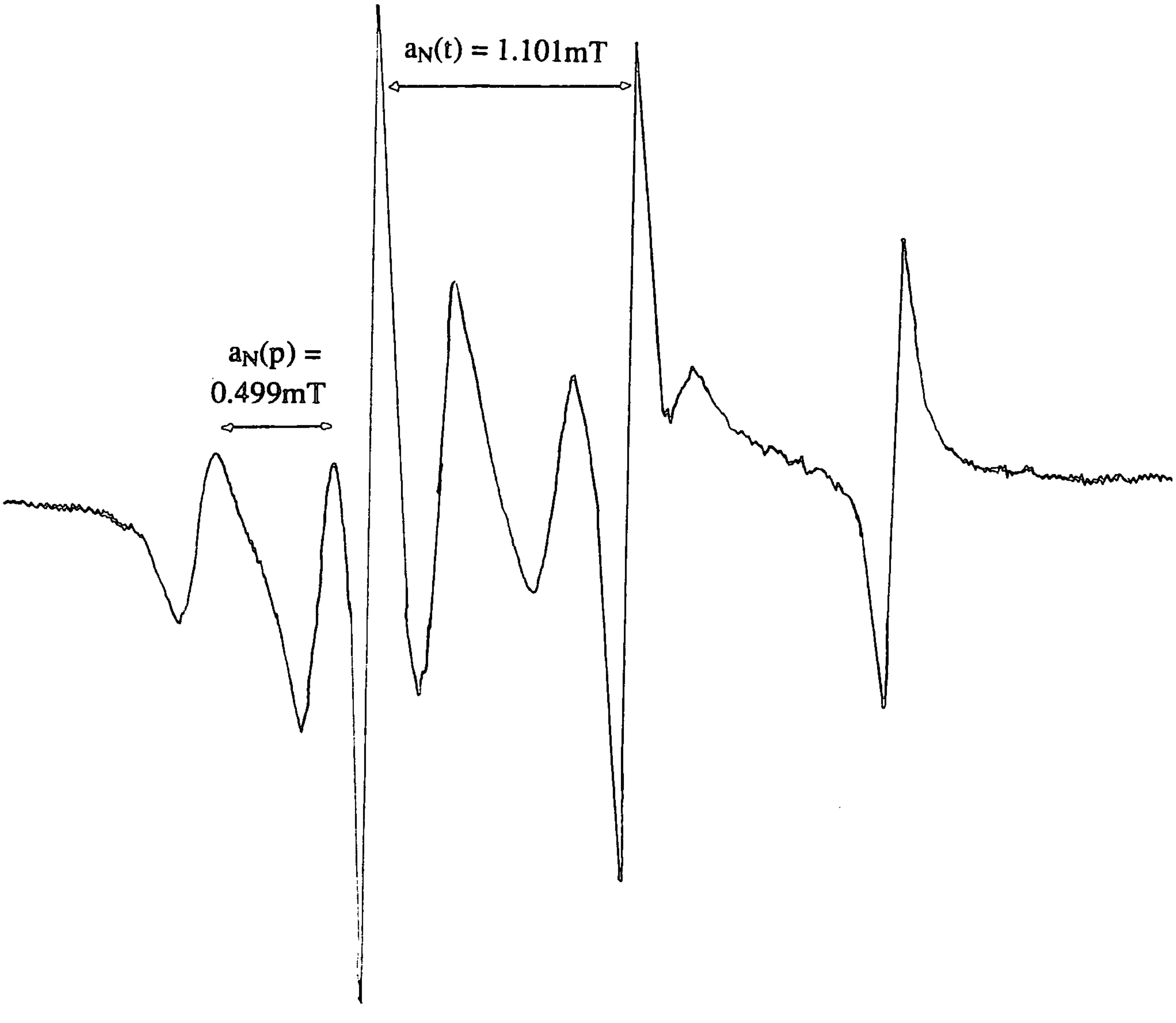
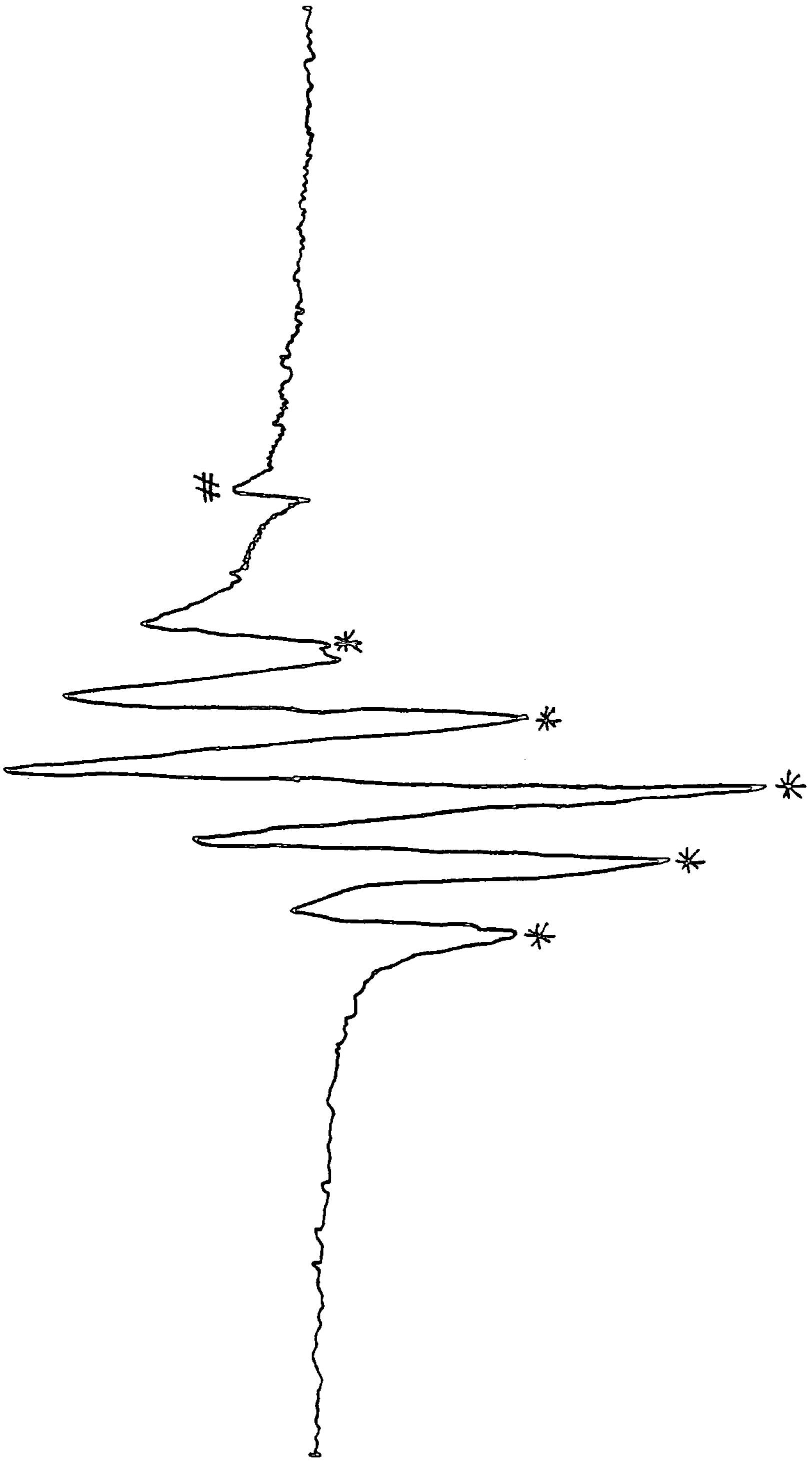


Figure 4.9 Esr spectrum of the rearranged product of p-$[\mathrm{SNSNC.C_6H_4.CNSSN}]^{\circ\circ}$

** indicates the 1:2:3:2:1 pentet arising from the bis-1,2,3,5-dithiadiazolyl, the rearrangement product*

 # indicates the remaining 1:1:1 triplet arising from some residual mixed diradical



4.2.2.3 Preparative reductions

Metathesis of *m*- and *p*- [SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ with two equivalents of [NBu_4]Cl provided the dichloride salts, [SNSNC.C_6H_4.CNSSN]Cl_2.

These chlorides were then reduced with half or one equivalent of $SbPh_3$ to yield the radical cations *m*- and *p*- [SNSNC.C_6H_4.CNSSN]Cl and the diradicals *m*- and *p*-[SNSNC.C_6H_4.CNSSN], respectively. The radical cations were isolable as dark purple and green solids (*m*- and *p*- respectively), whereas the diradicals were deeper in colour (purple-black and black) and significantly more moisture sensitive.

In comparison, attempts to prepare the radical cation, *p*-[SNSNC.C_6H_4.CNSSN][AsF_6], by metathesis of the dication, *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$, with one equivalent of Bu_4NCl followed by reduction with $SbPh_3$ were unsuccessful; reaction of one equivalent of Bu_4NCl with *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ yielded a salt of mixed stoichiometry, analysing as *p*- [SNSNC.C_6H_4.CNSSN][AsF_6]$_{0.5}$[Cl]$_{1.5}$ Similar salts, such as [PhCNSSN]$_3$[AsF_6]$_2$Cl, have been observed previously[15]. Conversely, metathesis of *m*- [SNSNC.C_6H_4.CNSSN]Cl_2 with one equivalent of $AgAsF_6$ followed by reduction gave a red-brown product which showed a 1:1:1 triplet only in its esr spectrum and gave poor elemental analyses. Attempts at recrystallisation from acetonitrile were unsuccessful due to the extreme moisture sensitivity of this material.

4.2.2.3.1 Attempted recrystallisations

Attempts to crystalise *p*-[SNSNC.C_6H_4.CNSSN] by high vacuum sublimation (10^{-7} torr, 110°C), electrocrystallisation (under constant current or fixed potential on a variety of substrates - Pt sheet, Pt wire and glass) and crystal growth (using [SNSNC.C_6H_4.CNSSN]Cl_2, $SbPh_3$ and various solvents) were unsuccessful, although crystal growth methods provided microcrystalline samples. As yet, similar attempts to grow crystals of the radical cation, *p*-[SNSNC.C_6H_4.CNSSN]Cl, have also been unsuccessful.

4.2.2.4 Magnetisation studies

Figure 4.10 shows the variation of magnetic susceptibility of *p*-[SNSNC.C_6H_4.CNSSN] with temperature. A fit to Curie-Weiss law behaviour can be made to the paramagnetic tail in the susceptibility plot, provided a constant corrective factor of -1.0×10^{-4} emu mol^{-1} is made. The latter contribution is believed to be due to a small concentration of ferromagnetic impurity and is likely to be responsible for the small structure observed in the susceptibility around 60 K. Magnetic susceptibility with characteristic Curie-tail behaviour has previously been observed in related bis-dithiadiazolyl radicals[2a,b,d,14]. Spin-paired bonding interactions between dithiadiazolyl radicals in the solid state lead to diamagnetic dimers in *p*-[NSSNC.C_6H_4.CNSSN][2a] and polymers in *p*-[SNSNC.C_6H_4.CNSNS][1a]. The residual paramagnetic response is attributable to the unpaired spins at lattice defects or polymer chain ends respectively and varies between 1 and 16% unpaired spins per molecule depending upon the degree of crystallinity[2]. In comparison the spin concentration per molecule in *p*-[SNSNC.C_6H_4.CNSSN] can be estimated at 3%, assuming a Curie-Weiss fit.

In contrast, *p*-[SNSNC.C_6H_4.CNSSN]Cl is strongly paramagnetic (figure 4.11); a plot of χ^{-1} versus temperature shows that the material follows a Curie-Weiss type behaviour above 160 K with θ=-65 K. The effective magnetic moment at higher temperatures can thus be estimated at 1.87 Bohr magneton, somewhat in excess of the 1.73 Bohr magneton expected of a spin 1/2 system with a g-factor close to 2.

Such a strong paramagnetic response from dithiadiazolyl radicals in the condensed phase is rare and has previously only been observed in liquid dithiadiazolyl radicals[16,17] and the salts [RCNSSN]$_3$Cl (R=Cl, CF_3)[18]. However, similar data have recently been observed by Passmore and co-workers for their related radical cations[19] [CF_3CNSSS][AsF_6] and [CF_3CSSSCCF_3][AsF_6]. Repulsive coulombic interactions between adjacent dithiadiazolyl radical-cations may be responsible for preventing the spin-paired dimerisation process in *p*-[SNSNC.C_6H_4.CNSSN]Cl although there would appear to be ample scope for intramolecular spin-charge separation.

Figure 4.10 Magnetic properties of *p*-[SNSNC.C_6H_4.CNSSN]

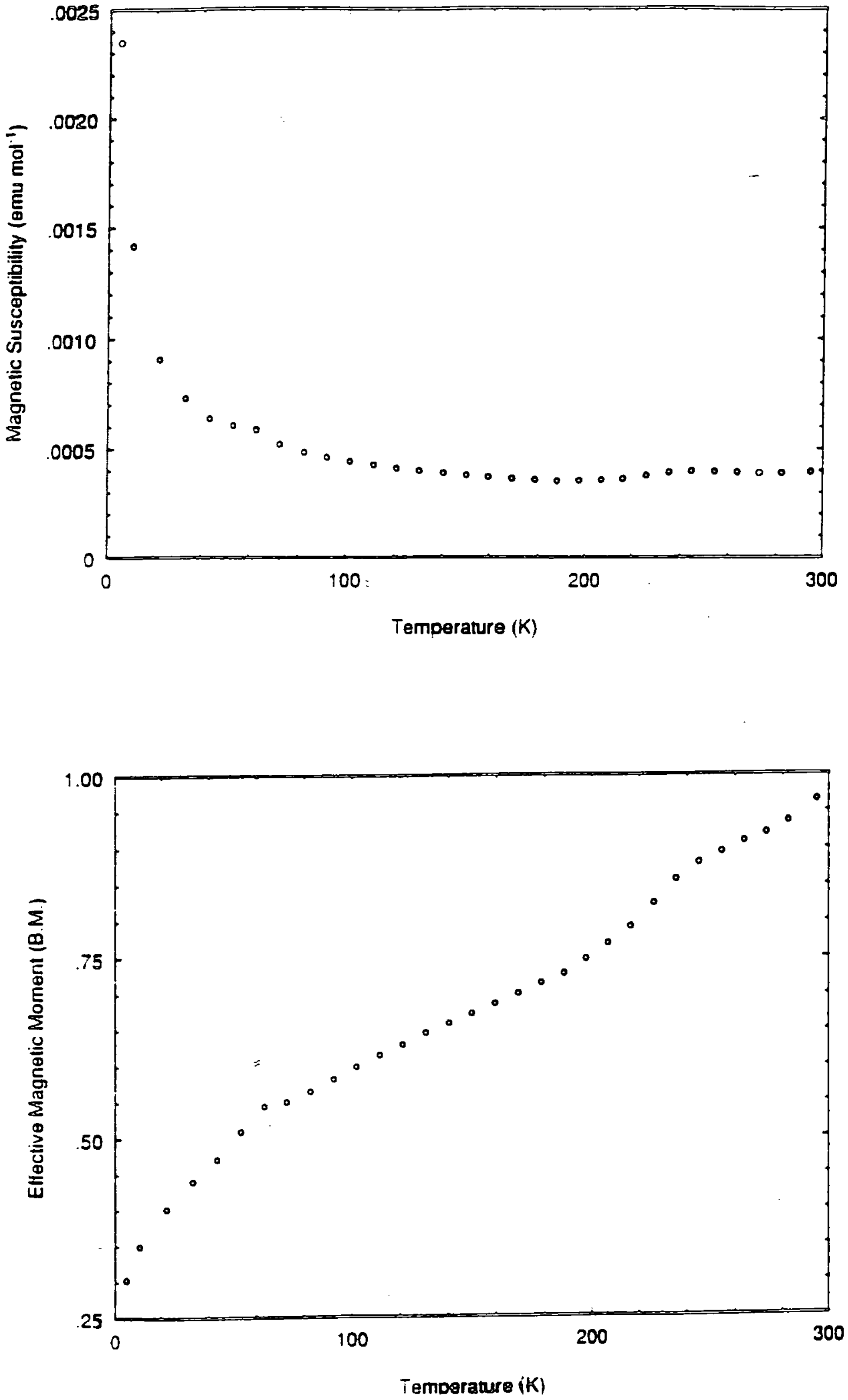
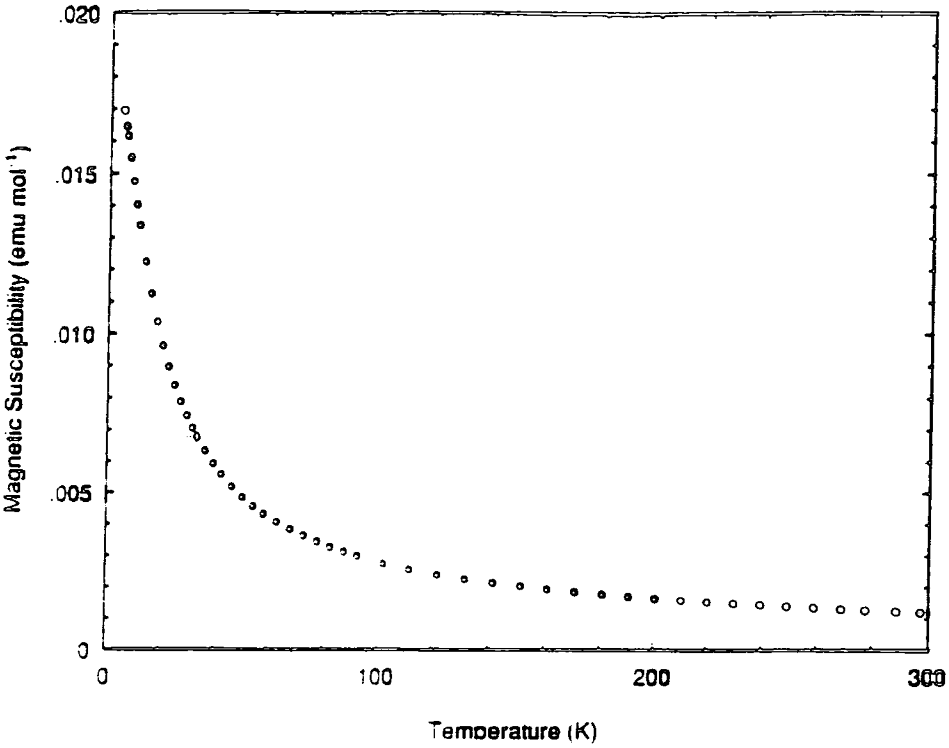
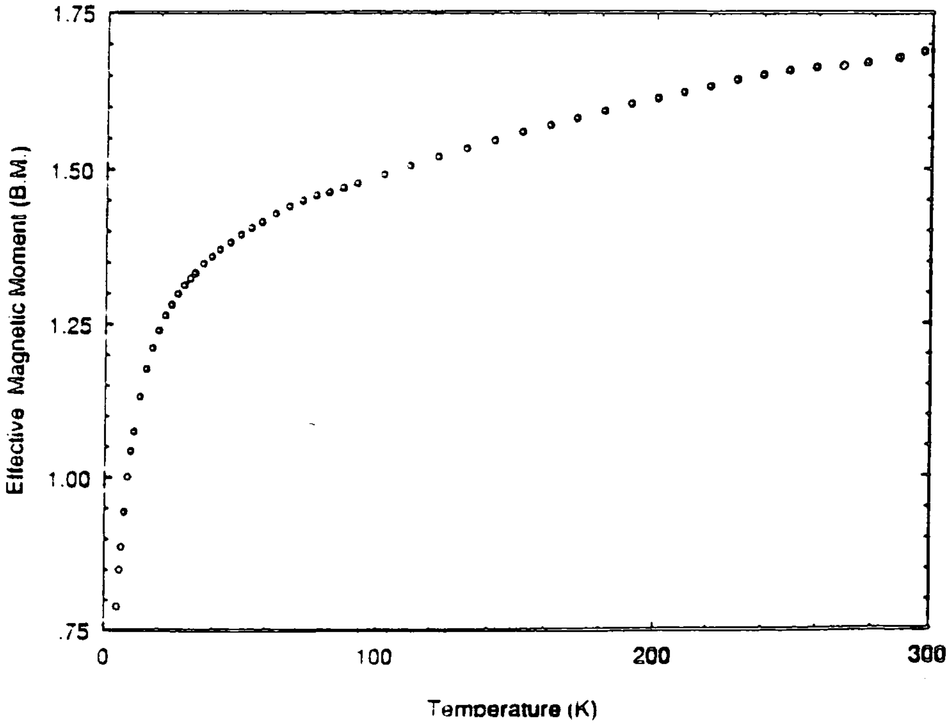


Figure 4.11 Magnetic properties of *p*-[SNSNC.C_6H_4.CNSSN]Cl





4.2.3 Solid state structure

The crystal structure of *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$.CH_3CN shows 1,2,3,5 -and 1,3,2,4- dithiadiazolylium rings held together through a phenylene unit (Figure 4.12). Bond distances and angles in both dithiadiazolylium rings are similar to those observed in related structures. Tables 4.1 to 4.5 give crystal data, including structure, solution, refinement, atomic coordinates, bond lengths, bond angles and thermal parameters.

Table 4.1 Crystal parameters and data collection/refinement for *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$.CH_3CN

Formula	$C_{10}H_7As_2F_{12}N_5S_4$	θ range unit cell	11.63-17.31°
M.W.	703.29	Space Group	P2$_1$/n
Crystal Size (mm)	0.50 x 0.05 x 0.05	Z	4
Crystal Form	Yellow Needle	D_c (g cm^{-3})	2.216
Instrument	Stoe-Siemens	F(000)	1360
Radiation	Cu(Kα)	μ/mm^{-1}	8.769
λ/Å	1.54178	T/K	170.0(10)
Scan Type	ω/θ	θ range for data	5.28 - 54.94°
Crystal System	Monoclinic	Data Measured	3374
a/Å	8.233(3)	Total Unique	2633
b/Å	16.742(6)	Total Observed	1715
c/Å	15.332(7)	Significance Test	
α/°	90	No. of Parameters	312
β/°	94.21(5)	ρ_{min}- ρ_{max}/eÅ^{-3}	-0.714- 0.895
γ/°	90	Weighting Scheme	
V/Å^3	2107.6(14)	R	0.0479
		R_w	0.1173

Figure 4.12 **The solid state structure of the *p*-[SNSNC.C_6H_4.CNSSN] dication, showing the atom numbering scheme**

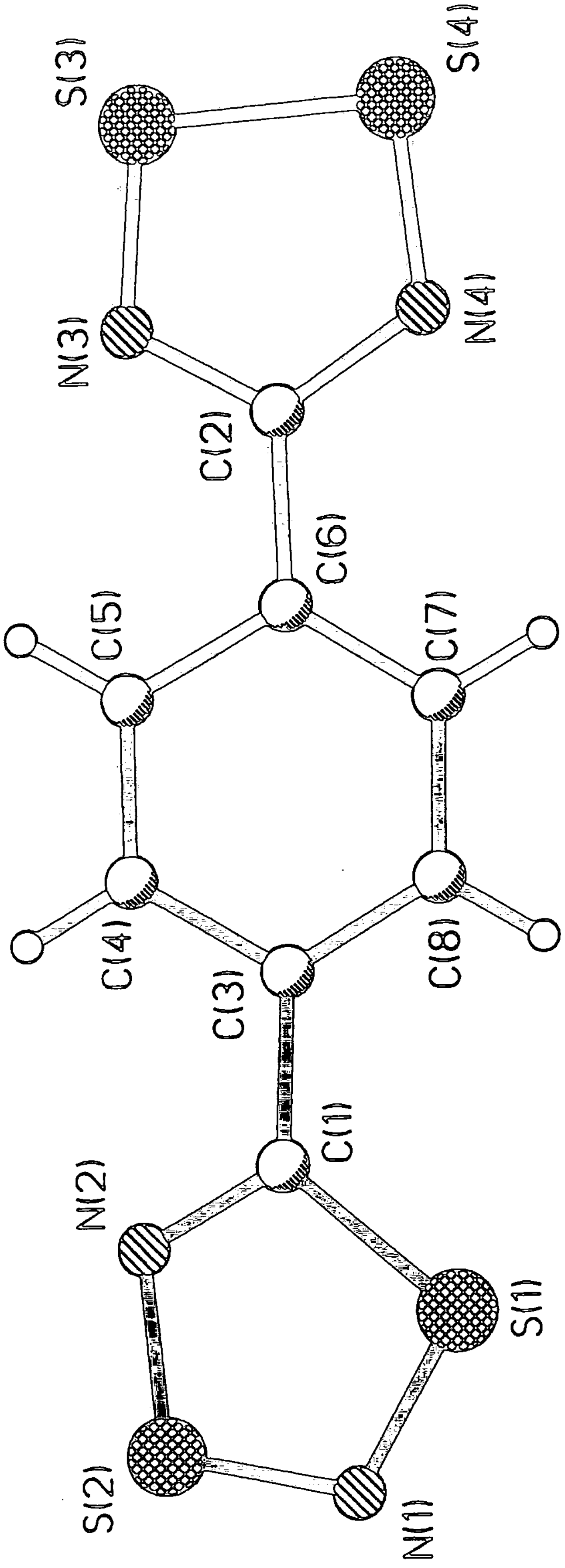


Figure 4.13 The solid state structure of the *p*-[SNSNC.C_6H_4.CNSSN] di-cation, showing attendant anions

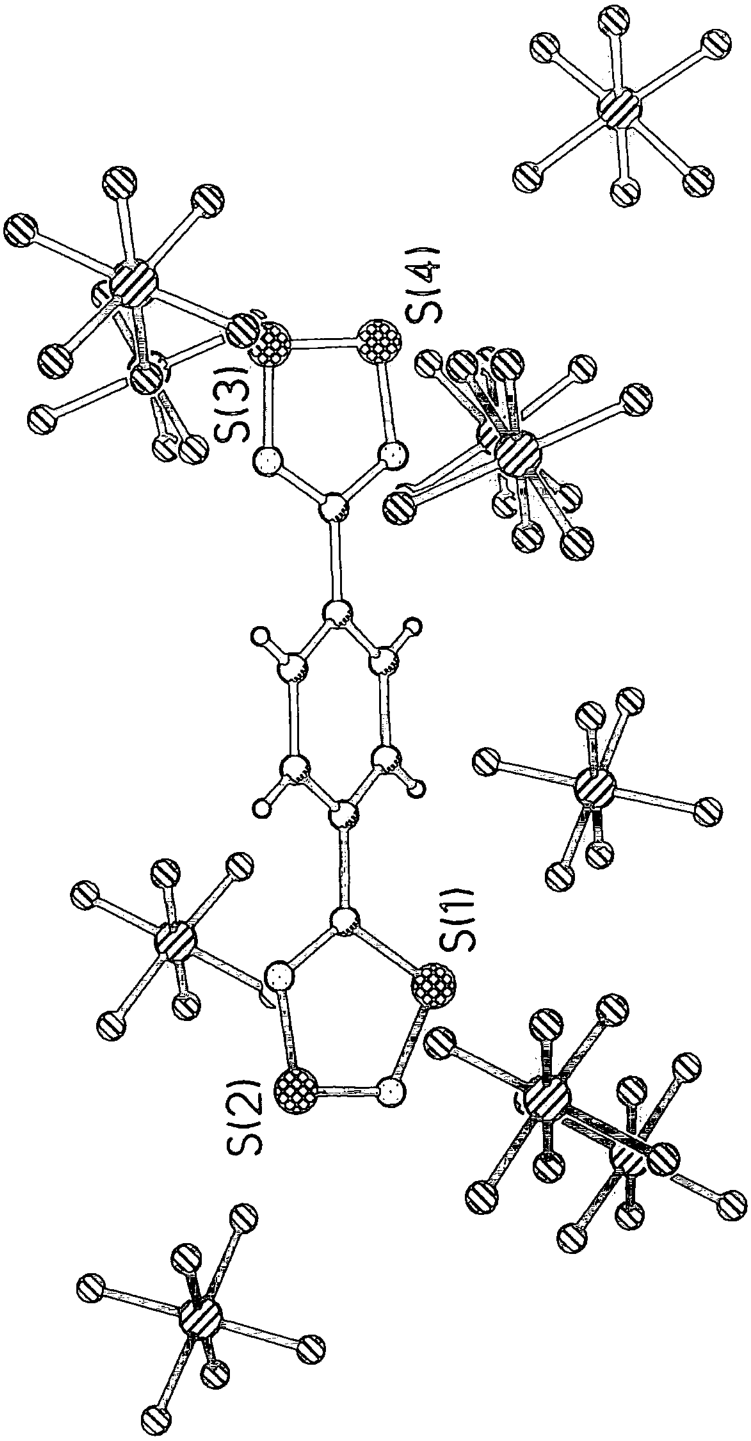


Figure 4.14 Packing of *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$, showing S···N interactions with an adjacent solvent molecule

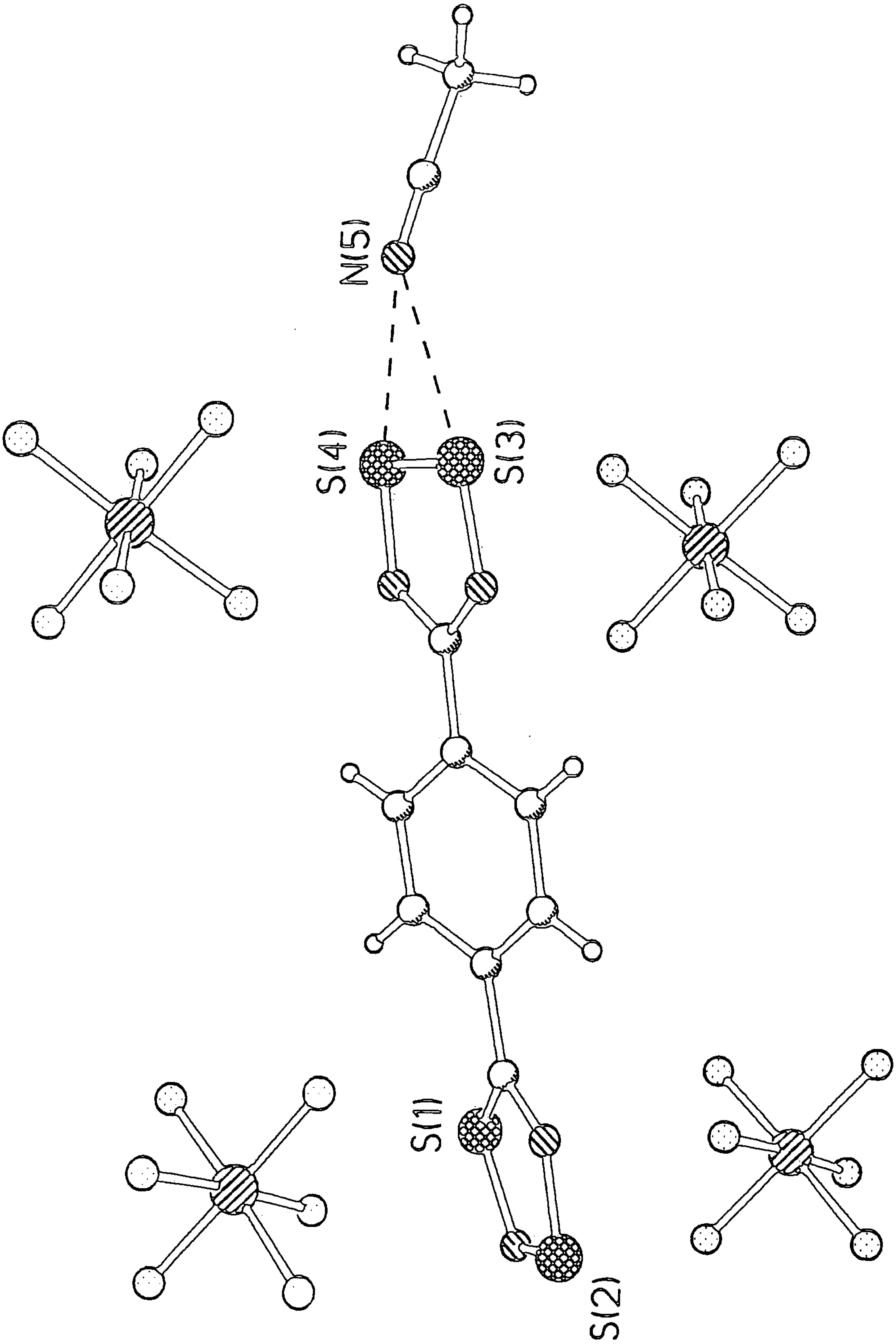


Table 4.2 Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{3}x10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
S(1)	6984(3)	5110.0(15)	1056.0(15)	48(2)
S(2)	7060(3)	3553(2)	1331(2)	52(2)
S(3)	5500(3)	7089.6(14)	6582.8(13)	40.6(13)
S(4)	5267(3)	8067.9(14)	5812.9(14)	40.4(13)
N(1)	7175(9)	4239(5)	641(5)	46(4)
N(2)	6733(9)	4015(4)	2201(5)	43(5)
N(3)	5778(9)	6491(4)	5820(4)	39(4)
N(4)	5516(8)	7608(4)	4931(4)	39(4)
C(1)	6657(10)	4793(5)	2105(5)	36(5)
C(2)	5769(10)	6814(5)	5018(5)	31(4)
C(3)	6408(10)	5332(5)	2835(5)	37(5)
C(4)	6797(11)	5072(6)	3673(6)	43(5)
C(5)	6614(11)	5552(6)	4380(5)	41(6)
C(6)	5953(10)	6318(5)	4249(5)	33(5)
C(7)	5522(10)	6576(5)	3408(5)	34(5)
C(8)	5741(11)	6086(5)	2705(5)	39(6)
As(1)	523.7(11)	7217.8(6)	5759.9(6)	40.0(6)
F(11)	219(8)	6276(3)	5893(5)	78(4)
F(12)	475(8)	7236(4)	4752(4)	71(4)
F(13)	1125(7)	7616(4)	6207(4)	67(3)
F(14)	1522(8)	7200(4)	6777(4)	70(4)
F(15)	2203(6)	6813(4)	5330(4)	65(3)
F(16)	1279(7)	8158(3)	5627(4)	65(4)
As(2)	8013.4(11)	5678.9(6)	8517.7(6)	40.0(6)
F(21)	6947(6)	5636(3)	7516(3)	56(3)
F(22A)	8450(50)	4700(16)	8564(15)	118(23)
F(23A)	6337(30)	5487(26)	9079(13)	115(9)
F(24A)	7559(54)	6681(15)	8537(16)	118(23)
F(25A)	9724(25)	5846(28)	8055(12)	115(9)
F(22B)	7472(36)	4690(12)	8593(12)	78(16)
F(23B)	6280(24)	5917(17)	8941(16)	76(7)
F(24B)	8570(38)	6625(13)	8368(12)	78(16)
F(25B)	9677(22)	5351(18)	8038(12)	76(7)
F(26)	9068(7)	5720(3)	9524(3)	57(3)
N(S)	4973(12)	8397(6)	7592(6)	67(7)

C(9)	5486(13)	8831(6)	8102(6)	50(7)
C(10)	6209(13)	9400(6)	8737(6)	60(7)

Table 4.3 Bond lengths (Å) and angles (degrees) in *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$.CH_3CN.

S(l)-N(l)	1.604(8)	S(l)-C(l)	1.733(9)
S(2)-N(l)	1.568(8)	S(2)-N(2)	1.582(7)
S(3)-N(3)	1.570(8)	S(3)-S(4)	2.020(4)
S(4)-N(4)	1.583(7)	N(2)-C(l)	1.312(11)
N(3)-C(2)	1.343(10)	N(4)-C(2)	1.351(11)
C(l)-C(3)	1.464(12)	C(2)-C(6)	1.459(12)
C(3)-C(4)	1.372(12)	C(3)-C(8)	1.385(12)
C(4)-C(5)	1.366(12)	C(5)-C(6)	1.402(12)
C(6)-C(7)	1.382(11)	C(7)-C(8)	1.377(12)
As(l)-F(12)	1.697(5)	As(l)-F(13)	1.701(5)
As(l)-F(ll)	1.708(6)	As(l)-F(14)	1.709(6)
As(l)-F(16)	1.711(5)	As(l)-F(15)	1.715(5)
As(2)-F(25A)	1.647(19)	As(2)-F(23B)	1.659(19)
As(2)-F(24B)	1.670(15)	As(2)-F(22A)	1.678(22)
As(2)-F(25B)	1.693(16)	As(2)-F(23A)	1.710(23)
As(2)-F(21)	1.714(5)	As(2)-F(26)	1.715(5)
As(2)-F(22B)	1.720(15)	As(2)-F(24A)	1.720(20)
N(5)-C(9)	1.127(12)	C(9)-C(10)	1.458(14)
N(l)-S(l)-C(l)	96.7(4)	N(l)-S(2)-N(2)	103.5(4)
N(3)-S(3)-S(4)	95.5(3)	N(4)-S(4)-S(3)	95.3(3)
S(2)-N(l)-S(l)	112.6(4)	C(l)-N(2)-S(2)	113.6(6)
C(2)-N(3)-S(3)	115.7(6)	C(2)-N(4)-S(4)	115.0(6)
N(2)-C(l)-C(3)	122.3(8)	N(2)-C(l)-S(l)	113.5(6)
C(3)-C(l)-S(l)	124.1(7)	N(3)-C(2)-N(4)	118.6(8)
N(3)-C(2)-C(6)	121.1(8)	N(4)-C(2)-C(6)	120.3(7)
C(4)-C(3)-C(8)	119.1(8)	C(4)-C(3)-C(l)	119.0(8)
C(8)-C(3)-C(l)	121.8(8)	C(5)-C(4)-C(3)	121.7(9)
C(4)-C(5)-C(6)	119.2(8)	C(7)-C(6)-C(5)	119.3(8)
C(7)-C(6)-C(2)	122.8(8)	C(S)-C(6)-C(2)	117.8(7)
C(8)-C(7)-C(6)	120.4(8)	C(7)-C(8)-C(3)	120.2(8)
F(12)-As(l)-F(13)	90.7(3)	F(12)-As(l)-F(ll)	88.4(3)
F(13)-As(l)-F(ll)	90.6(3)	F(12)-As(l)-F(14)	179.8(3)
F(13)-As(l)-F(14)	89.1(3)	F(ll)-As(l)-F(14)	91.5(3)
F(12)-As(l)-F(16)	91.8(3)	F(13)-As(l)-F(16)	89.7(3)

F(11)-As(1)-F(16)	179.7(3)	F(14)-As(1)-F(16)	88.3(3)
F(12)-As(1)-F(15)	90.4(3)	F(13)-As(1)-F(15)	178.9(3)
F(11)-As(1)-F(15)	89.3(3)	F(14)-As(1)-F(15)	89.8(3)
F(16)-As(1)-F(15)	90.4(3)	F(23B)-As(2)-F(24B)	94.5(10)
F(25A)-As(2)-F(22A)	89.8(12)	F(23B)-As(2)-F(25B)	173.9(8)
F(24B)-As(2)-F(25B)	90.5(10)	F(25A)-As(2)-F(23A)	175.1(8)
F(22A)-As(2)-F(23A)	88.5(12)	F(25A)-As(2)-F(21)	91.1(7)
F(23B)-As(2)-F(21)	87.8(8)	F(24B)-As(2)-F(21)	92.6(6)
F(22A)-As(2)-F(21)	95.2(8)	F(25B)-As(2)-F(21)	88.5(6)
F(23A)-As(2)-F(21)	93.7(7)	F(25A)-As(2)-F(26)	89.3(7)
F(23B)-As(2)-F(26)	91.8(8)	F(24B)-As(2)-F(26)	87.7(6)
F(22A)-As(2)-F(26)	84.8(8)	F(25B)-As(2)-F(26)	91.8(6)
F(23A)-As(2)-F(26)	85.9(7)	F(21)-As(2)-F(26)	179.6(3)
F(23B)-As(2)-F(22B)	88.3(10)	F(24B)-As(2)-F(22B)	175.7(8)
F(25B)-As(2)-F(22B)	86.5(10)	F(21)-As(2)-F(22B)	84.3(7)
F(26)-As(2)-F(22B)	95.5(7)	F(25A)-As(2)-F(24A)	92.0(12)
F(22A)-As(2)-F(24A)	176.6(9)	F(23A)-As(2)-F(24A)	89.5(12)
F(21)-As(2)-F(24A)	87.6(7)	F(26)-As(2)-F(24A)	92.4(7)
N(S)-C(9)-C(10)	177.4(11)		

The 1,2,3,5-dithiadiazolylium ring possesses bond lengths identical (within 0.01 Å) to that of the related [PhCNSSN][AsF_6][15] and *p*-[$C_6H_4(CNSSN)_2$][SbF_6]$_2$.2PhCN[20] cations. Although the CNSSN ring is completely planar within experimental error (r.m.s. deviation, Δ=0.001 Å), it is twisted some 16.7° out of plane with respect to the phenylene ring. This is similar to the twist angle observed in *p*- [$C_6H_4(CNSSN)_2$][SbF_6]$_2$.2PhCN (θ=15.8°) but different from the essentially planar cation in the [PhCNSSN][AsF_6] structure. Such rotation out of the molecular plane perhaps arises through a combination of secondary interactions and molecular packing forces. For example, the *p*- [Cl.C_6H_4.CNSSN][AsF_6][21] structure (analogous to [PhCNSSN][AsF_6]) does show a twist angle (θ=21.9(2)°) between phenylene and dithiadiazolylium rings. Indeed, PM3 molecular orbital calculations[14] have shown that the energy barrier to rotation about the C-C bond in such systems is low (below kT at room temperature) while the twist angle remains less than 30°.

Table 4.4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic temperature factor exponent takes the form- $2\pi^2(ha^{*2}U_{11}+...+2hka^*b^*U_{12})$.

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
S(1)	56(2)	47.2(15)	42.0(13)	3.4(11)	7.7(11)	-1.1(12)
S(2)	61(2)	43(2)	53.6(14)	-3.8(12)	15.5(13)	4.4(12)
S(3)	39.7(13)	48.0(15)	34.2(12)	0.3(10)	3.6(10)	-5.2(11)
S(4)	41.1(13)	41.0(13)	39.3(12)	-2.2(10)	4.0(10)	2.8(11)
N(1)	39(4)	58(5)	42(4)	-17(4)	5(3)	0(4)
N(2)	49(5)	32(5)	48(5)	-4(4)	3(4)	-1(4)
N(3)	36(4)	39(4)	43(4)	8(4)	5(3)	-5(3)
N(4)	35(4)	41(5)	42(4)	10(4)	1(3)	-5(4)
C(1)	24(5)	45(6)	40(5)	-4(4)	4(4)	8(4)
C(2)	25(4)	37(5)	32(4)	7(4)	-1(3)	-4(4)
C(3)	35(5)	32(5)	43(5)	8(4)	0(4)	1(4)
C(4)	41(5)	37(5)	49(5)	8(5)	-4(4)	10(4)
C(5)	42(6)	50(6)	31(5)	-2(4)	-2(4)	0(5)
C(6)	25(5)	35(5)	39(5)	1(4)	4(4)	-2(4)
C(7)	31(5)	33(5)	40(5)	6(4)	1(4)	1(4)
C(8)	45(6)	40(5)	31(5)	4(4)	-3(4)	-1(5)
As(1)	31.1(6)	39.4(7)	49.0(6)	2.1(5)	0.9(4)	0.9(5)
F(11)	74(4)	43(4)	120(5)	6(3)	26(4)	-19(3)
F(12)	80(4)	72(4)	56(4)	-8(3)	-39(3)	14(3)
F(13)	36(3)	78(4)	87(4)	-17(3)	9(3)	0(3)
F(14)	74(4)	86(5)	47(3)	6(3)	-15(3)	14(4)
F(15)	37(3)	78(4)	80(4)	-20(3)	5(3)	0(3)
F(16)	75(4)	42(3)	78(4)	2(3)	8(3)	-21(3)
As(2)	31.8(6)	47.4(7)	40.5(6)	0.6(5)	0.9(4)	-1.3(5)
F(21)	44(3)	75(4)	46(3)	-1(3)	-16(3)	-1(3)
F(22A)	175(23)	66(11)	101(10)	-16(8)	-65(13)	53(14)
F(23A)	62(9)	216(30)	66(8)	38(10)	-6(6)	-34(13)
F(24A)	175(23)	66(11)	101(10)	-16(8)	-65(13)	53(14)
F(25A)	62(9)	216(30)	66(8)	38(10)	-6(6)	-34(13)
F(22B)	105(16)	33(9)	89(8)	19(6)	-44(9)	-41(10)
F(23B)	34(7)	141(18)	54(9)	-51(11)	3(6)	16(10)
F(24B)	105(16)	33(9)	89(8)	19(6)	-44(9)	-41(10)
F(25B)	34(7)	141(18)	54(9)	-51(11)	3(6)	16(10)
F(26)	53(3)	75(4)	39(3)	8(3)	-13(2)	-8(3)
N(5)	73(7)	73(7)	57(5)	-12(5)	9(5)	-13(5)

C(9)	62(7)	48(6)	41(5)	-3(5)	5(5)	4(5)
C(10)	65(7)	53(7)	61(6)	-6(5)	-4(6)	-8(6)

Table 4.5 Atomic coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for hydrogen atoms for *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$.CH_3CN.

Atom	x	y	z	U
H(4)	7200(11)	4551(6)	3763(6)	51
H(5)	6928(11)	5370(6)	4948(5)	50
H(7)	5077(10)	7088(5)	3315(5)	41
H(8)	5437(11)	6263(5)	2135(5)	47
H(10A)	5890(71)	9260(25)	9328(9)	90
H(10B)	5818(66)	9945(8)	8583(27)	90
H(10C)	7410(13)	9382(30)	8731(33)	90

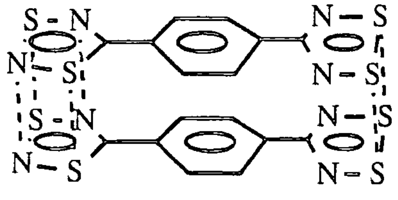
In a similar manner, the 1,3,2,4-dithiadiazolylium ring shows bond distances comparable (within 0.02 Å) to those found in [PhCNSNS][AsF_6][22], the most marked difference is a slight shortening of the CN distance at 1.312 Å (see Table 4.3). The CNSNS ring is also essentially planar (r.m.s. deviation, $\Delta = 0.011$ Å). In comparison with *p*-[C_6H_4(CNSSN)$_2$][SbF_6]$_2$.2PhCN, which shows an inversion centre (i.e. the two dithiadiazolylium rings are twisted in opposite senses to the phenylene plane), the mixed dication shows both rings twisted in the same sense. The 1,3,2,4-dithiadiazolylium ring is twisted by 25.1° with respect to the phenylene plane and the angle is close to that observed in [PhCNSNS][AsF_6].

The solvate molecule would appear to be associated with the 1,2,3,5-dithiadiazolylium ring, the acetonitrile N atom being in the CNSSN ring plane and showing close contacts to S(3) and S(4) at 2.73 Å and 2.81 Å respectively (figure 4.14). Such contacts are significantly shorter than the sum of the in-plane van der Waals radii[8] (3.20 Å). It was previously considered that electron donation processes to the 1,2,3,5-dithiadiazolylium cations to lead to shortening or lengthening of the SS bond[5] (via in-plane and out-of-plane secondary interactions respectively). However electron donation from MeCN to the dithiadiazolylium ring can be considered negligible, with the sulphur-sulphur distance in *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$.CH_3CN being 2.020(4) Å whilst that in [PhCNSSN][AsF_6][15] is 2.023(1) Å and that in [PhCNSSN]Cl[21] (which also shows in-plane interactions) is 1.990(5) Å. The presence of two solvate molecules in p-$[C_6H_4(CNSSN)_2][SbF_6]_2.2PhCN$ indicates stronger solvent interactions with the 1,2,3,5-dithiadiazolylium ring than with the 1,3,2,4-dithiadiazolylium ring. It appears that solvent molecules, like anions, interact more strongly with the 1,2,3,5-dithiadiazolylium ring in which there are adjacent sulphur atoms.

4.2.4 Differential scanning calorimetry

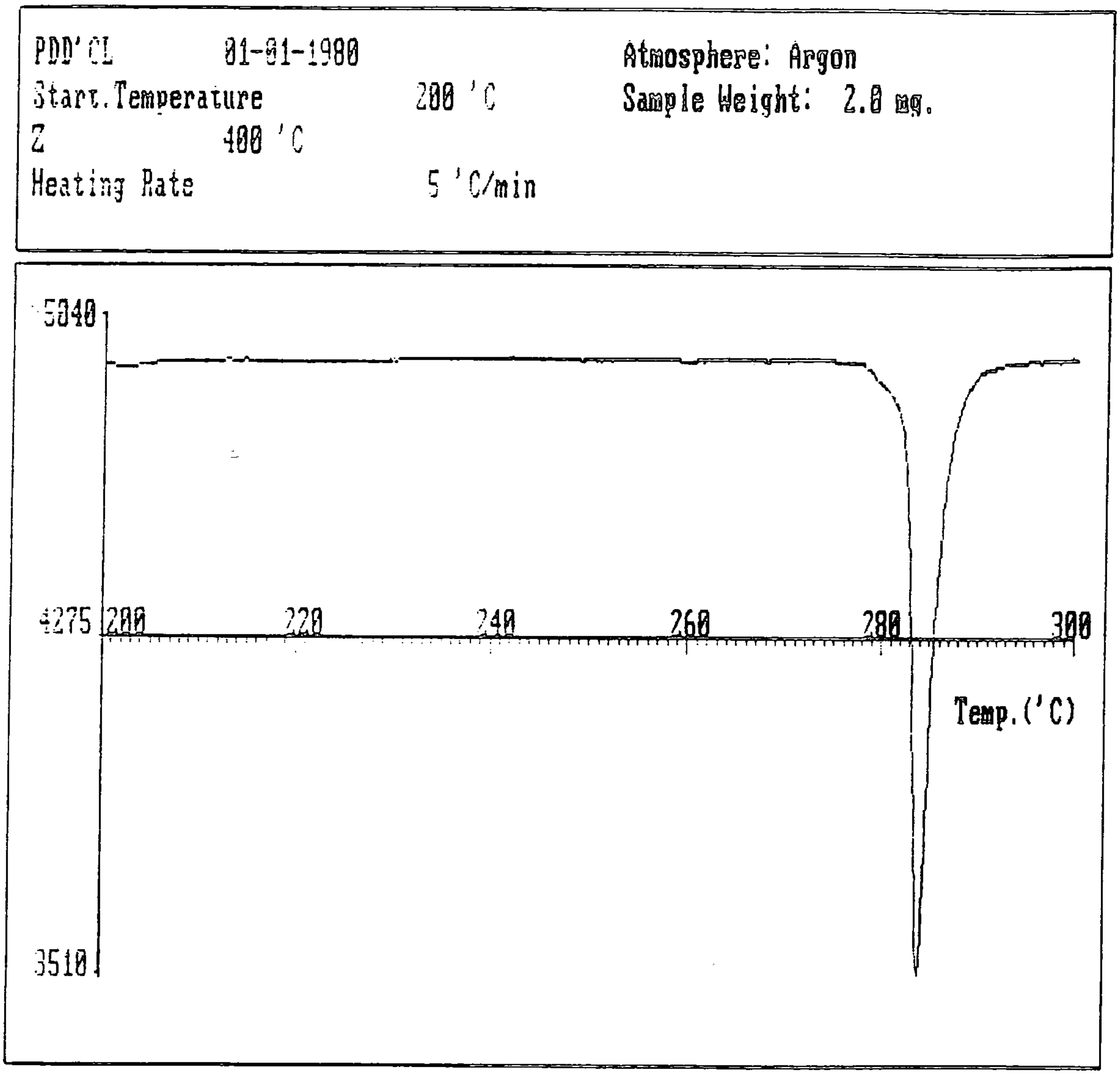
DSC measurements on a variety of 1,3,2,4-dithiadiazolyl/ium ring systems have shown that, in some cases, thermolysis leads to solid state rearrangement from the 1,3,2,4-isomer to its 1,2,3,5-counterpart[1c]. Such rearrangement has been attributed to secondary interactions in the solid state that facilitate rearrangement through a head-to-tail interaction between dithiadiazolyl rings[1c] (see figure 3.10). DSC measurements on the radical cation p-$[SNSNC.C_6H_4.CNSSN]Cl$ show an exothermic decomposition (280°C) to leave a brown tar (figure 4.15). There is no evidence for a possible rearrangement product. Such a decomposition is consistent with a cationic 1,3,2,4-dithiadiazolylium ring and a neutral 1,2,3,5-dithiadiazolyl radical, as indicated by both the c.v. and esr data. Since the radical cation, $[SNSNC.C_6H_4.CNSSN]Cl$, is paramagnetic in the solid state the type of molecular packing can be considered to be driven by coulombic cation-anion interaction terms rather than the spin-paired 1,2,3,5-dithiadiazolyl dimerisation process. This is not unexpected since the energy of dimerisation is low, whereas lattice-energy terms tend to be high.

DSC measurements on the mixed diradical, p-$[SNSNC.C_6H_4.CNSSN]$, also show a decomposition (261.5°C) to leave an oily tar (figure 4.16). On the basis of the previous proposals for solid state rearrangement[1c] it may be inferred that although the 1,3,2,4-dithiadiazolyl rings are held together through a spin-paired interaction (p-$[SNSNC.C_6H_4.CNSSN]$ is very weakly paramagnetic in the solid state) this does not involve a head-to-tail arrangement. We may thus consider an alternative structure, such as that shown below, in which the structure is determined by the head-to-head dimerisation of 1,2,3,5-dithiadiazolyl radicals and consequent head-to-head arrangement of 1,3,2,4-dithiadiazolyl rings.



Such a structure would not facilitate such rearrangement, but would allow the required spin-paired interactions that make this material only weakly paramagnetic.

Figure 4.15 DSC plot for p-[SNSNC.C_6H_4.CNSSN]Cl (arbitrary thermal units vs. temperature)



PDD'CL 01-01-1980

Start.Temperature 200 'C

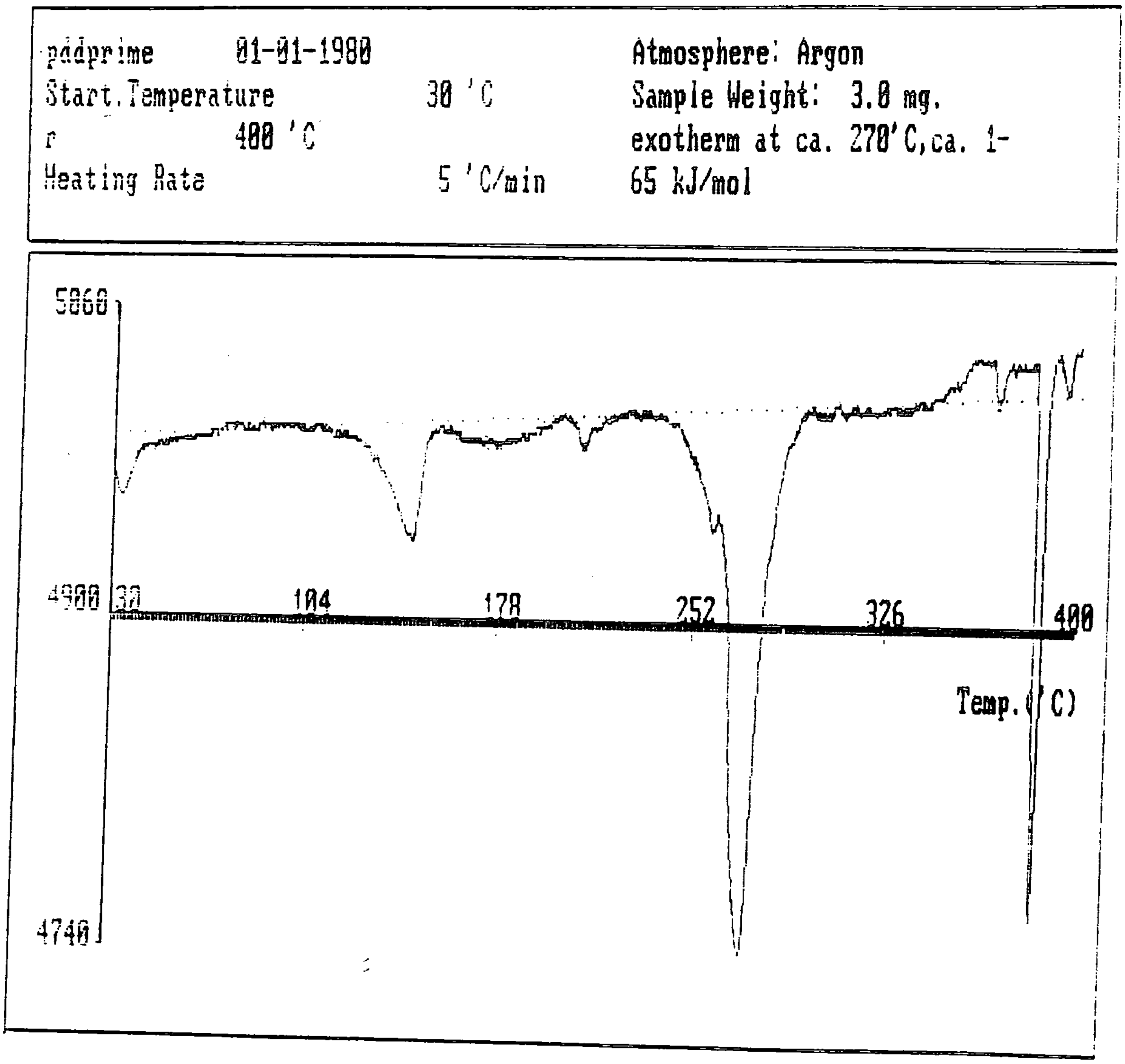
Z 400 'C

Heating Rate 5 'C/min

Atmosphere: Argon

Sample Weight: 2.0 mg.

Figure 4.16 DSC plot for p-[SNSNC.C_6H_4.CNSSN] (arbitrary thermal units vs. temperature)



```
pddprime        01-01-1980                    Atmosphere: Argon
Start.Temperature             30 'C           Sample Weight:  3.0 mg.
r               400 'C                        exotherm at ca. 270'C,ca. 1-
Heating Rate                   5 'C/min       65 kJ/mol
```

4.3 Conclusions and suggestions for further work

The reactions of $[SNS][AsF_6]$ with both para and meta-cyanophenylene 1,2,3,5-dithiadiazolylium hexafluoroarsenate(V) give the corresponding mixed 1,2,3,5 / 1,3,2,4-dithiadiazolylium salts in high yield (over 94% in both cases).

However, the reactions of $[SNS][AsF_6]$ with the cyanophenylene substituted radicals or chloride salts do not give the simple addition compounds but rather the mixed 1,2,3,5 / 1,3,2,4-dithiadiazolylium di-hexafluoroarsenate salts (together with sulphur and S_4N_4) and the cyanophenylene 1,2,3,5-dithiadiazolylium hexafluoroarsenate(V) salt (together with sulphur monochloride and $[S_3N_2]Cl$) respectively.

The former reaction can be rationalised by proposing the reduction of $[SNS]^+$ to give the unstable intermediate $[SNS]^\circ$ and its subsequent decomposition to sulphur, S_4N_4 and S_4N_2. The reducing agent is the 1,2,3,5-dithiadiazolyl radical, which is oxidised to give the corresponding dithiadiazolylium hexafluoroarsenate(V) salt.

The latter reaction, with $[NC.C_6H_4.CNSSN]Cl$, may be considered as a metathesis of $[SNS][AsF_6]$ with the chloride to yield the unstable intermediate, $\{[SNS]Cl\}$, which disproportionates to give $[S_3N_2]Cl$ and S_2Cl_2.

The reduction of *m* and *p*-$[NSNSC.C_6H_4.CNSSN]^{++}$ gives the corresponding radical cation and the diradical as isolable, characterisable solid products. The radical cation salts (chlorides) are paramagnetic with spin = $^1/_2$ (although the experimental magnetic moment is higher than that calculated for an S = $^1/_2$ paramagnet). The diradical contains only ca. 3% unpaired spins and its diamagnetism can be rationalised as resulting from spin pairing in the solid state (probably due to some type of dimerisation similar to that seen in the isomeric material *p*-$NSSNC.C_6H_4.CNSSN$[2a]). However, the thermal stability of the diradical (certainly with respect to rearrangement of the 1,3,2,4-dithiadiazolyl ring) suggests a head-to-head / tail-to-tail dimerisation with spin-pairing between isomeric rings on adjacent molecules.

As yet, there is no solid state structure of either of the diradicals or radical cations. However the para-substituted dication has been crystallised as the hexafluoroarsenate(V) salt, with one molecule of acetonitrile of crystallisation.

In order to explain unambiguously the magnetic properties of these systems a solid state structure, preferably of the radical cation, is required and preparation / crystallisation of other radical cation salts (such as $[AsF_6]^-$, $[S_3N_3]^-$ and $[metal(mnt)_2]^{2-}$) should be a future priority.

Another extension of this work could be the preparation of other mixed salts based on a variety of di and tri-cyano benzenes, for example, *sym*-tricyano benzene, *o*-dicyanobenzene and substituted dicyanobenzenes. The introduction of higher or lower symmetry substituents that are bulky or electronically unusual and the possibility of diradical cations, may well enhance the magnetic processes inherent in these systems. However, the need for structural data cannot be under emphasised, as subtle changes in substituent have a disproportionate effect on the molecular packing of these systems (see chapter 7).

A natural progression in this area is towards selenium-based heterocycles, which would exhibit enhanced interactions between adjacent radicals and radical cations. Preliminary work has begun on the use of $[NC.C_6H_4.CNSeSeN][AsF_6]$ to prepare spin = $^1/_2$ systems with improved intermolecular interactions (see chapter 6).

Metal complexes of 1,2,3,5-dithiadiazolyls are known, so a mixed radical cation could be coupled to a metal centre, with transfer of the unpaired electron to the 1,2,3,5-dithiadiazolylium ring, driven by some type of precipitation or metathesis process. Subsequent reduction of the cationic end and complexation of the product to another metal centre would allow for the construction of polymeric and oligomeric systems containing repeating units of two metal centres bridged by di-functional dithiadiazolyl radicals. However, this type of compound may prove extremely difficult to prepare (mainly because of the insolubility of the metal dithiadiazolyls).

4.4 Experimental

4.4.1 Starting materials

4.4.1.1 Preparation of *p*-$[NC.C_6H_4.CNSSN]Cl$

$Li[N(SiMe_3)_2]$ (13 g, 0.078 mol) and 1,4-$C_6H_4(CN)_2$ (10 g, 0.078 mol) were stirred in Et_2O (40 ml)at room temperature for 18 hours and then pumped to dryness to provide an off-white solid. This solid was slowly added to a solution of SCl_2 (10 ml, 0.155 mol) in CH_2Cl_2 (50 ml) with cooling to form an immediate orange precipitate which was filtered off and pumped to dryness. The crude product was then extracted exhaustively with SO_2 (to free it from any remaining LiCl) and washed liberally with CH_2Cl_2. Yield 13.5 g, 72%. I.R. ν_{max} (cm^{-1}): 2220m, 1285w, 1212w, 1150s, 1012m, 920m, 890s, 857s, 850s, 837sh, 740s, 720w, 685s, 552s, 520w, 455w, 405w. Mass spectrum (EI^+) (m/e) 205.86 (81.32), 159.92 (28.38), 127.97 (25.63), 101.98 (14.28), 100.97 (13.98), 77.91 (100.00), 74.98 (13.44), 49.99 (13.05), 45.95 (22.56). Calc. for $[NC.C_6H_4.CNSSN]Cl$; C, 39.75%; H, 1.66%; N, 17.39%. Obs. C, 39.11%, H, 1.71%, N, 17.20%.

4.4.1.2 Preparation of *m*-[NC.C_6H_4.CNSSN]Cl

Li[N($SiMe_3$)$_2$] (13.0 g, 0.078 mol) and 1,3-$C_6H_4(CN)_2$ (10.0 g, 0.078 mol) were stirred in Et_2O (40 ml) at room temperature for 18 hours and then pumped to dryness to provide an off-white solid. This solid was slowly added to an ice-cooled solution of SCl_2 (9 ml, 0.14 mol) in CH_2Cl_2 (50 ml) to form an immediate orange precipitate which was filtered off and pumped to dryness. The crude product was then extracted exhaustively with SO_2 and washed liberally with CH_2Cl_2. Yield 13.1 g, 70%. I.R. ν_{max} (cm^{-1}): 2232m, 1670m, 1307m, 1234m, 1206m, 1177m, 1136m, 1092m, 1000m, 969m, 910m, 895 s sh, 890s, 857s, 850m, 816s, 796m, 720 sh m, 716vs, 680m, 590m sh, 583m, 565m, 535m, 515w, 473w, 457w, 414w, 388w, 315m, 310w sh, 297w. Calc. for [NC.C_6H_4.CNSSN]Cl; C, 39.75%; H, 1.66%; N, 17.39%. Obs. C, 39.53%, H, 1.61%, N, 16.91%.

4.4.1.3 Preparation of *p*-[(NC).C_6H_4.CNSSN][AsF_6]

p-[NC.C_6H_4.CNSSN]Cl (1.21 g, 5.0 mmol) and $AgAsF_6$ (1.50 g, 5.1 mmol) were placed in one limb of a two-limbed reaction vessel and *l.* SO_2 condensed on. The reagents were stirred for 16 h at room temperature during which time a yellow-white precipitate formed under a yellow solution. The soluble material was filtered off and the residues washed with back-condensed *l.* SO_2. Eight such operations were required to remove all of the yellow colouration to give a residual white powder and yellow product from the extractate (after solvent removal). Yield 1.78 g, 90%. I.R. ν_{max}(cm^{-1}) 2244s, 1653w sh, 1607m, 1507w, 1445m sh, 1399vs, 1377vs, 1342w sh, 1333w sh, 1300w, 1285m, 1204m, 1182m, 1161m, 1018m, 938w, 921m, 852m, 849m, 814m, 703vs, 688vs sh, 677vs br, 617w, 574vw sh, 562m, 553m, 542w sh, 524vw, 398vs. This analysed as $C_8N_3H_4S_2AsF_6$: Calc. C, 24.31%, H, 1.01%, N, 10.63%, As, 18.73%.Found. C, 24.30%, H, 1.24%, N, 10.60%, As, 18.64%

4.4.1.4 Preparation of *m*-[(NC).C_6H_4.CNSSN][AsF_6]

m-[NC.C_6H_4.CNSSN]Cl (1.21 g, 5.0 mmol) and $AgAsF_6$ (1.50 g, 5.1 mmol) were placed in one limb of a two-limbed reaction vessel and *l.* SO_2 condensed on. The reagents were stirred for 16 h at room temperature during which time a yellow-white precipitate formed under a yellow solution. The soluble material was filtered off and the residues washed with back-condensed *l.* SO_2. A dozen such operations were required to remove all of the yellow colouration to give a residual white powder and yellow product from the extractate (after solvent removal). Yield 1.90 g, 96%. I.R. ν_{max}(cm^{-1}) 2260s, 1685m, 1606m, 1585vw, 1444vs, 1394vs, 1329vs, 1315w sh, 1214m, 1181m, 1146m, 1095m, 1058m, 999vw, 983m, 965w, 928m, 918m, 861m, 820m sh, 813m, 810w sh, 798m, 696m sh, 677vs br, 588m, 567m, 552m, 507vw, 480w, 462w, 398vs. This analysed as $C_8N_3H_4S_2AsF_6$: Calc. C, 24.31%, H, 1.01%, N, 10.63%, As, 18.73%.Found. C, 24.22%, H, 1.27%, N, 10.51%, As, 18.88%

4.4.2 Mixed salts

Preparation of *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$

[SNS]AsF_6 (0.680 g, 2.5 mmol) and *p*-[(NC).C_6H_4.CNSSN]AsF_6 (1 g, 2.5 mmol) were placed in one limb of a two-limbed reaction vessel and *l.* SO_2 condensed on. The reagents were stirred at room temperature for 18 hours during which time a pale yellow precipitate formed under a red solution. The soluble material was filtered off and the product washed with back-condensed SO_2 and then washed further with CH_2Cl_2. Yield 1.63 g, 97%. I.R. ν_{max}(cm^{-1}) : 1518m, 1400s, 1302w, 1205w, 1162m, 1020w, 990s, 922s, 888w, 852s, 845m, 832w, 800s, 749m, 700vs, 670s, 630w, 590w, 560w, 440w, 400s. Calc. for [SNSNC.C_6H_4.CNSSN][AsF_6]$_2$; C, 14.51%; N, 8.45%; H, 0.60%; As, 22.63%. Obs. C, 14.54%; N, 8.50%; H, 0.64%; As, 22.74%.

4.4.2.2 Preparation of *m*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$

[SNS]AsF_6 (0.554 g, 0.2 mmol) and *m*-[(NC).C_6H_4.CNSSN]AsF_6 (0.790 g, 0.2 mmol) were placed in one limb of a two-limbed reaction vessel and *l.* SO_2 condensed on. The reagents were stirred at room temperature for 18 hours during which time a pale yellow precipitate formed under a red solution. The soluble material was filtered off and the product washed with back-condensed SO_2 and then washed further with CH_2Cl_2. Yield 1.240 g, 94%. I.R. ν_{max}(cm^{-1}): 1772w, 1689m, 1654w, 1607m, 1582w, 1488m sh, 1410m sh, 1393vs, 1332w sh, 1301w sh, 1219m, 1181w, 1149m, 1118vw, 1094vw, 1030vw, 1009m, 998vw sh, 983w sh, 970m, 926m, 919m sh, 894m sh, 885m, 861w, 849m, 823m, 814m, 799s, 701vs br, 676m sh, 640m sh, 586m, 578m, 562m, 527vw, 455vw, 436w, 398vs br. Calc. for [SNSNC.C_6H_4.CNSSN][AsF_6]$_2$; C, 14.51%; N, 8.45%; H, 0.60%; As, 22.63%. Obs. C, 14.88%; N, 8.44%; H, 0.71%; As, 22.68%.

4.4.3 Derivatives of the mixed salts

4.4.3.1 Preparation of *p*-[SNSNC.C_6H_4.CNSSN]Cl_2

p-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ (1.00 g, 1.5 mmol) and $(Bu^t)_4NCl$ (1.00 g, 3.4 mmol) were placed in one limb of a two-limbed reaction vessel and acetonitrile (5 ml) added against a counter-flow of nitrogen. The mixture was stirred for 18 h during which time a pale orange solid formed under an orange-yellow solution. The soluble material was filtered off and the orange, residual product washed three times with back-condensed acetonitrile to yield a fine orange powder. Yield 0.500 g, 93%). I.R. $\nu_{max}(cm^{-1})$: 1682w, 1599vw, 1528vw, 1509w, 1428m, 1388vs, 1300m, 1214w, 1154w, 1120m, 1015m, 978m, 923m, 891m, 852m, 780w, 745m, 723w, 701w, 685m, 668w, 621w, 579w, 545w, 421m. Mass spectrum (EI+) (m/e): 283.69 (45.88), 237.75 (19.12), 205.81 (77.55), 159.87 (27.14), 127.92 (57.82), 101.95 (18.05), 100.94 (20.83), 77.88 (100.00), 63.89 (46.84), 49.97 (19.12), 45.94 (25.49). Calc. for *m*-$[SNSNC.C_6H_4.CNSSN]Cl_2$ C, 27.04%; H, 1.13%; N, 15.77%. Obs. C, 26.48%, H, 1.83%, N, 13.29%.

4.4.3.2 Preparation of *m*-$[SNSNC.C_6H_4.CNSSN]Cl_2$

m-$[SNSNC.C_6H_4.CNSSN][AsF_6]_2$ (0.675 g, 1.02 mmol) and $(Bu^t)_4NCl$ (0.670 g, 2.41 mmol) were placed in one limb of a two-limbed reaction vessel and acetonitrile (5 ml) added against a counter-flow of nitrogen. The mixture was stirred for 18 h during which time a pale orange solid formed under an orange-yellow solution. The soluble material was filtered off and the orange, residual product washed three times with back-condensed acetonitrile to yield a fine orange powder. Yield 0.300 g, 83%. I.R. $\nu_{max}(cm^{-1})$: 1680m, 1510vs br, 1420m, 1295m, 1220m, 1145w, 1090m, 1000m, 948m, 905m sh, 985m, 875m, 850m, 820m, 792m, 715vs, 675m, 652w, 627m, 576m sh, 572m, 551m, 420m br. Mass spectrum (EI+) (m/e): 283.69 (45.88), 237.75 (19.12), 205.81 (77.55), 159.87 (27.14), 127.92 (57.82), 101.95 (18.05), 100.94 (20.83), 77.88 (100.00), 63.89 (46.84), 49.97 (19.12), 45.94 (25.49). Calc. for *m*-$[SNSNC.C_6H_4.CNSSN]Cl_2$ C, 27.04%; H, 1.13%; N, 15.77%. Obs. C, 27.37%, H, 1.49%, N, 15.74%.

4.4.3.3 Attempted Preparation of *p*-$[SNSNC.C_6H_4.CNSSN][AsF_6]Cl$ by the reaction of $SNSAsF_6$ with *p*-$[(NC).C_6H_4.CNSSN]Cl$

p-$[(NC).C_6H_4.CNSSN]Cl$ (0.242 g, 1 mmol) and $SNSAsF_6$ (0.269 g, 1 mmol) were placed in on limb of a two-limbed reaction vessel and SO_2 condensed on. There was an immediate colour change to deep red-brown and after stirring for 16 h at room temperature a red-green dichroic solution and solid remained. Filtration followed by solvent removal gave a residual red-green solid (70 mg) and from the soluble material an orange solid (310 mg). The IR of red-green solid suggested $[S_3N_2][AsF_6]$, $\nu_{max}(cm^{-1})$: 1030vw, 955m, 940m, 845w, 800vw, 700m, 580m, 550w sh, 435w, 400w, 375s.

[An analogous reaction was conducted using the *meta* isomer and very similar results obtained.]

4.4.3.4 Attempted Preparation of *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]Cl by the metathesis of *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ with one equivalent of Bu_4NCl

p-[SNSNC.C_6H_4.CNSSN][AsF_6]$_2$ (0.331 g, 0.5 mmol) and Bu_4NCl (0.139 g, 0.5 mmol) were placed in one limb of a two-limbed vessel and MeCN (6 ml) syringed on against a counter-flow of nitrogen. After 16 h stirring there remained a residual, pale orange solid, which was washed with CH_2Cl_2 to remove pale yellow Bu_4NAsF_6 from the orange powder (80 mg). This analysed well as *p*-[SNSNC.C_6H_4.CNSSN][AsF_6]$_{0.5}$[Cl]$_{1.5}$: Calc. for C, 22.40%; H, 0.93%; N, 12.97%. Obs. C, 21.89%, H, 1.05%, N, 13.12%.

4.4.3.5 Attempted Preparation of *m*-[SNSNC.C_6H_4.CNSSN]$^{+\circ}$[AsF_6] by the reduction of *m*-[SNSNC.C_6H_4.CNSSN][AsF_6]Cl

m-[SNSNC.C_6H_4.CNSSN]Cl_2 (0.080 g, 0.23 mmol) and $AgAsF_6$ (0.067 g, 0.23 mmol) were placed in one limb of a two-limbed reaction vessel and liquid SO_2 condensed on. The reaction mixture was stirred for 16 h at room temperature to yield a pale pink solid under an orange solution. Repeated filtration and back condensation afforded a pale yellow sticky solid after solvent removal from the filtrate. Several solvents were used in an attempt to obtain this material as a workable solid but none gave good results so Ph_3Sb (50 mg, 0.014 mmol) was added directly and CH_2Cl_2 syringed on. This mixture gave a red-brown insoluble solid (35 mg, 32%) almost immediately, the esr signal (in MeCN at RT) of which was a 1:1:1 triplet indicative of a 1,3,2,5-dithiadiazolyl. An attempt at recrystallisation (from MeCN) failed as the material decomposed upon warming.

4.4.3.6 Attempted Preparation of *p*-[SNSNC.C_6H_4.CNSSN]$^{+\circ}$[AsF_6] by the reaction of $SNSAsF_6$ with *p*-[NSSNC.C_6H_4.CN]

p-[NSSNC.C_6H_4.CN] (65 mg, 0.3 mmol) and $SNSAsF_6$ (75 mg, 0.3 mmol) were placed together in one limb of a two-limbed reaction vessel and liquid SO_2 was condensed onto them at liquid nitrogen temperature. An immediate deep orange-red colour was observed and this gave way after 16 h stirring as a deep green-brown solid precipitate formed. A pale yellow insoluble material (85 mg) remained after solvent removal and washing with CH_2Cl_2 (4x5 ml). The red soluble material gave up an oily red-orange material (15 mg) upon solvent removal *in vacuo*. The yellow solid was identified as *p*-[NSSNC.C_6H_4.CN][AsF_6] by IR, ν_{max} (cm^{-1}): 2255m, 1690m, 1560s sh, 1405s, 1290w, 1188vw, 1168m, 1045vw, 1020w, 926m, 860sh m, 852m, 805w, 742m, 700vs br, 565w, 550w, 500w, 399vs, 332vw, 298vw br.

The red-orange needles were identifed as mainly S_4N_4 by their IR, ν_{max} (cm^{-1}) 928s, 728m, 700s, 690m sh, 550s, 542m.

4.4.3.7 Preparation of *p*-$[SNSNC.C_6H_4.CNSSN][Br]_2$

p-$[SNSNC.C_6H_4.CNSSN][AsF_6]_2$ (100 mg ,0.15 mmol) and Bu_4NBr (100 mg, 0.30 mmol) were stirred together in MeCN (8 ml). An immediate deep red-brown colouration was observed and after 16 h there remained a deep crimson solid under an orange solution. Filtration and back washing with MeCN (3x8 ml) gave a deep crimson residual solid. A small quantity of a brown oil was removed from the red-brown residual powder by continuous extraction with CH_2Cl_2. Yield 55 mg, 83%. I.R. ν_{max} (cm^{-1}): 1673m, 1598w, 1559w, 1505m, 1301m, 1242w, 1212w, 1151s, 1117m, 1087m, 1013m, 975s, 921m, 886m, 850m br, 824w, 772m, 741m, 723m, 683m, 667w, 619m, 578m, 542m, 468w, 453vw, 431vw, 416m. Mass spectrum (m/e in CI$^+$): 284.8 (2.41) (parent ion), 223.9 (1.17), 205.84 (1.95), 146.0 (12.62) (1,4-dicyanobenzene + NH_4), 77.9 (1.95), 52.1 (1.17).

Calc. for $[SNSNC.C_6H_4.CNSSN][Br]_2$: C, 21.74%; H, 1.00%; N, 12.68%. Found C, 21.72%; H, 1.06%; N, 12.68%. (averaged values.)

4.4.3.8 Preparation of *p*-$[SNSNC.C_6H_4.CNSSN][F_3CSO_3]_2$

p-$[SNSNC.C_6H_4.CNSSN]Cl_2$ (72 mg, 0.2 mmol) and $Ag[F_3CSO_3]$ (104 mg, 0.4 mmol) were placed together in one limb of a two-limbed reaction vessel and liquid SO_2 was condensed onto them at liquid nitrogen temperature. An immediate deep orange colour was observed and the solution stirred for 16 h, during which time a floculent white precipitate appeared. Repeated filtration and back condensation of liquid SO_2 removed only a little of the pale yellow product so the solvent was removed and CH_3CN (5 ml) added. Further back-extractions (x3) removed all of the yellow colouration from the residual white powder and a subsequent wash with CH_2Cl_2 was required to remove a slight oilyness from the bright yellow powder Yield 60 mg, 51% I.R. ν_{max} (cm^{-1}): 1697m, 1518m, 1462vs, 1396s, 1377vs, 1261s, 1235s br, 1221s, 1170m, 1021s, 987m, 922w, 891w, 851w, 800w, 761w, 748w, 722m, 687w, 669vw, 637m, 574m, 557vw, 517m, 435w, 412vw.

Mass spectra showed only dicyanobenzene (m/e = 146 in EI$^+$) and S_4 (m/e = 128 in EI$^+$).

4.4.4 Reduction products

4.4.4.1 Preparation of p-[SNSNC.C_6H_4.CNSSN]

p-[SNSNC.C_6H_4.CNSSN]Cl_2 (300 mg, 0.85 mmol) and Ph_3Sb (300 mg, 0.85 mmol) were placed in one limb of a two limbed reaction vessel and CH_2Cl_2 (5 ml) added. The mixture was stirred in the dark for 16 h, filtered and the grey-green product washed with back condensed CH_2Cl_2 (3x5 ml). Yield 210 mg, 78%. I.R. ν_{max} (cm^{-1}):1516m, 1413s, 1099s, 937m, 903w, 851w, 833w, 804m, 782m, 723m, 648w, 594w, 510m, 460m. Calc. for [SNSNC.C_6H_4.CNSSN]: C, 33.80%; H, 1.41%; N, 19.72%. Found C, 33.56%; H, 1.48%; N, 19.90%.

4.4.4.2 Preparation of p-[SNSNC.C_6H_4.CNSSN] Cl

p-[SNSNC.C_6H_4.CNSSN]Cl_2 (375 mg, 1.1 mmol) and Ph_3Sb (186 mg, 0.5 mmol) were placed in one limb of a two limbed reaction vessel and CH_2Cl_2 (5 ml) added. The mixture was stirred in the dark for 2 h, filtered and the grey-green product washed with back condensed CH_2Cl_2 (4x5 ml). Yield 300 mg, 89%. I.R. ν_{max} (cm^{-1}): 1772w, 1689m, 1654w, 1607m, 1582w, 1488m sh, 1410m sh, 1393vs, 1332w sh, 1301w sh, 1219m, 1181w, 1149m, 1118vw, 1094vw, 1030vw, 1009m, 998vw sh, 984m sh, 885m, 861w, 849m, 823m, 814m, 799s, 701s br, 676m sh, 640m sh, 586m, 562m, 527vw, 455vw, 436w, 398vs br. Calc. for [SNSNC.C_6H_4.CNSSN]Cl : 30.05%C, 1.25%H, 17.53%N. Found: 30.48%C, 1.55%H, 17.65%N.

4.4.4.3 Preparation of m-[SNSNC.C_6H_4.CNSSN]

p-[SNSNC.C_6H_4.CNSSN]Cl_2 (35 mg, 0.1 mmol) and Ph_3Sb (35 mg, 0.1 mmol) were placed in one limb of a two limbed reaction vessel and MeCN (5 ml) added. The mixture was stirred in the dark for 2 h, filtered and the purple-black product washed with back condensed MeCN (4x5 ml). Yield 12 mg, 43%. I.R. ν_{max} (cm^{-1}): 1679s br, 1503m, 1409vs, 1286m, 1233s, 1202s, 1102s, 1020s, 896w, 849w, 830w, 804m, 797m, 785m, 722s, 708m, 693m, 680m, 615w, 602vw, 513vw, 456vw, 413vw. (Found C, 29.65%; H, 2.29%; N, 16.14%.Calc. C, 33.80%; H, 1.41%; N, 19.72%.)

4.4.4.4 Preparation of m-[SNSNC.C_6H_4.CNSSN] Cl

m-[SNSNC.C_6H_4.CNSSN]Cl_2 (75 mg, 0.2 mmol) and Ph_3Sb (37 mg, 0.1 mmol) were placed in one limb of a two limbed reaction vessel and MeCN (5 ml) added. The mixture was stirred in the dark for 1 h, filtered and the purple product washed with back condensed MeCN (4x5 ml). Yield 52 mg, 77%. I.R. ν_{max} (cm^{-1}):1516m, 1413s, 1099s, 937m, 903w, 851w, 833w, 804m, 782m, 723m, 648w, 594w, 510m, 460m. Calc. for [SNSNC.C_6H_4.CNSSN]Cl : 30.05%C, 1.25%H, 17.53%N. Found: 30.04%C, 1.92%H, 17.52%N.

4.4.4.5 Preparation of *p*-[NSSNC.C_6H_4.CN]

p-[NSSNC.C_6H_4.CN]Cl (1.00 g, 4.1 mmol) and Ph_3Sb (0.73g ,2.1 mmol) were placed in a Schlenk and MeCN (15 ml) added. The mixture was stirred for 16 h, filtered and the maroon product washed with MeCN (4x5 ml). Yield 780 mg, 91%. I.R. ν_{max} (cm^{-1}) 2222s, 1605s, 1438s sh, 1415s, 1362vs, 1310m, 1262s, 1195w sh, 1188m, 1170s, 1135s, 1103m, 1015m, 998w, 905w, 890vw, 848vs, 832vs, 816s, 788vs, 747w, 728m, 680w, 647m, 642m sh, 532s, 500s, 440m, 430m, 390m. Calc. for [NC.C_6H_4.CNSSN] : 46.59%C, 1.95%H, 20.37%N. Found: 46.90%C, 1.90%H, 20.01%N

4.4.4.5 Preparation of *m*-[NSSNC.C_6H_4.CN]

m-[NSSNC.C_6H_4.CN]Cl (1.00 g, 4.1 mmol) and Ph_3Sb (0.73 g, 2.1 mmol) were placed in a Schlenk and MeCN (15 ml) added. The mixture was stirred for 16 h, filtered and the deep purple product washed with MeCN (4x5 ml). Yield 740 mg, 87%. I.R. ν_{max} (cm^{-1}) 2230s, 1438s sh, 1365s sh 1315m, 1298m, 1264m, 1208m, 1202m, 1180m, 1172m, 1130m, 1120m, 1102m, 1098m sh, 1022w, 1000w, 990w, 955m, 938m, 930w, 918w, 905s, 842vs, 840m sh, 814vw, 809vs, 795vs, 777vs br, 750w, 735m, 727m sh, 700w sh, 687vs, 673w, 669w, 570s, 562s, 512s, 480m, 455m, 445m, 390vw, 385vw. Calc. for [NC.C_6H_4.CNSSN]: 46.59%C, 1.95%H, 20.37%N. Found: 47.00%C, 1.98%H, 20.21%N

4.5 References

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Chapter 5

The preparation and characterisation of the first dithia / diselenadiazolylium salts and their reduction products

5.1 Introduction

The rationale behind the study of dithiadiazolylium salts has already been outlined in several of the preceding chapters, with particular emphasis on multi-dithiadiazolylium species; for example, the 1,3,2,4-isomers in chapter 3 and the so-called mixed 1,2,3,5- / 1,3,2,4- dithiadiazolyliums in chapter 4.

Oakley and co-workers have recently developed the syntheses of diselenadiazolyl / ium derivatives, containing one[1] and two[2] cationic or radical centres. This has resulted in the preparation of multi-radicals with semi-conducting properties[2a], the room temperature resistivity of p-$[(NSeSeNC)_2C_6H_4]^{\circ\circ}$ is quoted as ca. 100 Ωcm. These selenium based materials have more diffuse d-orbitals available for intermolecular, intra-stack interactions than their sulphur analogues, thereby leading to greater dimensionality and so potentially more interesting solid-state properties.

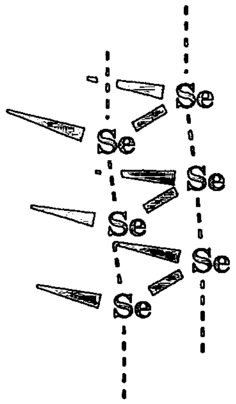


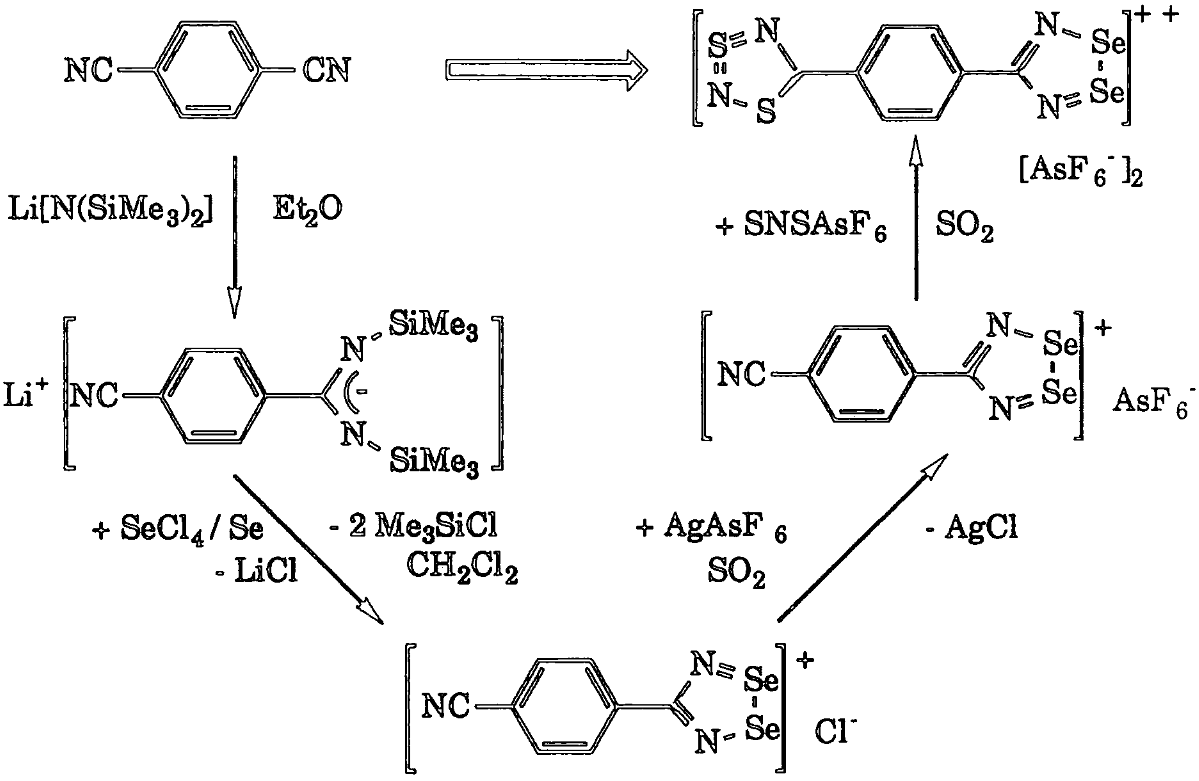
Figure 5.1

Potential
Infinite Intrastack
Interactions
In Diselenadiazolyls

However, the desired overlap of 1,2,3,5-dithia / diselenadiazolyl radicals, with co-facial CNEEN rings (E=S or Se) forming infinite chains of interacting radicals (as in figure 5.1), has yet to be achieved, although the cyanophenylene substituted diselenadiazolyls[3] come close to this type of structure (see figure 7.2 for examples).

The reactions of $[SNS][AsF_6]$ with cyanophenylene-substituted 1,2,3,5- dithiadiazolyliums outlined in the previous chapter, and the analogous methods used by Oakley and co-workers to prepare the cyanophenylene substituted 1,2,3,5- diselenadiazolyliums[3], suggested that the corresponding mixed phenylene bridged 1,2,3,5-diselenadiazolylium / 1,3,2,4-dithiadiazolylium salts might be prepared by an analogous route (see scheme 5.1). This chapter describes preliminary investigations into that route.

The very promising magnetisation data obtained from the radical cation salts of the sulphur analogues adds further urgency to the study of these mixed sulphur / selenium dications and their reduction products. The electronic, magnetic and structural properties of this new family of compounds were therefore investigated, and they form the other main topic of this chapter.



Scheme 5.1 Synthesis of the mixed 1,2,3,5 / 1,3,2,4 - diselena / dithiadiazolylium salts.

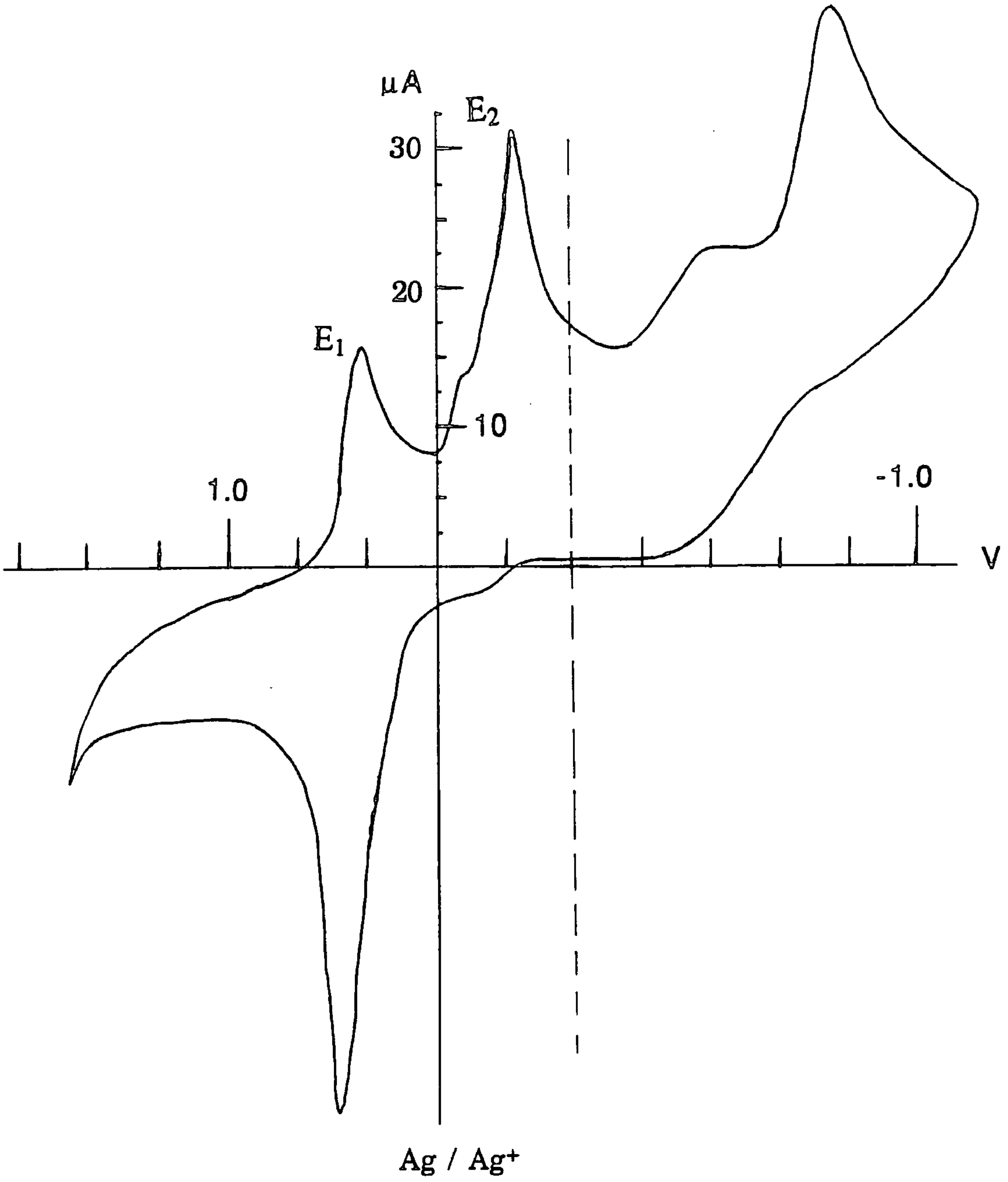
5.2 Results and Discussion

5.2.1 General Reactivity

Although the preparation of the parent cation, [*p*-(NC).C_6H_4.CNSeSeN]Cl, was straightforward with no significant deviation from the methods employed in the syntheses of cyanophenyl dithiadiazolyliums (as outlined in chapter 4), the subsequent metathesis with silver hexafluoroarsenate(V) was problematic. This difficulty was probably due to the lability of the N-Se bonds in the diselenadiazolylium ring and to the affinity of silver cations for selenium. These factors may have resulted in the loss of silver selenide (in spite of the low solubility of AgCl in liquid SO_2) and the breakdown of the product. Several attempts were made to reduce the levels of an oily brown contaminant in this product, by using shorter reaction times and washing with CH_2Cl_2. However, no significant improvement in yield or product quality could be achieved.

The subsequent reaction with [SNS][AsF_6] was relatively clean and high yielding, giving a good quality product in the space of a few hours.

Figure 5.2 Cyclic voltammogram of *p*-[SNSNC.C_6H_4.CNSeSeN][AsF_6]$_2$ in MeCN at -13C with [NBu_4][BF_4] supporting electrolyte. $E_{red}(1)$= +0.705 V, $E_{red}(2)$= +0.245 V, *vs.* standard saturated calomel electrode



5.2.2 Reduction products

5.2.2.1 Cyclic voltammetry

In acetonitrile solution at -13°C with $[Bu_4N]BF_4$ as supporting electrolyte, two discrete, reversible reduction peaks were observed for $[SNSNC.C_6H_4.CNSeSeN][AsF_6]_2$. This voltammogram is shown in figure 5.2.

The 1,2,3,5-diselenadiazolylium ring is reduced first, $E_{1/2}$= +0.70V relative to the S.S.C.E.. The comparable value of +0.595 V obtained for the sulphur analogue in chapter 4 (see fig 4.5) is somewhat lower.

The second reduction is, again, at a relatively low potential, $E_{1/2}$= +0.25V, compared with the sulphur analogue (+0.30V) and those of other para-substituted phenylene dithiadiazolyliums, $X.C_6H_4.CNSSN$, X=Me $E_{1/2}$= 0.30V, X=F $E_{1/2}$= 0.34V[4] . Both of these reductions are reversible and therefore, as in the case of the mixed 1,2 / 1,3 sulphur dications (chapter 4), there is no electronic coupling between the rings. So both the diradical and radical cation should be isolable.

In addition to the two reduction bands expected for this system there is a shoulder evident on the second reduction peak. This may be due to the presence of a trace quantity of $[SNSNC.C_6H_4.CNSNS]^{2+}$, which could arise from any dicyanobenzene remaining in the *p*-$[(NC).C_6H_4.CNSeSeN]$ when it reacts with $[SNS][AsF_6]$. The anomalous esr data outlined below could be explained in this way also.

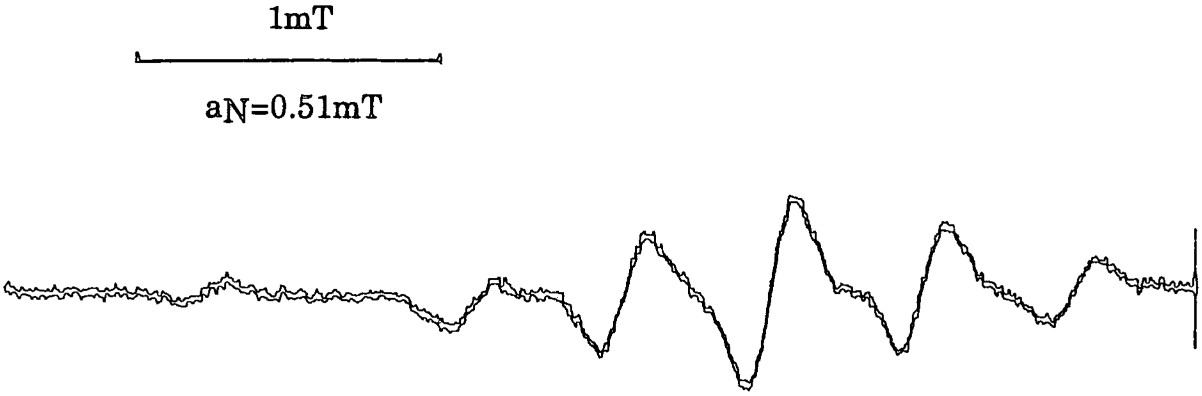
A similar study of the material obtained from photolysis of the mixed diradical, $[NSeSeNC.C_6H_4.CNSNS]^{\circ\circ}$, proved to be inconclusive. Only a broad shoulder was visible in the C.V. of $[Se_2N_2C.C_6H_4.CN_2S_2][Br_3]_2$; this was probably due to the insolubility of the tribromide salt in acetonitrile.

5.2.2.2 Electron spin resonance

Electron spin resonance spectra for the reduction products of the $[SNSNC.C_6H_4.CNSeSeN]^{2+}$ dication depended highly upon solvent. In toluene (fig. 5.3) a weak 1:1:1 triplet was just visible together with a more discernable 1:2:3:2:1 pentet when the dichloride was reduced with an excess of triphenylantimony. Neither heating nor cooling resolved this ambiguity and the poor solubility of the radicals limited the quality of the spectra obtained.

In acetonitrile a very strong triplet was seen, with a rather weak pentet just visible underneath (fig. 5.4). No rearrangement was observed, even with heating or in samples exposed to bright sunlight for several hours.

Figure 5.3 Esr spectrum of p-[SNSNC.C$_6$H$_4$.CNSeSeN]Cl$_2$ in toluene with an excess of Ph$_3$Sb



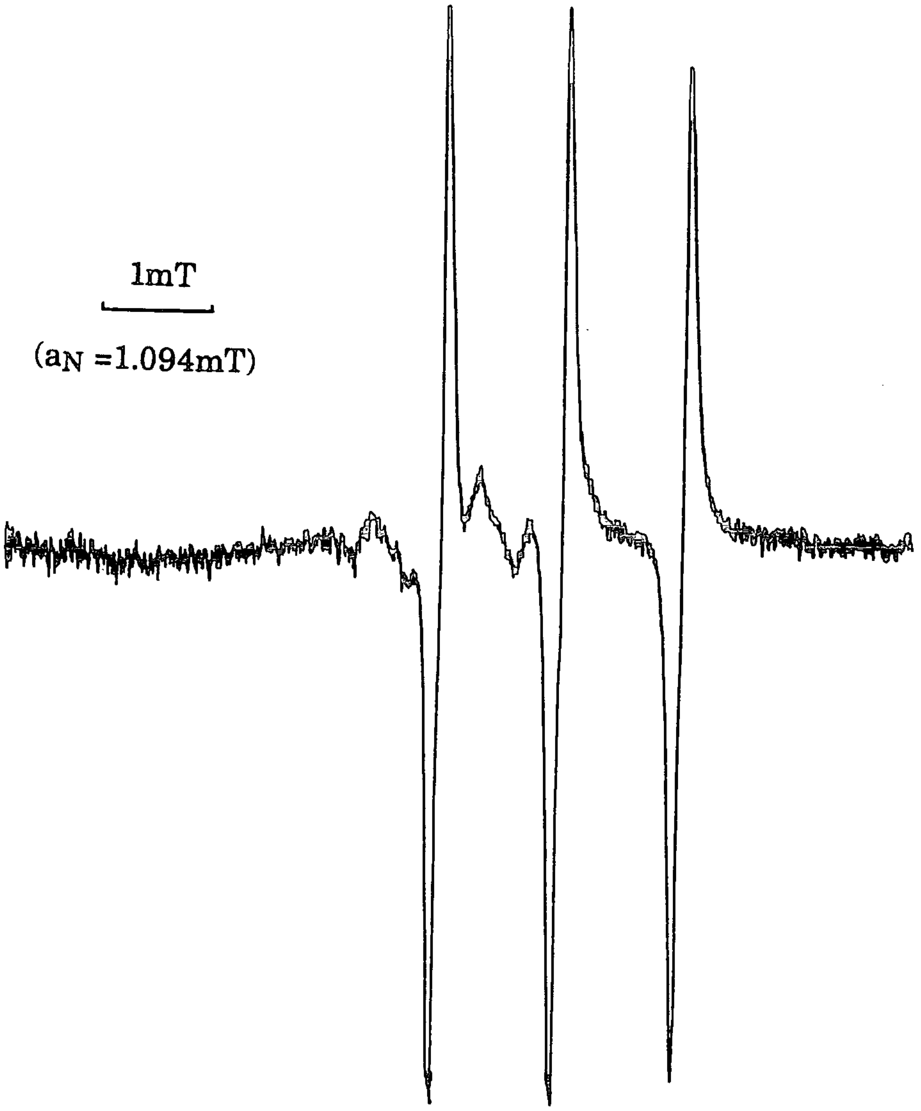


Figure 5.4 Esr spectrum of *p*-[SNSNC.C_6H_4.CNSeSeN]Cl_2 in acetonitrile with an excess of Ph_3Sb

This apparent absence of rearrangement may be due to the very low solubility of the reduction products; in dilute solution the diradicals may not be able to get close enough to each other in order to undergo the bi-molecular rearrangement seen in other 1,3,2,4-dithiadiazolyls (see section 3.2.3).

This solvent dependency could be explained by association of the diselenadiazolyl radicals in solution, as shown in figure 5.5. If such association were to occur then the esr spectrum of the diradical would show only the 1:1:1 triplet due to the free 1,3,2,4-dithiadiazolyl radicals.

Furthermore, the pentet, which should be of the same order of magnitude as any triplet for the radical cation as well as the diradical, is far weaker than the triplet in acetonitrile solution. Association of diradicals should be more pronounced for the selenium isomer than for its sulphur analogue, as the selenium d-orbitals are more diffuse and so allow for greater inter molecular overlap.

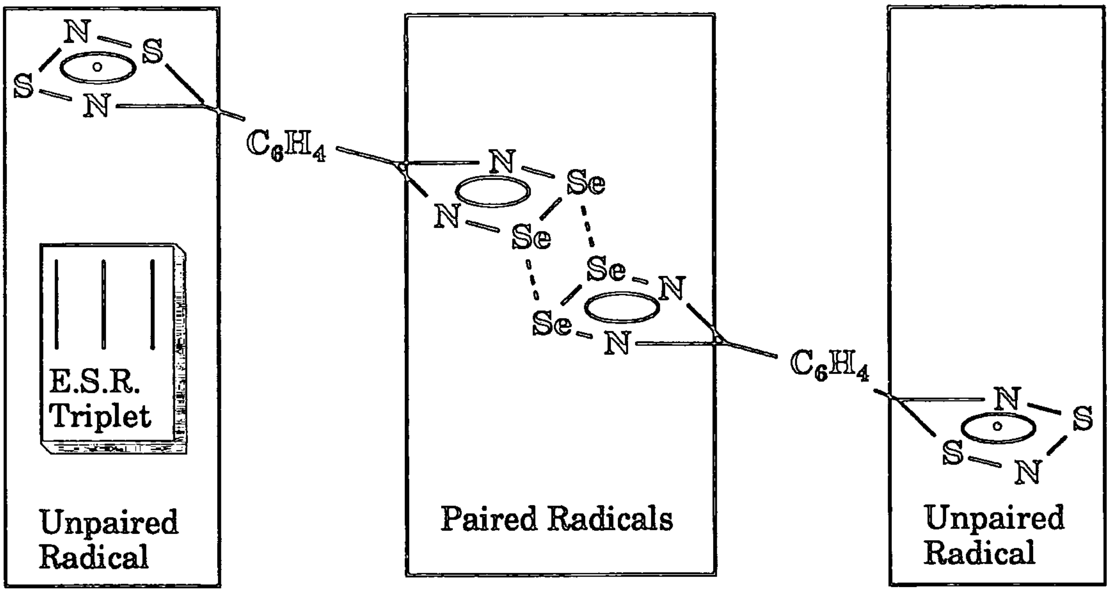


Figure 5.5 Esr triplet observed for associated diradicals in solution.

In toluene, a far less coordinating solvent, the diradical is much less soluble and so only the pentet associated with the radical cation is observed.

An alternative explanation is that the strong triplet observed in acetonitrile solution may be due to the reaction of $[SNS][AsF_6]$ with a trace quantity of dicyanobenzene contaminating the $[NC.C_6H_4.CNSeSeN][AsF_6]$. The contaminant would give, $[SNSNC.C_6H_4.CNSNS]^{\circ\circ}$, a known[5] compound, which is much more soluble in acetonitrile[6] than the mixed selenium / sulphur analogue; a very small amount would give a relatively strong esr triplet.

The dication prepared by the [SNS][AsF_6] reaction was shown, by IR and elemental analysis, to be highly pure and only a pentet was observed in the esr spectrum of the reduction product of [NSeSeN.C_6H_4.CNSNS]Cl_2 in toluene, which indicates that there was very little [SNSNC.C_6H_4.CNSNS]$^{\circ\circ}$ solublised. It should be noted, however, that [SNSNC.C_6H_4.CNSNS] is far less soluble[6] in toluene than it is in acetonitrile. The lack of an esr triplet does not, of necessity, imply that no [SNSNC.C_6H_4.CNSNS] was present. Furthermore, less than 1% of impurity would account for the esr and CV data obtained, so the presence of [SNSNC.C_6H_4.CNSNS]$^{2+}$ seems to be the most likely explanation for these apparently anomalous results.

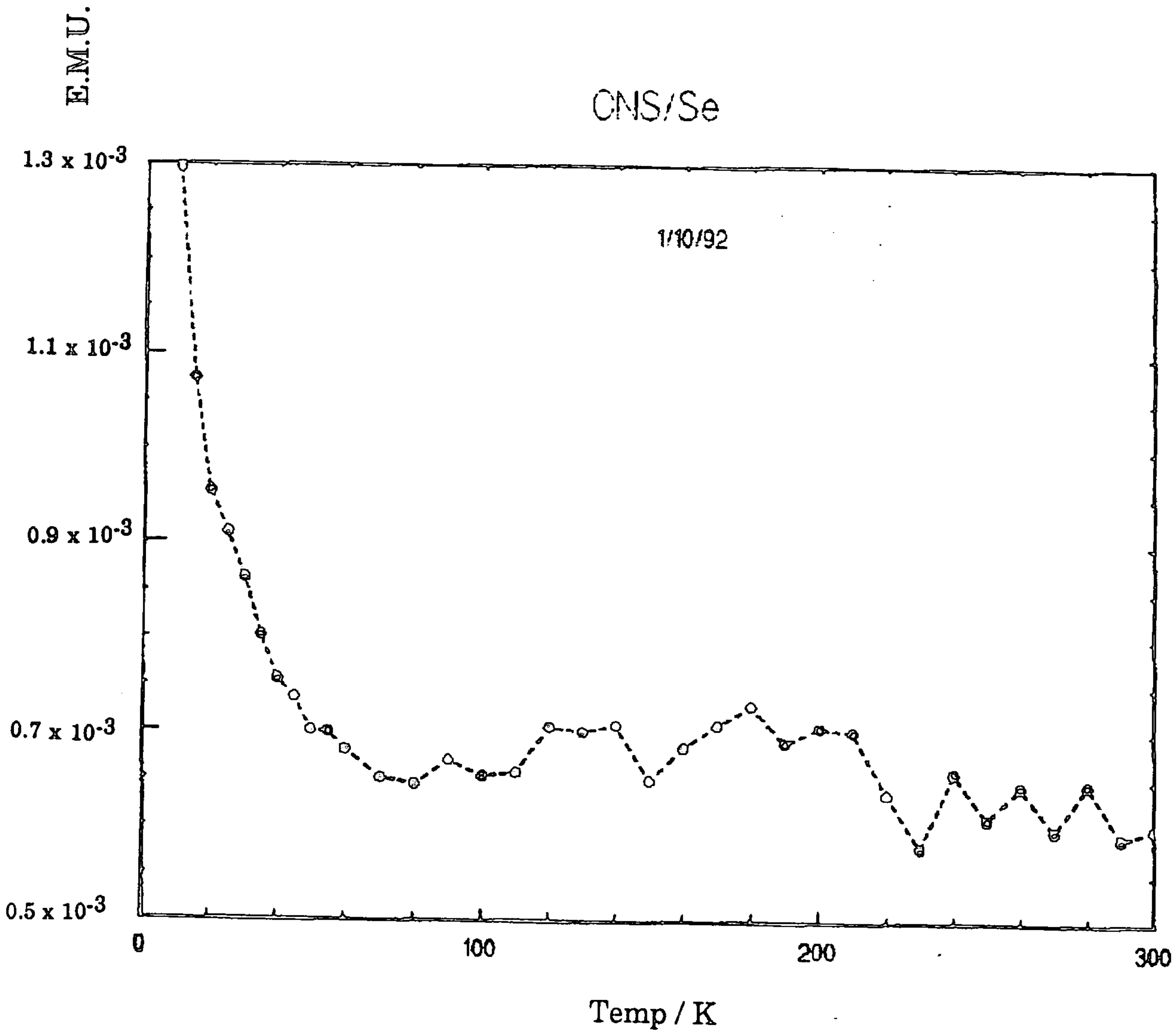
5.2.2.3 Magnetisation studies

Preliminary Gouy balance data for these reduced species suggested similar behaviour to that of the sulphur systems, as outlined in chapter 4, with a diamagnetic response for the diradical and a paramagnetic response for the chloride salt of the radical cation.

Very recently, preliminary variable-temperature magnetisation data have become available for the radical cation and these also suggest behaviour similar to that of the sulphur system. At low temperatures a paramagnetic response is clearly visible but the measurements are less reliable above 100 K and so Curie-Weiss behaviour cannot, as yet, be accurately established. It should also be noted that a diamagnetic response, albeit with a small increase in magnetisation at very low temperatures, was obtained for a sample of the radical cation that had been standing for a week before measurements were made. This emphasises the increased moisture sensitivity of the selenium / sulphur system compared to the sulphur / sulphur analogue.

It can be seen, therefore, that the current magnetisation data cannot definitely confirm the expected magnetic properties of the selenium based system and cannot help us to draw any parallels in moving from sulphur to selenium. Further measurements need to be made in order to verify these magnetic properties and to determine whether the increased potential of selenium atoms for inter molecular interactions does improve the magnetic properties of the selenium containing system.

Figure 5.6 The magnetic properties of *p*-[SNSNC.C_6H_4.CNSeSeN]Cl



5.2.2.4 Preparative reductions

Both the radical cation, $[NSeSeNC.C_6H_4.CNSSN]Cl$, and the diradical, $[NSeSeNC.C_6H_4.CNSSN]$, were obtained as highly moisture sensitive solids, in moderate yield (60-80%), by reduction of the dichloride salt using half or one equivalent of triphenylantimony in CH_2Cl_2 solution.

5.2.2.5 Attempted photolytic rearrangement of $[NSeSeNC.C_6H_4.CSNSN]$ to $[NSeSeNC.C_6H_4.CNSSN]$

The esr evidence (i.e. a lack of thermal or photolytic isomerisation of $[NSeSeNC.C_6H_4.CSNSN]$ in solution) seemed to suggest that the insolubility of the diradical may prevent a preparative-scale rearrangement. An initial attempt was made to obtain the rearranged product by UV photolysis in CH_2Cl_2 solution over a period of four days. However, characterisation of the products proved impossible, either by CV or esr (the two most accurate tests of the nature of the product) or by oxidation using AsF_5 followed by characterisation of the hexafluoroarsenate(V) salt. This aspect of the work is thus inconclusive. Elemental analysis of the tribromide salt, prepared by oxidation with bromine, did, however, suggest that the $[Se_2N_2C.C_6H_4.CN_2S_2]$ unit had remained in tact.

5.3 Conclusions and suggestions for further work

Evidence for the preparation of the first binary 1,3,2,4-dithia / 1,2,3,5-diselenadiazolyliums and their reduction products has been obtained by the use of CV, esr, IR and elemental analysis. The radical cations in particular seem to be of considerable interest as building blocks for the preparation of novel magnetic and electronic materials and therefore warrant further investigation. Further work on the esr and DSC of these radicals is required in order to study their rearrangement properties.

A more productive approach to the preparation of the mixed 1,2,3,5-dithia / 1,2,3,5-diselenadiazolyliums could either be by direct sublimation of the diradical (which should rearrange at the required temperature) or by photolysis of the radical cation (as it is more soluble).

The synthetic methodology applied to the *para*-dicyanobenzene system could well be used in the preparation of further interesting compounds e.g. derivatives of *sym*-$(NC)_3.C_6H_3$, *o*-$(NC)_2.C_6H$ or *m*-$(NC)_2.C_6H_4$.

5.4 Experimental

5.4.1 Preparation of [*p*-(NC).C_6H_4.CNSeSeN]Cl

p-$(NC)_2.C_6H_4$ (1.28 g, 0.01 mol) and $LiN(SiMe_3)_2$ (1.67 g, 0.01 mol) were stirred together in Et_2O (30 ml) for 18 hr and the solvent removed *in vacuo* to yield an off-white powder. This solid was scraped directly into an ice-cooled, stirred solution of selenium metal (0.79 g, 0.01 mol) and $SeCl_4$ (2.21 g, 0.01 mol) in CH_2Cl_2(40 ml). A rapid reaction occurred and stirring was continued for a further 16 h during which time a brownish orange solid was precipitated. This solid was filtered off under nitrogen, washed with CH_2Cl_2 (3 x 10 ml) and then pumped to dryness. Continuous extraction with liquid SO_2 freed the pale orange-brown product from any residual LiCl. A further extraction with CH_2Cl_2 removed a little reddish oily material and the residual brown solid (1.75 g, 52%) analysed well as the desired product. Found 12.81%N, 28.41%C, 1.13%H. Calc. 12.52%N, 28.63%C, 1.19%H.

IR ν_{max} (cm^{-1}): 2230s, 1665s br, 1465s sh, 1455s sh, 1420w br, 1345s br, 1305m, 1290m, 1190m sh, 1185m, 1115m, 1090w, 1042w, 1021m br, 850s, 840m sh, 818w sh, 782m, 768m, 731m sh, 672m, 610w, 568m, 549m, 532m, 438m, 402vw, 350w sh. Mass spectra: CI^+ (m/e): 302.7 (2.34) [(H_2NC).C_6H_4.CNSeSeN]H^+, 300.7 (2.01) [*p*-(NC).C_6H_4.CNSeSeN]H^+, 147.0 (4.37), 146.0 (44.97) [NC.C_6H_4.CN]NH_4^+. EI^+ (m/e): 301.27 (5.44), 299.7 (5.12), 171.7 (6.14), 159.7 (17.40), 157.7 (15.17), 128.0 (100), 74.9 (13.3), 50.0 (13.8)

5.4.2 Preparation of [*p*-(NC).C_6H_4.CNSeSeN][AsF_6]

[*p*-(NC).C_6H_4.CNSeSeN]Cl (0.770 g, 2.3 mmol) and $AgAsF_6$ (0.678 g, 2.3 mmol) were placed in one bulb of a two-limbed reaction vessel and liquid SO_2 (5 ml) was condensed onto the mixture. A yellow colouration was observed immediately and after stirring for 5 minutes a pale yellow solid / solution remained. After a further 5 minutes the solution produced a deep brown oily material. Repeated filtration and washing of the residual solids with back-condensed solvent (4 x 5 ml) removed a pale yellow solid and a highly soluble deep brown material from the residual white silver chloride. The deep brown impurity was removed by a single wash with very cold liquid SO_2 to leave a pale yellow powder (0.600 g, 50%). This analysed well as the desired product. Found 8.11%N, 19.24%C, 0.90%H. Calc. 8.58%N, 19.60%C, 0.82%H. IR ν_{max} (cm^{-1}): 2240m, 1690m, 1660m sh, 1465s sh, 1415m, 1378m, 1365m, 1349m, 1138m, 1020m, 870sh m, 856m, 804m, 769m, 702vs br, 543m, 512w, 431w, 398vs.

5.4.3 Preparation of *p*-[SNSNC.C_6H_4.CNSeSeN][AsF_6]$_2$

[*p*-(NC).C_6H_4.CNSeSeN][AsF_6] (0.310 g, 0.6 mmol) and [SNS][AsF_6] (0.170 g, 0.6 mmol) were placed in one bulb of a two-limbed reaction vessel and liquid SO_2 was condensed on at liquid nitrogen temperature. The mixture was stirred and allowed to warm to room temperature. Within 5 minutes all of the reagents has dissolved. After stirring for a further 18 h a yellow solid had precipitatated out. Solvent removal yielded a yellow powder which was washed with CH_2Cl_2 (5 ml) to remove a small quantity of pale brown soluble material. The residual pale yellow solid was dried *in vacuo*, yield 0.400g (83%). This analysed well as the desired product. Found 7.31%N, 12.70%C, 0.55%H. Calc. 7.41%N, 12.71%C, 0.53%H. IR ν_{max} (cm^{-1}): 1612m, 1510vs, 1426vs, 1408vs, 1366vs, 1319m, 1301m, 1222m, 1212m, 1143m, 1126m, 1074w br, 1019m, 989s, 967w, 917m, 890m, 870w, 858m, 837w, 804s, 797s, 780vw, 752m, 745m, 701vs br, 681vs sh, 676s sh, 662m sh, 637m, 621vw, 588m, 576m, 561m, 509vw, 450m, 440m, 404vs, 375vw, 348w.

5.4.4 Preparation of *p*-[SNSNC.C_6H_4.CNSeSeN]Cl_2

p-[SNSNC.C_6H_4.CNSeSeN][AsF_6]$_2$ (0.860 g, 1.1 mmol) and [Bu_4N]Cl (0.680 g, 2.5 mmol) were placed with a stirrer bar in one bulb of a two-limbed reaction vessel and acetonitrile (8 ml) was syringed onto the reactants against a counterflow of dry nitrogen. An immediate chocolate brown colour was observed, which remained during continued stirring (for a further 2 h). The resulting red-brown solution was isolated by filtration and back-condensed solvent (2 x 5 ml) was used to wash the residual brown solid free of a brown-white solid. Solvent removal followed by continual extraction with acetonitrile of the brown residues, yielded a brown powder (0.420 g, 82%), which analysed as the dichloride. Found: 12.18%N, 21.34%C, 1.53%H. Calc. 12.48%N, 21.40%C, 0.87%H. IR ν_{max} (cm^{-1}): 1678m, 1605m, 1528w, 1403m, 1315m sh, 1235m, 1129m, 1017w, 984m, 871w, 854m, 785m, 740m, 722m, 702m, 672m, 615w, 578w, 453w, 423m.

5.4.5 Preparation of *p*-[SNSNC.C_6H_4.CNSeSeN]Cl

p-[SNSNC.C_6H_4.CNSeSeN]Cl_2 (0.196 g, 0.44 mmol) and Ph_3Sb (0.076g, 0.22 mmol) were placed in one bulb of a two-limbed reaction vessel and CH_2Cl_2 (8 ml) was syringed onto them. An immediate black colouration was observed and the reagents were stirred for 18 h in the dark to give a black powder under a brown solution, which was removed by filtration. Back-condensation of solvent followed by filtration (5 x 8 ml) removed a brown material from the residual black powder, which was washed further by continuous extraction with acetonitrile in a closed extractor. This yielded a fine black residual powder (0.120 g, 66%) which analysed well as the monochloride. Found 13.63%N, 23.30%C, 1.52%H. Calculated: 13.55%N, 23.24%C, 0.97%H.

5.4.6 Preparation of *p*-[SNSNC.C_6H_4.CNSeSeN]

p-[SNSNC.C_6H_4.CNSeSeN]Cl_2 (0.097 g, 0.22 mmol) and Ph_3Sb (0.080g, 0.23 mmol) were placed in one bulb of a two-limbed reaction vessel and CH_2Cl_2 (8 ml) was syringed onto them. An immediate black colouration was observed and the reagents were stirred for 18 h in the dark to give a black powder under a brown solution, which was removed by filtration. Back-condensation of solvent followed by brief stirring and filtration (4 x 8 ml) removed a brown material from the residual purple-gold powder (0.070 g, 86%), which did not analyse well as the diradical. Found 12.76%N, 26.53%C, 1.76%H. Calculated: 14.83%N, 25.47%C, 1.05%H. A further extraction with acetonitrile only decreased product quality. The mass spectrum of this compound showed only dicyanobenzene (m/e 146 in CI^+). IR ν_{max} (cm^{-1}): 1683vs, 1604m, 1575w, 1558w, 1532m, 1408m, 1302m, 1211w, 1170w, 1123m, 1080w, 1047w, 1017w, 984w, 850m, 765w, 722s, 625vw, 614w, 578vw, 545vw, 446vw, 412vw.

5.4.7 Attempted Photolytic Rearrangement of *p*-[SNSNC.C_6H_4.CNSeSeN] to *p*-[NSSNC.C_6H_4.CNSeSeN]

p-[SNSNC.C_6H_4.CNSeSeN]Cl_2 (0.100 g, 0.22 mmol) and Ph_3Sb (0.090g, 0.25 mmol) were placed in one bulb of a two-limbed reaction vessel and CH_2Cl_2 (8 ml) was syringed onto them. An immediate black colouration was observed and the reagents were stirred for 3 h in the dark to give a black powder under a brown solution.Filtration removed a red, oily material. The residual black suspension was then stirred for a further four days under broadband UV illumination. The insoluble black product (0.072 g, 92%) was isolated by filtration, washed with back-condensed solvent (2 x 8 ml) and dried *in vacuo*. Elemental analysis suggested that the diradical system had remained in tact: found 12.53%N, 24.46%C, 1.63%H; calc. 14.82%N, 25.41%C, 1.06%H.

Solution state esr of the product proved impossible as it was insoluble in toluene and acetonitrile (even when iodine was added - this usually aids solution of these multi-radicals [7]).

A sample of the product (50 mg) was stirred in SO_2 solution with an excess of AsF_5 (ca. 500mg) for 16 h to yield a yellow solid under an olive green solution. The solid could not be isolated as it became intractable upon solvent removal.

5.4.7 Attempted Oxidation of *p*-[NSSNC.C_6H_4.CNSeSeN] with Br_2 / SO_2

p-[NSeSeNC.C_6H_4.CNSSN] (0.026 g, 0.07 mmol) was placed in one bulb of a two limbed reaction vessel and an excess of Br_2/SO_2 mixture condensed onto it. The reagents were stirred for 5 minutes to yield an orange solid from which the solvent and unreacted bromine were removed to leave a pale brown powder (0.020 g, 34%) that analysed fairly well as the tribromide salt. Found: 6.50%N, 11.18%C, 0.85%H. Calc.: 6.53%N, 11.20%C, 0.47%H.

The material could not be characterised by cyclic voltammetery as it was insufficiently soluble in acetonitrile.

5.5 References

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(c) A.W. Cordes and R.T. Oakley, *Acta. Cyst.*, 1990, **C46**, 699.
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Chapter 6

Novel preparations of some acyclic thiazenes

6.1 Introduction

During the examination of the reactivity of [SNS][AsF_6] with various alkyl and aryl nitriles the reactions of [SNS][AsF_6] with metal / metalloid cyanides have been studied, albeit to a limited extent. A.W. Luke[1] has investigated the reactions of [SNS][AsF_6] with $[Ni(CN)_4]^{2-}$, $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$ with limited success, and J.M. Rawson[2] those with $Hg(CN)_2$. Products of theses reactions have not as yet been fully characterised.

As an extension of that work the reactions of PhHgCN, Ph_3SnCN and Na[Ph_3BCN] with [SNS][AsF_6] were examined, *vide infra*, as this may lead to the preparation of a compound containing a dithiadiazolylium cation bound to a metal or metalloid centre. This metal dithiadiazolylium could be a dithiadiazolylium transfer reagent.

Such a transfer reagent would have wide-ranging synthetic utility as well as being of interest in its own right. For example, it could react with a halogenated alkyl or aryl compound (equation 6.1).

$$\text{Y-M-CN} \xrightarrow{\text{SNSAsF}_6} [\text{Y-M-CNSNS}][\text{AsF}_6] \xrightarrow[\text{- Y-M-X}]{\text{R-X}} [\text{R-CNSNS}][\text{AsF}_6]$$

[Eq. 6.1]

However, the reaction of [SNS][AsF_6] with PhHgCN gave an unexpected product, [Ph.SNSNSNS.Ph][AsF_6], **1**, and led to further investigation of the preparation of acyclic sulphur-nitrogen compounds with aryl or alkyl capping groups.

6.1.1 Background

The chemistry of $(SN)_x$ has been widely studied[3], particularly over the past 25 years, mainly as it was the first nonmetallic material found to exhibit metallic conductivity (ca. 1000-3000 S cm^{-1} depending upon crystallinity)[4], with a T_c for superconductivity[5] of 0.26 K. With these novel properties in mind several classes of linear sulphur-nitrogen compounds have been prepared. Previous work in this area is summarised in table 6.1. Many workers have attempted to mimic the useful properties of $(SN)_x$ whilst reducing its sensitivity to hydrolysis, its insolubility and the hazards of preparation.

Each strategy employed to mitigate the detrimental properties of $(SN)_x$ and so allow for the incorporation of these systems into large scale, multifunctional molecular arrays (such as those in the proposed 'molecular' computers[10]) has involved the use of substituted or unsubstituted phenylenes or thiophenes, serving either as chain terminators or "spacers".

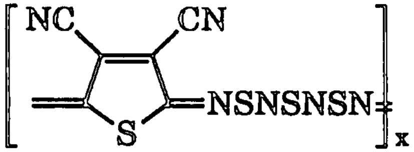
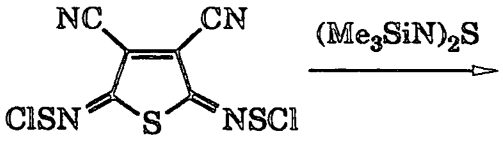
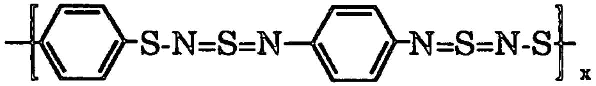
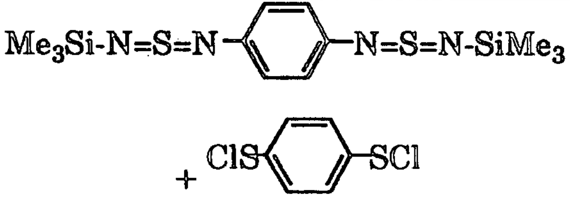
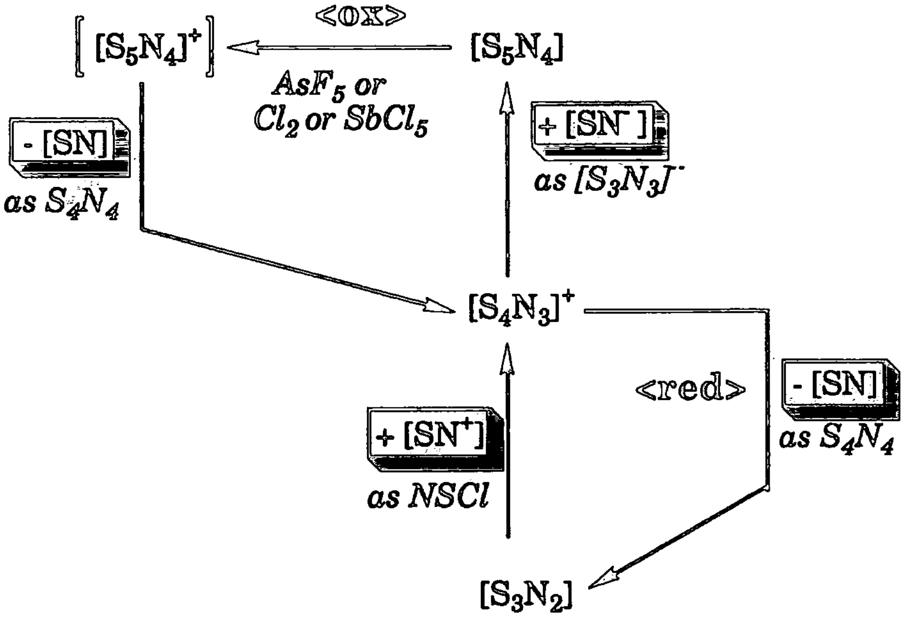
System	Examples	Yield (%)	Ref.s	Preparative Route
Linear Azathienes	ArNSNSNSNAr Ar = Ph p-Me-C_6H_4	 32 38	6	$\mathrm{ArNSO} \xrightarrow{\mathrm{LiN(SiMe_3)_2}} \mathrm{ArN{=}S{=}NSiMe_3} \xrightarrow{\mathrm{SCl_2}} \mathrm{(ArNSN)_2S}$
Linear Thiazenes	[ArSNSNSNSAr][Cl] Ar =p-Me-C_6H_4 p-Cl-C_6H_4	 80-90 40	7	$\mathrm{ArSCl} \xrightarrow{\mathrm{(Me_3SiN)_2S}} \mathrm{ArSNSNSNSAr}$
Polymeric Thiazenes with Thiophene and Phenylene Spacers		66	8	
			9	

Table 6.1 Examples of acyclic thiazenes, azathienes and polymeric thiazenes with heterocyclic spacer groups

These compounds have been isolated in yields ranging from 20% to 90%, but some of the larger chains are susceptible to loss of sulphur or nitrogen atoms and also to cyclisation, rendering them unstable, e.g. $Ar_2N_6S_5$[11]. A systematic approach to the synthesis of the higher thiazenes and azathienes (and their corresponding cations) would be of considerable interest.

6.2 Proposed synthetic routes

The possibility of lengthening or shortening of thiazene chains by the use of a variety of chemical methods (such as addition reactions, oxidations and reductions) can be envisioned. Some of these possibilities are summarised in scheme 6.1.



Scheme 6.1 Proposed chain lengthening / shortening reactions of thiazenes (aryl groups are omitted for clarity and $[Ar_2S_4N_3]^+$ is used as an example).

The use of the $[NS_2Cl_2]^+$ cation as a precursor to aryl and alkyl substituted dithianitronium salts as well as short cationic SN chains with aryl or alkyl terminating groups could also be readily explored.

Phenyl transfer reagents such as PhLi or Ph_4Sn could be used in an attempt to phenylate the cation directly and various trimethylsilyl-substituted sulphur diimides such as $^tBuNSNSiMe_3$ could also be used to prepare linear cations (see equations 6.2 and 6.3).

$$[NS_2Cl_2]^+ \quad + \quad 2\,PhLi \quad \xrightarrow{-\,2\,LiCl} \quad [PhSNSPh]^+ \qquad \text{[Eq. 6.2]}$$

$$[NS_2Cl_2]^+ \quad + \quad 2\,{}^tBuNSNSiMe_3 \xrightarrow{-\,2\,Me_3SiCl} \left[{}^tBuNSNSNSNSN{}^tBu\right]^+$$

[Eq. 6.3]

6.2.1 Chain shortening

It could be possible to shorten the S_aN_b backbone in a *cationic* species by reduction:

$$[Ar_2S_aN_b]^+ \xrightarrow{<red>} \left[Ar_2S_aN_b\right] \xrightarrow{-\,{}^1/_4\,S_4N_4} Ar_2S_{a-1}N_{b-1}$$

[Eq. 6.4]

In order to reduce the length of a *neutral* species oxidation is required, followed by loss of an SN unit (perhaps as S_4N_4). This could possibly be achieved by the use of AsF_5 or $SbCl_5$ as an oxidant:

$$Ar_2S_xN_y \xrightarrow{<ox>} \left[\,[Ar_2S_xN_y]^+\,\right] \xrightarrow{-\,{}^1/_4\,S_4N_4} [Ar_2S_{x-1}N_{y-1}]^+$$

[Eq. 6.5]

Both of the steps in this reaction would be driven by a gain in lattice energy, firstly through the formation of an ionic material and secondly through the small diameter and similarity in size of the $[Ar_2S_xN_y]^+$ cation and the counter ion.

6.2.2 Chain lengthening

It should be possible to convert a shorter SN backbone into a longer *cation* with one further SN unit by the addition of $[SN^+]$. This type of reaction would be driven by the relative stability of the ionic product compared with the neutral starting material and highly reactive $[SN]^+$. In a similar manner the addition of $[SN]^-$ to a cationic species, e.g. $[Ar_2S_4N_3]^+$, could possibly generate the next highest homologue, $[Ar_2S_5N_4]$. See scheme 6.1 for postulated reactions.

Chlorothiazene in the presence of $AgAsF_6$ has been shown[12] to be a good source of $[SN]^+$. The salt improves activity by the formation of $[SN][AsF_6]$ and insoluble AgCl. Salts of the anion $[S_3N_3]^-$ could provide a source of 'SN^-', with S_4N_4 generated as a by-product. The formation of S_4N_4 appears to be a good driving force for many reactions, in spite of its thermodynamic instability relative to S_8 and N_2; witness the wide variety[13] of preparations of S_4N_4.

In theory, chain-lengthening reactions may also be used more generally, for example, with aryl-substituted azathienes (linear SN compounds containing more nitrogen atoms than sulphur in the backbone) as well as thiazenes (where there are at least as many sulphur atoms present). However, preliminary work undertaken as part of these studies showed that the preparation and purification of the longer SN chains (e.g. $Ar_2S_5N_4$ and $Ar_2N_4S_3$) is difficult, leading to products with extreme variations in carbon analyses obtained. That work is not included here.

The reactions of $[SNS][AsF_6]$ with some metalloid cyanides will now be described and preliminary work will be reported on the use of $(NSCl)_3$ as a source of $[SN^+]$ for its incorporation into linear thiazenes.

6.3 Discussion of results

6.3.1 Reactions of $[SNS][AsF_6]$ with metalloid cyanides

The reactions of $[SNS][AsF_6]$ with Ph_3SnCN and PhHgCN gave products showing a broad IR band at ca. 2150 cm^{-1} and no evidence of the $[CNSNS]^+$ functionality, characteristic[14] IR bands at ca. 450, 580, 800, 880 and 1200 cm^{-1} being absent.

With PhHgCN a deep blue-gold dichroic solid was isolated and subsequently recrystallised from CH_2Cl_2 to yield golden, diamond shaped crystals. They were shown, by single crystal X-ray structure determination, to be of $[Ph.SNSNSNS.Ph][AsF_6]$ (**1**).

However, as is the case for many of these aryl-substiuted thiazenes, elemental analysis of this product was variable (see table 6.2) and the deep blue powder appeared, in the first instance, to analyse closer to the formulation of [PhHgCNSNS] (**2**) than $[PhSNSNSNSPh][AsF_6]$ (**1**).

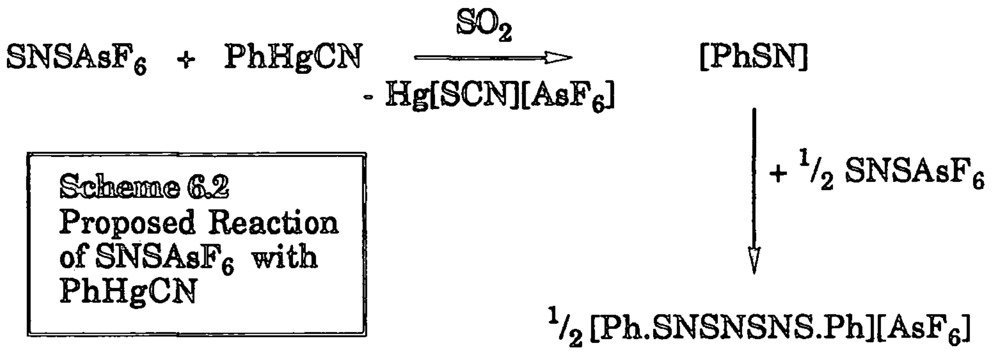
Element	Observed analysis	**1**	**2**
N	6.75	8.19	7.35
C	22.56	28.00	22.64
H	1.92	1.96	1.30

Table 6.2 Microanalytical data obtained for the blue product of the reaction of $[SNS][AsF_6]$ with PhHgCN and those calculated for **1** and **2**.

[*Note;* In contrast, the materials prepared by the reaction of $(NSCl)_3$ with $Ar_2S_3N_2$ (Ar = *o*- or *p*-$[O_2N.C_6H_4.]$) followed by metathesis with $AgAsF_6$ did analyse well as $[Ar_2S_4N_3][AsF_6]$ (**3a**).]

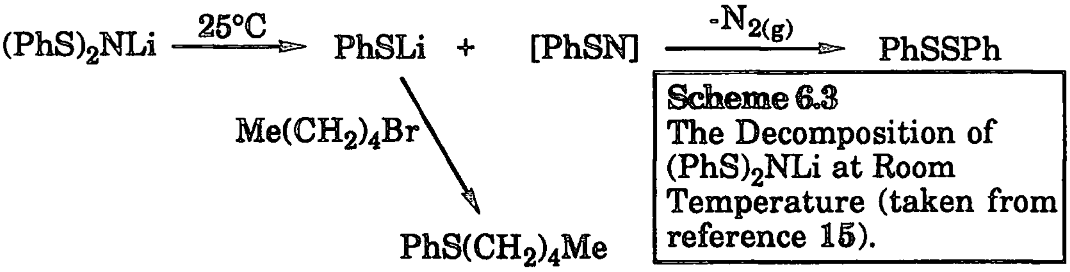
It would appear, therefore, that PhHgCN and Ph_3SnCN are acting as phenylating agents rather than dieneophiles in the presence of $[SNS]^+$. This is not very surprising as several halo-substituted organometallics behave as alkyl or aryl transfer reagents in organic synthesis and [C≡N]$^-$ is a pseudo halide.

The broad, intense band at ca. 2130 cm^{-1} observed in the IR spectra of the products could well be due to thiocyanate. The C≡N group may have abstracted a sulphur atom, presumably from [SNS]$^+$, leaving [SN]$^+$, which may then couple with the phenylate anion (from PhHgCN) to form PhSN; the latter compound may then react with half an equivalent of [SNS]$^+$ to give the resulting cationic, linear thiazene (see scheme 6.2).



Scheme 6.2
Proposed Reaction of $SNSAsF_6$ with PhHgCN

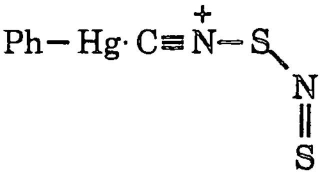
The compound PhS≡N, thiazyne, has been reported[15] as a reactive intermediate generated by the decomposition of $(PhS)_2NLi$.



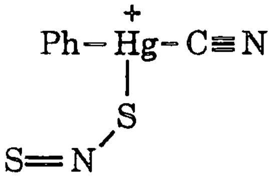
Scheme 6.3
The Decomposition of $(PhS)_2NLi$ at Room Temperature (taken from reference 15).

Compound 1, identified by its IR spectrum, lustrous appearance and elemental formulation, was produced also when PhHgCl reacted with $[SNS][AsF_6]$. The yield of this reaction is similar to that of PhHgCN with $[SNS][AsF_6]$, suggesting that both reactions proceed by a similar mechanism and mitigating against any interaction of [SNS]$^+$ with free or complexed C≡N.

Further support for a mechanism independent of C≡N comes from the lack of evidence for the formation of a dithiadiazolylium ring as the product of the reaction with PhHgCN. A cyclic compound would be expected as at least a minor product if complexation of [SNS]$^+$ with the terminal nitrogen of the nitrile, were to occur through the intermediate shown below.



The intermediate is less likely to contribute to the addition of $[SN]^+$ to the phenyl group than would a complex containing $[SNS]^+$ bound directly to mercury. In the latter case the two reacting moieties would be held close together by the mediating mercury centre.



Whether the desulphurisation of $[SNS]^+$ is in fact mediated by its complexation to the mercury centre would be difficult to substantiate absolutely. Perhaps ^{199}Hg nmr at low temperature could elucidate this. Three-coordinate mercury is known[16] and stable complexes are readily formed with sulphur donors[16]. Considering the metal's affinity for sulphur, the abstraction of S prior to addition of phenylene to $[SNS]^+$ seems likely. However, the mechanism involving coordination of $[SNS]^+$ to C≡N cannot be ruled out, certainly for the reaction with PhHgCN. Mercury analyses of a variety of these products were irreproducable and so inconclusive.

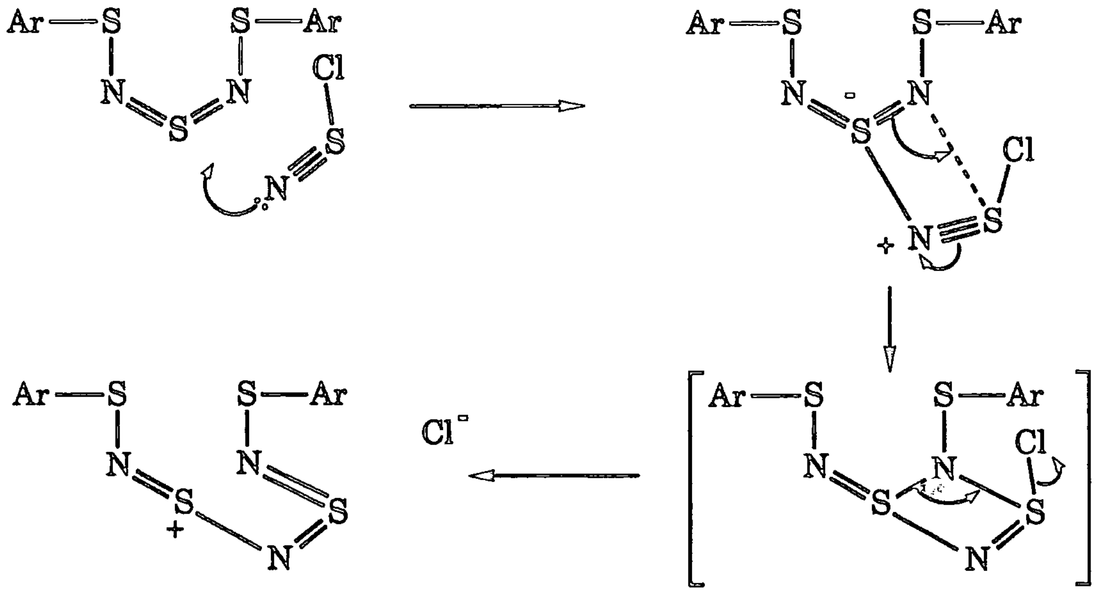
The reactions of $[SNS][AsF_6]$ with Ph_3SnCN and $Na[Ph_3B.CN]$ were much less well defined and the products were not readily characterised, generally being intractable oils. Even when isolated as solids they gave irreproducible elemental analyses.

6.3.2 Chain lengthening reactions utilising $(NSCl)_3$ as a source of $[SN]^+$

Although $(NSCl)_3$ is a covalent molecule it may act as a source of $[SN]^+$ when reacting with Ar.SNSNS.Ar [Ar= p-$(O_2N).C_6H_4$.] to give the chain-lengthened compound [Ar.SNSNSNS.Ar][Cl], **3b**, in 87% yield. Metathesis with $AgAsF_6$ gives the corresponding hexafluoroarsenate(V) salt, $[Ar.SNSNSNS.Ar][AsF_6]$, **3a**, which is very similar in appearance to the phenyl analogue, **1**, i.e. a golden blue-black solid.

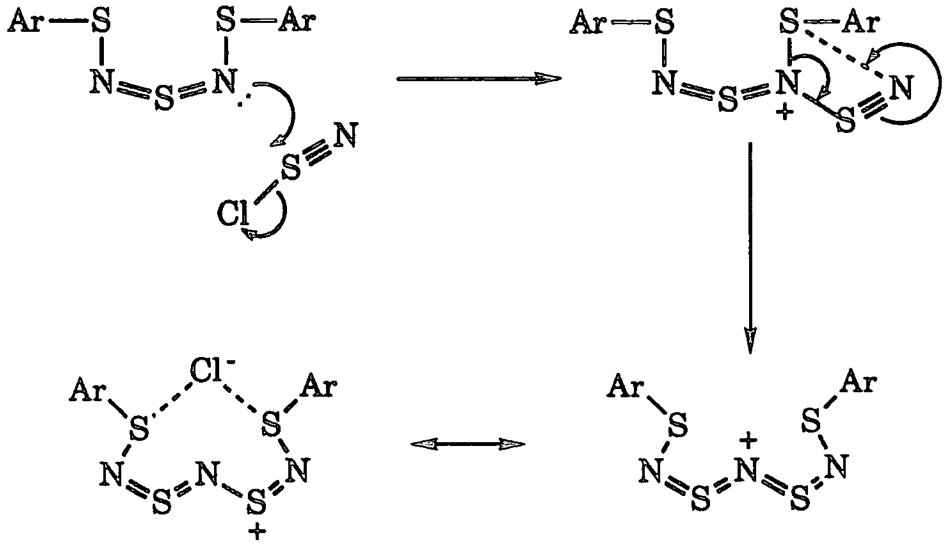
This reaction could occur by nucleophilic attack via one of two routes.

(i) The thiazyl chloride nitrogen attacks at the central sulphur on the $Ar_2S_3N_2$ molecule (which is the most electrophilic as it is adjacent to two nitrogens, the other two sulphur atoms being between a single nitrogen and an aryl group).



Scheme 6.4 Postulated mechanism for the nucleophilic attack of $(NSCl)_3$ on $Ar_2S_3N_2$

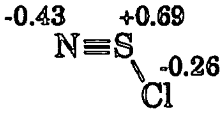
(ii) One of the nitrogens in $Ar_2S_3N_2$ attacks the sulphur in thiazyl chloride monomer.

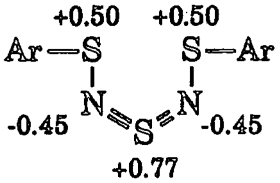


Scheme 6.5 Postulated mechanism for the nucleophilic attack of $Ar_2S_3N_2$ on $(NSCl)_3$

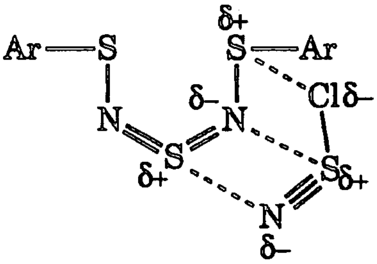
There are at least three reasons for suggesting a hybrid of these two mechanisms, in which the latter dominates.

(a) Molecular orbital calculations, at the PM3 level[17], on single crystal X-ray data[18] for $Ph_2S_3N_2$, with one self-consistent field, and on NSCl (minimising to a structure with an S-Cl bond at 2.08 Å, an S-N bond length of 1.46 Å and Cl-S-N angle of 108.5°) reveal partial charges, viz.:

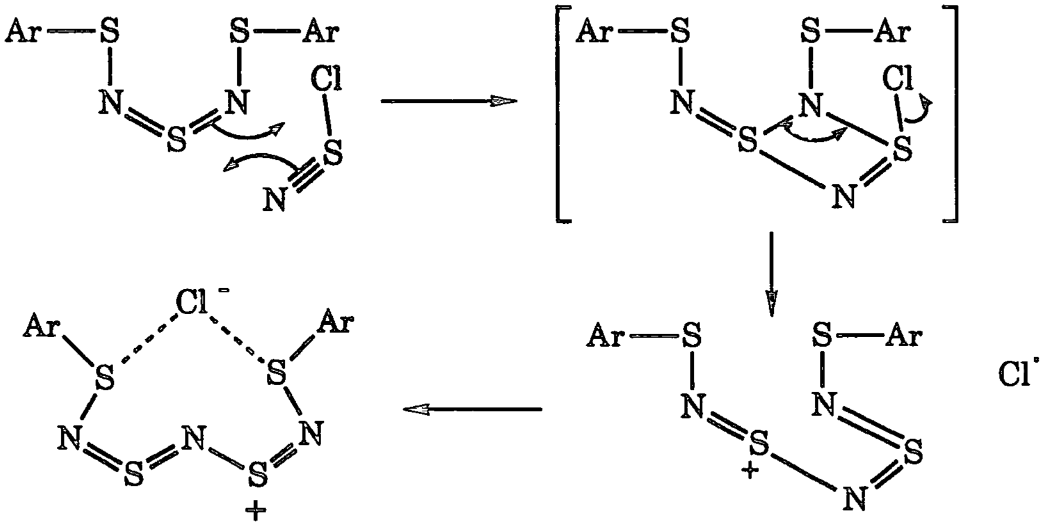




These results indicate little difference between the charges on the atoms involved in the reaction (for mechanism (i) a nitrogen atom, with a charge of -0.45, attacks a sulphur atom, with a charge of +0.69, and for (ii) the charges are -0.43 and +0.77 for nitrogen and sulphur respectively). Furthermore,the partial charge distribution suggests that there may be stability gained by association of the two molecules :



This coulombic attraction may then promote a cyclisation, to give an unstable four-membered cyclic intermediate, which could then ring open with loss of a chloride ion to give the product directly .



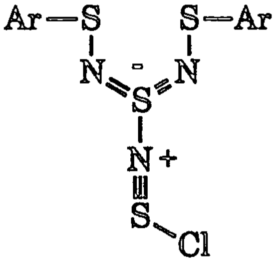
Scheme 6.6 Proposed mechanism for the formation of $[Ar_2S_4N_3]Cl$ from $Ar_2S_3N_2$ and $(NSCl)_3$

There is a precedent for this type of four-membered SN intermediate as several PSN heterocycles and sulphur diimines are claimed[19] to rearrange via a similar species.

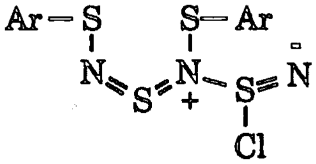
The mechanism, facilitated by the attraction of partial charges in solution, would also explain the relative reactivities of the *ortho-* and *para-*nitro substituted phenylene reagents. The *ortho* system is expected to have greater steric (and electronic) bulk in a position adjacent to the chlorine atom of the incoming thiazyl chloride in the proposed intermediate, thus resulting in the observed relative inertness of $(NSCl)_3$ to the *ortho* isomer.

With $AgAsF_6$ present, *vide infra*, attack on the thiazyl chain is more facile: mechanism (ii) accords with this observation by showing that incipient $[SN][AsF_6]$ does not require room in which to begin the attack.

(b) The intermediates and transition states generated by the two proposed mechanisms appear to differ somewhat in stability, (i) giving rise to an intermediate containing unusually high oxidation states:



This five-coordinate inter-anionic sulphur would be very unstable, whereas the intermediate generated by the other mechanism, (ii), seems to be more feasible:



(c) There are two possible, chemically equivalent nucleophilic sites on $Ar_2S_3N_2$ - so the approach of the thiazyl chloride unit into their vicinity is more probable in this case of mechanism (ii) than the attack of the thiazyl chloride nitrogen on the single sulphur in the $Ar_2S_3N_2$ molecule.

Reaction of $(NSCl)_3$ *with* $(p\text{-}O_2N.C_6H_4).SNSNS.(p\text{-}O_2N.C_6H_4)$

The IR spectrum of the product, 3a, identifies it (table 6.3) as the linear thiazene rather than a simple addition compound (as shown in scheme 6.4) .

Aryl substituent	*p*-Me	*p*-Cl	*p*-NO_2	H	*o*-NO_2	*p*-NO_2
Counter ion	$[Cl]^-$	$[Cl]^-$	$[Cl]^-$	$[AsF_6]^-$	$[AsF_6]^-$	$[AsF_6]^-$
Assignment						
ν_{as}	1082	1078	1066	1067	1069	1080
ν_s	723	730	728	749	736	741
	500	482	475	505	487	480
	357	....	362	....	....	....
	977	970	972	978	984	985
Reference	7	7	a	a	a	a

Notes: a - this work

Table 6.3 S-N vibrations (cm^{-1}) observed in the IR spectra of some $[Ar_2S_4N_3][X]$ salts.

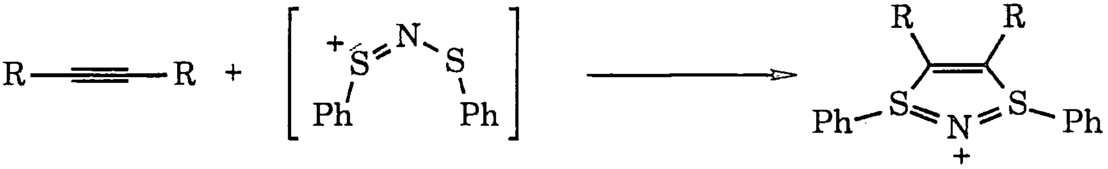
With (o-$O_2N.C_6H_4$).SNSNS.(o-$O_2N.C_6H_4$)

With the nitro group in the *ortho* position it appears that the $Ar_2S_3N_2$ chain is much less reactive toward $(NSCl)_3$ than with the *para* derivative. This could be due to the steric bulk of the substituent preventing the approach of an NSCl unit in solution.

So in this case one equivalent of $AgAsF_6$ must be added in order for any reaction to occur. The presence of $AgAsF_6$ allows for the formation of $[SN]AsF_6$ *in situ*, which is in far higher concentration than any [SN][Cl] present and is much more reactive than the NSCl monomer. This allows for facile insertion of an $[SN]^+$ unit to give the corresponding thiazene cation.

6.3.3 Attempted preparation of phenylated $[SNS]^+$

The bis-phenyl dithianitronium salt, $[PhSNSPh]^+$, the first member of the family of aryl-substituted linear thiazenes, could well provide a route into some aryl substituted CSN heterocycles, by analogy with $[SNS]^+$, for example:



[Eq. 6.6]

The steric bulk of the phenyl groups should reduce reactivity of the cation but these aryl substituents should not have such a marked electronic effect as the chlorine atoms in $[ClSNSCl]^+$ (see section 1.2.7). So nitriles may be reactive enough to give bis-aryl dithiadiazolylium salts, providing the cyano-substituent is small enough, e.g. Me, CF_3.

The availability of a convenient route[12] to $[Cl_2S_2N][AsF_6]$ allowed for some experimentation in the synthesis of the $[PhSNSPh]^+$ cation. Reactions of $[Cl_2S_2N][AsF_6]$ with phenyl lithium and tetraphenyl tin (both versatile phenylating reagents) were attempted.

However, the reaction with phenyl lithium resulted only in an oily, intractable product. Tetraphenyl tin did give a deep blue lustrous powder, but this was shown, by the presence of a broad IR band at ca. 3320 cm^{-1}, to be extensively hydrolysed.

6.3.4 Structure and bonding in $[PhSNSNSNSPh][AsF_6]$

The structure of $[PhSNSNSNSPh][AsF_6]$ (**1**) was determined by single crystal X-ray diffraction. Crystal data, refined atomic coordinates, bond lengths and angles, anisotropic thermal parameters and hydrogen atom coordinates for $[PhSNSNSNSPh][AsF_6]$ are given in tables 6.4 to 6.8, respectively. The structure of the cation, $[PhSNSNSNSPh]^+$, and the solid state packing are given in figures 6.1 and 6.2, respectively.

Table 6.4 Crystal structure determination of $[PhSNSNSNSPh][AsF_6]$

Formula	$C_{12}H_{10}N_3F_6S_4As$	2θ range for unit cell / °	20-25 °
M.W.	513.4	Space Group	P_{nma}
Crystal Size (mm)	0.16x0.24x0.56	Z	4
Crystal Form	Gold / Black	D_c (gcm^{-3})	1.851
Instrument	Stoe-Siemens	F(000)	1016
Radiation	Mo(Kα)	μ/mm^{-1}	2.33
λ(Å)	0.71073	T/K	240
Scan Type	ω/θ	2θ range for data	0-50 °
Crystal System	Orthorhombic	Total Data Measured	7487
a/ Å	17.3546(11)	Total Unique	1768
b/ Å	6.7359(7)	Total Observed	1531
c/ Å	15.7608(9)	Significance Test	$F_o>4\sigma(F_o)$
α/°	90	No. of Parameters	152
β/°	90	ρ_{min}- ρ_{max}/e $Å^{-3}$	(-0.29)-(0.41)
γ/°	90	Weighting Scheme	
V/ $Å^3$	1842.4	R	0.0318
		R_w	0.0350

Figure 6.1 Solid state structure of [PhSNSNSNSPh][AsF_6], showing atom numbering scheme

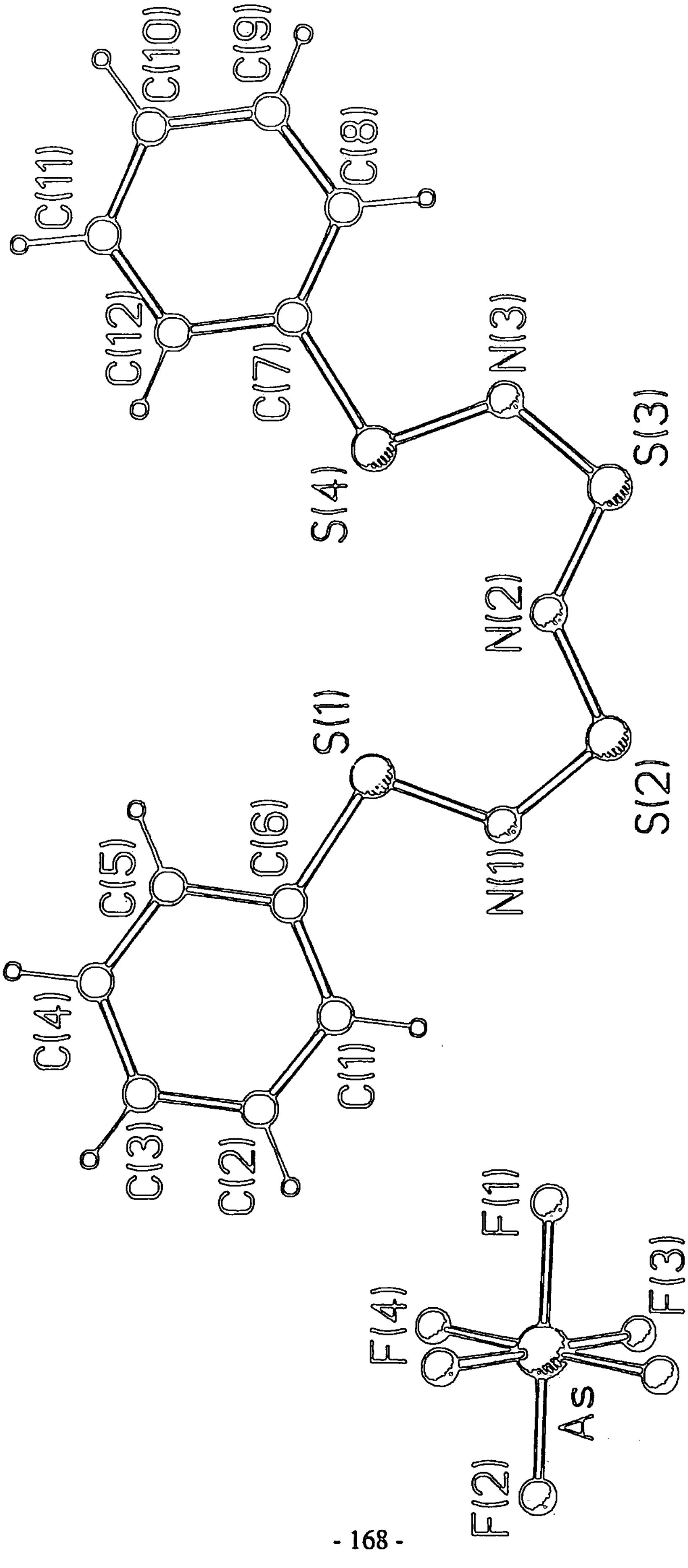


Table 6.5 Atomic coordinates for [PhSNSNSNSPh][AsF_6]

Atom	x	y	z
C(1)	2419(1)	2500	4582(2)
C(2)	2869(2)	2500	3857(2)
C(3)	3661(2)	2500	3911(2)
C(4)	4018(2)	2500	4696(3)
C(5)	3583(2)	2500	5424(2)
C(6)	2782(2)	2500	5365(2)
S(1)	2299(1)	2500	6344(1)
N(1)	1403(1)	2500	6055(2)
S(2)	757(1)	2500	6743(1)
N(2)	1207(2)	2500	7627(2)
S(3)	872(1)	2500	8570(1)
N(3)	1597(1)	2500	9150(2)
S(4)	2450(1)	2500	8728(1)
C(7)	3045(2)	2500	9637(2)
C(8)	2766(2)	2500	10459(2)
C(9)	3293(2)	2500	11120(2)
C(10)	4077(2)	2500	10949(3)
C(11)	4341(2)	2500	10135(3)
C(12)	3827(2)	2500	9463(2)
As	884(1)	2500	2253(1)
F(1)	913(1)	2500	3326(1)
F(2)	840(1)	2500	1181(1)
F(3)	177(1)	733(1)	2281(1)
F(4)	1584(1)	738(4)	2231(1)

Table 6.6 Bond lengths (Å) and angles (degrees) in [PhSNSNSNSPh][AsF_6]

C(1)-C(2)	1.384(5)	C(1)-C(6)	1.387(4)
C(2)-C(3)	1.378(6)	C(3)-C(4)	1.383(6)
C(4)-C(5)	1.374(5)	C(5)-C(6)	1.393(5)
C(6)-S(1)	1.755(3)	S(1)-N(1)	1.622(3)
N(1)-S(2)	1.560(3)	S(2)-N(2)	1.596(3)
N(2)-S(3)	1.597(3)	S(3)-N(3)	1.555(3)
N(3)-S(4)	1.622(3)	S(4)-C(7)	1.766(3)
C(7)-C(8)	1.383(4)	C(7)-C(12)	1.384(5)
C(8)-C(9)	1.386(5)	C(9)-C(10)	1.386(5)
C(10)-C(11)	1.363(6)	C(11)-C(12)	1.385(6)

C(2)-C(1)-C(6)	118.6(2)	C(1)-C(2)-C(3)	120.8(3)
C(2)-C(3)-C(4)	120.1(4)	C(3)-C(4)-C(5)	120.1(3)
C(4)-C(5)-C(6)	119.5(3)	C(1)-C(6)-C(5)	120.8(3)
C(1)-C(6)-S(1)	124.5(2)	C(5)-C(6)-S(1)	114.7(2)
C(6)-S(1)-N(1)	102.1(1)	S(1)-N(1)-S(2)	119.6(2)
N(1)-S(2)-N(2)	104.8(1)	S(2)-N(2)-S(3)	129.4(2)
N(2)-S(3)-N(3)	104.6(2)	S(3)-N(3)-S(4)	119.9(2)
N(3)-S(4)-C(7)	101.7(1)	S(4)-C(7)-C(8)	123.7(3)
S(4)-C(7)-C(12)	114.4(3)	C(8)-C(7)-C(12)	121.9(3)
C(7)-C(8)-C(9)	118.3(3)	C(8)-C(9)-C(10)	120.0(3)
C(9)-C(10)-C(11)	120.9(4)	C(10)-C(11)-C(12)	120.2(4)
C(7)-C(12)-C(11)	118.7(4)		

Table 6.7 Anisotropic thermal parameters ($Å^2 x 10^3$) for [PhSNSNSNSPh][AsF_6]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	49(2)	46(3)	47(2)	0	1(1)	0
C(2)	71(3)	42(2)	50(2)	0	8(2)	0
C(3)	68(2)	49(3)	60(2)	0	24(2)	0
C(4)	48(2)	70(4)	76(3)	0	11(2)	0
C(5)	45(2)	64(3)	57(2)	0	-2(2)	0
C(6)	43(2)	35(2)	46(2)	0	1(1)	0
S(1)	39(1)	46(1)	43(1)	0	-3(1)	0
N(1)	41(1)	44(2)	47(1)	0	-2(1)	0
S(2)	37(1)	64(1)	47(1)	0	-4(1)	0
N(2)	40(2)	56(2)	44(1)	0	-2(1)	0
S(3)	37(1)	64(1)	47(1)	0	3(1)	0
N(3)	45(2)	47(2)	46(1)	0	4(1)	0
S(4)	40(1)	52(1)	41(1)	0	2(1)	0
C(7)	42(2)	41(2)	45(2)	0	-1(1)	0
C(8)	48(2)	41(2)	49(2)	0	-1(2)	0
C(9)	64(2)	47(3)	49(2)	0	-11(2)	0
C(10)	62(2)	53(3)	80(3)	0	-31(2)	0
C(11)	42(2)	96(4)	84(3)	0	-10(2)	0
C(12)	46(2)	92(4)	61(2)	0	5(2)	0
As	31(1)	61(1)	49(1)	0	3(1)	0
F(1)	59(1)	140(3)	53(1)	0	-5(1)	0
F(2)	75(2)	176(4)	49(1)	0	6(1)	0
F(3)	72(1)	89(2)	104(1)	5(1)	-11(1)	-34(1)
F(4)	72(1)	111(2)	122(1)	-23(1)	-10(1)	40(1)

Table 6.8 Hydrogen atoms: atomic coordinates ($\times10^4$) and isotropic thermal parameters (Å x 10^3) in [PhSNSNSNSPh][AsF_6]

	x	y	z	U
H(1)	1867	2500	4542	57
H(2)	2626	2500	3309	65
H(3)	3967	2500	3403	71
H(4)	4570	2500	4732	77
H(5)	3829	2500	5970	66
H(8)	2222	2500	10569	55
H(9)	3115	2500	11697	64
H(10)	4438	2500	11411	78
H(11)	4886	2500	10027	89
H(12)	4010	2500	8888	80

The cation shows a similar structure to the previously described[21] 4-tolyl derivative, [MeC_6H_4.SNSNSNS.C_6H_4Me]Cl, but the cation of 1 is completely planar and also possesses a plane of symmetry perpendicular to the cation plane through N(2) (figure 6.1). The lower symmetry of the tolyl system, described by Mayerle *et. al.*[21], can be thought of as arising from perturbations of the geometry, induced by strong cation-anion interactions particularly those involving S(2) and S(3) on the cation (at 3.056(3) and 3.237(3) Å respectively), whereas in solid 1 there are negligible interactions involving the 'hard' [AsF_6]$^-$ anion with the 'soft' S atoms in the cation. The closest S···F contact is 3.120 Å.

The cations pack in planes of wave-like chains along the z-axis with [AsF_6]$^-$ anions located in the interstices, which run parallel to the y-axis throughout the structure (figure 6.2). Although the inter-plane distance, at 3.37 Å, should facilitate intermolecular contacts, the staggered nature of the structure minimises such cation-cation interactions. Instead, the capacity for S···N secondary bonding is satisfied internally. Within the S_4N_3 chain there are several strong intramolecular contacts, including both S···S and S···N: S(1)-S(4) (3.766(4) Å), S(1)-N(2) and S(4)-N(2) (at 2.771(5) Å and 2.769(5) Å respectively). The strong secondary S···N interactions between atoms on the delocalised chain can be considered as having both covalent and electrostatic contributions. Figure 6.3 shows the net atomic charges.

Figure 6.2 Molecular packing of [PhSNSNSNSPh][AsF$_6$], seen in projection along the b axis.

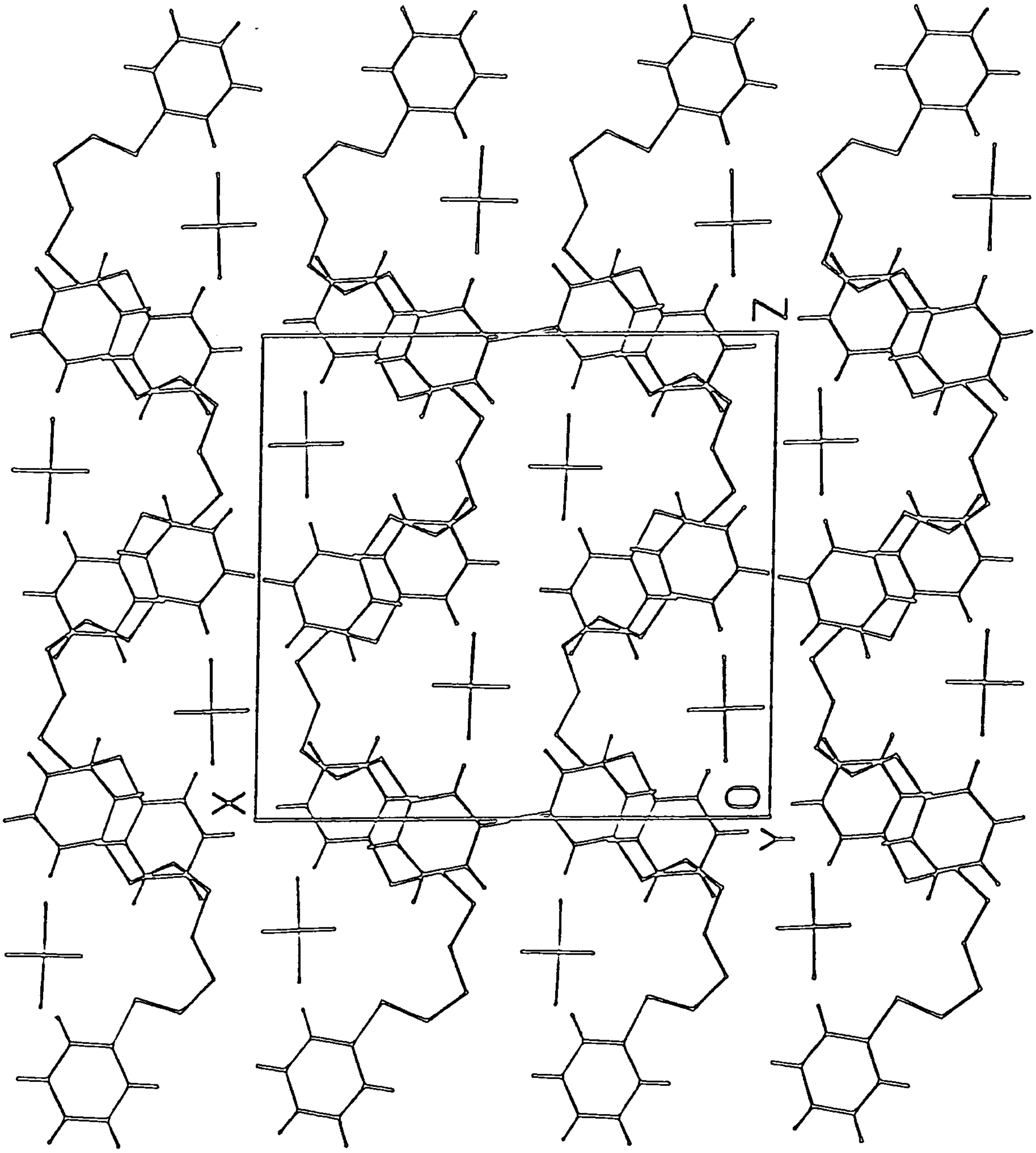
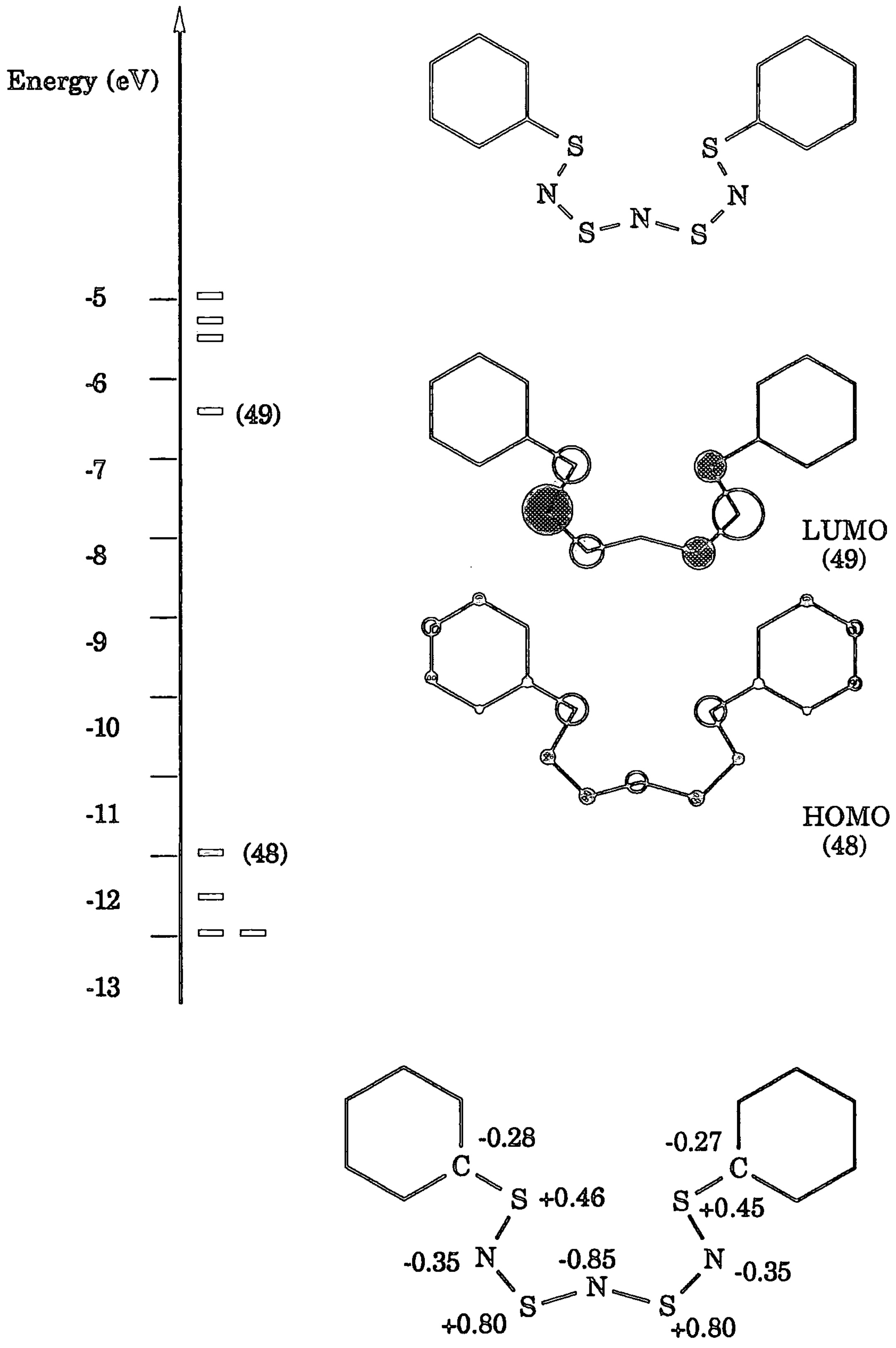


Figure 6.3 Frontier molecular orbitals and partial charges of the CSNSNSNSC chain in [PhSNSNSNSPh][AsF$_6$].



PM3 molecular orbital calculations[17] on this structure indicate several features of interest. The first, and possibly most important, is the S(1)-S(4) bonding interaction of the HOMO. Mayerle *et.al.*[21] previously proposed that the horse-shoe configuration of the [RSNSNSNSR]$^+$ cation is preferred to the zig-zig-zag-zag configuration found[3] in $(SN)_x$ because the former achieves the maximum packing efficiency within the lattice. In 1 the bonding interaction between S(1) and S(4), indicated by the MO calculations, appears to be a major factor in determining the structural conformation.

The calculated charge distribution (figure 6.3) in [PhSNSNSNSPh]$^+$ is quite unusual; it shows strong bond polarisation of the type $S^{\delta+}\cdots N^{\delta-}$, which may explain the inversion of N(2) into the acyclic U-shape of the S_4N_3 chain, as shown below (fig. 6.4). This allows strong secondary interactions of N(2) with both S(1) and S(4) as observed in the crystal structure. Such strong bond polarisation and intramolecular interaction are characteristic of SN chain chemistry. In particular this bond polarisation and the secondary interactions between S(1) and N(2) may provide a convenient explanation of the loss of an SN unit as observed[21] in the hydrolytic decomposition of [Me.C_6H_4.SNSNSNS.C_6H_4.Me]Cl to provide [Me.C_6H_4.SNSNS.C_6H_4.Me] i.e. through loss of the N(1)-S(2) fragment (in the molecule illustrated in figure 6.4) and formation of a formal S(1)-N(2) bond.

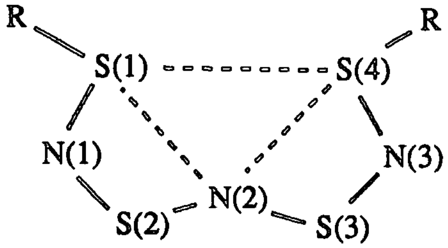


Figure 6.4 The U-shape conformation of the cation in 1 arising from intramolecular S···S and S···N interactions.

6.4 Conclusions and suggestions for further work

The reaction of [SNS][AsF_6] with PhHgCN does not result in the expected cycloaddition compound, PhHgCNSNS, but rather the acyclic, phenylated compound, [PhSNSNSNSPh][AsF_6]. Further investigations into the preparation of these SN chains using $(NSCl)_3$ as a source of [SN]$^+$ leads to the preparation of [$Ar_2S_4N_3$][Cl], in high yield, from the corresponding neutral $Ar_2S_3N_2$ chain. This reaction requires the addition of $AgAsF_6$ when using more sterically hindered aryl groups. (For example Ar = *o*-$O_2N.C_6H_4$ did not appear to react with $(NSCl)_3$ even after two weeks and required an equivalent of $AgAsF_6$ to be added in order to give a chain-lengthened product, whereas the reaction with $Ar_2S_3N_2$ when Ar=*p*-$O_2N.C_6H_4$ was complete within 18 hours.)

The particular reaction could possibly be extended to acyclic azathienes, e.g. $Ar_2N_4S_3$, and higher thiazenes, e.g. $Ar_2S_5N_4$, to produce longer chain cations not readily available by conventional routes.

The solid state structure of $[PhS_4N_3Ph][AsF_6]$ reveals U-shaped planar cations arranged in staggered sheets. This conformation is rationalised using PM3 molecular orbital calculations, with intramolecular $^{\delta+}S \cdots N^{\delta-}$ interactions accounting for the shape.

Further work on these systems could include (as outlined above) the synthesis of longer cationic thiazene and azathiene chains and their matching to anionic species, such as $[S_3N_3]^-$. Further developments may include the use of $[S_3N_3]^-$ salts as potential chain lengthening reagents (see scheme 6.1) and complexation of the U-shaped $[Ph_2S_4N_3]^+$ cation with transition metals.

The reaction of $[SNS][AsF_6]$ with metal cyanides such as $K[Ag(CN)_2]$ or $Au(CN)_2$ may be more fruitful in the preparation of dithiadiazolylium transfer reagents.

6.5 Experimental

6.5.1 Reactions of [SNS][AsF$_6$] with metal and metalloid cyanides

6.5.1.1 Preparation of PhHgCN

PhHgCl (3.51 g, 0.01 mol) and AgCN (1.5 g, 0.01 mol) were stirred for 3 d at room temperature in MeCN (15 ml) to provide a grey-purple suspension. The AgCl was filtered off at a water-pump using a Zitex filter. Evaporation of the filtrate *in vacuo* provided a white solid, which analysed as PhHgCN (2.85 g, 84%).IR ν_{max} (cm^{-1}): 1460mbr, 1335w, 1310w, 1160w, 1083w, 1060w, 1028m,999m, 909m, 860w, 805w, 770w, 730vs, 690vs, 610w, 455s, 395vs.(Found: C, 27.59%; H, 1.58%; N, 4.55%. Calc.: C,27.68%; H, 1.66%; N, 4.61%).

6.5.1.2 Preparation of Ph_3SnCN

Triphenyltin chloride (3.85 g, 0.01 mol) and KCN (0.63 g, 0.01 mol) were stirred, under air in methanol (30 ml) for 4 d at room temperature. The resultant white solid was filtered, on a 'Zitex' membrane, at the pump, washed with water (200 ml) and with methanol (20 ml) - a little solid was washed though. After drying for 12 h *in vacuo* there remained a fine, white powder (3.22 g, 86%) which analysed well as the cyanide. Found: C, 60.07%; H, 3.96%; N, 3.39%. Calc.: C, 60.69%; H, 4.02%; N, 3.79%. The IR indicated a trace of solvent and the presence of a thiocyanate group, ν_{max} (cm^{-1}) : 3050w, 2160w, 1445m, 1370sh, 1070w, 1025w, 1000w, 730s, 695s, 692s, 460sh,s, 455s.

6.5.1.3 Reaction of PhHgCN with [SNS][AsF_6]

Phenylmercury (II) cyanide (0.303 g, 1.0 mmol) and [SNS][AsF_6] (0.270 g, 1.01 mmol) were placed in a two limbed reaction vessel. Liquid SO_2 (10 ml) was condensed on and immediately a red colour was observed which became increasingly purple and then deep blue upon stirring for 24 h. Solvent removal and extraction of the blue product with CH_2Cl_2 (in a closed extractor) gave a pale blue residue and a deep blue filtrate, from which was obtained the deep blue solid [PhSNSNSNSPh][AsF_6] (165 mg, 65% yield based on PhHgCN). The solid was recrystallised from CH_2Cl_2 by slow solvent removal to yield blue-gold diamond-shaped, lustrous crystals, which were identified by X-ray analysis. IR ν_{max} (cm^{-1}): 1733w, 1668w, 1652vw, 1595vw, 1564w, 1306w, 1280vw, 1183m, 1067m, 1023w sh, 978s, 820m, 749s, 698vs br, 556m, 505m, 398vs.

6.5.1.4 Reaction of Ph_3SnCN with [SNS][AsF_6]

Triphenyltin cyanide (0.370 g, 0.001 mol) and [SNS][AsF_6] (0.278 g, 0.001 mol) were stirred in liquid SO_2 for 14 h to give a deep green solution (with some white solid at the edges). Solvent removal gave a sticky, green-black oil. Solvent, CH_2Cl_2 (4 ml), was syringed on and the oil was taken up to give a greyish green solution from which no solid could be obtained by cooling (-10°C for 2h). Hexane (4 ml) was added (after removal of the CH_2Cl_2) and this solublised a pale blue-green material, which was filtered off and pumped dry yielding a green powder. This material gave variable elemental analyses and the IR spectrum showed extensive hydrolysis.

6.5.1.5 Reaction of PhHgCl with [SNS][AsF_6]

Phenylmercury (II) chloride (0.313 g, 1 mmol) and [SNS][AsF_6] (0.267 g, 1 mmol) were placed in a two limbed reaction vessel. Liquid SO_2 (10 ml) was condensed on and immediately a pink-grey colour was observed which became increasingly red-brown and then deep blue-brown upon stirring for 16 h. Filtration and solvent removal separated an oily blue-black solid from the residual grey powder (162 mg). The oily solid furnished a deep blue powder (211 mg) upon washing with CH_2Cl_2 (5 ml) and it was washed further by exhaustive continuous extraction over a period of 7 days (again with CH_2Cl_2). The filtrate gave a golden-blue solid (140 mg, 55% based on PhHgCl), the green-blue residue (25 mg) was severely hydrolysed after an attempt at recrystallisation from liquid SO_2. The IR spectrum of the blue material was as expected for $[Ph_2S_4N_3][AsF_6]$: ν_{max} (cm^{-1}): 1660m, 1565m, 1440m sh, 1308w, 1175m, 1068m, 1005w sh, 975s, 920w, 890w, 820m, 745s sh, 692vs br, 555m, 506m, 396vs. Elemental analysis confirmed the formulation : Found C, 28.15%; H, 2.13%; N, 8.03%.Calc. C, 28.08%; H, 1.97%; N, 8.19%.

6.5.1.6 The reaction of sodium cyanotriphenylborate with $[SNS][AsF_6]$

Sodium cyanotriphenylborate obtained from Lancaster Synthesis (at unspecified purity) appeared crystalline under the microscope but its analysis was poor: 3.89%N (4.81), 68.89%C (78.38), 6.02%H (5.20). A single recrystallisation from toluene / Et_2O improved the elemental analyses: 4.22%N, 72.14%C, 5.86%H, but recovery was low (<50%) so a further recrystallisation of the sample was not attempted.

Upon adding $[SNS][AsF_6]$ (200 mg, 0.75 mmol) to sodium cyanotriphenylborate (220 mg, 0.68 mmol) the yellow-white, heterogeneous solid mix rapidly became grey in colour. A deep olive green colour resulted when SO_2 was condensed onto the mixture and a dirty brown solid and solution remained after stirring for 14 h. Filtration, repeated washing with back-condensed solvent and solvent removal gave a yellow solid residue. IR suggested $NaAsF_6$, with a little hydrolysis apparent [ν_{max} (cm^{-1}): 402vs, 713vs, 1402m, 3000-3300 br]. The deep brown filtrate gave up an intractable brown oil. IR showed extensive hydrolysis and the presence of $[AsF_6]^-$ ν_{max} (cm^{-1}): 3500-3100m br, 3070m, 3045m, 2240w, 2130m, 1970w, 1890w, 1825vw, 1595m, 1020m, 1000m, 905sh, 890m, 735m, 695s br, 640m, 620m, 605m, 580m, 555m, 475w, 400m (also present were multiple, broad bands superimposed on a very broad band between 1700 and 1100cm^{-1}).

6.5.2 *Attempted preparations of $[Ph_2S_2N][AsF_6]$*

6.5.2.1 Reaction of PhLi with $[Cl_2S_2N][AsF_6]$

To a stirred suspension of $[Cl_2S_2N][AsF_6]$ (50 mg, 0.15 mmol) in hexane (5 ml) was added 0.2 ml of 1.48 M PhLi (0.3 mmol) in hexane. No immediate reaction was observed but after stirring for 72 h and filtration there remained an oily, off-white solid and pale orange solution. The solvent was removed *in vacuo* and CH_2Cl_2 (5 ml) added. After sonication and filtration a white residual powder (20 mg) remained with an intractable, oily red-orange material given up by the filtrate upon solvent removal.

6.5.2.2 Reaction of Ph_4Sn with $[Cl_2S_2N][AsF_6]$

Ph_4Sn (107 mg, 0.25 mmol) and $[Cl_2S_2N][AsF_6]$ (170 mg, 0.5 mmol) were stirred in liquid SO_2 for 72h to give a deep red solution. After solvent removal, CH_2Cl_2 (5 ml) was added and the red, oily solid washed three times with back-condensed solvent. A further washing with CCl_4 (5 ml) was attempted but this yielded only a red-purple oily material. Application of SO_2 and CH_2Cl_2 to the material gave a deep blue lustrous powder. This material was shown (by an intense, broad IR band at 3323 cm^{-1}) to be extensively hydrolysed.

6.5.3 Chain lengthening using $(NSCl)_3$

6.5.3.1 General Preparation of $(Ar)_2S_3N_2$ (Ar=*p*-, *o*-$O_2N.C_6H_4$-)

ArSCl (1.66 g, 8.8 mmol) and $Me_3SiNSNSiMe_3$ (1.0 g, 4.4 mmol) were dissolved, separately, in CH_2Cl_2 (10 ml) and the diimide solution added dropwise to the stirred solution of the sulphuryl chloride over a period of several minutes. The yellow solution slowly darkened to deep orange and finally to red. Solvent removal *in vacuo* gave a red-green dichroic solid (1.64 g), which was washed with hexane (in a closed extractor) to leave a red-orange solid (0.78 g, 48%). This analysed as the required product. Found C, 39.33%; H, 2.42%; N, 15.03%.Calc. C, 39.13%; H, 2.17%; N, 15.21%.

6.5.3.2 Reaction of $(p\text{-}O_2N.C_6H_4)_2S_3N_2$ with $(NSCl)_3$ (Ar=*p*-$O_2N.C_6H_4$-)

ArSNSNSAr (368 mg, 1 mmol) and $(NSCl)_3$ (82 mg, 0.33 mmol) were placed in a Schlenk tube and stirred in CH_2Cl_2 for 18 h at room temperature to provide a brown solid under a red solution. The solvent was removed *in vacuo* and the crude product exhaustively extracted with hexane. Recovered yield 342 mg, 76%. IR ν_{max} (cm^{-1}): 1600m, 1572m, 1505s, 1400w, 1338s, 1286m, 1172w, 1107m, 1066s, 1004m, 972m, 865m, 850s, 744m,738s,728s,717s, 720m, 620w, 545m, 475m, 455m, 362m, 330w. (Found C, 32.35%; H, 1.99%; N, 15.94%.Calc. C, 32.02%; H, 1.78%; N, 15.56%).

6.5.3.3 Metathesis of $[(p\text{-}O_2N.C_6H_4)_2S_4N_3][Cl]$ to give the $[AsF_6]$ salt (Ar=*p*-$O_2N.C_6H_4$-)

[ArSNSNSNSAr]Cl (100 mg, 0.22 mmol) and $AgAsF_6$ (70 mg, 0.23 mmol) were stirred in one limb of a two-limbed reaction vessel in liquid SO_2 to give an immediate blue solution. Stirring was continued for 18 h then filtration provided an orange-white residue (contaminated AgCl) and a blue filtrate. Evaporation of the solvent provided golden, blue-black crystals of $[ArSNSNSNSAr][AsF_6]$ (Recovered yield 80 mg, 60%).IR ν_{max}

(cm^{-1}): 1679m, 1597s, 1576vs, 1509vs, 1288vs, 1176s, 1146s, 1106m, 1080m, 985m, 853vs, 804w, 741s, 698vs, 621m, 548m, 480m, 400vs. (Found C, 24.59%; H, 1.68%; N, 10.56%. Calc. C, 23.88%; H, 1.33%; N, 11.60%).

6.5.3.4 Reaction of $(o\text{-}O_2N.C_6H_4)_2S_3N_2$ with $(NSCl)_3$ in the presence of $AgAsF_6$

$(o\text{-}O_2N.C_6H_4)SNSNS(o\text{-}O_2N.C_6H_4)$ (656 mg, 1.8 mmol) and $(NSCl)_3$ (146 mg, 0.6 mmol) were placed in a Schlenk tube and stirred in CH_2Cl_2 for 14 days at room temperature with no apparent colour change. The solvent was removed *in vacuo*, $AgAsF_6$ (530 mg, 1.8 mmol) added and the mixture stirred in CH_2Cl_2 for a further 2 days. During this time a white solid was precipitated and the blue-green solution was filtered off. The filtrate was pumped to dryness to yield a deep green-blue solid, which was washed with hexane (3 x 5 ml) and then dried *in vacuo*. Yield = 0.85 g, 78%. IR ν_{max} (cm^{-1}): 1589s, 1569s, 1513s, 1459s, 1308s, 1191m, 1171m, 1152s, 1069m, 1040m, 984s, 877w, 854vs, 814w, 790vs, 768s, 736s sh, 700vs br, 592m br, 570m, 542w, 512m, 487w sh, 452m, 398vs. (Found C, 23.78%; H, 1.43%; N, 11.80%. Calc. C, 23.88%; H, 1.33%; N, 11.61%).

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Chapter 7

The reaction of 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolylium hexafluoroarsenate (V) with tetramethylammonium fluoride: the X-ray crystal structure of 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl

7.1 Introduction

Although many alkyl and aryl dithiadiazolylium salts are known[1], for example the chloride, bromide, iodide, hexachloroantimonate(V) and hexafluoroarsenate(V), the fluoride has never been isolated and fully characterised.

Several attempts have been made[2] to prepare 4-phenyl-1,2,3,5-dithiadiazolylium fluoride, [D]F, and there is somewhat circumstantial evidence for its preparation and that of the analogous compound, $[D]_3F$.

$$AgF_2 + [Ph\text{-}CN_2S_2]_2 \xrightarrow{CCl_4} [Ph\text{-}CN_2S_2]_3F + [Ph\text{-}CN_2S_2]F \qquad [Eq.\ 7.1]$$

Another attempted fluorination[2], using N_2F_4 in liquid SO_2, has given the fluorosulphite salt as the major product (equation 7.2).

$$3N_2F_4 + 2\,[Ph\text{-}CN_2S_2]_2 + 4SO_2 \xrightarrow{SO_2} 4\,[Ph\text{-}CN_2S_2]SO_2F_3 + 3N_2 \qquad [Eq.\ 7.2]$$

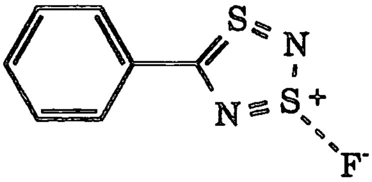
A dithiadiazolylium fluoride would be of interest in the study of the covalent - ionic barrier in the various dithiadiazolyliums. It would provide a useful insight into bonding in these compounds. Therefore, it was considered to be of interest as a target molecule.

7.2 Results and discussion

The availability of a small quantity of dry $[Me_4N]F$ presented an opportunity for the synthesis of a dithiadiazolylium fluoride by a previously untried metathesis reaction:

$$[Me_4N]F + [Ar\text{-}CN_2S_2][AsF_6] \longrightarrow [Me_4N][AsF_6] + [Ar\text{-}CN_2S_2]F \qquad [Eq.\ 7.3]$$

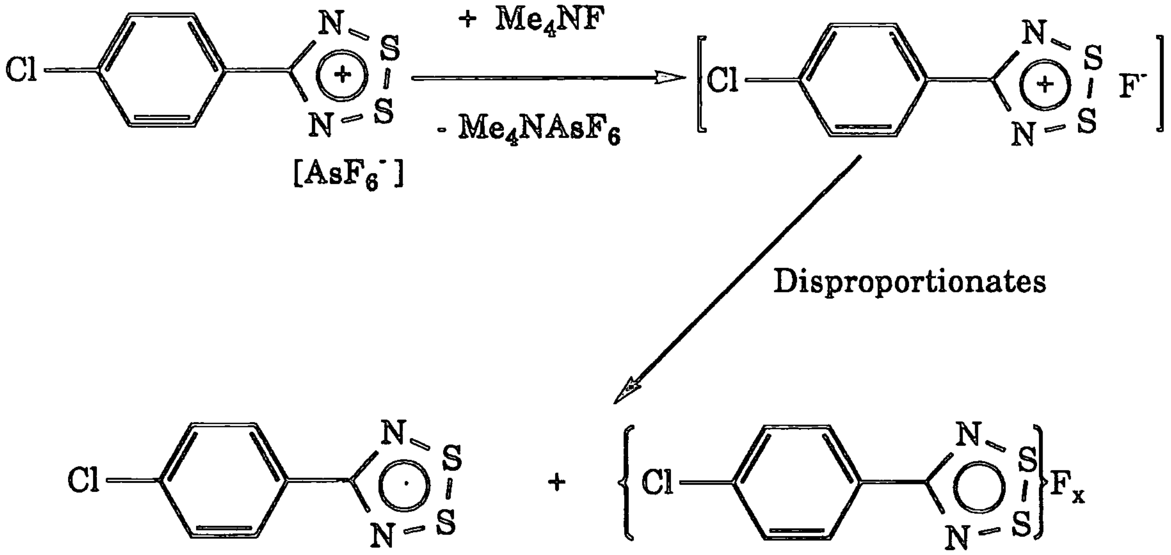
Both 1,2,3,5 and 1,3,2,4-dithiadiazolylium salts were used, with the 1,3,2,4-isomer favoured initially - as the positive charge is more localised on the S3 atom (in the usual labelling convention) allowing for association of the fluoride anion with one centre.



However, the oily red solid obtained from the reaction of 5-phenyl-1,3,2,4-dithiadiazolylium hexafluoroarsenate(V) with $[Me_4N]F$ proved to be extremely sensitive to moisture; rhombic crystals, obtained by slow solvent extraction with acetonitrile, decomposed to give a colourless rhombic shell and a polycrystalline interior.

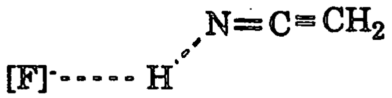
In comparison, when 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolylium hexafluoroarsenate(V) reacted with $[Me_4N]F$ an immediate colour change occurred to give a deep red solid which was isolated by filtration. This material was then recrystallised from acetonitrile using the temperature 'ripple' technique described in chapter 2. The crystals obtained were subsequently found to be split, but they were recrystallised in a similar manner from CH_2Cl_2 to give needles suitable for single crystal X-ray diffraction studies. These red-black needles were air-stable, which suggested that they were not of a simple ionic fluoride. They were later confirmed to be of the 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl radical, $(p\text{-}Cl.C_6H_4.CNSSN)_2$ (or *p*Cl-D).

A possible explanation for the isolation of this unexpected product from a simple metathesis reaction is that a transient fluorinated dithiadiazolylium species, formed by metathesis, disproportionates to give a perfluorinated dithiadiazolyl and the observed free radical.



[Eq. 7.4]

^{19}F nmr was utilised in an attempt to rationalise this reaction; $[AsF_6]^-$ was observed in both the red recrystallised material and the reaction mixture, as a 1:1:1:1 quartet between (-)62 and (-)69 ppm. Anionic fluoride was observed in the $[Me_4N]F$ starting material at (-)76ppm together with another resonance at (-)148ppm. The latter resonance could be due to solvent association.


$[F]^- \cdots\cdots H \cdots N{=}C{=}CH_2$

Both the reaction mixture and the recrystallised dithiadiazolyl contained the pentet associated with $[AsF_6]^-$ and resonances at (-)151 and (-)138 ppm, although the former was much less intense than that seen for $[Me_4N]F$. The singlet at (-)138 ppm seems to be the most likely candidate for a $[p\text{Cl-DF}_x]$ species. The fluorine (or fluorines) are most likely to be bound to sulphur as the nmr resonance would broaden if they were coupled to nitrogen. Rapid fluoride exchange in solution may account for the singlet in the nmr.

Crystals of another compound were obtained from above solid $[p\text{Cl-D}][AsF_6]$ in a crystal growth experiment using $[p\text{Cl-D}][AsF_6]$ and $[Me_4N]F$ in an upside down 'dog'; where a solution of $[Me_4N]F$ in CH_2Cl_2 was allowed to diffuse over solid $[p\text{Cl-D}][AsF_6]$. These colourless needles were of a size suitable for single crystal X-ray diffraction, but they were subsequently found to be heavily twinned. Insufficient material remained after crystal picking for elemental analyses or IR. However mass spectrometry revealed the presence of the para-chlorophenyldithiadiazolylium cation.

The appearance and extreme air-sensitivity of this colourless material strongly suggested that it may have been the per-fluorinated dithiadiazolyl proposed in equation 7.4.

7.3 Solid state structure of 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl

Although the aryl-1,2,3,5-dithiadiazolyls are well known and well characterised compounds, the only crystal structure which had been determined, until recently, was that of phenyl-1,2,3,5-dithiadiazolyl[3]. Results were not entirely satisfactory as the R value was 8.2%. However, at about the time that this work was conducted Oakley and co-workers[4] prepared several cyano-substituted aryl dithiadiazolyls and diselenadiazolyls, obtaining good single crystals of these by sublimation. A comparison of the intramolecular bond distances in these systems is given in table 7.1.

The crystal parameters for 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl are given in table 7.2, the atomic coordinates in table 7.3, the bond lengths and angles in table 7.4, anisotropic thermal parameters in table 7.5 and atomic coordinates plus isotropic displacement parameters for the hydrogen atoms in table 7.6. Figure 7.1 shows the atom numbering scheme used for the eclipsed dimer units.

Figure 7.1 The 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl dimer unit showing the atom numbering scheme

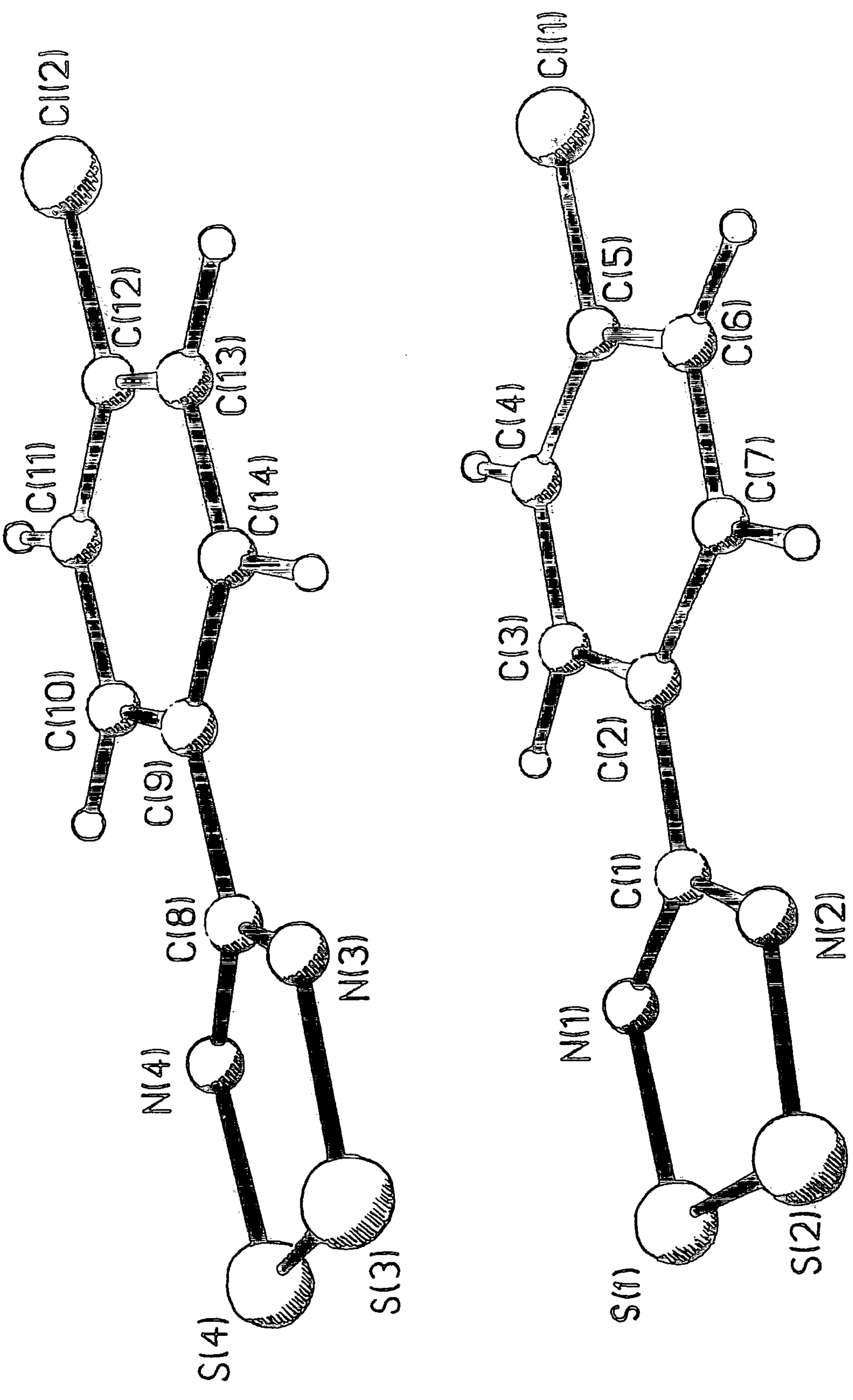


Table 7.1 Selected bond distances (Å) in aryl 1,2,3,5-dithiadiazolyls (see below for atom numbering scheme)

Bond	Ph	*p*-Cl-C_6H_4	*p*-CN-C_6H_4	*m*-CN-C_6H_4
S_1-S_2	2.089	2.085(2)	2.08	2.08
S_1-N_1	1.625	1.635(3)	1.63	1.64
S_2-N_2	1.625	1.632(3)	1.63	1.62
C-N_1	1.337	1.333(5)	1.34	1.33
C-N_2	1.330	1.333(5)	1.33	1.34
Ref	3	This Work	4	4

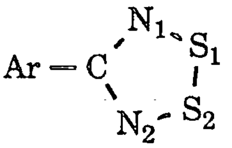


Table 7.2 Crystal parameters and data collection / refinement for 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl

Formula	$C_{14}H_8Cl_2N_{44}S_4$	θ range for unit cell	21.28 - 24.27°
M.W.	431.38	Space Group	C2/c
Crystal Size (mm)	0.27x0.19x0.12	Z	8
Crystal Form	Red	D_c (gcm^{-3})	1.755
Instrument	Stoe-Siemens	F(000)	1744
Radiation	Cu(Kα)	μ/mm^{-1}	8.409
λ(Å)	1.54184	T/K	113.0(10)
Scan Type	ω/θ	θ range for data	4.25-64.91°
Crystal System	Monoclinic	Total Data Measured	4023
a/Å	20.859(4)	Total Unique	2667
b/Å	9.971(2)	Total Observed	2658
c/Å	15.736(3)	Significance Test	$F_o>4\sigma(F_o)$
α/°	90	No. of Parameters	217
β/°	103.12(3)	ρ_{min}- ρ_{max}/eÅ^{-3}	(-0.454)-(0.376)
γ/°	90	Weighting Scheme	
V/Å^3	3264.6(11)	R	0.0420
		R_w	0.0585

As expected there is little significant difference in the bond lengths for the phenyl and para-substituted phenyl dithiadiazolyls (see table 7.1). The solid state structure of the corresponding cation (as the [AsF$_6$]$^-$ salt) has recently been determined[5]. As expected, the S-N and S-S bond distances (2.010(5)Å and 1.587(7)Å respectively) are shorter in the cation, whereas the C-N bond is slightly longer at 1.341(9)Å. Such changes in bond length are readily explained in terms of occupancy of the SOMO based on the dithiadiazolyl ring which is antibonding in S-N and S-S, but bonding in C-N.

Table 7.3 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl(1)	6451.5(5)	4167.9(9)	6221.7(6)	33.5(6)
C1(2)	5963.4(6)	6817.1(10)	7823.3(6)	39.5(8)
S(1)	5855.4(5)	-1542.8(9)	9932.0(6)	26.6(6)
S(2)	6855.1(5)	-1472.2(9)	10110.3(6)	30.3(6)
S(3)	6684.4(5)	817.4(9)	11440.5(6)	27.5(6)
S(4)	5685.2(5)	587.2(9)	11299.4(6)	26.7(6)
N(1)	5818(2)	-411(3)	9178(2)	25(2)
N(2)	6944(2)	-361(3)	9367(2)	29(2)
N(3)	6708(2)	2018(3)	10736(2)	25(2)
N(4)	5582(2)	1782(3)	10588(2)	26(2)
C(1)	6389(2)	43(4)	8977(2)	25(2)
C(2)	6415(2)	1037(3)	8286(2)	21(2)
C(3)	5846(2)	1571(4)	7914(2)	26(2)
C(4)	5855(2)	2535(4)	7276(2)	27(2)
C(5)	6442(2)	2946(4)	7012(2)	26(2)
C(6)	7019(2)	2411(4)	7362(2)	28(2)
C(7)	7002(2)	1457(4)	8000(2)	27(2)
C(8)	6130(2)	2373(3)	10392(2)	22(2)
C(9)	6088(2)	3469(3)	9755(2)	23(2)
C(10)	5493(2)	3968(4)	9450(2)	27(2)
C(11)	5445(2)	5015(4)	8853(2)	28(2)
C(12)	6006(2)	5520(4)	8566(2)	26(3)
C(13)	6607(2)	5037(4)	8859(2)	29(3)
C(14)	6647(2)	4010(4)	9453(2)	26(2)

Table 7.4 Bond lengths (Å) and angles (degrees) in (p-$Cl.C_6H_4.CNSSN)_2$.

Cl(1)-C(5)	1.742(4)	C1(2)-C(12)	1.742(4)
S(1)-N(1)	1.635(3)	S(1)-S(2)	2.085(2)
S(2)-N(2)	1.632(3)	S(3)-N(3)	1.634(3)
S(3)-S(4)	2.093(2)	S(4)-N(4)	1.638(3)
N(1)-C(1)	1.333(5)	N(2)-C(1)	1.333(5)
N(3)-C(8)	1.334(5)	N(4)-C(8)	1.342(5)
C(1)-C(2)	1.475(5)	C(2)-C(3)	1.391(6)
C(2)-C(7)	1.398(5)	C(3)-C(4)	1.390(5)
C(4)-C(5)	1.382(5)	C(5)-C(6)	1.395(6)
C(6)-C(7)	1.385(5)	C(8)-C(9)	1.481(5)
C(9)-C(10)	1.390(6)	C(9)-C(14)	1.398(5)
C(10)-C(11)	1.403(5)	C(11)-C(12)	1.380(6)
C(12)-C(13)	1.390(6)	C(13)-C(14)	1.385(5)

N(1)-S(1)-S(2)	94.02(13)	N(2)-S(2)-S(1)	95.16(13)
N(3)-S(3)-S(4)	94.94(13)	N(4)-S(4)-S(3)	94.29(13)
C(1)-N(1)-S(1)	114.1(3)	C(1)-N(2)-S(2)	113.3(3)
C(8)-N(3)-S(3)	113.6(2)	C(8)-N(4)-S(4)	113.8(3)
N(2)-C(1)-N(1)	123.3(3)	N(2)-C(1)-C(2)	117.8(3)
N(1)-C(1)-C(2)	118.8(4)	C(3)-C(2)-C(7)	119.3(3)
C(3)-C(2)-C(1)	119.6(3)	C(7)-C(2)-C(1)	121.1(4)
C(2)-C(3)-C(4)	120.9(3)	C(5)-C(4)-C(3)	118.7(4)
C(4)-C(5)-C(6)	121.7(3)	C(4)-C(5)-Cl(1)	118.6(3)
C(6)-C(5)-Cl(1)	119.7(3)	C(7)-C(6)-C(5)	118.8(3)
C(6)-C(7)-C(2)	120.5(4)	N(3)-C(8)-N(4)	123.4(3)
N(3)-C(8)-C(9)	118.6(3)	N(4)-C(8)-C(9)	118.0(3)
C(10)-C(9)-C(14)	119.3(3)	C(10)-C(9)-C(8)	120.4(3)
C(14)-C(9)-C(8)	120.2(4)	C(9)-C(10)-C(11)	121.1(4)
C(12)-C(11)-C(10)	118.0(4)	C(11)-C(12)-C(13)	122.1(3)
C(11)-C(12)-C1(2)	119.1(3)	C(13)-C(12)-C1(2)	118.8(3)
C(14)-C(13)-C(12)	119.3(3)	C(13)-C(14)-C(9)	120.2(4)

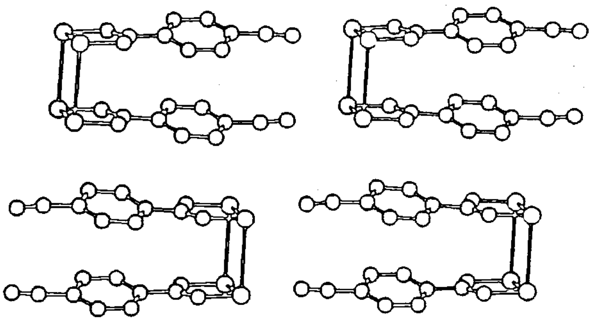
Table 7.5 Anisotropic displacement parameters (Å^2 x 10^3) for (p-Cl.C_6H_4.CNSSN)$_2$. The anisotropic temperature factor exponent takes the form $-2\pi^2(ha^{*2}U_{11}+...+2hka^*b^*U_{12})$.

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cl(1)	39.1(6)	27.8(5)	34.5(5)	6.1(4)	9.6(4)	-4.5(4)
Cl(2)	56.7(8)	27.2(5)	35.5(5)	9.2(4)	10.1(5)	-1.0(5)
S(1)	26.0(6)	21.3(5)	32.6(5)	2.5(3)	3.0(4)	-2.4(3)
S(2)	25.6(6)	30.3(5)	35.3(5)	5.6(4)	5.1(4)	5.5(4)
S(3)	28.3(6)	24.4(5)	29.7(5)	2.2(3)	1.6(4)	0.4(4)
S(4)	26.8(6)	23.6(5)	30.7(5)	5.2(3)	8.1(4)	0.6(4)
N(1)	26(2)	21(2)	29(2)	0.2(12)	2.4(13)	-2.2(13)
N(2)	22(2)	34(2)	32(2)	3.7(14)	9.0(14)	1.4(14)
N(3)	23(2)	21(2)	32(2)	0.1(12)	4.2(13)	-4.1(13)
N(4)	27(2)	20(2)	30(2)	8.8(12)	5.4(13)	4.3(13)
C(1)	25(2)	22(2)	30(2)	-5.2(15)	9(2)	-2(2)
C(2)	23(2)	18(2)	23(2)	-2.7(13)	3.1(14)	1.5(15)
C(3)	24(2)	24(2)	30(2)	-2.4(14)	10(2)	-2.6(15)
C(4)	24(2)	28(2)	29(2)	0(2)	5(2)	1(2)
C(5)	33(2)	21(2)	26(2)	-3.8(14)	10(2)	-5(2)
C(6)	30(2)	27(2)	28(2)	-5(2)	9(2)	-7(2)
C(7)	24(2)	27(2)	31(2)	-4.9(15)	6(2)	1(2)
C(8)	25(2)	16(2)	27(2)	-4.5(14)	5.8(15)	-1.2(15)
C(9)	27(2)	15(2)	27(2)	-1.7(13)	8(2)	0.1(14)
C(10)	29(2)	21(2)	33(2)	-1.8(15)	10(2)	0(2)
C(11)	31(2)	23(2)	31(2)	0.6(15)	4(2)	4(2)
C(12)	39(3)	16(2)	25(2)	1.5(14)	7(2)	-2(2)
C(13)	35(3)	24(2)	31(2)	-1.4(15)	12(2)	-8(2)
C(14)	24(2)	24(2)	32(2)	-2.2(15)	5(2)	-1(2)

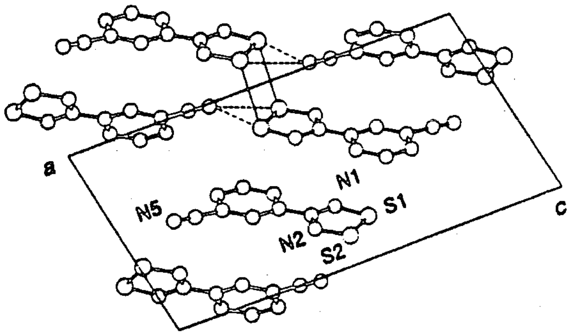
Table 7.6 Atomic coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for hydrogen atoms

	x	y	z	U
H(3)	5450(2)	1277(4)	8096(2)	31
H(4)	5470(2)	2899(4)	7030(2)	33
H(6)	7414(2)	2692(4)	7168(2)	33
H(7)	7387(2)	1089(4)	8242(2)	33
H(10)	5116(2)	3598(4)	9648(2)	33
H(11)	5043(2)	5361(4)	8655(2)	34
H(13)	6982(2)	5404(4)	8656(2)	35
H(14)	7051(2)	3675(4)	9653(2)	32

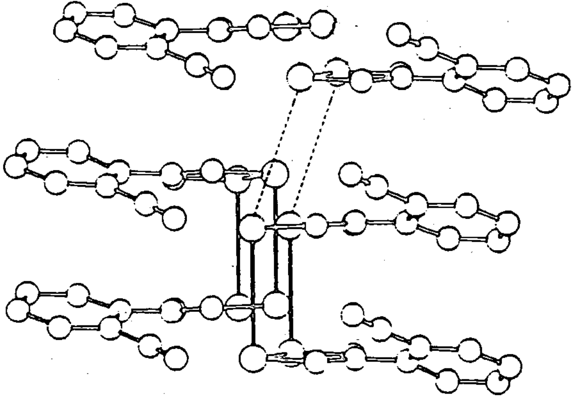
Figure 7.2 Solid state packing in some related dithia / diselenadiazolyls



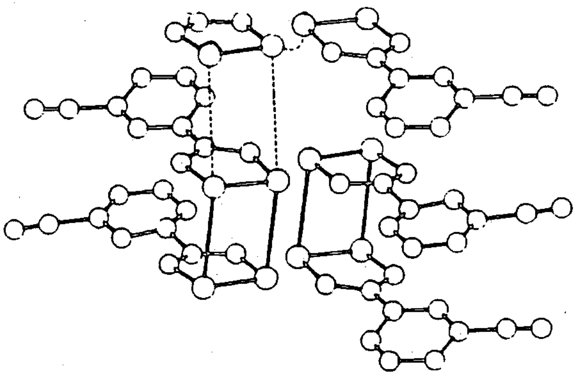
In *p*- (CN).C_6H_4.CNSeSeN ribbons of dimeric units (connected by head to tail CN···Se interactions) stack in an anti-parallel fashion



In *m*- (CN).C_6H_4.CNSSN dimer pairs are formed in an non-eclipsed fashion which is mediated by inter-dimer CN···S interactions



In *o*- (CN).C_6H_4.CNSeSeN there arise pseudo-vertical arrays of dimeric units (connected by inter-dimer Se···Se interactions)



In *m*- (CN).C_6H_4.CNSeSeN stacks of dimer pairs are almost vertical (and are mediated by Se···Se and CN···Se interactions)

7.3.2 Gross structure

As normal in the mono-functional aryl -1,2,3,5-dithiadiazolyls, dimerisation occurs by means of S···S interactions between, in this case, coplanar, eclipsed molecules. Examples of dithiadiazolyl structures are shown in figure 7.2.

The S···S interactions in 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl are of the order of those observed in the related systems, viz. 3.062 Å and 3.135 Å, as compared to 3.06 Å and 3.14 Å in the phenyl analogue and 3.23Å (mean) in the para-cyano analogue.

There are also four S···N interactions (at 3.060 Å) between pairs of dimer units leading to the formation of loose tetramers (as shown in figure 7.3). Such in-plane interactions have not been previously observed in dithiadiazolyls, although sulphur and selenium have been seen to interact with nitrile nitrogens in several recent structures (e.g. in cyanophenyl substituted analogues[4] and in $(NC)_2C=CNSNS$ - see chapter 3). These are in the plane of the molecule and are shorter than those observed in the phenyl system (3.17 and 3.07 Å) where a single nitrogen interacts, out of plane, with two sulphurs.

Furthermore, there are S···Cl interactions both perpendicular (figures 7.4, 7.5 and 7.6) and parallel to the plane of the molecule. The perpendicular interactions are shorter (3.487 Å and 3.347 Å, compared to 3.609 Å and 3.548 Å) and give rise to a structure containing alternating perpendicular tetrameric units (see figs 7.5 and 7.6). The difference in interaction distances could be explained partly by the anisotropy of the van der Waals radius of the chlorine atom. This radius is greater perpendicular to the plane of the C-Cl bond (this is due to the effective radius being greater out of the plane of the C-Cl bond than in it, i.e. ca. 1.78 Å compared to 1.58 Å[6]). Such anisotropy in the van der Waals radius facilitates a greater interaction out of plane of the molecule than in plane.

It can be seen that a simple change in aryl substituent causes a considerable change in the packing of this type of radical, as observed by Oakley and co-workers for their cyano-substituted dithia/diselenadiazolyls[4] - see figure 7.2. Further investigation into the effect of substituent on the packing in aryl dithiadiazolyls and related species should provide an insight into possibilities of preparing new materials with multi-dimensional properties (particularly useful in the development of novel electronic and magnetic materials).

Figure 7.3 Tetramers formed by S···N interactions between dimer units of 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl

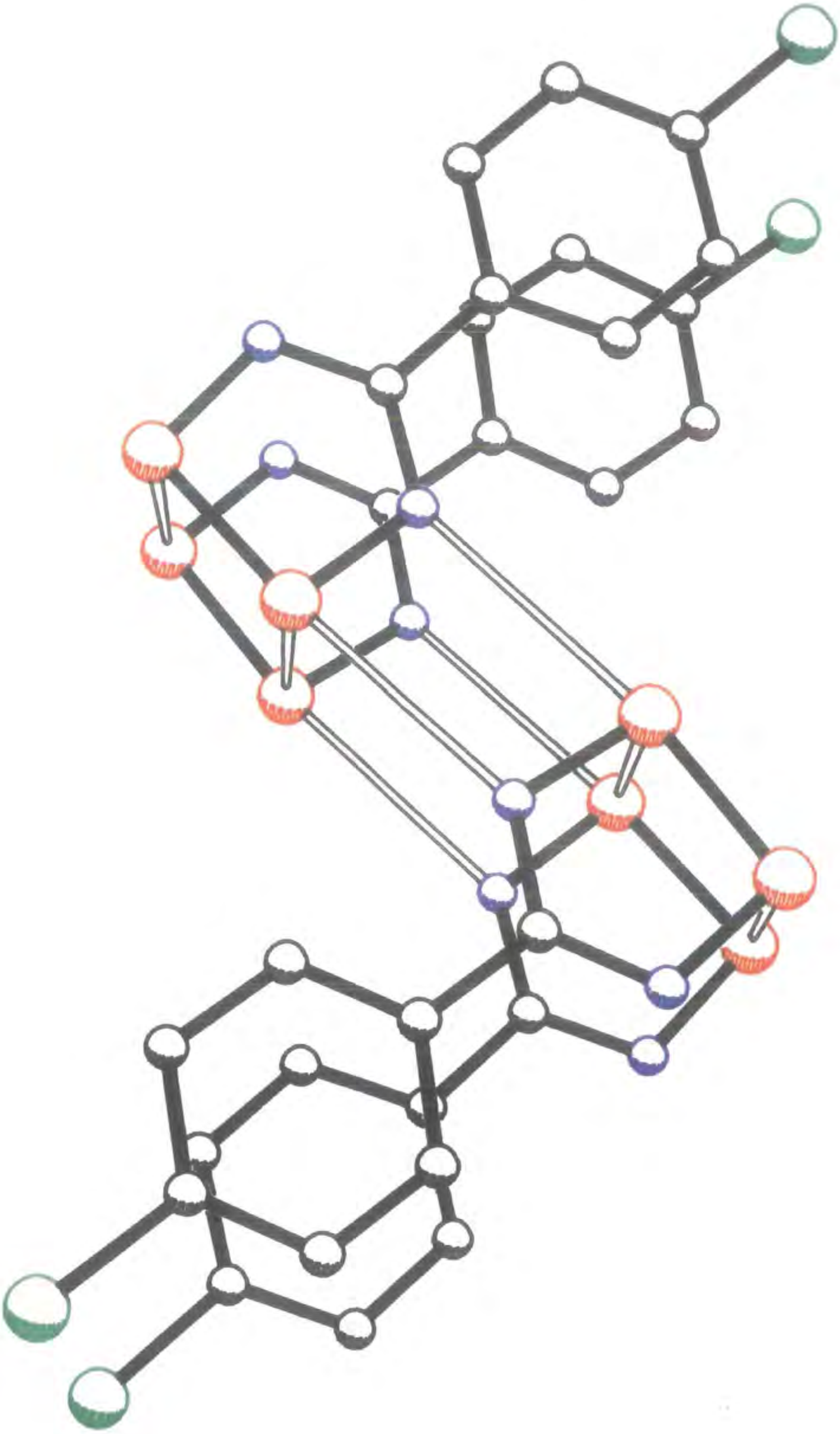


Figure 7.4 Out of plane S···Cl interactions in the solid state structure of 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl

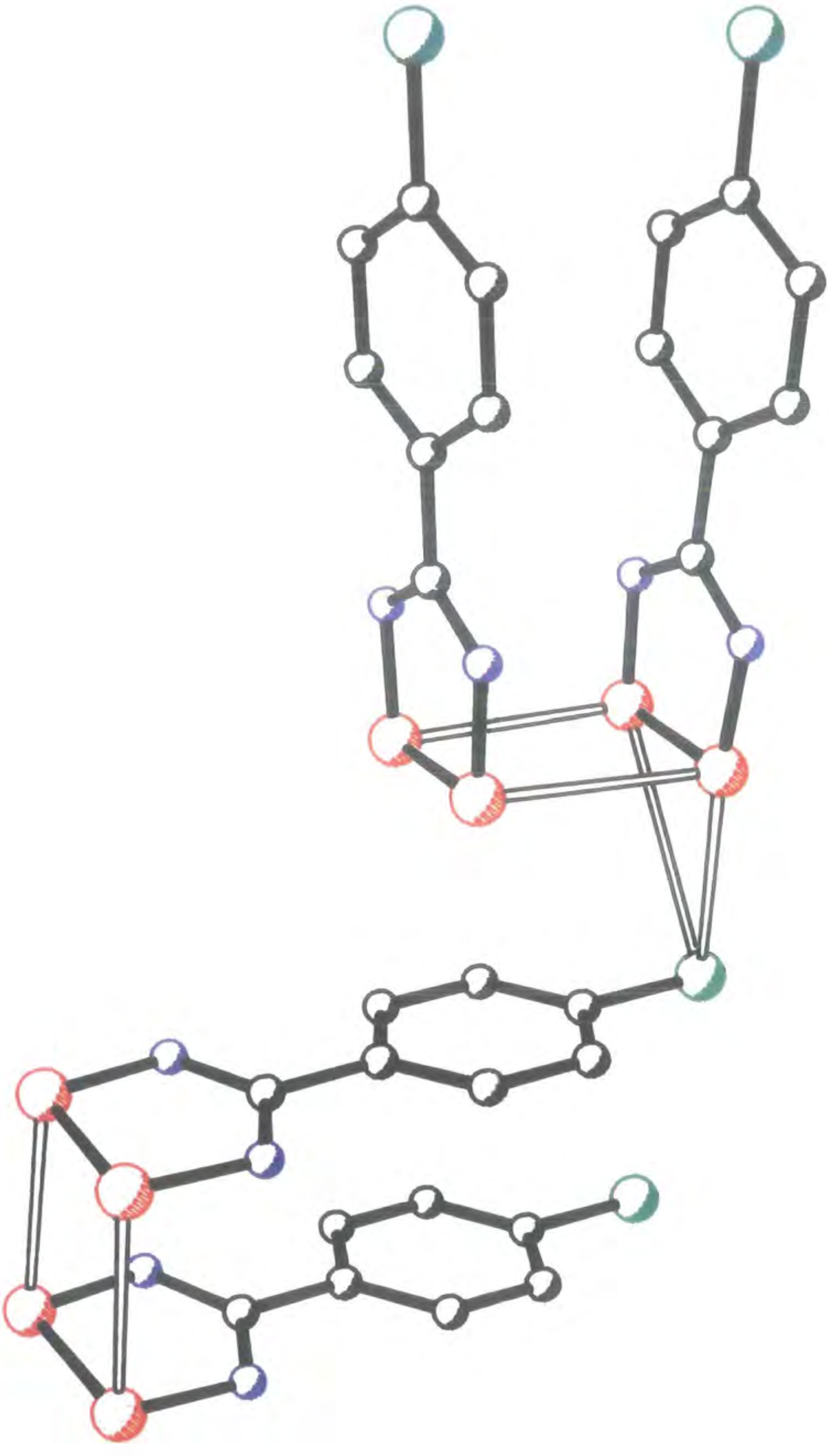


Figure 7.5 Packing in 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl, showing the out of plane S···Cl interactions in the solid state.

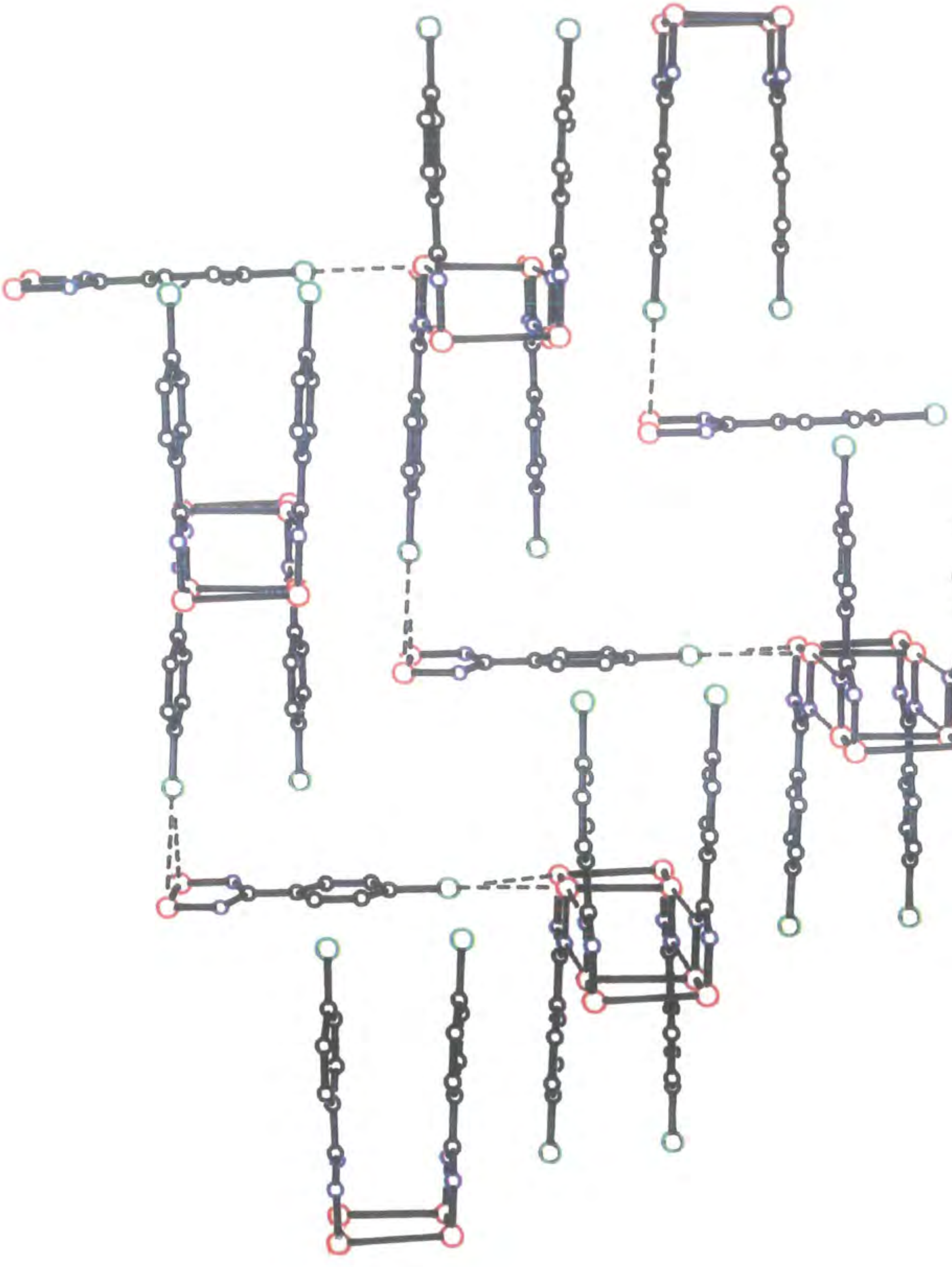
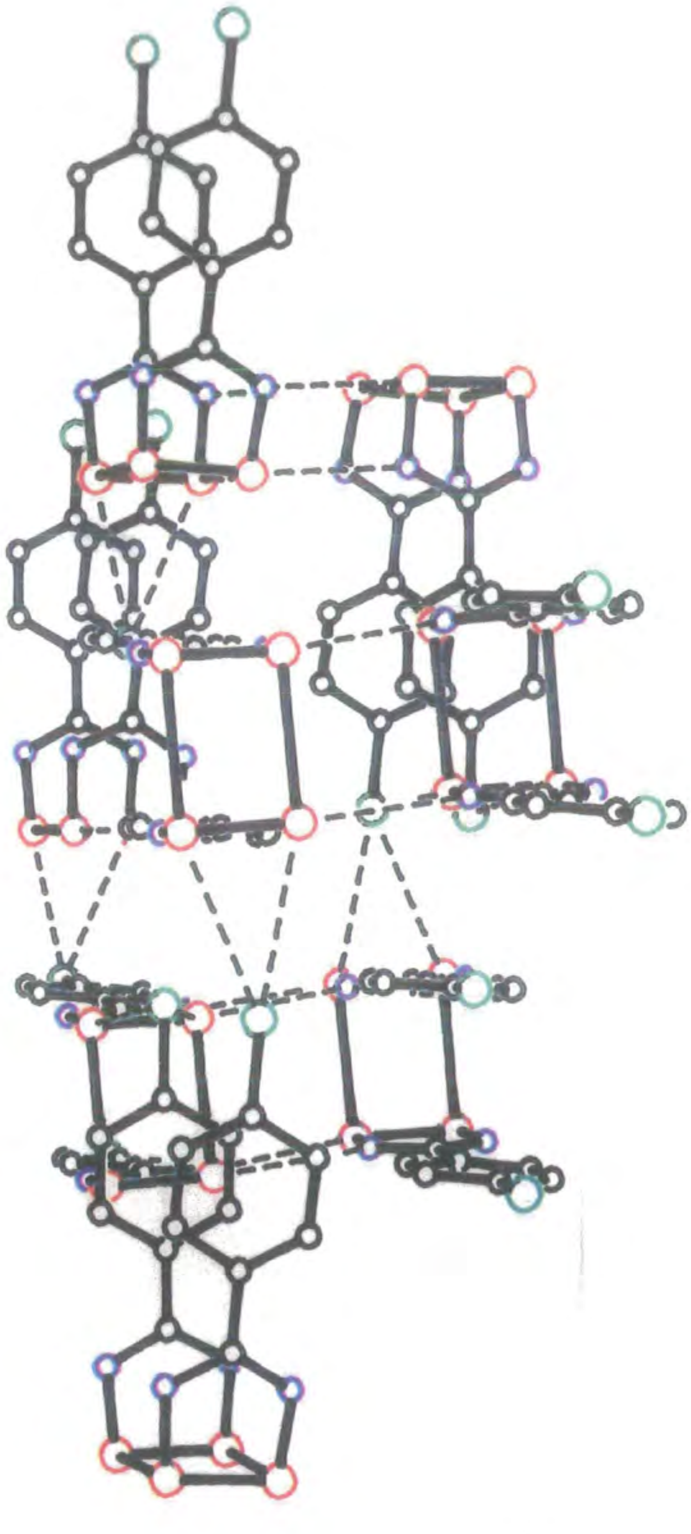


Figure 7.6 Alternative view of the packing in 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolyl, showing the out of plane S···Cl interactions in the solid state.



7.4 Conclusions and suggestions for further work

4-(4-Chlorophenyl)-1,2,3,5-dithiadiazolyl is an unexpected product of the reaction of $[Me_4N]F$ with 4-(4-chlorophenyl)-1,2,3,5-dithiadiazolylium hexafluoroarsenate. This reaction may proceed via metathesis of the dithiadiazolylium to the fluoride followed by disproportionation to yield a perfluorinated CN_2S_2 ring and the observed product.

In order to fully characterise the products of this complex reaction any dithiadiazolyl present could be sublimed out and the $[Me_4N]AsF_6$ removed by washing with an appropriate solvent. The remaining material could then be characterised (by ^{19}F nmr, elemental analysis and single crystal X-ray diffraction).

Although the solid state structure of 4-(4-chloro-phenyl)-dithiadiazolyl is similar to those of other aryl dithiadiazolyls already studied it contains unusual S··N interactions, similar to those seen in $(NC)_2C{=}CNSNS)$.

7.5 Experimental

7.5.1 Reaction of $[Me_4N]F$ with $[p\text{-}Cl.C_6H_4.CNSSN][AsF_6]$

$[p\text{-}Cl.C_6H_4.CNSSN][AsF_6]$ (1.500 g, 3.75 mmol) and $[Me_4N]F$ (0.300g, 3.8 mmol) were placed in one limb of a two-limbed reaction vessel and acetonitrile (8 ml) was syringed onto the mixture. This was stirred for 18 h to yield a dichroic red-green solid and solution. After solvent removal *in vacuo* CH_2Cl_2 was added and the material washed several times by repeated filtration and back-condensation of solvent (4 x 5 ml) to yield an orange-green lustrous filtrate (0.500 g) and a dark red residual solid (1.050g). The red material was exhaustively extracted with CH_2Cl_2 to give a pale yellow insoluble powder (700 mg) and a red-green extractate, which was recrystallised by slow removal of solvent from a saturated solution in CH_2Cl_2 to yield red needles. These crystals were found to be suitable for single crystal X-ray diffraction and their structure shown to be that of $[p\text{-}Cl.C_6H_4.CNSSN]$. The IR of the red-green material was recorded (ν_{max} / cm^{-1}): 1740vw, 1655vw, 1626vw, 1593m br, 1493m, 1404m, 1304w, 1238w, 1261w, 1245w, 1175w, 1165w, 1142m, 1134m, 1103w, 1092m, 1016m, 972vw, 928vw, 905w, 846s, 838s sh, 809s, 779vs, 720s, 649m, 631vw, 550w br, 510m, 486m, 428w, 400w, 220m.

Deep red-green dichroic needles were also obtained from acetonitrile (by simple warming and cooling) and these analysed well as $[p\text{-}Cl.C_6H_4.CNSSN]_2[F]$: Found 37.27%C, 1.93%H, 12.36%N; calc. 37.33%C, 1.75%H, 12.45%N. ($[p\text{-}Cl.C_6H_4.CNSSN]$ calc. 38.79%C, 1.85%H, 12.93%N.)

However, this material did not diffract as the crystals were split.

7.5.2 Crystal growth of [Me_4N]F with [*p*-$Cl.C_6H_4.CNSSN$][AsF_6] in CH_2Cl_2

[*p*-$Cl.C_6H_4.CNSSN$][AsF_6] (ca. 15 mg) and [Me_4N]F (ca. 20 mg) were placed in separate bulbs of a two-limbed reaction vessel and CH_2Cl_2 (8 ml) was syringed onto each. After equilibration the whole apparatus was inverted and the solutions allowed to diffuse together through a medium porosity glass frit. After twelve weeks colourless needles had formed amongst the orange powder on the [*p*-$Cl.C_6H_4.CNSSN$][AsF_6] side. These were submitted loose for single crystal X-ray diffraction but they gave no diffraction effects. Also further samples were laboriously picked in the glove box and mounted under dry nitrogen in Lindemann capillaries. These crystals were found to be twinned or intergrown and they did not provide enough data to give a crystal index. Their mass spectrum was also obtained, CI^+ m/e (intensity): 301.91 (0.39), 154.97 (1.99) - corresponds to [$Cl.C_6H_4.CS$]$^+$ or [$Cl.C_6H_4.CN.NH_4$]$^+$ (chemical ionisation with NH_4^+).

7.5.3 Reaction of [Me_4N]F with [$C_6H_5.CNSNS$][AsF_6]

[$C_6H_5.CNSNS$][AsF_6] (0.180 g, 0.5 mmol and Me_4NF (0.038 g, 0.5 mmol) were placed in one limb of a two-limbed reaction vessel and CH_2Cl_2 (8 ml) was syringed onto the mixture to give an immediate brown colour. This was stirred for 18 h to yield a pale yellow solid and a deep red-brown solution. Repeated filtration and back-condensation of solvent (4 x 5 ml) followed by solvent removal *in vacuo* gave a deep red oily filtrate (30 mg) and a pale yellow residual solid (110 mg).

7.5.5 Reaction of [Me_4N]F with [$C_6H_4(SNS)$][AsF_6]

[$C_6H_4(SNS)$][AsF_6] (0.172 g, 0.5 mmol) prepared by the route outlined in appendix 2, and Me_4NF (0.047 g, 0.6 mmol) were placed in one limb of a two-limbed reaction vessel and acetonitrile (8 ml) was syringed onto the mixture to give an immediate red-brown colour. This was stirred for 18 h to yield a white solid and a pale orange solution. Repeated filtration and back-condensation of solvent (4 x 8 ml) followed by solvent removal *in vacuo* gave a red-brown oily filtrate and a colourless residual solid. Continuous extraction of the red material with CH_2Cl_2 removed a dirty white solid (81 mg) from an oily brown intractable solid.

7.6 References

1. A.W. Luke, PhD. thesis, University of Durham, 1992 (Introductory chapter and references therein).

2. I.B.Gorrell, Ph.D. Thesis, University of Durham, 1989.

3 A. Vegas, A. Perez-Salazar, A.J. Banister and R. G. Hey, *J. Chem. Soc., Dalton Trans.* 1980, 1812

4. A.W. Cordes, R.T. Oakley, R.C. Haddon, R. G. Hicks and T.T.M. Palstra, *Inorg Chem* 1992, 31, 1802

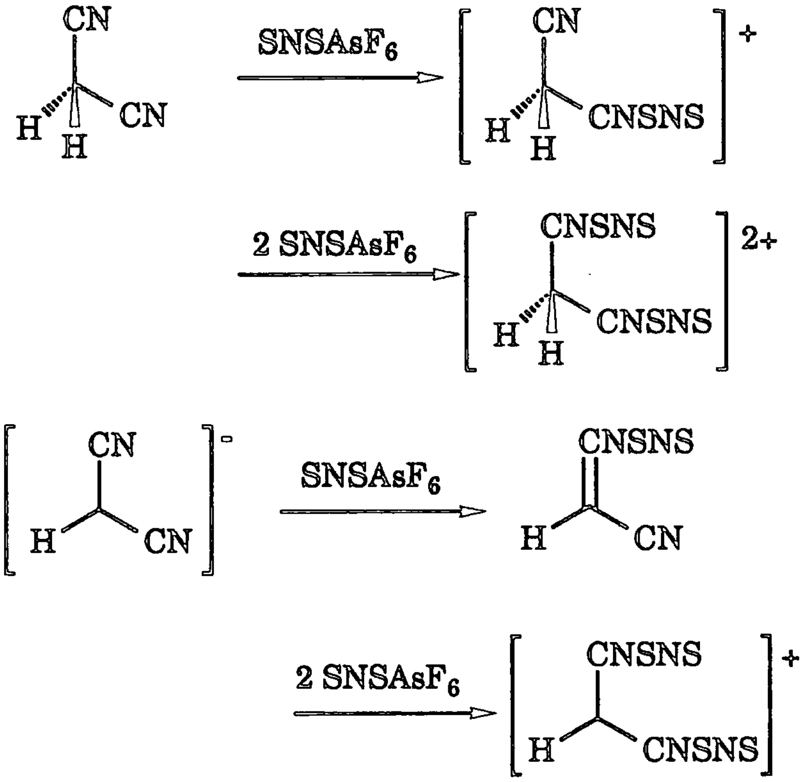
5. M.B. Hursthouse, C.E.F. Rickard, A.J. Banister, A.W. Luke and J.M. Rawson, *Acta. Cryst. Sect. C*, submitted for publication.

6. S.C. Nyburg and C.H. Fraeman, *Acta Cryst* 1985, B41, 274

Appendix 1: The Reactions of [SNS][AsF$_6$] with (NC)$_2$CH$_2$ and Na[(NC)$_2$CH]

A1.1 Introduction

In order to prepare 'model' compounds for those prepared by the reaction of [SNS][AsF$_6$] with K[C(CN)$_3$] (see chapter 3), malononitrile, (NC)$_2$CH$_2$, and the sodium salt of its corresponding anion (Na[HC(CN)$_2$]) were reacted with one and two equivalents of [SNS][AsF$_6$].



Eq. A1.1

Eq. A1.2

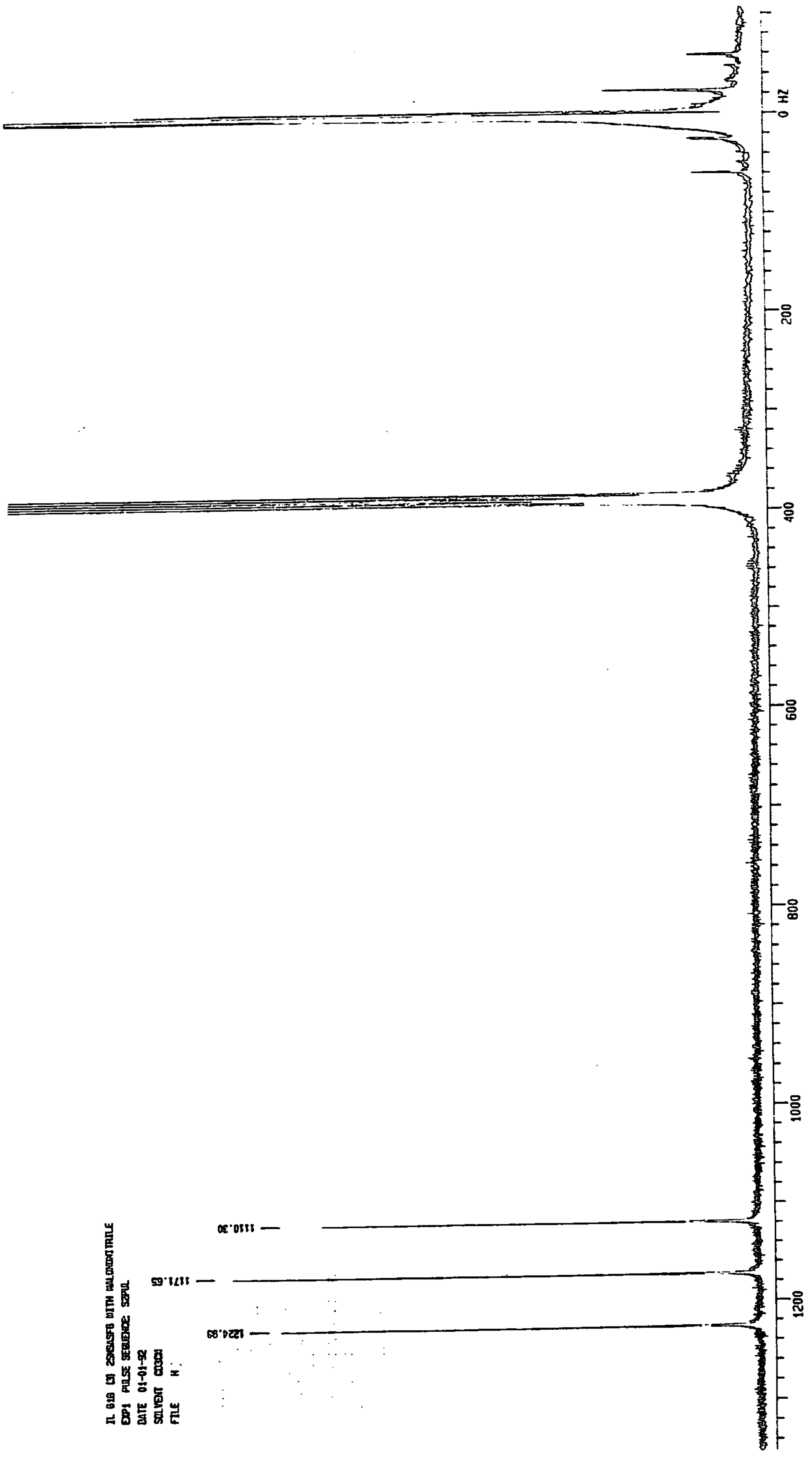
A1.2 Results and Discussion

Although the products of the [SNS]$^+$ reactions with malononitrile in both 1:1 and 1:2 stoichiometeries seemed to be homogeneous powders a persistent, broad, N-H stretch was observed in all IR spectra. This suggested that hydrolysis had occured and so the work was postponed in favour of more promising reactions.

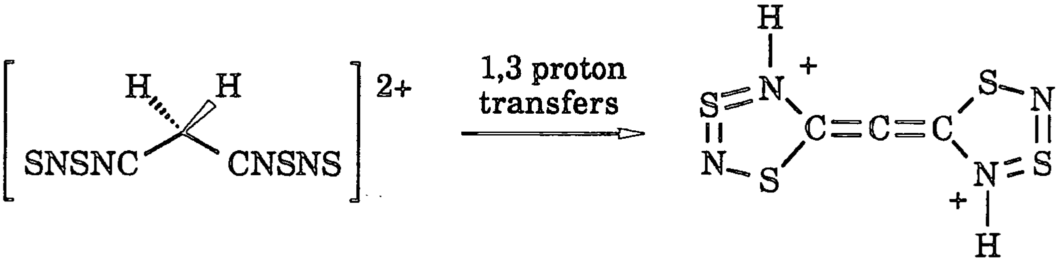
However, the elemental analyses of the 1:2 adduct of malononitrile strongly suggested that the product was 'clean' so a ^{1}H nmr was run.

This revealed a sharp 1:1:1 triplet indicative of the N-H coupling, as observed by A.W. Luke in his work on the hydrolysis products of dithiadiazolylium salts[1] (see fig A1.1).

FigureA1.1 ^1H nmr spectrum of compound 1 (solvent MeCN-d_3)



Furthermore, no methylene protons were observed (in both MeCN and CH_2Cl_2 solutions), which suggested that two 1,3-proton shifts may have occurred, with the dithiadiazolylium nitrogens abstracting a proton each from the highly acidic methylene group.



Eq. A1.3 (1)

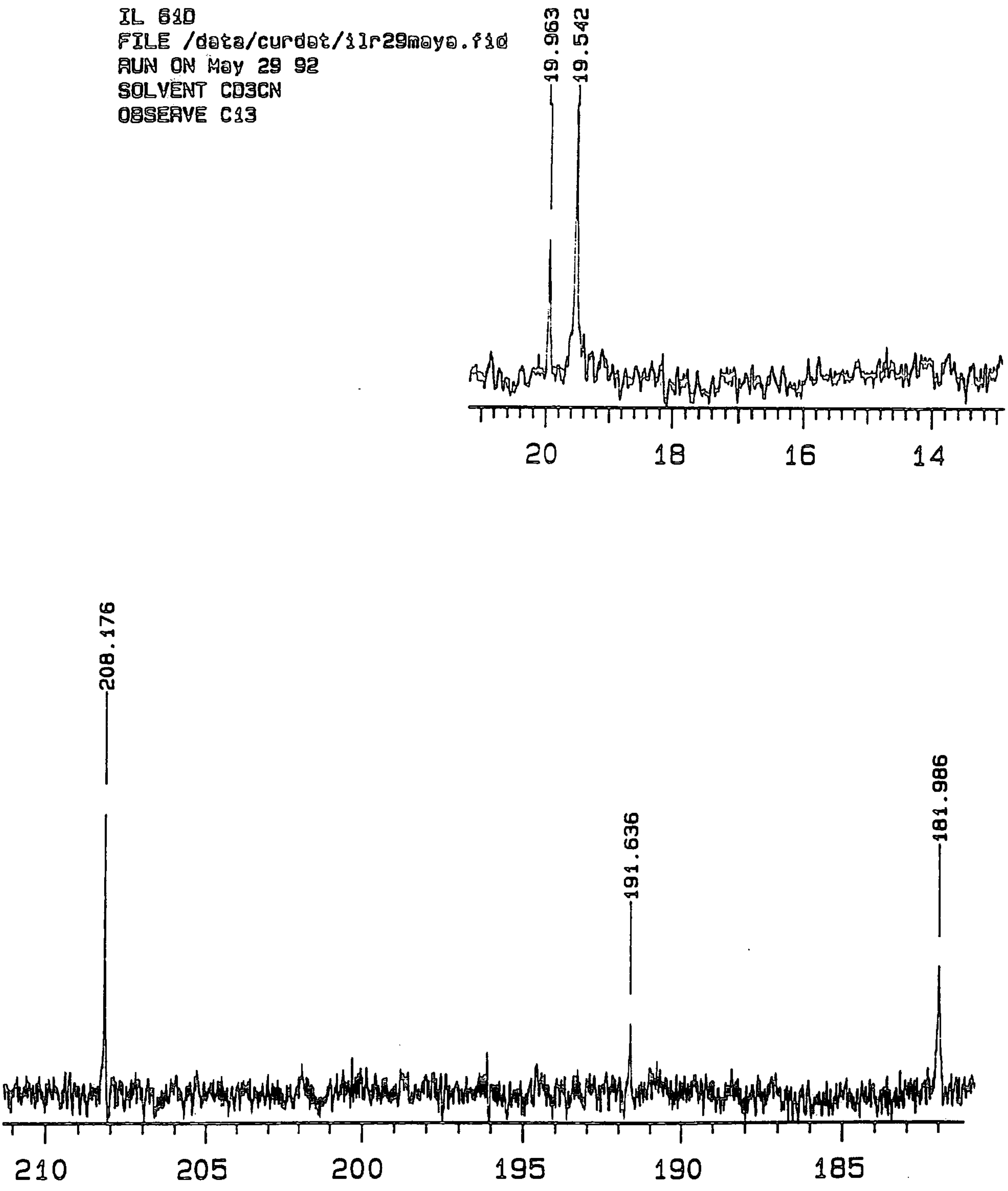
This would lead to an allene dication - with a dithiadiazolylium ring bonded to an alpha carbon by a double bond as in $(NC)_2C{=}CNSNS$ (see chapter 3). This is a highly unusual system.

In order to confirm this a proton decoupled ^{13}C spectrum of 1 was determined at high concentration (>250mg in acetonitrile), on a Brucker VXR400S spectrometer for a large number of transients (100000). In spite of the addition of $Cr(acac)_2$, as a spin-relaxant (to increase the intensity of the allene carbon reasonance), only the dithiadiazolylium carbons could be positively identified[1] (see fig.A1.2 and table A1.1) as no similar systems have been previously characterised. However the allene was tentatively assigned as the peak at 192ppm (it was of approximately half the intensity of the dithiadiazolium reasonance at 208ppm - the absence of protons allowing for intesity to be proportional to number of carbons).

Table A1.1 ^{13}C nmr data for $[C{=}(CN(H)SNS)_2][AsF_6]_2$

Peak (ppm)	Tentative Assignment
19.54	$Cr(acac)_2$ (Methyl)
19.96	$Cr(acac)_2$ (Methyl)
181.99	$Cr(acac)_2$ (Carbonyl)
191.64	Allene Carbon
208.18	Dithiadiazolium Carbon

Figure A1.2 ^{13}C nmr spectrum of $[C{=}(CN(H)SNS)_2][AsF_6]_2$



No methylene carbons were observed in any of the ^{13}C spectra which suggests the formation of an allene, together with proton transfer to the dithiadiazolyl ring. Elemental analysis strongly suggest that a 2:1 adduct has been formed. However, the absence of a characteristic IR band at ca. 2200 cm^{-1} oblivates against the formation of a simple allene (although the chrged dithiadiazolylium rings may cause a considerable shift in this frequency). Repeated attempts at recrystallisation (from a variety of solvents and by crystal growth) failed to produce crystals suitable for X-ray diffraction so no solid state data are available at this time. The reactions of $[SNS]^+$ with $Na[(NC)_2CH]$ were not considered to be adequately promising so were not pursued.

A1.3 Conclusions and Suggestions for Further Work

The reactions of $(NC)_2CH_2$ and $Na[(NC)_2CH]$ with $SNSAsF_6$ warrant further investigation as the multications and/or radicals may well have interesting properties. Of particular interest is the dication, 1, which may possibly be an allene bound to two protonated dithiadiazolylium cations. Derivatisation and/or crystallisation of this compound should be possible given sufficient time [perhaps the use of acetonitrile - 1,2-dichloro-benzene as a recrystallisation system may prove useful (see chapters 4 and 5)].

An alternative explanation is that this allene when formed dimerises to give six membered ring (this would carry a charge of +4 and so seems an unlikely proposition).

A1.4 Experimental

Starting Materials

Preparation of $Na[(NC)_2CH]$

To a stirred solution of $(NC)_2CH_2$ (2.0g, 0.030mol) in THF (20ml) was added NaH (0.75g, 0.031mol) slowly over a period of 5 min. Rapid effervescence ocurred and the solution became yellow in colour. After stirring for 18 h a whitish-yellow solid remained under a pale yellow solution. This was filtered, washed with THF and dried *in vacuo* to yield an off white solid (2.56g, 95%). This solid analysed reasonably well as NaC_3N_2H; Calc.: 31.82%N, 40.92%C, 1.26%H, 26.10%Na found 29.48%N, 38.90%C, 1.26%H, 26.63%Na

Addition Reactions

Malononitrile with one equivalent of $[SNS][AsF_6]$

Malononitrile (50mg, 1.0mmol) was stirred with $[SNS][AsF_6]$ (276mg, 1.0mmol) in liquid SO_2 in a two limbed reaction vessel for 18 h to yield a deep red solution over a red solid. Solvent removal followed by addition of CH_2Cl_2 (3ml) and sonication gave a red oily solid and red-brown solution. This oily solid was intractable and the entrained solvent could not be removed by sonication or by washing with a variety of solvents.

Malononitrile with two equivalents of [SNS][AsF_6]

Malononitrile (48mg, 0.9mmol) was stirred with [SNS][AsF_6] (510mg, 1.8mmol) in liquid SO_2 in a two limbed reaction vessel for 18 h to yield a dark brown solution over a black solid. Solvent removal followed by addition of CH_2Cl_2 (3ml) and sonication gave a black powder and brown solution. Filtration and repeated back-extraction followed by solvent removal gave a black residual powder (360mg, 66%) and an oily brown filtrate. Solvents used in attempted recrystallisations included: SO_2, $CFCl_3$, MeCN, SO_2/SO_2F_2. Analysis; Calc. for $C_3H_2N_4S_4As_2F_{12}$: 9.33%N, 6.00%C, 0.34%H, 24.96%As Found 9.19%N, 5.75%C, 1.03%H, 23.08%As

IR data $\nu_{max}(cm^{-1})$: 3320s br, 3230m sh, 1670m, 1632m, 1600m sh, 1515s sh, 1405vs sh, 1373vs sh, 1308m, 1270m, 1220m, 1155m, 1150m sh, 1085w, 995m, 978m, 953m, 920w, 905w, 852m, 802s, 780m, 702 vs br, 580m sh, 450s, 398vs. ^1H nmr data: triplet at 5.86ppm J_{NH}=53.3Hz. ^{13}C data: 208.2ppm, 191.6ppm, 182.0ppm, 20.0ppm, 19.5ppm.

Reaction of Na[$(NC)_2CH$] with one equivalent of [SNS][AsF_6]

Na[$(NC)_2CH$] (25mg, 0.3mmol) was stirred with [SNS][AsF_6] (76mg, 0.3mmol) in liquid SO_2 in a two limbed reaction vessel. An immediate red-brown colour was observed and the solution stirred for 18 h to yield a dark red solution over an white solid. Solvent removal followed by addition of CH_2Cl_2 (3ml) and sonication gave an intractable brown oily solid.

Reaction of Na[$(NC)_2CH$] with two equivalents of [SNS][AsF_6]

Na[$(NC)_2CH$] (16.5mg, mmol) was stirred with [SNS][AsF_6] (100mg, mmol) in liquid SO_2 in a two limbed reaction vessel. An immediate yellow-orange colour was observed which deepend to red within 1 h with a white solid precipitating out. Filtration and repeated back-extraction followed by solvent removal followed by addition of CH_2Cl_2 (3ml) and sonication gave an intractable red, oily solid.

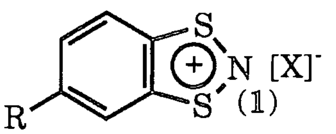
A1.5 References

1. A.W. Luke, unpublished results

Appendix 2 The Preparation of Some Dithiazolium Salts

A2.1 Introduction

Benzo-1,3,2-dithiazol-2-yl[1,2,3] (BDTA,1) and its derivatives have generated recent interest as stable planar radicals which have potential[1] for use in the preparation of so-called 'organic metals'.



(1)

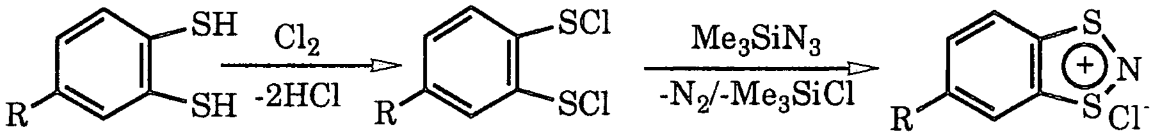
a: R=Me,X=Cl
b: R=Me,X=AsF_6
c: R=H,X=Cl
d: R=H,X=AsF_6

Figure A2.1 Benzo-1,3,2-dithiazol-2-ylium salts prepared during the course of this work.

For example, one of the best known donor anions is TCNQ$^-$ [4,5] and BDTA readily forms charge transfer complexes with TCNQ[1] (see equation A2.1).

[Eq. A2.1]

The BDTAs may be prepared readily from the corresponding dithiol[1].



[Eq. A2.2]

Also, S.T. Wait has prepared salts containing dithiadiazolylium cations and donor anions (particularly promising results were obtained using the trisulphur trinitride anion[6], which is itself close to planar). Therefore, the dithiazolium cations may well form interesting (and perhaps charge transfer) salts with $[S_3N_3]^-$.

Further derivatisation to the hexafluoroarsenate(V) salt should provide a more stable, reactive reagent which may give a $[S_3N_3]^-$ salt when metathesised with $[Pr_4N]S_3N_3$.

A2.2 Discussion of results

When reacted with $[Pr_4N]S_3N_3$ both **1b** and **1d** gave blue products which were highly moisture sensitive (both decomposed even when sealed under nitrogen). Attempts at crystal growth of the tolyl derivative by

(i) slow diffusion of saturated solutions of reagents together through a medium porosity frit,

(ii) slow solvent removal, and

(iii) a temperature ripple (see chapter 2)

gave either powders or, in the case of the ripple, green crystals of S_4N_4 (characterised by IR and mass spectroscopy).

Also observed during crystal growth was a deep blue solution, which formed when petroleum ether condensed on isolated, solid $[Pr_4N]S_3N_3$. This may have been due to the photodecomposition[7] of $[S_3N_3]^-$ to $[S_3N]^-$ so this may add to the deep blue colours observed. However, this process took several weeks, compared with 15min or so reaction time, and the elemental analyses obtained indicate the trisulphur trinitride salt to be present. IR spectroscopy cannot distinguish[8] between $[S_3N_3]^-$ and $[S_3N]^-$ anions as readily as UV/visible or Raman.

Only a trial-scale reaction was attempted using **1d**; which yielded an interesting (albeit very air sensitive) mixture of golden and blue products, therefore the potential of this system could not be accurately judged.

A2.3 Conclusion

The reactions of the BDTA hexafluoroarsenate(V) salts with $Pr_4N[S_3N_3]$ appear to be promising as the products are deeply coloured, lustrous, dichroic solids, however, they are also very sensitive to moisture (as expected for $[S_3N_3]^-$ salts - they may ring-open and polymerise or oxidise to give $[S_3N_3O_3]^-$). Because of the air-sensitive nature of these materials crystallisation and purification proved difficult and so the dithiazoliums were passed over in favour of more interesting and / or more readily handleable materials.

A2.4 Experimental

Benzo-1,3,2-dithiazolium chloride and its methyl analogue were prepared using the general method outlined by Wolmerhäuser *et. al.*[1].

$[Pr_4N]S_3N_3$ was prepared as outlined in the literature[8], but with some minor modifications[9].

Preparation of 6-methyl-benzo-1,3,2-dithiazolium chloride (1a)

Chlorine gas was passed through a stirred, ice-chilled solution of 3,4-dithiotoluene (1 ml, 7.5 mmol) in CCl_4 (70 ml) for 2 hr and the solution became increasingly yellow and finally orange. A deep yellow, intractable oil remained on solvent removal and addition of CH_2Cl_2 (10 ml) gave an orange solution. Slow addition of trimethylsilyl azide (0.7 ml,5.3 mmol) from a syringe to the chilled solution resulted in rapid effervescence and a colour change to bright yellow. Filtration at the pump followed by extraction with CH_2Cl_2 yielded a bright yellow powder (1.10 g, 72%). Found 39.26%C, 6.18%N, 2.74%H; calc. 41.27%C, 6.88%N, 2.97%H. Infra-red indicated some hydrolysis (ν_{max} / cm^{-1}): 1520m, 1330m, 1075m, 1020br, 840m, 770s, 725w, 655m.

Derivatisation of 1a to hexafluoroarsenate (V) salt (1b)

1a (0.96 g, 4.7 mmol) and $AgAsF_6$ (1.43 g, 4.8 mmol) were stirred together in SO_2 for 24 hr. The whitish pink ppt was filtered off and doubly back-extracted leaving an almost white solid (AgCl). Upon solvent removal the deep orange-brown solution yielded a yellow solid (1.61 g, 96%). Infra-red indicated a pure sample (strong, sharp bands) (ν_{max} / cm^{-1}): 1595m, 1580m, 1395m, 1380m, 1332s, 1210m, 1090m, 1050m, 1030m, 880m, 818vs, 778s, 773s, 695vs,br. No hydrolysis was apparent in the IR after 24hr exposure.

Reaction of 1b with $[Pr_4N]S_3N_3$

$[Pr_4N]S_3N_3$ (0.200 g, 0.63 mmol) and 1b (0.228 g, 0.63 mmol) were stirred in acetonitrile (5 ml) with deep blue crystals forming almost immediately. The deep blue solution lightened (becoming more turquoise) during the reaction (15 min). Upon solvent removal there remained a heterogenous turquoise-blue solid mixed with a little green material. A yellow solid and green solution were washed out by continuous extraction with 40/60° pet. ether (leaving a deep blue residual solid). The product was fully soluble in CH_2Cl_2 and solvent removal gave a blue powder (120 mg, 63%). Analysis was reasonable: Found 25.98%C, 17.68%N, 2.01%H; calc. 27.44%C, 18.28%N, 1.97%H. Infra-red was good with intense, sharp bands (ν_{max} / cm^{-1}): 1090m, 945m, 902w, 890m, 872w, 808m, 712vs, 702m, 690m, 662s, 632s.

Benzo-1,3,2-dithiazolium chloride(1c)

Dry nitrogen was passed through stirred, ice-cooled solution of benzene-1,2-dithiol ('500mg', 3.52 mmol) in CCl_4 (30 ml) and then chlorine passed for 1 hr. Solvent removal gave a yellow solid and an orange oil. These were taken up in CH_2Cl_2 (5 ml) and trimethylsilyl azide (0.6 ml, 4.5 mmol) was slowly syringed in. The effervescence and heat evolved forced off all solvent and so a further portion of CH_2Cl_2 (10 ml) was added and stirring continued. The yellow solid was filtered at the pump and dried *in vacuo.* to yield 900 mg, (>100% - based on '500mg' quoted on the dithiol label, the dithiol was not weighed (as it has quite a stench) and excess azide was used). Analysis confirmed the product as 1c. Found 37.44%C, 6.90%N, 2.09%H; calc. 38.20%C, 7.42%N, 2.12%H. Again sharp, well defined IR bands were obtained (ν_{max} / cm^{-1}): 1525m, 1420m, 1330m, 1080m, 1050m, 1020m, 962m, 940m, 860w, 755vs, 700w, 555w, 485w, 448m, 398m.

Derivatisation of 1c to the hexafluoroarsenate(V) salt(1d)

1c (650 mg, 3.45 mmol) and $AgAsF_6$ (1.02 g, 3.44 mmol) were stirred together in liquid SO_2 for 24 hr and the resulting yellow solution decanted off leaving a white precipitate. Repaeted washing of the precipitate with back-condensed solvent (3x5 ml) removed all traces of yellow colour from the white solid. Solvent removal gave a lemon-yellow solid (1.01 g, 85%). Found 19.71%C, 3.69%N, 1.19%H; calc. 21.00%C, 4.08%N, 1.17%H.

Reaction of 1d with $[Pr_4N]S_3N_3$

$[Pr_4N]S_3N_3$ (56 mg, 0.17 mmol) and 1d (63 mg, 0.18 mmol) were stirred in acetonitrile (2 ml) for 2hr. Cooling and filtration gave a golden brown solid residue and the filtrate gave up green-blue crystals upon solvent removal. However both of these solids appeared to decompose within several hours under nitrogen.

A2.5 References

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4. J. Ferraris, D.O. Cowan, V. Walatka Jnr. and J.H. Perlstein, *J. Am. Chem. Soc.*, 1973, 95, 948.
5. M.R. Bryce, *Chem. Brit.*, 1988, 781.
6. A.J. Banister, W. Cleg g, Z.V. Hauptman, A.W. Luke and S.T. Wait, *J. Chem. Soc., Chem. Commun.*, 1989, 351.
7. J.Boyes and T. Chivers, Personal Communication.
8. J.Boyes and T. Chivers, *Inorg. Chem.*, 1978, 17, 318 .
9. S.T. Wait, Ph.D. Thesis, University of Durham,1989.

Appendix 3

First Year Induction Courses: October 1989

The course consists of a series of one hour lectures on the services available in the department.

1. Departmental organisation
2. Safety matters
3. Electrical appliances and infrared spectroscopy
4. Chromatography and microanalysis
5. Atomic absorption and inorganic analysis
6. Library facilities
7. Mass spectroscopy
8. Nuclear magnetic resonance
9. Glass blowing techniques

Appendix 4 (☼ indicates lectures attended by the author)

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS

1st October 1989 to 31st July 1990

Palmer, Dr. F. (University of Nottingham) 17.10.89
Thunder and Lightning

Floriani, Prof. C. (University of Lausanne) 25.10.89
Molecular Aggregates - A Bridge Between Homogeneous and Heterogeneous Systems

Badyal, Dr. J. P. S. (University of Durham) 01.11.89
Breakthroughs in Heterogeneous Catalysis

Greenwood, Prof. N. N. (University of Leeds) 09.11.89
Novel Cluster Geometries in Metalloborane Chemistry

Bercaw, Prof. J. E. (California Institute of Technology) 10.11.89
Synthetic and Mechanistic Approaches to Ziegler - Natta Polymerization of Olefins

Becher, Dr. J. (University of Odense) 13.11.89
Synthesis of New Macrocyclic Systems Using Heterocyclic Building Blocks

Parker, Dr. D. (University of Durham) 16.11.89
Macrocycles, Drugs and Rock 'n' Roll

Cole-Hamilton, Prof. D. J. (University of St. Andrews) 29.11.89
New Polymers from Homogeneous Catalysis

Hughes, Dr. M. N. (King's College, London) 30.11.89
A Bug's Eye View of the Periodic Table

Graham, Dr. D. (B. P. Research Centre) *How Proteins Adsorb to Interfaces*	04.12.89
Powell, Dr. R. L. (ICI) *The Development of C.F.C. Replacements*	06.12.89
Butler, Dr. A. (University of St. Andrews) *The Discovery of Penicillin : Facts and Fancies*	07.12.89 *
Klinowski, Dr. J. (University of Cambridge) *Solid-State NMR Studies of Zeolite Catalysts*	13.12.89
Huisgen, Prof. R. (Universität München) *Recent Mechanistic Studies of [2 + 2] Additions*	15.12.89
Perutz, Dr. R. N. (University of York) *Plotting the Course of C-H Activations with Organometallics*	24.01.90
Dyer, Dr. U. (Glaxo) *Synthesis and Conformation of C-Glycosides*	31.01.90
Holloway, Prof. J. H. (University of Leicester) *Noble Gas Chemistry*	01.02.90
Thompson, Dr. D. P. (University of Newcastle upon Tyne) *The Role of Nitrogen in Extending Silicate Crystal Chemistry*	07.02.90
Lancaster, Rev. R. (Kimbolton Fireworks) *Fireworks - Principles and Practice*	08.02.90 *
Lunazzi, Prof. L. (University of Bologna) *Application of Dynamic NMR to the Study of Conformational Enantiomerism*	12.02.90
Sutton, Prof. D. (Simon Fraser University, Vancouver) *Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium*	14.02.90

Crombie, Prof. L. (University of Nottingham) 15.02.90
The Chemistry of Cannabis and Khat *

Bleasdale, Dr. C. (University of Newcastle upon Tyne) 21.02.90
The Mode of Action of some Anti - Tumour Agents

Clark, Prof. D.T. (ICI Wilton) 22.02.90
Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Arena)

Thomas, Dr. R. K. (University of Oxford) 28.02.90
Neutron Reflectometry from Surfaces

Stoddart, Dr. J. F. (University of Sheffield) 01.03.90
Molecular Lego *

Cheetham, Dr. A. K. (University of Oxford) 08.03.90
Chemistry of Zeolite Cages

Powis, Dr. I. (University of Nottingham) 21.03.90
Spinning Off in a Huff : Photodissociation of Methyl Iodide

Bowman, Prof. J. M. (Emory University) 23.03.90
Fitting Experiment with Theory in Ar-OH

German, Prof. L. S. (Soviet Academy of Sciences) 09.07.90
New Syntheses in Fluoroaliphatic Chemistry : Recent Advances in the Chemistry of Fluorinated Oxiranes

Platanov, Prof. V.E. (Soviet Academy of Sciences, Novosibirsk 09.07.90
Polyfluoroindanes : Synthesis and Transformation

Rozhkov, Prof. I. N. (Soviet Academy of Sciences, Moscow) 09.07.90
Reactivity of Perfluoroalkyl Bromides

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COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS

1st August 1990 to 31st July 1991

Macdonald, Dr. W.A. (ICI Wilton) 11.10.90
Materials for the Space Age *

Bochmann, Dr. M. (University of East Anglia) 24.10.90
Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls *

Soulen, Prof. R. (South Western University, Texas) 26.10.90
Preparation and Reactions of Bicycloalkenes

Jackson, Dr. R.F.W. (University of Newcastle upon Tyne) 31.10.90
New Synthetic Methods : α-Amino Acids and Small Rings

Logan, Dr. N. (University of Nottingham) 01.11.90
Rocket Propellants *

Kocovsky, Dr. P. (University of Uppsala) 06.11.90
Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals *

Gerrard, Dr. D. (British Petroleum) 07.11.90
Raman Spectroscopy for Industrial Analysis

Scott, Dr. S.K. (University of Leeds) 08.11.90
Clocks, Oscillations and Chaos *

Bell, Prof. T. (SUNY, Stoney Brook, USA) 14.11.90
Functional Molecular Architecture and Molecular Recognition

Pritchard, Prof. J. (Queen Mary & Westfield College) 21.11.90
Copper Surfaces and Catalysts

Whitaker, Dr. B.J. (University of Leeds) *Two-Dimensional Velocity Imaging of State-Selected Reaction Products*	28.11.90
Crout, Prof. D. (University of Warwick) *Enzymes in Organic Synthesis*	29.11.90
Pringle, Dr. P.G. (University of Bristol) *Metal Complexes with Functionalised Phosphines*	05.12.90 *
Cowley, Prof. A.H. (University of Texas) *New Organometallic Routes to Electronic Materials*	13.12.90 *
Alder, Dr. B.J. (Lawrence Livermore Labs., California) *Hydrogen in all its Glory*	15.01.91
Sarre, Dr. P. (University of Nottingham) *Comet Chemistry*	17.01.91
Sadler, Dr. P.J. (Birkbeck College London) *Design of Inorganic Drugs : Precious Metals, Hypertension & HIV*	24.01.91
Sinn, Prof. E. (University of Hull) *Coupling of Little Electrons in Big Molecules : Implications for the Active Sites of Metalloproteins and other Macromolecules*	30.01.91 *
Lacey, Dr. D. (University of Hull) *Liquid Crystals*	31.01.91 *
Bushby, Dr. R. (University of Leeds) *Biradicals and Organic Magnets*	06.02.91 *
Petty, Dr. M.C. (Durham University) *Molecular Electronics*	14.02.91 *
Shaw, Prof. B.L. (University of Leeds) *Syntheses with Coordinated, Unsaturated Phosphine Ligands*	20.02.91 *

Brown, Dr. J. (University of Oxford) 28.02.91
Can Chemistry Provide Catalysts Superior to Enzymes?

Dobson, Dr. C.M. (University of Oxford) 06.03.91
NMR Studies of Dynamics in Molecular Crystals

Markam, Dr. J. (ICI Pharmaceuticals) 07.03.91
DNA Fingerprinting

Schrock, Prof. R.R. (M.I.T.) 24.04.91
Metal-Ligand Multiple Bonds and Metathesis Initiators

Hudlicky, Prof. T. (Virginia Polytechnic Institute) 25.04.91
Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products

Brookhart, Prof. M.S. (University of North Carolina) 20.06.91
Olefin Polymerizations, Oligomerizations and Dimerizations Using Electrophilic Late Transition Metal Catalysts

Brimble, Dr. M.A. (Massey University, New Zealand) 29.07.91
Synthetic Studies Towards the Antibiotic Griseusin-A

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1st October 1991 to 31st July 1992

Burton, Prof. D.J. (University of Iowa, USA) 12.09.91
Fluorinated Organometallic Reagents

Adcock, Prof. J.L. (University of Tennessee, USA), 12.09.91
Aerosol Direct Fluorination

Salthouse, Dr. J.A. (Manchester University), 17.10.91
Son et Lumiere - a Demonstration Lecture *

Keeley, Dr. R. (Metropolitan Police Forensic Science), 03.10.91
Modern Forensic Science

Johnson, Dr. B.F.G. (Edinburgh University), 06.11.91
Cluster-Surface Analogies *

Butler, Dr. A.R. (St. Andrews University), 07.11.91
Traditional Chinese Herbal Drugs: a Different Way of Treating Disease

Koch, Prof. H. F. (Ithaca College, USA), 8.11.91
Relative Leaving Abilities of fluoride Ion Versus Proton Transfer, in the Neutralisation of Carbanions, Generated in Alcohols

Gani, Prof. D. (St. Andrews University), 13.11.91
The Chemistry of PLP-Dependant Enzymes

More OFerrall, Dr. R. (University College, Dublin), 20.11.91
Some Acid-Catalysed Rearrangements in Organic Chemistry

Ward, Prof. I.M. (Leeds University), 28.11.91
The Science & Technology of Orientated Polymers

Grigg, Prof. R. (Leeds University), 04.12.91
Palladium Catalysed Cyclisation and Ion Capture Processes *

Smith, Prof. A.L. (ex-Unilever), 05.12.91
Soap, Detergents and Black Puddings

Cooper, Dr. W.D. (Shell Research), 11.12.91
Colloid Science, Theory, and Practice *

Snyder, Mr. C.E. (U.S. Air Force, Ohio), 09.01.92
Perfluoropolyethers

Long, Dr. N.J. (Exeter University), 16.01.92
Metallocenophanes-Chemical Sugar-tongs

Harris, Dr. K.D.M. (St Andrews University), 22.01.92
Understanding the Properties of Solid Inclusion Compounds *

Holmes, Dr. A. (Cambridge University), 29.01.92
Cycloaddition Reactions in the Service of the Synthesis of Piperidine and Indolizidine Natural Products

Anderson, Dr. M. (Shell Research, Sittingbourne), 30.01.92
Recent Advances in the Safe and Selective Chemical Control of Insect Pests

Fenton, Dr. D.E. (Sheffield University), 12.02.92
Polynuclear Complexes of Molecular Clefts as Models for Copper Biosites *

Saunders, Dr. J. (Glaxo Group Research Limited), 13.02.92
Molecular Modelling in Drug Discovery

Thomas, Prof. E.J. (Manchester University), 19.02.92
Application of Organo-Stannanes to Organic Synthesis *

Vogel, Prof. E. (University of Cologne), 20.02.92
Porphyrins: Molecules of Interdisciplinary Interest.

Nixon, Prof. J.F. (University of Sussex), 25.02.92
Phosphaalkynes, New Building Blocks in *
Inorganic and Organometallic Chemistry

Hitchman, Prof. M.L. (Strathclyde University), 26.02.92
Chemical Vapour Deposition

Billingham, Dr. N.C. (University of Sussex), 05.03.92
Degradable Plastics - Myth or Magic

Fielding, Dr. H.C. (ICI, Chemicals & Polymers), 10.03.92
Fluoropolymer Membranes

Thomas, Dr. S.E. (Imperial College, London), 11.03.92
Recent Advances in Organoiron Chemistry *

Hamm, Dr. R.A. (ICI Imagedata), 12.03.92
Electronic Photography - An Image of the Future.

Maskill, Dr. H. (Newcastle University), 18.03.92
Mechanistic Studies of Organic Group Transfer Reactions

Knight, Prof. D.M. (Durham University), 07.04.92
Interpreting Experiments: The Beginning of Electrochemistry

Marhold, Dr. A. (Bayer Co., Leverkusen), 30.04.92
Fluorine Chemistry in the Bayer Company

Gehert, Dr. J-C. (Ciba Geigy, Basel), 13.05.92
Some Aspects of Industrial Agrochemical Research

And so to bed....

“..Of the making of books there is no end
and much study wearies the body”
Eccl. 12 v 11

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