The synthesis and reactivity of some 1,2,3,5 - and 1,3,2,4-dithiadiazolium salts

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The Synthesis and Reactivity of some 1,2,3,5- and 1,3,2,4-dithiadiazolium salts.

by

Jeremy Michael Rawson.

A thesis submitted for the degree of Ph.D. to the University of Durham.

August 1990

To Ian,for getting me into this
in the first place...

To my family for their encouragement,
enthusiasm and patience...

And to Alison,
for being special,
and for being there.

> " It was the sort of afternoon that most scientists experience from time to time. It was half past three and everyone else in the lab seemed to have disappeared. It was raining outside, and the chemicals I'd ordered three weeks ago still hadn't turned up. Nothing for it but to repair to the library and catch up with some reading until I could decently go home..."
>
> New Scientist (24.6.89).

Acknowledgements

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I have also been particularly privileged to have had the technical and practical expertise of Dr. Z.V. Hauptman to whom I am particularly indebted.

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Last, but not least, I am indebted to the Isle Of Man Board Of Education for funding my research over the last three years.

Memorandum

The work carried out in this thesis was carried out by me in the Chemistry Department of the University of Durham between October 1987 and July 1990 and at the Centre National de Recherche Scientifique in Toulouse between January and April 1990. I declare that the work has not been submitted previously for a degree at this, or any other, University. This thesis is my original work, except where acknowledged by reference. The copyright of this thesis rests with the author. No quotation from it 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:

"Reaction of $N(SCl)_2^+$ salts with Tin(II) Chloride: A New Preparative Route to Salts of the SNS^+ Cation."
A.J. Banister and J.M. Rawson; J. Chem. Soc., Dalton Trans., 1990, 1517.

"The Preparation of Salts of the 5,5'-(1,4-Phenylene) Bis(1,3,2,4-Dithiadiazolylium) Dication and of its 1,2- and 1,3- Phenylene Analogues; The Preparation and X-Ray Crystal Structure of the Stacked Neutral 5,5'-(1,4-phenylene) Bis (1,3,2,4-Dithiadiazole)."
A.J. Banister, J.M. Rawson, W. Clegg and S.L. Birkby; J. Chem. Soc., Dalton Trans., submitted for publication.

"Dithiadiazoles: Members of a New Family of Free Radicals"
A.J. Banister and J.M. Rawson; Chemistry in Britain, submitted for publication.

" The Structures of $[PhCN_2S_2]_2[Pt(mnt)_2]$ and $[(p\text{-}Cl.C_6H_4.CN_2S_2)_2Cl][Pt(mnt)_2]$"
A.J. Banister, J.M. Rawson and W.Clegg, Acta. Cryst., in preparation.

"The Synthesis of [SNS][CF_3SO_3] and the Redetermination of the Structure of [S_6N_4][CF_3SO_3]$_2$. A Comparison of the Reactivity of [SNS][X] Salts (X= AsF_6, $SbCl_6$, $AlCl_4$ and CF_3SO_3). The Preparation and a Cyclic Voltammetric Study of Some Novel 1,3,2,4-Dithiadiazolylium Salts, $RCNSNS^+$ (R= C_6H_5, *p*-Cl.C_6H_4, *p*-Br.C_6H_4, *p*-F.C_6H_4 and C_6F_5) and a Comparison with Their 1,2,3,5-Dithiadiazolylium Analogues."
A.J. Banister, B. Ayres, M.I. Hansford, Z.V. Hauptmann, J.M. Rawson and M. Hursthouse; in preparation.

The following parts of this work were also presented as posters at the following meetings:

" The Preparation and Reactivity of 1,4-Phenylene Bis(1,3,2,4-Dithiadiazolium) Hexafluoroarsenate(V)."
J.M. Rawson; University of Strathclyde Inorganic Graduate Symposium, 1989.

" The Preparation, Crystal Structure and Solid State Properties of 1,4-Phenylene Bis(1,3,2,4-Dithiadiazole) and Related Species."
J.M. Rawson and R. Whitehead; SERC Molecular Electronics Initiative, Grant Holders Workshop, University of Durham, 1990.

Abbreviations

The following abbreviations are used in this thesis:

Ar	aryl
^{n}Bu	normal butyl
^{t}Bu	tertiary butyl
C.I.	chemical ionisation
Cp	cyclopentadienyl
-CNSNS	the 1,3,2,4-dithiadiazole/ium ring system
-CNSSN	the 1,2,3,5-dithiadiazole/ium ring system
C.V.	cyclic voltammetry
D.S.C.	differential scanning calorimetry
E.I.	electron impact
HOMO	highest occupied molecular orbital
i.r.	infra-red; all i.r. absorption frequencies (ν) are measured in cm^{-1}.
l.	liquid
LUMO	lowest unoccupied molecular orbital
Me	methyl
MNDO	modified neglect of diatomic overlap
mnt	maleonitriledithiolate [cis-1,2-dicyano-1,2-ethylenedithiolate]
n.m.r.	nuclear magnetic resonance
Ph	phenyl
^{n}Pr	normal propyl
^{i}Pr	iso-propyl
R	alkyl (or aryl) substuent
r.T.	room temperature
SOMO	singly occupied molecular orbital
T.H.F.	tetrahydrofuran
w.r.t.	with respect to

The synthesis and reactivity of some 1,2,3,5- and 1,3,2,4-dithiadiazolium salts.

by Jeremy Michael Rawson.

Abstract

The reaction of $N(SCl)_2^+$ salts with $SnCl_2$ provided a new route to the SNS^+ synthon; an important reagent in the synthesis of inorganic sulphur-nitrogen containing heterocycles.

The reactions of C_6H_5CN and C_6F_5CN with a variety of SNS^+ salts (AsF_6^-, $SbCl_6^-$ and $AlCl_4^-$) were examined. Both $[SNS][AsF_6]$ and $[SNS][SbCl_6]$ reacted in high yield to give the 1,3,2,4-dithiadiazolium salts ($Ar.CNSNS^+$) whereas $[SNS][AlCl_4]$ did not readily provide the analagous heterocycle. Reduction of these 1,3,2,4-dithiadiazolium cations provided the isostructural 1,3,2,4-dithiadiazole radicals which then underwent rearrangement to the 1,2,3,5-dithiadiazole. This isomerisation process was monitored by e.s.r. spectroscopy.

Reaction of two or three equivalents of$[SNS][AsF_6]$ with dicyanoaromatics (*o,m* and *p*-$C_6H_4(CN)_2$, $NC.C_6H_4.C_6H_4.CN$ and *p*-$C_6F_4(CN)_2$) or 1,3,5-tricyanobenzene yielded the novel bis- and tris-(dithiadiazolium) cations respectively. 1,4-phenylene bis(1,3,2,4-dithiadiazolium) hexafluoroarsenate(V) was readily converted to a variety of other salts by anion metathesis and its reduction yielded the neutral bis(dithiadiazole) which was characterised by a single crystal X-ray structure determination.

Reaction of 4-phenyl-1,2,3,5-dithiadiazolium hexafluoroarsenate(V) with $[Et_4N][Pt(mnt)_2]$ and $[Et_4N]_2[Pt(mnt)_2]$ produced $[PhCN_2S_2][Pt(mnt)_2]$ and $[PhCN_2S_2]_2[Pt(mnt)_2]$ respectively; the latter compound was characterised by an X-ray structure. The reaction of $[PhCN_2S_2]Cl$ with $[Et_4N][Pt(mnt)_2]$ in the presence of excess $[PhCN_2S_2]Cl$ yielded $[(PhCN_2S_2)_2Cl][Pt(mnt)_2]$. Crystals of the analagous compound, $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl][Pt(mnt)_2]$, were large enough for an X-ray structure determination and this provided the second example of the planar cation, $[(ArCN_2S_2)_2Cl]^+$.

In comparison the reaction of phenyldithiadiazole, $(PhCN_2S_2)_2$, with $Pd(PPh_3)_4$ led to the formation of $Pd_3(PhCN_2S_2)_2(PPh_3)_4$; the solid state structure of which shows three square planar Pd centres held together by two bridging $PhCN_2S_2$ ligands.

The reaction of [$PhCN_2S_2$]Cl with a variety of P and N containing materials was also examined and the synthesis of P containing analogues of the CN_2S_2 ring was attempted, leading to the formation of the $PN_2S_2^+$ heterocycle.

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CHAPTER 6 THE ATTEMPTED FORMATION OF PHOSPHORUS CONTAINING SULPHUR-NITROGEN HETEROCYCLES 116

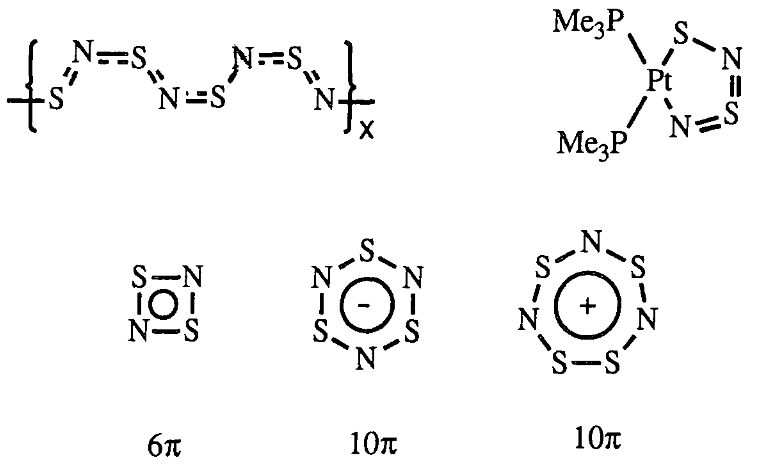
CHAPTER ONE

INTRODUCTION

Introduction

The chemistry of sulphur-nitrogen materials is an extensive and expanding area of study with many compound types - rings and chains, anions and cations, neutral molecules and free radicals[1]. Within this great variety, there are several systems of special current interest; for instance, poly(sulphurnitride)[2], metal-sulphur-nitrogen complexes[3] and delocalised rings[4] (see Fig1.1). Dithiadiazoles are closely related to this last category and my research has been involved in the synthesis and reactivity of these materials.

Figure 1.1: S/N chemistry takes many and varied forms



Most delocalised sulphur-nitrogen rings belong to a Hückel series, where the ring possesses a delocalised π system of electrons. However these rings do not necessarily need to be 6π aromatic but may belong to any of the $(4n+2)\pi$ electron systems. Figure 1.1 shows a variety of these rings and their formal π electron count.

However, of these materials, there would appear to be one exception; this is the delocalised $S_6N_4^{2+}$ cation; this species is known with a variety of anions[5] but all the solid state structures are based on two $S_3N_2^{+\bullet}$ rings with each ring formally providing one electron for a unique type of π-π^* interaction involving four sulphur atoms (see figure 1.2). These structures also frequently show secondary cation-anion interactions between the bridging sulphur atoms and the anions. The relevant SOMO overlap diagram shows a bonding interaction between the rings which rationalises the parallel ring geometry.

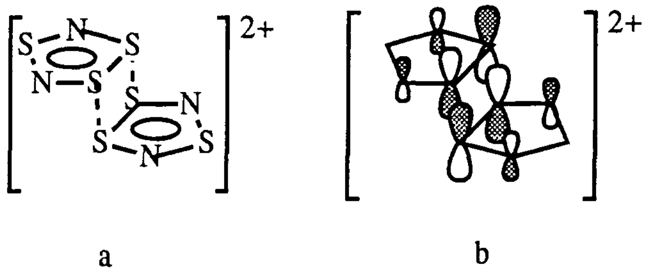


Figure 1.2: Structure (a) and Bonding (b), showing the SOMO interactions in $[S_6N_4]^{2+}$

A particularly striking feature of this $S_6N_4^{2+}$ ring system is that the interaction between the two rings is so weak (ΔH dimerisation = -47(±7)kJmol^{-1})[6] that it results in incomplete association of the rings both in solution and in the solid state. These $S_3N_2^{+\bullet}$ radicals are easily detected by electron spin resonance[7], and a detailed analysis[8] has indicated that most of the spin density of the unpaired electron lies on the two nitrogen atoms; nitrogen being more electronegative than sulphur[9].

The search for structural analogues of $S_6N_4^{2+}$ was first directed towards the dithiadiazolium cations (see Fig. 1.3) as these on reduction lead to the neutral 7π dithiadiazole free radicals which are isoelectronic with an $S_3N_2^{+\bullet}$ unit:

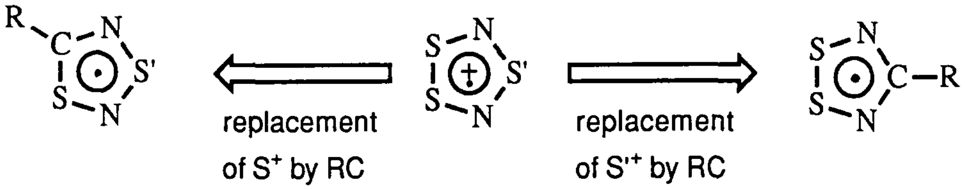


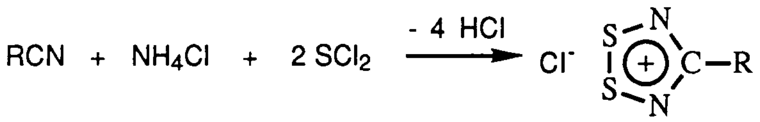
Figure 1.3: Replacement of S$^+$ in $S_3N_2^{+\bullet}$ by an RC unit produces the isoelectronic 1,3,2,4- or 1,2,3,5-dithiadiazole radicals.

By structurally replacing S$^+$ by an RC group we may form either a 1,3,2,4-dithiadiazole or a 1,2,3,5-dithiadiazole, as indicated in Figure 1.3.

1,2,3,5-dithiadiazolium salts

Chlorides of the 1,2,3,5-dithiadiazolium cations, RCNSSN$^+$, are readily prepared[10] by the reaction of SCl_2 or S_2Cl_2 with amidinium salts, amidines or silylated amidines. These conditions conveniently occur in a one-pot reaction from benzonitrile, ammonium chloride and sulphur dichloride.:

Eqn. 1.4:

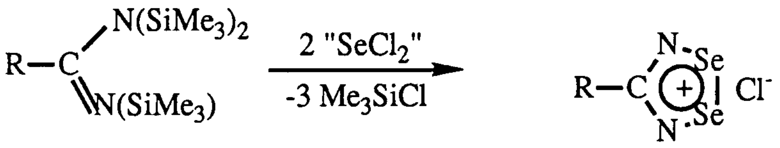


The yield ,typically 35%, can be improved considerably by adding a tertiary base e.g.1,8-diazabicyclo[5,4,0] undec-7-ene[11] which scavenges the HCl formed as a by product.

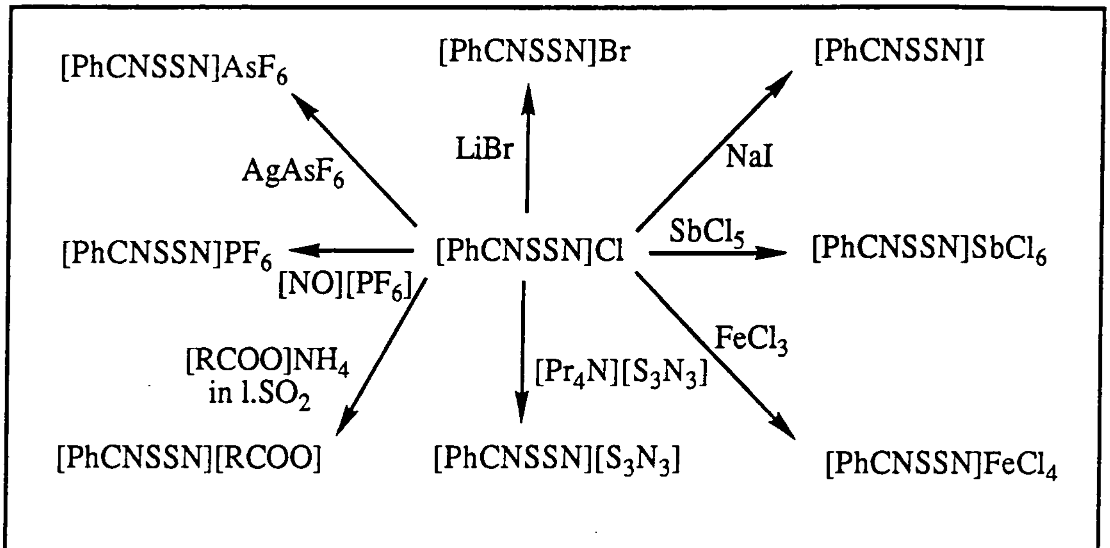
The mixture of NH_4Cl and SCl_2 acts as a source of thiazyl chloride and this reagent as the trimer can be used for a variety of other heterocyclis syntheses; it has been shown to be a useful reagent[12,13] in the synthesis of a variety of other heterocyclic species such as $S_5N_5^+$ and $RCN_3S_2Cl_2$.

Recently[14,15] the reaction of silylated amidines with SCl_2 has been proven to be a high yield route to these dithiadiazolium cations and can also be used to introduce selenium into the ring instead of sulphur; a 1:1 mixture of $SeCl_4$ and Ph_3Sb being a source of $SeCl_2$:

Eqn. 1.5:



These dithiadiazolium (or diselenadiazolium) cations, as the chloride salt, are readily converted to a variety of other salts by anion metathesis reactions[10,16] (see scheme1.6):



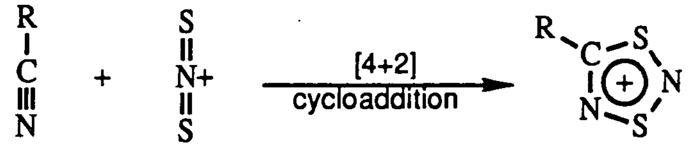
Scheme 1.6: Some metathesis reactions of [PhCNSSN]Cl

As with many other sulphur-nitrogen compounds these materials are brightly coloured and the progress of many reactions can be followed by inspection. It is an interesting feature that the donor capacity of the anion can be estimated from the colour of the $RCN_2S_2^+$ salts; weakly donor ('hard') anions such as BF_4^-, AsF_6^- and ClO_4^- yield brightly coloured salts (typically orange-red in the case of $RCNSSN^+$ cations) whereas more strongly donating anions produce red, burgundy, brown and black salts.

Synthesis of 1,3,2,4-dithiadiazolium salts

Salts of the 1,3,2,4-dithiadiazolium cation are readily prepared from nitriles and dithianitronium salts [17] via a [4+2] cycloaddition reaction:

Eqn. 1.7:

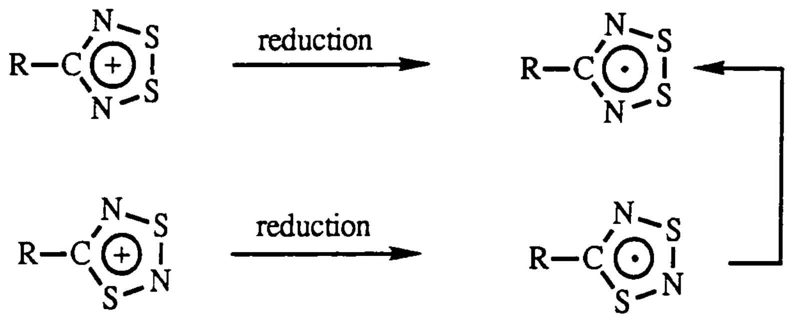


The chemistry and reactivity of these dithianitronium salts and the 1,3,2,4-dithiadiazolium cations are discussed more fully in later chapters (see Chapters 2.1, 3.1 and 4.1):

However before the advent of the SNS^+ synthon few salts of this type had been prepared[18] and they were formed from more esoteric routes.

Dithiadiazoles: synthesis and structure

Reduction of either the 1,3,2,4- or 1,2,3,5-dithiadiazolium salts with a variety of chemical reducing agents[16,17,19] yields the corresponding dithiadiazole:



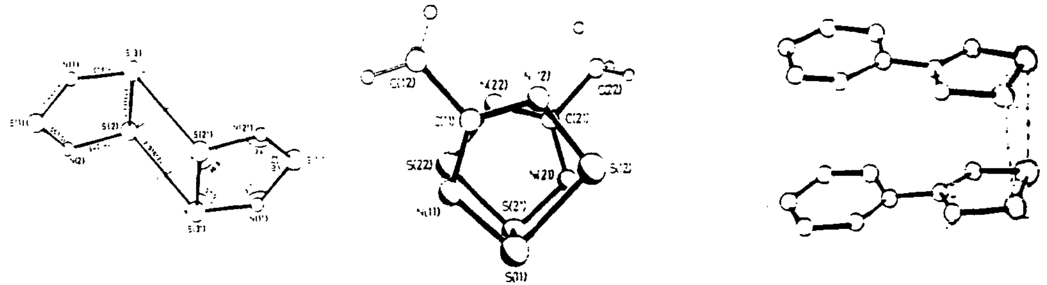
Scheme 1.8: Reduction of both 1,2,3,5- and 1,3,2,4- dithiadiazolium salts yields the corresponding radicals. However the 1,3,2,4-dithiadiazole radical can undergo rearrangement to the 1,2,3,5-isomer.

Typically these radicals are purple-brown in solution. However the 1,3,2,4-dithiadiazoles have been shown to be photochemically unstable w.r.t. rearrangement to their 1,2,3,5-dithiadiazole counterparts[17] and thus the chemistry of this isomeric form has been little studied.

On the other hand the 1,2,3,5-dithiadiazole materials have been well characterised and appear to have an unusual and diverse chemistry:

A variety of solid state dithiadiazoles are known and have been characterised by X-ray analysis. As expected they have a variety of similarities with the isoelectronic $S_6N_4^{2+}$ cation, in that they are dimeric in the solid state and are held together through weak S...S interactions. However rather than taking up a trans arrangement, as observed in $S_6N_4^{2+}$, the rings take up a cis-oid conformation with the rings held together through either one (e.g. $(MeCNSSN)_2$[19] and $(CF_3CNSSN)_2$[20]) or two S...S interactions ($(PhCNSSN)_2$[21]) see Figure 1.9:

Figure 1.9: A Structural Comparison of $S_6N_4^{2+}$ and its isoelectronic $[RCN_2S_2]_2$ counterparts.



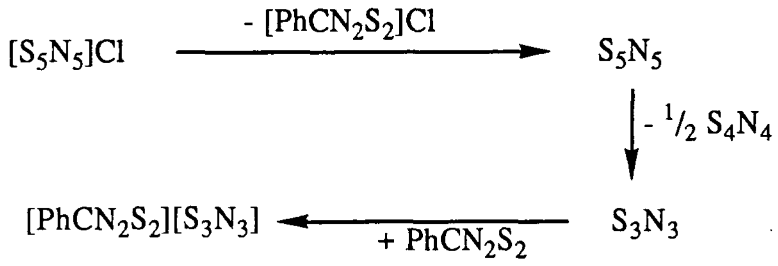
$S_6N_4^{2+}$ $[MeCN_2S_2]_2$ $[PhCN_2S_2]_2$

In these materials there are also further interactions between dimer pairs, somewhat akin to those between cation and anion in $S_6N_4^{2+}$. Other dithiadiazoles such as $^tBuCNSSN$ are paramagnetic liquids at room temperature[17] and this can be attributed to either steric hindrance (e.g. ^tBu,which blocks dimerisation) or to electron-withdrawing effects (e.g. CF_3) which destabilise the oligomerisation process.

Reactions of dithiadiazoles

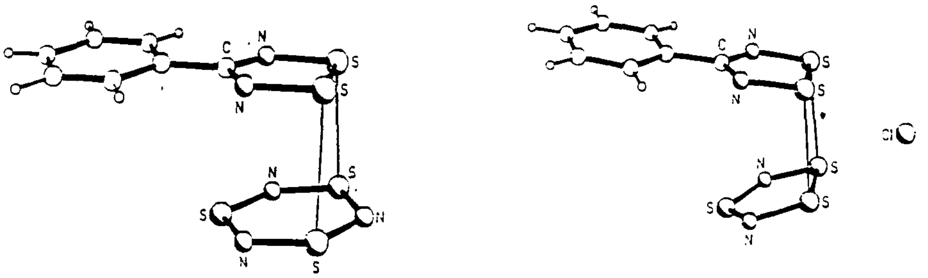
Dithiadiazoles have been shown to be dehalogenating agents[22]; reacting with both elemental chlorine and bromine, as well as SO_2Cl_2, to give the corresponding dithiadiazolium cation. More interestingly they can also dehalogenate other sulphur-nitrogen materials such as $[S_5N_5]Cl$ and $[S_4N_3]Cl$ [22]. However in these cases the process is not simple and contraction of the binary S/N ring also occurs and the dithiadiazole moiety shows itself to also act as a radical trap:

Scheme 1.10: $[PhCN_2S_2]_2$ is able to act as a dechlorinating agent but also as a radical trap; $[S_5N_5]Cl$ being reduced to S_5N_5 which undergoes ring contraction to S_3N_3 which is then trapped by $[PhCN_2S_2]_2$ to form $[PhCN_2S_2][S_3N_3]$.



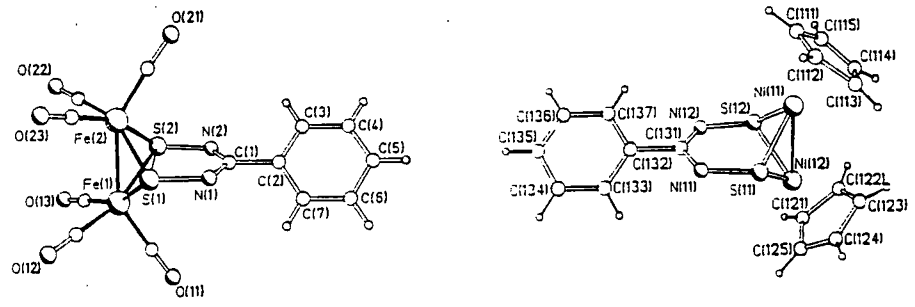
The structures of [PhCNSSN][S_3N_3] and [PhCNSSN][S_3N_2]Cl both show pseudo-planar structures and the formation of these materials has induced work into the preparation of low dimensional organic metals based on sulphur-nitrogen heterocycles [23].

Figure 1.11: Solid State Structures of [$PhCN_2S_2$][S_3N_3] and [$PhCN_2S_2$][S_3N_2]Cl



A variety of dithiadiazoles also undergo insertion reactions with a nitrogen plasma, to give the RCN_3S_2 ring system[19]. Metals have also been shown to undergo insertion into the dithiadiazole SS bond[3b,24] and have led to some unusual species with the PhCNSSN moiety acting as a bidentate, bridging ligand:

Figure 1.12: X-ray Crystal Structures of $Fe_2(CO)_6(PhCN_2S_2)$ and $Cp_2Ni_2(PhCN_2S_2)$; showing the $PhCN_2S_2$ unit as a bidentate bridging ligand.



Consequently the dithiadiazole ring would appear to be a novel system whose chemistry is diverse and unusual with ring expansions, metal complexations, dehalogenations and which show a variety of solid state secondary interactions. Perhaps more importantly the dithiadiazolium/ole system would appear to be providing some low dimensional, pseudo-planar materials whose physical solid-state properties may prove as exciting and unusual as those of $(SN)_x$ which, itself, has attracted industrial interest through a variety of possible applications[2].

The work which now follows describes an investigation into the preparation of new dithiadiazolium salts and their reduced ,*free radical*, dithiadiazole counterparts, including the consequent reactivity of these species, with the formation of low dimensional materials as a synthetic target.

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CHAPTER TWO

THE SNS^+ SYNTHON

2.1 Introduction

[SNS][AsF$_6$]

The dithianitronium cation,as the AsF$_6^-$ salt , has been found to react with a wide variety of unsaturated organic groups, especially nitriles[1-4], alkynes[1-4] and alkenes[5] to produce heterocyclic cations I, II, III and IV respectively in essentially quantitative yields as shown in figure 2.1.1.

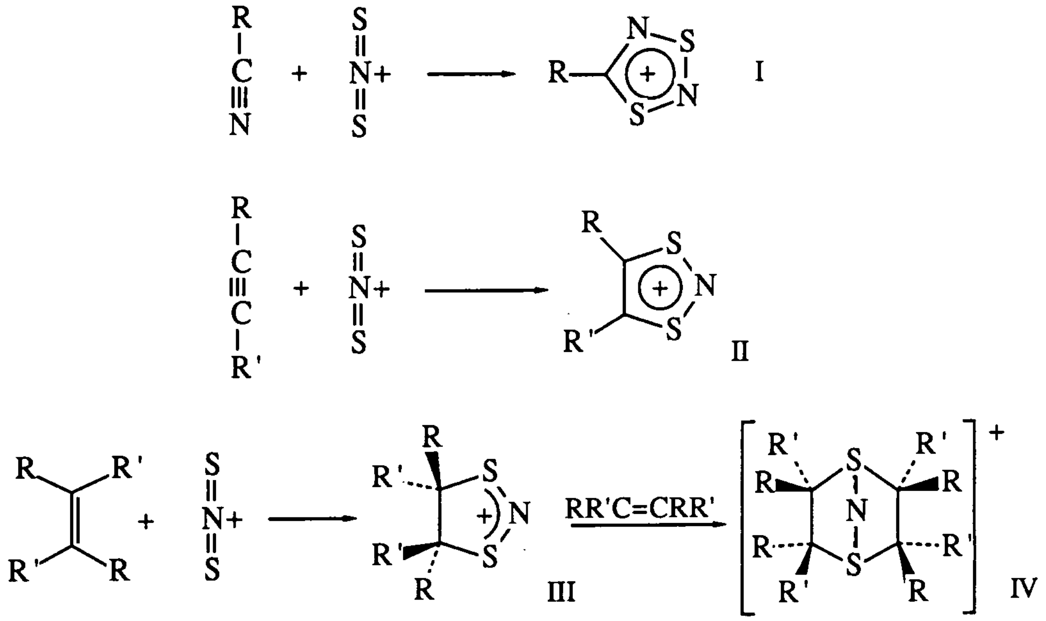


Figure 2.1.1. Cycloaddition reactions of the SNS$^+$ cation with a variety of unsaturated organic groups (nitriles, alkynes and alkenes) are well-known; see text.

Ring formation has been shown to occur via a concerted symmetry -allowed [4+2] cycloaddition process[5] involving one of the mutually perpendicular orbitals of SNS$^+$ (comparable with those of CO$_2$ and NO$_2^+$) and those of the other unsaturated group. This is perhaps best illustrated from a Frontier Orbital approach, see figure 2.1.2. Cyclisation occurs via a reverse electron-demand process where the primary interaction is electron donation from the olefin HOMO into the SNS$^+$ LUMO . These sort of interactions have been observed in other S/N cycloaddition reactions, particularly with norbornadiene[6-9].

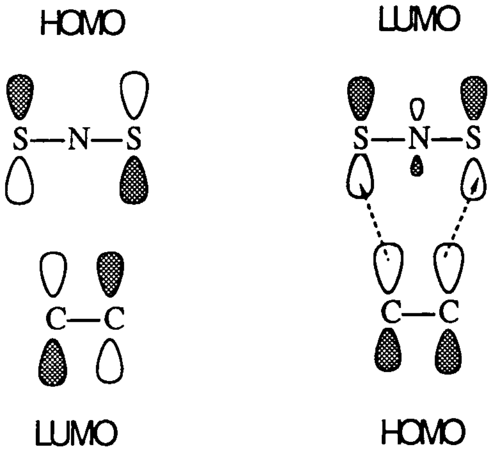


Figure 2.1.2. Frontier Orbital Interactions between SNS$^+$ and an olefin.
Similar interactions are observed for other organic groups such as nitriles but the orbital coefficients will have different values.

They are, however, the reverse of those seen in most "organic" cyclisation processes[7] where the major interaction is electron donation from the diene HOMO. It is interesting to note that isovalent NO_2^+ and CS_2 have not been observed to undergo related cycloaddition processes ,despite having similar orbital symmetries[10,11], and this may be a consequence of the fact that SNS$^+$ is one of very few triatomics having relatively electropositive terminal atoms; a comparison of orbital characteristics is shown in figure 2.1.3:

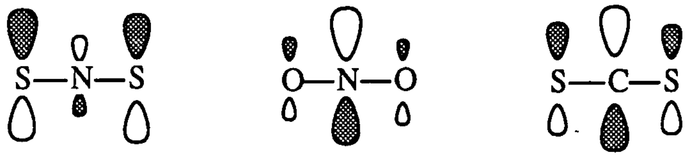


Figure 2.1.3. The LUMOs of SNS$^+$, ONO$^+$ and CS_2 all show the same symmetry, but only SNS$^+$ has electropositive terminal atoms.

We can see, therefore, that since SNS$^+$ has possibly a special position in heterocyclic synthesis, the development of high yield preparations of SNS$^+$ salts is of vital importance in making the formation of a wider range of such S/N containing materials possible.

The first dithianitronium salt to be prepared in high yield[12] was [SNS][AsF_6], according to equations 2.1.4 and 2.1.5; the solvent being liquid SO_2:

Eqn. 2.1.4. $[S_8][AsF_6]_2 + NaN_3 \longrightarrow [SNS][AsF_6] + NaAsF_6 + N_2 + {}^3/_4 S_8$

Eqn. 2.1.5. ${}^1/_2\ S_8 + S_4N_4 + 6AsF_5 \longrightarrow 4\,[SNS][AsF_6] + 2\ AsF_3$

The yields were 20% and 80+% respectively but the hazardous nature of this preparation; involving either NaN_3,or S_4N_4 and AsF_5,has led to the development of other routes to this cation.

Other published SNS$^+$ salts

[SNS][$SbCl_6$] was first synthesised[13] in unspecified yield by the reaction of S_7NH, S_7NBCl_2 or 5,8-$S_6(NH)_2$ with $SbCl_5$ in liquid SO_2 but the reaction of $(NSCl)_3$ with $SbCl_5$ and elemental sulphur ,in the correct molar ratio, in methylene chloride is a more convenient route[14]; readily producing [SNS][$SbCl_6$] in higher yield; 50% (see equation 2.1.6):

Eqn. 2.1.6. $(NSCl)_3 + 3SbCl_5 \longrightarrow 3\,[NSCl][SbCl_5] \xrightarrow{{}^3/_8\,S_8} 3\,[SNS][SbCl_6]$

The quoted intermediate, NSCl.$SbCl_5$, can be considered as [SN]$SbCl_6$ since the reaction of [SN][$SbCl_6$] or [SN][AsF_6] with sulphur itself leads to SNS$^+$ salts.

Having observed that the reaction of SN$^+$ with elemental sulphur yields the SNS$^+$ cation , the syntheses of a variety of SN$^+$ salts[15,16] have consequently been attempted, eventually leading to the formation of the first "organic" SNS$^+$ reagent[17], see equation 2.1.7:

Eqn. 2.1.7. $(NSCl)_3 + 3[Ag][CF_3SO_3] + {}^3/_8\ S_8 \longrightarrow 3\,[SNS][CF_3SO_3]$

Unfortunately yields of this salt have been poor and isolation proved difficult due to the similar solubilities of [SNS][CF_3SO_3] and the major by-product, [S_6N_4][CF_3SO_3]$_2$. Moreover the triflate salt is extremely air sensitive (even more so than [SNS][AsF_6]) and its applications would therefore appear minor.

Summarising, we can see that the [4+2] cycloaddition reactions of the dithianitronium cation are ideal for the generation of S/N containing heterocycles but the synthesis of suitable SNS^+ reagents has been something of a problem; the only high yield (>50%) preparation requires the use of both explosive S_4N_4 and highly toxic AsF_5.

Consequently our research has been targeted at the development of new routes to these SNS^+ salts and, in particular, to the dechlorination of $N(SCl)_2^+$ salts:

Proposed Synthesis of SNS^+ from $N(SCl)_2^+$ salts

Salts of the type $N(SCl)_2^+X^-$ (X^-= $AlCl_4^-$, $FeCl_4^-$ and $SbCl_6^-$) are readily prepared[18-20] from the reaction of $(NSCl)_3$ with SCl_2 and a Lewis acid such as $AlCl_3$, $FeCl_3$ or $SbCl_5$ respectively (see equations 2.1.8-10):

Eqn. 2.1.8. $(NSCl)_3 + 3SCl_2 + 3AlCl_3 \longrightarrow 3\,[N(SCl)_2][AlCl_4]$

Eqn. 2.1.9. $(NSCl)_3 + 3SCl_2 + 3FeCl_3 \longrightarrow 3\,[N(SCl)_2][FeCl_4]$

Eqn. 2.1.10 $(NSCl)_3 + 3SCl_2 + 3SbCl_5 \longrightarrow 3\,[N(SCl)_2][SbCl_6]$

All salts are readily isolated in 80-100% yield with further purification often being unnecessary and thus these materials seemed ideal starting materials for reduction to the analogous SNS^+ systems.

The following results describe the formation of $N(SCl)_2^+$ salts and the attempted dechlorination of these $N(SCl)_2^+$ salts using a variety of reagents and under varying conditions.

2.2 Results and Discussion

2.2.1. Preparation of $[N(SCl)_2][AsF_6]$

$[N(SCl)_2][AsF_6]$ has previously been prepared[21,22] from the reaction of $[SN][AsF_6]$ with SCl_2 in liquid SO_2 and also by the reaction of $[SNS][AsF_6]$ with elemental chlorine (see equations 2.2.1a and 2.2.1b):

Eqn. 2.2.1a $[SN][AsF_6] + SCl_2 \xrightarrow{\text{liquid } SO_2} [N(SCl)_2][AsF_6]$

Eqn. 2.2.1b $[SNS][AsF_6] + Cl_2 \xrightarrow{\text{liquid } SO_2} [N(SCl)_2][AsF_6]$

However the prior preparation and isolation of $[SN][AsF_6]$, in 2.2.1a, involves the use of $AgAsF_6$ which is expensive and hazardous to make[23] (it requires the use of AsF_5) and consequently has few advantages (it does not require the use of explosive S_4N_4) over the present preparation of $[SNS][AsF_6]$[12]. Similarly the formation of $[N(SCl)_2][AsF_6]$ by the direct halogenation of $[SNS][AsF_6]$ is unsuitable since the interest in the preparation of this bis(chlorosulphur)nitrogen cation is as a potential route to the dithianitronium cation itself.

$[N(SCl)_2]AsF_6$ was therefore prepared in 80% recoverable yield from the simple anion metathesis reaction between $[N(SCl)_2][FeCl_4]$ and $[^tBu_4N][AsF_6]$ in methylene chloride:

Eqn. 2.2.1c $[N(SCl)_2][FeCl_4] + [^tBu_4N][AsF_6] \longrightarrow [^tBu_4N][FeCl_4] + [N(SCl)_2][AsF_6]$

2.2.2 Preparation of $[N(SCl)_2]_2[SeCl_6]$

This was prepared in an analogous manner to the $AlCl_4^-$, $FeCl_4^-$ and $SbCl_6^-$ salts as described in the literature[18] according to equation 2.2.2a; the required salt precipitating as a fine yellow powder and recovered in high yield (84%).

Eqn. 2.2.2a $^2/_3\ (NSCl)_3 + 2SCl_2 + SeCl_4 \longrightarrow [N(SCl)_2]_2[SeCl_6]$

2.2.3 Preparation of $[N(SCl)_2][BF_4]$

This was prepared by a similar anion metathesis to that in 2.2.1; using $[N(SCl)_2][AlCl_4]$ and $NaBF_4$:

Eqn. 2.2.3a $[N(SCl)_2][AlCl_4] + NaBF_4 \longrightarrow NaAlCl_4 + [N(SCl)_2][BF_4]$

Purification was by brief extraction with CH_2Cl_2 to provide a 50% recoverable yield of $[N(SCl)_2][BF_4]$. An increased yield could undoubtedly be obtained by using an analogous tetraalkylamonium salt, the increased solubility of the by-product producing a more facile separation.

2.2.4 Reduction of $[N(SCl)_2][SbCl_6]$ with Mg

$[N(SCl)_2][SbCl_6]$ was stirred with an excess of magnesium turnings in liquid SO_2 in an attempted preparation of $[SNS][SbCl_6]$. After a period of 20 hours the soluble products were separated from the insolubles (unreacted $[N(SCl)_2][SbCl_6]$ and Mg turnings) and identified mostly as S_4N_4 and sulphur halides by infra-red spectroscopy and observation. It was inferred that a small amount of decomposition had occured, according to equation 2.2.4a:

$$\text{Eqn. 2.2.4a} \quad Mg + 2N(SCl)_2^+ \longrightarrow {}^1/_2\, S_4N_4 + 2SCl_2 + Mg^{2+}$$

This is in agreement with the thermal decomposition products of $[N(SCl)_2][AsF_6]$ which have been published elsewhere[21]; the comparative thermal stabilities of AsF_6^- and $SbCl_6^-$ salts are discussed in Chapter 3.2.4.

2.2.5 Reduction of $[N(SCl)_2][AlCl_4]$ with Ph_3Sb

Reaction of $[N(SCl)_2][AlCl_4]$ with Ph_3Sb in liquid SO_2 produced an immediate red-green solution which, on filtration and removal of solvent, provided metallic-green microcrystals of $[S_6N_4][AlCl_4]_2$.

2.2.6 Reduction of $[N(SCl)_2][SbCl_6]$ with $SnCl_2$

Reaction of $[N(SCl)_2][SbCl_6]$ with anhydrous tin(II) chloride in liquid SO_2 produced an essentially quantitative yield of $[SNS][SbCl_6]$ over a period of 18 hours, according to equation 2.2.6a.The products were readily separated as $[SNS][SbCl_6]$ is insoluble in SO_2 whilst $SnCl_4$ itself is a liquid.

$$\text{Eqn. 2.2.6a} \quad [N(SCl)_2][SbCl_6] + SnCl_2 \longrightarrow [SNS][SbCl_6] + SnCl_4$$

It is possible to envisage the reaction occuring via insertion of the $SnCl_2$ unit between the terminal chlorines of $N(SCl)_2^+$ followed by either a concerted or stepwise loss of the two chlorine atoms, as proposed in figure 2.2.6b. However it is also possible that a consecutive chloride abstraction takes place via a non-symmetric intermediate as is also portrayed in figure 2.2.6b.

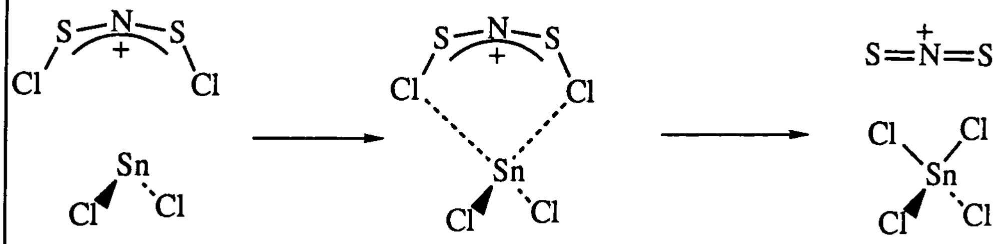
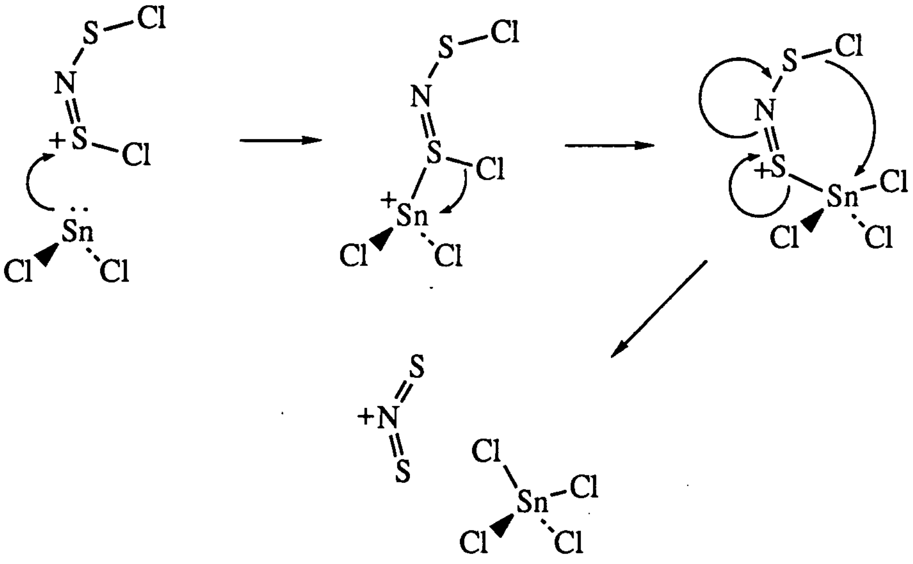


Figure 2.2.6b.
Possible reaction mechanisms for the dechlorination of $N(SCl)_2^+$ by $SnCl_2$.
A concerted mechanism (above) or a stepwise mechanism (below):



The precise reaction mechanism is not known at the present time and some further experiments would be required to determine the exact nature of the reduction pathway.

As in the case of [SNS][$AlCl_4$] and [SNS][AsF_6] (see 2.2.7 and 2.2.11) ; [SNS][$SbCl_6$] shows some cation-anion interactions in the solid state. Its crystal structure is shown in figure 2.2.6c.

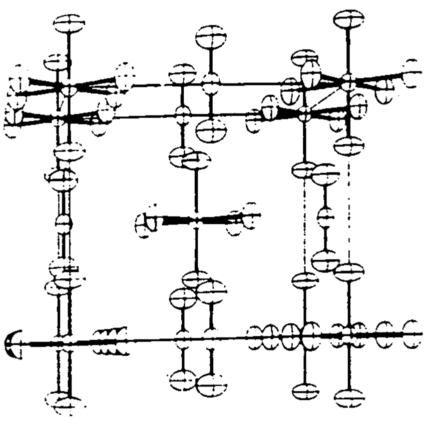


Figure 2.2.6c
Packing Diagram of $[SNS][SbCl_6]$, showing a linear, symmetric SNS^+ cation:

S(1)-N	1.463 A
S(2)-N	1.463A
$S(1)\hat{N}S(2)$	180.0°

ref. 26

2.2.7 Reduction of $[N(SCl)_2][AlCl_4]$ with $SnCl_2$

Reduction of $[N(SCl)_2][AlCl_4]$ with $SnCl_2$ was carried out in CH_2Cl_2 and produced $[SNS][AlCl_4]$ in ca. 85% yield. However in liquid SO_2 the yield was greatly reduced (ca.40%) and a large proportion of $[S_6N_4]$ $[AlCl_4]_2$ was observed.This tends to suggest that $[S_6N_4][AlCl_4]_2$ is the thermodynamically prefered product but intermediate salts may be isolated by selective precipitation; see equations 2.2.7a-c:

Eqn. 2.2.7a $$N(SCl)_2^+ + SnCl_2 \longrightarrow SNS^+ + SnCl_4$$

Eqn. 2.2.7b $$SNS^+ + N(SCl)_2^+ \longrightarrow S_3N_2Cl^+ + (SCl)^+$$

Eqn. 2.2.7c $$S_3N_2Cl^+ + {}^1/_2SnCl_2 \longrightarrow S_3N_2^+ + {}^1/_2SnCl_4$$

The low solubility of $[SNS]AlCl_4$ in CH_2Cl_2 precludes the formation of $S_3N_2Cl^+$ and $S_3N_2^{+\bullet}$salts whereas in liquid SO_2 $[S_6N_4][AlCl_4]_2$ is formed as the major product. $[SNS]AlCl_4$ was first prepared by Thewalt et al.[24] from the reaction of S_4N_4 with $AlCl_3$ in CH_2Cl_2 (the major component being $[S_2N_2][AlCl_3]_2$) and the crystal structure[25] (figure 2.2.7d) shows essentially linear SNS^+ cations with some S...Cl interactions.

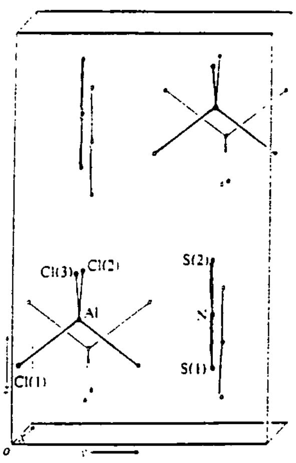


Figure 2.2.7d
Packing Diagram of [SNS][$AlCl_4$], showing S...Cl interactions between cation and anion.

S(1)-N	1.464 Å
S(2)-N	1.472Å
$S(1)\hat{N}S(2)$	179.5°

shortest S...Cl 3.26Å*

*compare sum of van der Waal's radii; 3.6Å.

ref. 25

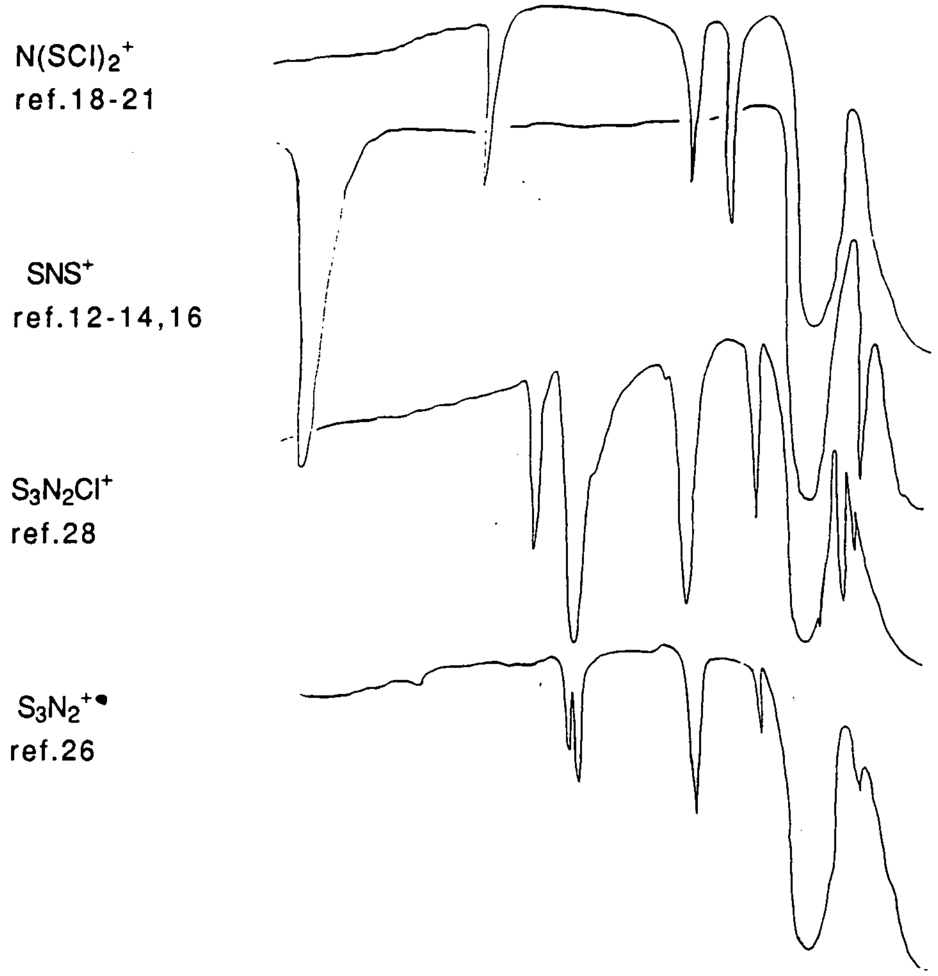
2.2.8. Reduction of [$N(SCl)_2$]$_2$[$SeCl_6$] with $SnCl_2$

Reduction of the $SeCl_6^{2-}$ salt with $SnCl_2$ in both CH_2Cl_2 and liquid SO_2 produced a pale green-yellow precipitate of [S_3N_2Cl]$_2$[$SeCl_6$] in agreement with the proposed mechanism above (equation 2.2.7a-c). Attempts to precipitate out intermediate [SNS]$_2$[$SeCl_6$] were unsuccesful.

2.2.9. Reduction of [$N(SCl)_2$][$FeCl_4$] with $SnCl_2$

Reaction of [$N(SCl)_2$][$FeCl_4$] with $SnCl_2$ in CH_2Cl_2 produced a mixture of [SNS][$FeCl_4$], [S_3N_2Cl][$FeCl_4$] and some [S_6N_4][$FeCl_4$]$_2$; identified by infra-red spectroscopy. Infra-red absorption data was found to be an ideal method of ready determination of the reaction products as each cation; $N(SCl)_2^+$, SNS^+, $S_3N_2Cl^+$ and $S_3N_2^{+\bullet}$; has its own distinctive absorption pattern, as shown in diagram 2.2.9a.

Figure 2.2.9a. Infra-red absorption bands of simple sulphur-nitrogen compounds often allow ready differentiation between various materials. In particular, we see here the distinctive i.r. frequencies associated with the products of reduction of $N(SCl)_2^+$ salts with $SnCl_2$:



2.2.10. Reduction of $[N(SCl)_2][BF_4]$ with $SnCl_2$

This reaction yielded $[S_3N_2Cl][BF_4]$ after being stirred for 18 hours at room temperature with $SnCl_2$ in dichloromethane. On removal of the CH_2Cl_2 and replacement with SO_2, a green-brown solution soon formed, which yielded green-black microcrystals of $[S_6N_4][BF_4]_2$ on evaporation of the solvent. This transformation is also in accordance with equations 2.2.7a-c.

2.2.11. Reduction of $[N(SCl)_2^+][AsF_6]$ with $SnCl_2$

Having seen that reduction of $N(SCl)_2^+$ salts with $SnCl_2$ seems to be solvent dependent to a large extent, CH_2Cl_2 was chosen in preference to liquid SO_2 for this reaction (although $[SNS][AsF_6]$ is known to be stable in SO_2) since $[SNS][AsF_6]$ has a much lower solubility in this solvent. After 18 hours stirring at room temperature with temperature with $SnCl_2$, $[N(SCl)_2][AsF_6]$ produced $[SNS][AsF_6]$ in 70% recoverable yield; the solubles containing only minimal quantities of $[S_6N_4][AsF_6]_2$, plus some $[SNS][AsF_6]$ and $SnCl_4$.

The crystal structure[27] of $[SNS][AsF_6]$ (see fig. 2.2.11a) shows some S...F cation-anion interactions but the strength of the As-F bond w.r.t. the metal-chlorine bond in the anion of other salts (e.g. $[SNS][AlCl_4]$ and $[SNS][SbCl_6]$; see Chapter 2.2.7 and 2.2.6) should be taken into account when comparing the reactivity of these different salts (Chapters 3.2.4 and 4.2.1-2).

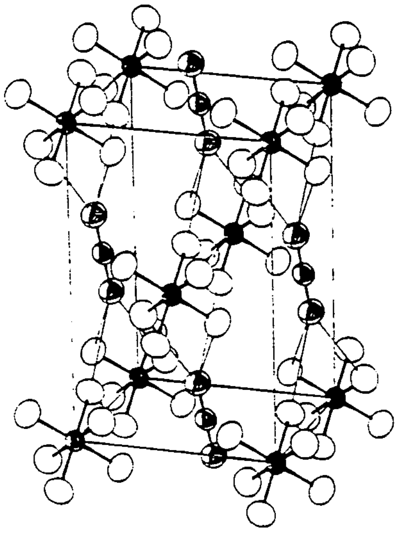


Figure 2.2.11a
Packing Diagram of $[SNS][AsF_6]$, showing S...F interactions between cation and anion.

S(1)-N	1.480(3) Å
S(2)-N	1.480(3)Å
$S(1)\hat{N}S(2)$	180.0°
shortest S...F	3.007(5)Å*

*compare sum of van Der Waal's radii; 3.2 Å.

ref. 27

Indeed it would appear that the strength of the metal-halogen bond, in the counterion, affects the reactivity of the SNS^+ reagent. This would appear to be particularly prevalent in the case of $[SNS][AlCl_4]$, where a variety of side products are observed which have been attributed to initial halide loss from the $AlCl_4^-$ anion.

2.3 Conclusions

Reactions of $N(SCl)_2^+$ salts with $SnCl_2$ would appear to be a general high yield route to the formation of new SNS^+ reagents. The ability to change the corresponding anion in the starting material by simple anion metathesis means that a variety of highly soluble and inexpensive dithianitronium salts could soon be safely prepared to replace or complement $[SNS][AsF_6]$. Meanwhile the preparation of $[SNS][AsF_6]$,itself, is now a simple procedure which avoids hazardous reagents and high pressure apparatus, whilst permitting the use of readily available $(NSCl)_3$§.

By monitoring the reduction by n.m.r. or e.s.r. it should be possible to confirm, or otherwise, the proposed reaction mechanism.

---

§ see Appendix 1.

2.4 Experimental

2.4.1: Preparation of $[N(SCl)_2][AsF_6]$

$[N(SCl)_2][FeCl_4]$ (0.347g, 1 mmol) was stirred with $[^nBu_4N][AsF_6]$ (0.431g, 1 mmol) in CH_2Cl_2 for 18 hours at room temperature. The yellow product was filtered off and washed with CH_2Cl_2(5x5ml) to remove $[^nBu_4N][FeCl_4]$. The product had an i.r. spectrum comparable to that in the literature.

Yield: 0.270 g, 80%

i.r.: ν(max): 1120(m), 720(m),690(vs), 655(ms), 525(s), 505(s), 495(s), 380(vs)

elemental analysis: $NS_2Cl_2AsF_6$ F.W.: 338

required: N: 4.1% S:18.9% Cl: 21.0% As:22.2% F: 33.7%

observed: N: 4.0% S: ----- Cl: ----- As: ----- F: -----

2.4.2: Preparation of $[N(SCl)_2]_2[SeCl_6]$

$(NSCl)_3$ (0.543 g, 6.6 mmol) and $SeCl_4$ (2.21 g, 10 mmol) were stirred in $SOCl_2$(30 ml) in a round-bottomed flask and SCl_2 added. The mixture was taken to reflux for 6 hours before allowing to cool. On cooling a lemon-yelllow powder of the required product, $[N(SCl)_2]_2[SeCl_6]$, was formed which was filtered off and washed with small quantities of ice-cold $SOCl_2$.

Yield: 4.956 g, 84%

i.r.: ν(max): 1136(m), 730(s), 720(m), 660(s), 650(m), 524(s), 510(s), 495(s).

elemental analysis: $N_2S_4Cl_{10}Se$ F.W.: 590

required: N: 4.7% S: 21.7% Cl: 60.1% Se: 13.4%

observed: N: 4.8% S: ----- Cl: ----- Se: -----

The product was primarily identified by its distinctive i.r. absorption bands.

2.4.3: Preparation of $[N(SCl)_2][BF_4]$

$[N(SCl)_2][FeCl_4]$ (0.347g, 1mmol) was stirred with NaBF4 (0.110 g, 1 mmol) in CH_2Cl_2 for 18 hours at room temperature. The yellow product was filtered off and extracted with CH_2Cl_2 in a sealed extractor.

Yield: 0.118 g, 50%

i.r.: ν(max): 1136(m), 730(s), 720(m), 660(s), 650(m), 524(s), 510(s), 495(s).

elemental analysis: $NS_2Cl_2BF_4$ F.W.: 236

required: N: 5.9% S: 27.1% Cl: 30.1% B: 4.7% F: 32.2%

observed: N: 6.1% S: ----- Cl: ----- B: ----- F: -----

2.4.4: Reduction of $[N(SCl)_2][SbCl_6]$ with Mg

$[N(SCl)_2][SbCl_6]$ (0.483g, 1 mmol) was stirred with an excess of magnesium turnings (0.030 g, 1.25 mmol) in SO_2 for 20 hours at room temperature. The soluble products were filtered off to leave a yellow precipitate of unreacted $[N(SCl)_2][SbCl_6]$ which was briefly washed with back-condensed SO_2. The soluble products were identified as S_4N_4 (by i.r.), and sulphur halides (by their distinctive odour).

i.r. ν(max): 1160(m), 928(s), 770(w), 760(w), 720(m), 700(ms), 617(w), 550(s).

2.4.5: Reduction of $[N(SCl)_2][AlCl_4]$ with Ph_3Sb

$[N(SCl)_2][AlCl_4]$(0.318g, 1mmol) and Ph_3Sb (0.353g, 1mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and liquid SO_2 (ca.5ml) was condensed in. On warming to room temperature a red-green solution soon formed which, on filtration and removal of solvent, yielded metallic microcrystals of $[S_6N_4][AlCl_4]_2$ and some Ph_3SbCl_2. Small samples of the product were isolated by pasteur separation for analysis.

i.r.: ν(max): 1195(m), 1160(m), 1050(s), 1030(m), 974(s), 928(s), 880(m), 680(m), 645(s), 590(m), 540(m), 530(w), 437(m).

elemental analysis: $N_4S_6Al_2Cl_8$ F.W.: 586

required: N: 9.6% S: 32.8% Al: 9.2% Cl: 48.5%

observed: N: 9.5% S: ----- Al: ----- Cl: -----

2.4.6.:Preparation of $[SNS][SbCl_6]$

$[N(SCl)_2][SbCl_6]$(1.460 g, 3.02mmol) and $SnCl_2$ (0.574 g, 3.02mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and liquid SO_2 (ca.5ml) was condensed in. The reaction mixture was stirred for 36h. to produce highly insoluble $[SNS][SbCl_6]$ under a red solution. The red solubles were filtered off and the yellow product washed with SO_2 by back-condensation before exhaustive extraction with SO_2 in a sealed extractor.

Yield: 0.874g, 70%.

i.r.:ν(max): 1480(s), 376(vs), 345(vs).

elemental analysis: NS_2SbCl_6 F.W.: 412.75

required: N: 3.4% S: 15.5% Sb: 29.5% Cl: 52.6%

observed: N: 3.4% S: 15.4% Sb: 29.7% Cl: 52.0%

2.4.7: Preparation of $[SNS][AlCl_4]$

$[N(SCl)_2][AlCl_4]$(0.318g, 1mmol) and $SnCl_2$ (0.190g, 1mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and CH_2Cl_2 (5ml) was syringed in. The reaction mixture was stirred at room temperature for 24h to give a yellow precipitate of $[SNS][AlCl_4]$ and a quantity of highly soluble red by-product which was readily removed by filtration. The product was extracted in a sealed extractor^8 with CH_2Cl_2 for 24h to remove any traces of $SnCl_4$ and minor side-products (mostly $[S_6N_4][AlCl_4]_2$).

Yield : 0.213g, 86%.

i.r.: ν(max): 1494(s), 470(s,br), 380(s).

elemental Analysis: NS_2AlCl_4 F.W.: 247

required:	N: 5.7%	S: 25.9%	Al: 10.9%	Cl: 57.5%
observed:	N: 5.4%	S: -----	Al: 10.9%	Cl: -----

2.4.8: Reduction of $[N(SCl)_2]_2[SeCl_6]$ with $SnCl_2$

$[N(SCl)_2]_2[SeCl_6]$(0.295g, 0.5mmol) and $SnCl_2$ (0.190g, 1mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and CH_2Cl_2 (5ml) was syringed in. The reaction mixture was stirred at room temperature for 24h to give a yellow-green precipitate ($[S_3N_2Cl]_2[SeCl_6]$) which was readily removed by filtration. The product was washed with CH_2Cl_2 (3x3ml) to remove any traces of $SnCl_4$ and minor side-products (mostly $[S_6N_4][SeCl_6]$).

i.r.: ν(max): 1125(m), 1032(s), 1020(s), 675(s), 570(ms), 564(m), 517(m).

elemental Analysis: $N_4S_6SeCl_8$ F.W.:611

required:	N: 9.2%	S: 31.4%	Se: 12.9%	Cl: 46.4%
observed:	N: 9.3%	S: -----	Se: -----	Cl: -----

A similar reaction was observed to occur in liquid SO_2, although this took place rather more rapidly.

2.4.9: Reduction of $[N(SCl)_2][FeCl_4]$ with $SnCl_2$

$[N(SCl)_2][FeCl_4]$(0.347g, 1mmol) and $SnCl_2$ (0.190g, 1mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and CH_2Cl_2 (5ml) was syringed in. The reaction mixture was stirred at room temperature for 24h to give a variety of products, identified by infra-red spectroscopy as; $[SNS][FeCl_4]$, a larger quantity of $[S_3N_2Cl][FeCl_4]$ and also $[S_6N_4][FeCl_4]_2$.

i.r.: ν(max):1490(m)[c] 1130(m)[a], 1070(s,br)[a], 1030(s)[a,b], 965(m)[a], 715(m)[a], 650(m)[b], 570(w)[a], 375(s)[a,c].

a: $[S_6N_4][FeCl_4]_2$ b: $[S_3N_2Cl][FeCl_4]$ c: $[SNS][FeCl_4]$

2.4.10: Reduction of $[N(SCl)_2][BF_4]$ with $SnCl_2$

$[N(SCl)_2][BF_4]$(0.236g, 1mmol) and $SnCl_2$ (0.190g, 1mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and CH_2Cl_2 (5ml) was syringed in. The reaction mixture was stirred at room temperature for 24h to give a yellow precipitate and a quantity of highly soluble red by-product which was readily removed by filtration. The crude material was identified as predominantly $[S_3N_2Cl][BF_4]$ by infra-red. On addition of SO_2 to this crude product a deep solution soon formed which on evaporation yielded green-black microcrystals of $[S_6N_4][BF_4]_2$.

i.r.: crude material:ν(max): 1150(m)[a,b], 1100(s), 1065(s)[a], 1030(s)[a,b], 1020(s)[a,b], 970(s)[a], 800(w)[a], 765(s)[a], 735(s)[a], 725(s)[a], 570(m)[a,b], 530(m)[a], 520(m)[b], 460(w)[b], 380(s), 360(s).

a: $[S_6N_4][BF_4]_2$ b: $[S_3N_2Cl][BF_4]$

2.4.11: Reduction of $[N(SCl)_2][AsF_6]$

$[N(SCl)_2][AsF_6]$(g, 1mmol) and $SnCl_2$ (0.190g, 1mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and CH_2Cl_2 (5ml) was syringed in. The reaction mixture was stirred at room temperature for 24h to give a yellow precipitate of $[SNS][AsF_6]$ and a quantity of highly soluble red by-product which was readily removed by filtration. The product was extracted in a sealed extractor[8] with CH_2Cl_2 for 4h to remove any traces of $SnCl_4$ and minor side-products (mostly $[S_6N_4][AsF_6]_2$).

Yield : 0.187g, 70%.

i.r.: ν(max):1495(m), 1090(w), 818(w), 700(vs), 385(s).

elemental Analysis: NS_2AsF_6 F.W.: 267

required:	N: 5.2%	S: 24.0%	As: 28.1%	F: 42.7%
observed:	N: 5.0%	S: -----	As: -----	F: -----

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CHAPTER THREE

THE PREPARATION OF SOME SIMPLE DITHIADIAZOLIUM SALTS

3.1 Introduction

The reaction of [SNS][AsF_6] with simple organic and inorganic nitriles is well documented[1-5]; the reactions proceeding in high yield to produce 1,3,2,4-dithiadiazolium salts; $RCNSNS^+$ (R:= H, I, Me, CF_3 and ^tBu).

Parallel to this work, research in Durham[6] has been carried out on other RCN compounds where R is an aryl group (R:= phenyl, 9-anthracenyl, *p*-methylphenyl, *p*-bromophenyl, *p*-chlorophenyl etc.) or an alkyl group (R:= Pr and CCl_3) ; again the $RCNSNS^+$ salts were synthesised in high yield. A summary of results are given in Table 3.1.1:

Table 3.1.1.: The preparation of previously known 1,3,2,4-dithiadiazolium ring systems; $RCNSNS^+$

R	Reagent	Time	Yield	Ref.
H	[SNS][AsF_6]	1 hr	93%	5
I	[SNS][AsF_6]	1 hr	89%	5
^tBu	[SNS][AsF_6]	1 hr	89%	4,5
CF_3	[SNS][AsF_6]	14d	97%	5
CCl_3	[SNS][AsF_6]	2d	*	6
Me	[SNS][AsF_6]	1d	100%	1,2,3,5
Me	[SNS][CF_3SO_3]	1d	30%	6
Ph	[SNS][AsF_6]	8hr	60%	6
Ph	[SNS][CF_3SO_3]	2hr	74%	6
p-Cl.C_6H_4	[SNS][AsF_6]	*	*	6
p-Br.C_6H_4	[SNS][AsF_6]	*	*	6
p-Me.C_6H_4	[SNS][AsF_6]	*	*	6
p-$NO_2C_6H_4$	[SNS][AsF_6]	*	*	6
9-$C_{14}H_9$	[SNS][AsF_6]	2hr	?	6

All reactions were carried out in liquid SO_2 at room temperature.

* unspecified

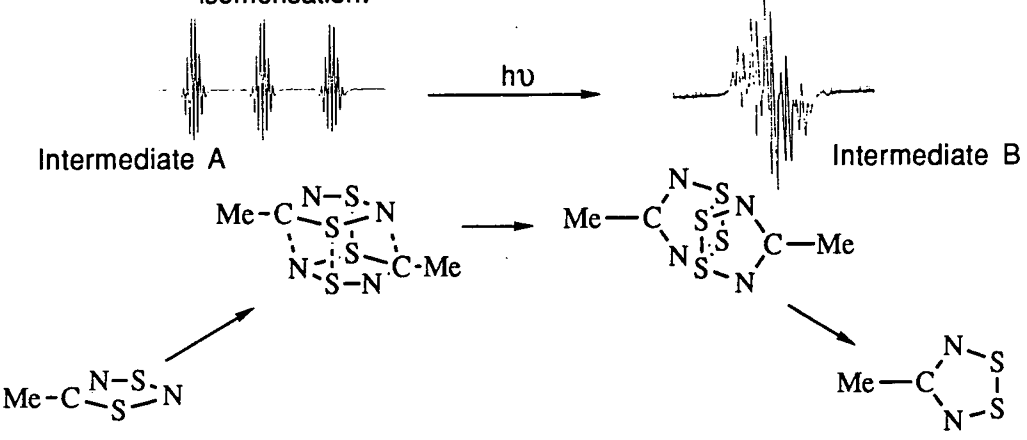
? a variety of products were formed due to cycloaddition addition reactions at the anthracenyl double bonds, as well as the nitrile group.

Reduction of these 1,3,2,4-dithiadiazolium cations[1-4] has led to the preparation of the corresponding 1,3,2,4-dithiadiazoles which have been characterised by e.s.r. spectroscopy:

The 1,3,2,4-dithiadiazole radical produces a simple triplet spectrum associated with a radical based on N(2) as proposed by MNDO calculations. However these 1,3,2,4-

dithiadiazole radicals are unstable w.r.t. isomerisation[2] to their well known 1,2,3,5-dithiadiazole counterparts and this process[10] is "thermally symmetry forbidden" but "photochemically symmetry allowed". The rearrangement process has been postulated[2] to proceed through the dimeric intermediates A and B (figure 3.1.2) to give the equivalent 1,2,3,5-dithiadiazole.

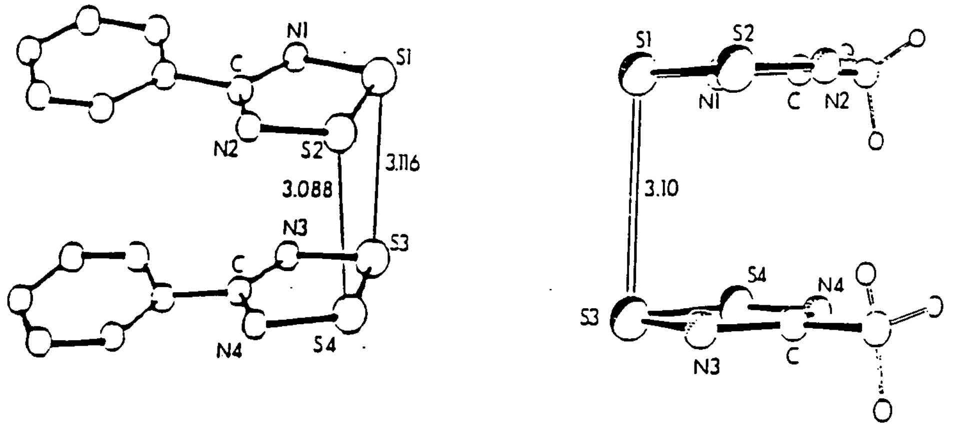
Figure 3.1.2: E.S.R. spectra of 4-methyl-1,3,2,5-dithiadiazole and 4-methyl-1,2,3,5-dithiadiazole; showing their associated radical structures and the proposed dimeric intermediates in the photochemical isomerisation.



The 1,2,3,5-dithiadiazoles themselves produce more complex e.s.r. spectra, viz. a 1:2:3:2:1 quintet due to splitting of the free electron by two equivalent N^{14} nuclei. In the case of [MeCNSSN], each of the five lines then undergoes subsequent hyperfine splitting with the methyl protons. Similar coupling is also seen in the 1,3,2,4-isomer.

The 1,3,2,4-dithiadiazoles would appear to be inherently unstable with many forming black insoluble polymers at higher concentrations[2] (e.g. greater than 1 molal) if they do not rearrange first. Consequently the solid state structures of these 1,3,2,4-dithiadiazoles have not yet been determined. In contrast a variety of structures of the 1,2,3,5-dithiadiazole radicals are known and all of these dimerise in the solid state through weak S...S interactions. The crystal structures of [PhCNSSN]$_2$ and [MeCNSSN]$_2$ are shown in figure 3.1.3.:

Figure 3.1.3: X-ray crystal structures of $[PhCNSSN]_2$ and $[MeCNSSN]_2$



ref 20

ref 21

In order to attempt to isolate such solid state 1,3,2,4-dithiadiazole radicals, several points were taken into consideration:

Firstly the radical should have a high molecular weight; both $^tBuCNSSN$ and $^tBuCNSNS$ are paramagnetic liquids at room temperature whilst lower molecular weight 1,3,2,4-dithiadiazole radicals are more volatile and are also more susceptable to decomposition and hydrolysis.

Secondly the use of electron-withdrawing substituents may stabilise these free-radical materials and hence promote the formation and isolation of these elusive species.

In this chapter the preparation of $RCNSNS^+$ salts (R:= C_6H_5 and C_6F_5) from the corresponding nitrile and SNS^+ are discussed, with a comparison of $[SNS][AsF_6]$, $[SNS][SbCl_6]$ and $[SNS][AlCl_4]$ reagents.The preparation and characterisation of the associated free radicals are also documented.

Results and Discussion

3.2.1. Preparation of $[PhCNSNS][AsF_6]$

Reaction of $[SNS][AsF_6]$ with neat PhCN at room temperature soon yielded a crude olive-green product; identified as $[PhCNSNS][AsF_6]$ which was isolated as lime-green microcrystals, by washing with CH_2Cl_2, in 90% recoverable yield (c.f. previous reports of 60%[6]). The highly-coloured solubles were identified by infra-red spectroscopy as predominantly $[PhCNSNS][AsF_6]$, although there was some evidence for trace amounts of $[S_6N_4][AsF_6]_2$.

Eqn.3.2.1a $$PhCN \quad + \quad [SNS][AsF_6] \longrightarrow [Ph\overline{CNSNS}][AsF_6]$$

3.2.2. Attempted Crystal Growth of $[PhCNSNS][AsF_6]$

Small crystals of $[PhCNSNS][AsF_6]$ were prepared by refluxing and then slowly cooling a saturated CH_2Cl_2 solution of $[PhCNSNS][AsF_6]$ to -25°C. The air-sensitive crystals were picked in a dry nitrogen atmosphere and mounted in Lindemann capillaries. However the oscillation photographs showed a very weak scattering pattern and the crystals were found to be unsuitable for a full X-ray analysis. (But see Appendix 5).

3.2.3 Preparation of $[PhCNSNS][SbCl_6]$

No reaction was observed between neat PhCN and $[SNS][SbCl_6]$ at room temperature. However, after refluxing the mixture for 3-4 hours all the $[SNS][SbCl_6]$ reacted to give a clear green-brown solution. On cooling, a precipitate of $[PhCNSNS][SbCl_6]$ formed under a dark solution and this was isolated as pale green microcrystals in 85% yield by washing with CH_2Cl_2.

Eqn.3.2.3a $$PhCN \quad + \quad [SNS][SbCl_6] \longrightarrow [Ph\overline{CNSNS}][SbCl_6]$$

Larger crystals could be grown by slow CH_2Cl_2 extraction in a sealed extractor.

Obviously $[SNS][SbCl_6]$ reacts in a similar manner to $[SNS][AsF_6]$, although the longer reaction time at elevated temperatures may slightly increase the number of side-reactions. This is evidenced by the smell of SCl_2 and the formation of dense white fumes on opening the reaction vessel; possibly due to some decomposition of the $[SNS][SbCl_6]$, see equation 3.2.3b:

$$\text{Eqn.3.2.3b} \quad 4\ [SNS][SbCl_6] \xrightarrow[\text{dec.}]{\text{heat}} SCl_2 + S + 2\ SbCl_5 + [S_6N_4][SbCl_6]_2$$

This type of decomposition is further evidenced by dark green highly soluble impurities in the crude product; typical of $[S_6N_4]^{2+}$ salts.

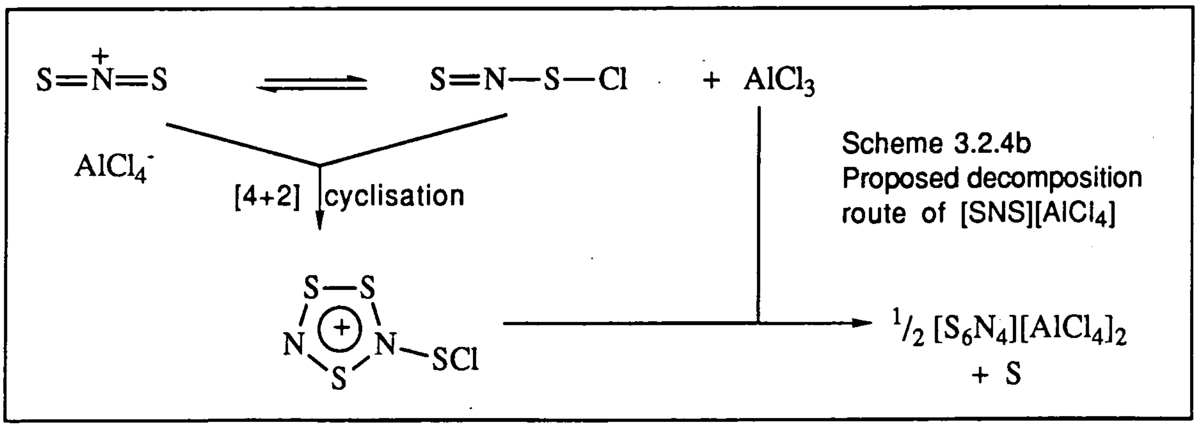
3.2.4 Reaction of PhCN with $[SNS][AlCl_4]$

As with $[SNS][AsF_6]$, this reaction occured rapidly at room temperature but in this case a wide variety of products were observed but a small quantity of $[PhCNSNS][AlCl_4]$ (colourless platelets) and green $[S_6N4][AlCl_4]_2$ were isolated from the intractable black mass (observed in other reactions of $[SNS][AlCl_4]$[19]) by washing with CH_2Cl_2 and identified by infra-red analysis.

The variety of products can be explained in terms of the extended decomposition of $[SNS][AlCl_4]$ in solution, as observed at higher temperatures with the analagous $[SNS][SbCl_6]$ salt; see fig. 3.2.4a.

$$\text{Eqn.3.2.4a} \quad 4\ [SNS][AlCl_4] \xrightarrow[\text{dec.}]{\text{rm.T.}} SCl_2 + S + 2\ AlCl_3 + [S_6N_4][AlCl_4]_2$$

Sulphur, SCl_2 and $AlCl_3$ can then recombine to give polysulphur cations of the type S_6^{2+}, S_7^+, S_8^{2+} etc.[12-14] whilst $AlCl_3$ is a potential Friedel-Crafts catalyst for aromatic ring substitution[15]. This ease of halide loss from the anion may well be the first step in the decomposition of these SNS^+ salts[16] followed by cyclisation of the intermediate [SNSCl] with more SNS^+ to form $[S_6N_4]^{2+}$, as outlined in the scheme below:



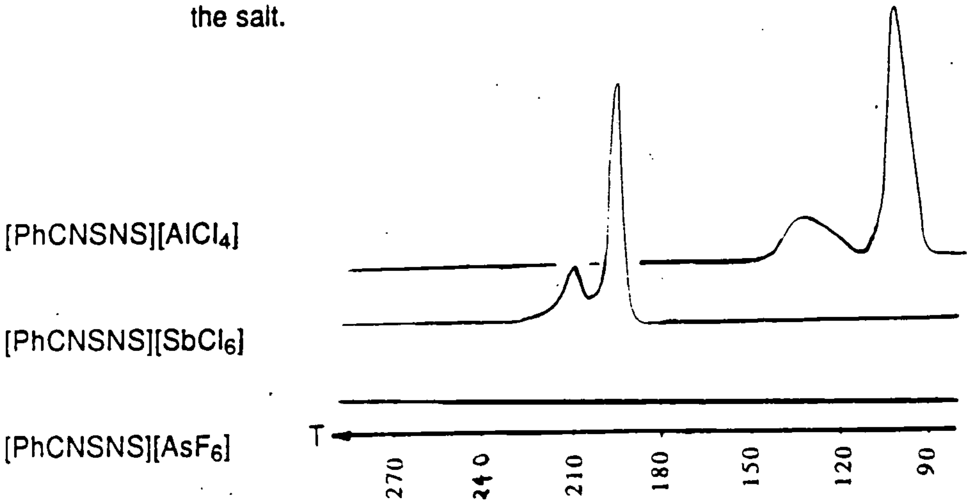
Scheme 3.2.4b
Proposed decomposition route of $[SNS][AlCl_4]$

Furthermore, it has been shown[18] that $[S_5N_5]Cl$ can be conveniently prepared by dissolving $[S_5N_5][AlCl_4]$ in THF; the $AlCl_4$ salt breaking down to give the chloride anion and a THF.$AlCl_3$ adduct.

The stability of the anion w.r.t. halide loss would appear to be a major factor in determining the ease and cleanliness of reaction; the easier halide loss occurs, the greater the number of by-products. This is highlighted by the strength of the secondary interactions in the solid state (see chapter2.2.6,7 and 11); the strongest secondary interactions being in $AlCl_4^-$ and $SbCl_6^-$ salts. This stability is also carried through from the dithianitronium salts to the dithiadiazolium salts:

$[PhCNSNS][AsF_6]$ is stable up to 300°C whereas $[PhCNSNS][SbCl_6]$ decomposes at c.190°C (see figure 3.2.4b). On opening the aluminium capsule some white fumes indicative of $SbCl_5$ were observed plus some tarnishing of the capsule itself, indicative of the break-down of $SbCl_6^-$ anions to $SbCl_5$ and Cl^-. It would therefore be anticipated that $[PhCNSNS][AlCl_4]$ would decompose at even lower temperatures as the Lewis acidity of $AlCl_3$ is weaker than that of $SbCl_5$. Indeed, although $[PhCNSNS][AlCl_4]$ could not be isolated from the reaction of $[SNS][AlCl_4]$ with PhCN, it could be prepared by anion metathesis from the chloride salt by reaction with $AlCl_3$. The D.S.C. trace shows decomposition of the salt at 105°C as expected:

Figure 3.2.4c: Differential Scanning Calorimetry traces of three phenyl-1,3,2,5-dithiadiazolium salts; AsF_6^-,$SbCl_6^-$ and $AlCl_4^-$ showing the effect of the strength of the Lewis acid in the anion on the stability of the salt.



3.2.5. Preparation of $[C_6F_5CNSNS][AsF_6]$

Again an instantaneous reaction between $[SNS][AsF_6]$ and C_6F_5CN was observed and yielded crude brown $[C_6F_5CNSNS][AsF_6]$. On washing with CH_2Cl_2 and a trace of SO_2, white $[C_6F_5CNSNS][AsF_6]$ was obtained (94%) as highly air-sensitive microcrystals. Larger crystals could be obtained by the slow evaporation of a saturated CH_2Cl_2 solution.

Eqn.3.2.5a $C_6F_5CN + [SNS][AsF_6] \longrightarrow [C_6F_5CNSNS][AsF_6]$

3.2.6. Preparation of $[C_6F_5CNSNS][SbCl_6]$

No reaction occurred between C_6F_5CN and $[SNS][SbCl_6]$ at room temperature (c.f. chapter 3.2.3) but heating to elevated temperatures (ca.100°C) over a period of 3-4 hours induced reaction which provided an olive solution. On cooling, an olive green precipitate of impure $[C_6F_5CNSNS][SbCl_6]$ was observed which yielded a lime microcrystalline powder (82%) after washing with CH_2Cl_2.

Eqn.3.2.6a $C_6F_5CN + [SNS][SbCl_6] \longrightarrow [C_6F_5CNSNS][SbCl_6]$

Differential Scanning Calorimetry again showed decomposition of the $SbCl_6$ salt at c.140°C whilst the AsF_6 salt showed no signs of decomposition up to 300°C.

3.2.7. Reaction of C_6F_5CN with $[SNS][AlCl_4]$

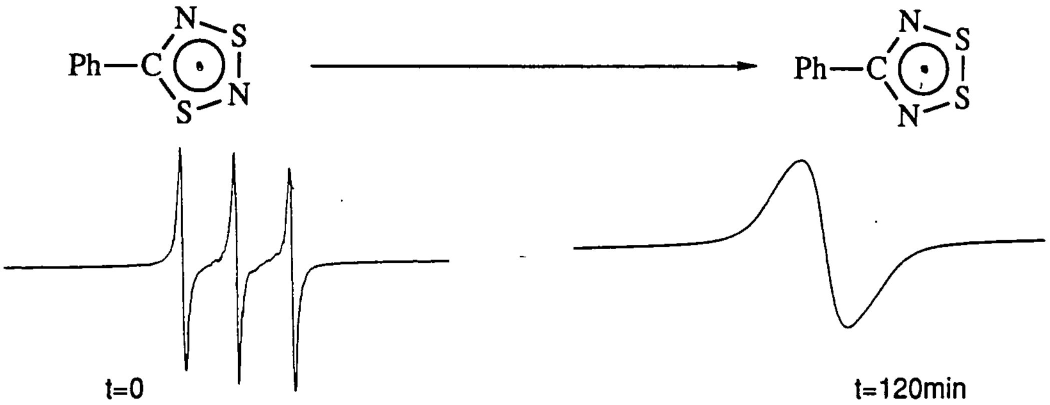
Both $[SNS][AsF_6]$ and $[SNS][SbCl_6]$ reacted in a similar fashion with C_6F_5CN and C_6H_5CN and consequently the formation of a black intractable material was not unexpected when $[SNS][AlCl_4]$ was reacted with C_6F_5CN (c.f. chapter 3.2.4.). Small quantities of what was presumably $[C_6F_5CNSNS][AlCl_4]$ as well as $[S_6N_4][AlCl_4]_2$ could be extracted out with CH_2Cl_2.

3.2.8. Reduction of $[PhCNSNS][AsF_6]$

Reduction of $[PhCNSNS][AsF_6]$ with Ph_3Sb in the presence of $^tBu_4NCl$ occurred readily in toluene upon slight warming. An e.s.r. spectrum of the initial mixture showed a three line 1:1:1 triplet; typical of a 1,3,2,4-dithiadiazole. On standing for several hours rearrangement took place to the 1,2,3,5-dithiadiazole radical, observed as a broad unresolved band at room temperature but which shows hyperfine coupling at lower temperatures.

The e.s.r. spectra of this rearrangement are shown in figure 3.2.8a (over).

Figure 3.2.8a: Rearrangement of the 5-phenyl-1,3,2,4-dithiadiazole radical into the 4-phenyl-1,2,3,5-dithiadiazole radical; as observed by e.s.r. spectroscopy.



The lower intensity of the signal for the 1,2,3,5-dithiadiazole, accompanied with the formation of a red-black oil is indicative of one or more side reactions during the rearrangement process as seen in other 1,3,2,4-dithiadiazoles.

Isolation of the 1,3,2,4-dithiadiazole moiety was not achieved although small quantities of the phenyl-1,2,3,5-dithiadiazole were isolated by sublimation.

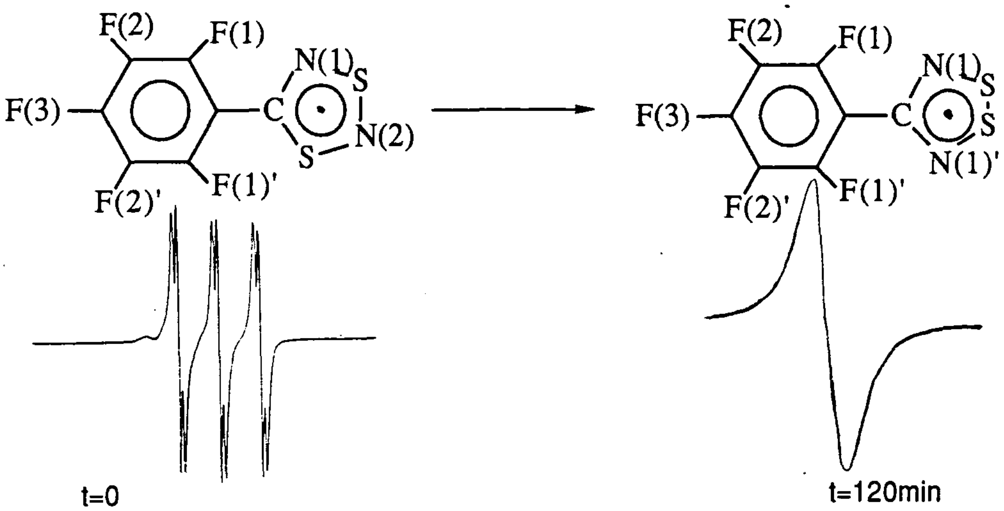
3.2.9 Reduction of [C_6F_5CNSNS][AsF_6]

E.s.r. tube reduction of [C_6F_5CNSNS][AsF_6] with Ph_3Sb in the presence of ^{t}Bu$_4$NCl in toluene produced an initial brown solution of the C_6F_5CNSNS radical; observed as a 1:1:1 triplet of doublets:

Coupling of the electron, based on nitrogen N(2), to ring fluorines would explain this spectrum. But more precisely, we might expect that significant coupling to *ortho* or *meta* fluorine nuclei would produce a triplet of triplets. Consequently we can propose that the largest hyperfine splitting constant is that between N(2) and the fluorine nucleus in the *para* position, F(3)

Again rearrangement of this radical was observed to the 1,2,3,5-dithiadiazole over a period of several hours and the spectra are shown in figure 3.2.9a (over).

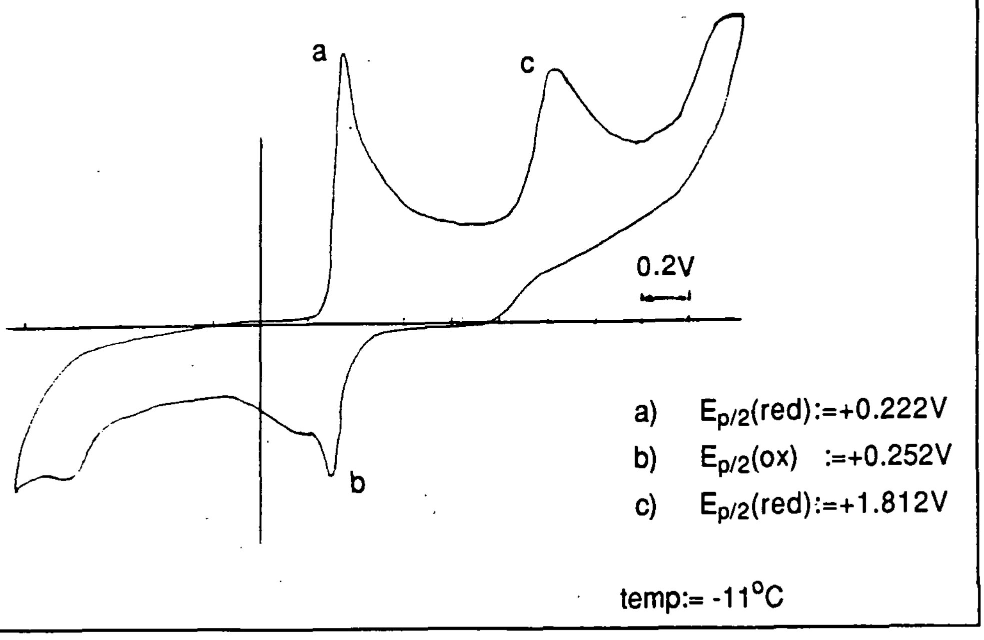
Figure 3.2.9a: Rearrangement of the 5-pentafluorophenyl-1,3,2,4-dithiadiazole radical into the 4-pentafluorophenyl-1,2,3,5-dithiadiazole radical; as observed by e.s.r. spectroscopy



3.2.10 Cyclic Voltammetry study of [PhCNSNS][AsF$_6$]

A cyclic voltammogram of [PhCNSNS][AsF$_6$] in CH$_3$CN, using a [^{t}Bu$_4$N][BF$_4$] supporting electrolyte, showed a reversible reduction peak at $E_{p/2}$(red):= +0.222V, with the equivalent oxidation peak at $E_{p/2}$(ox):= +0.252V (see diagram 3.2.10a). This redox behaviour is similar to those seen in other 1,3,2,4-dithiadiazolium/ole species and has been associated with the formation and subsequent oxidation of the 1,3,2,4-dithiadiazole radical:

Figure 3.2.10a: Cyclic voltammogram of [PhCNSNS][AsF$_6$] in CH$_3$CN.

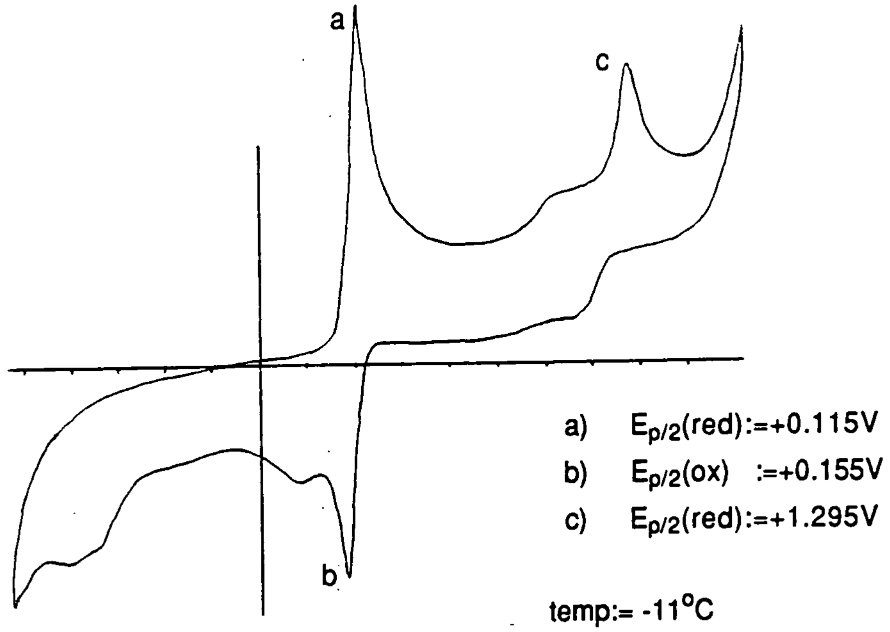


A second reduction peak is observed at $E_{p/2}$(red):= +1.812V, and can be assigned to the formation of $PhCNSNS^-$; this reduction is not reversible, although this could be due to subsequent reaction with $PhCNSNS^+$ to give two neutral $PhCNSNS^•$ radicals. This is likely as cyclic voltammograms of the neutral $PhCNSSN^•$ species show this reduction to be partially reversible[6] whilst the analogous $PhCNSSN^+$ system shows an irreversible reduction for the same process.

3.2.11 Cyclic Voltammetry study of $[C_6F_5CNSNS][AsF_6]$

A similar study of the pentafluorophenyl-1,3,2,4-dithiadiazolium cation showed a similar process occuring; with a reversible first reduction to the neutral $C_6F_5CNSNS^•$ radical followed by irreversible reduction to the $C_6F_5CNSNS^-$ anion (see diagram 3.2.11a).

Figure 3.2.11a: Cyclic voltammogram of $[C_6F_5CNSNS][AsF_6]$ in CH_3CN.



However due to the electron-withdrawing capabilities of the perfluorophenyl substituent these reductions take place at lower potentials i.e. $E_{p/2}$(red):= +0.115V and $E_{p/2}$(red):= +1.295V for the first and second reductions respectively.

This ease of reduction is indicative of stabilisation of the radical species and, although the neutral $C_6F_5CNSNS^•$ radical was not isolated during the course of this work, it is anticipated that its stability should be significantly higher than many other dithiadiazole species.

3.3 Conclusions

Both [SNS][AsF_6] and [SNS][$SbCl_6$] react in high yield with liquid nitriles; C_6H_5CN and C_6F_5CN; to produce the expected aryl dithiadiazolium cations. The reactions of [SNS][$AlCl_4$] unfortunately indicate a large degree of decomposition products which have been attributed to facile halide loss from the $AlCl_4^-$ anion. The utilisation of low temperature reactions, to minimise anion fragmentation, may partially alleviate this problem but the synthesis of further SNS^+ salts with "hard" anions would appear to be a more fruitful course of action.

The high reactivity of [SNS][AsF_6] with both C_6H_5CN and C_6F_5CN suggests that the electronic effects of the aryl group have little effect on the reactivity of this [4+2] cycloaddition and this reaction should work equally well with electron withdrawing substituents as with electron pushing substituents.

However the electron-withdrawing C_6F_5 substituent has a significant effect on the chemistry of the dithiadiazolium cation with the half-wave reduction potential dropping from +0.222 V in $C_6H_5CNSNS^+$ to +0.115V in $C_6F_5CNSNS^+$.

[SNS][$SbCl_6$] also shows a highly reactive chemistry, but one which is hampered by low solubility; the lack of a suitable solvent for this $SbCl_6^-$ salt may prove to be a problem with solid nitrile species; see chapter 4.

3.4 Experimental

3.4.1. Preparation of [PhCNSNS][AsF_6]

[SNS][AsF_6] (0.267g, 1mmol) was placed in one leg of a two limbed reaction vessel and PhCN (0.5ml) was syringed in to give an immediate brown solution. The mixture was stirred for 3 hours at room temperature before being washed with CH_2Cl_2 to yield lime green microcrystalline [PhCNSNS][AsF_6].

Yield: 0.33g, 90% F.W. 370

i.r.:ν(max): 1595(m), 1405(s), 1345(w), 1325(w), 1297(w), 1260(w), 1215(w), 1190(m), 1170(w), 1100(m), 1070(w), 1000(m), 985(s), 913(m), 888(m), 840(w), 797(s), 772(vs), 697(vs,br), 670(s), 645(m), 635(m), 610(w), 583(w), 440(s), 400(vs).

elemental analysis: $C_7H_5N_2S_2AsF_6$

required:					
C: 22.7%	H: 1.4%	N: 7.6%	S: 17.3%	As: 20.3%	F: 30.8%
observed:					
C: 22.5%	H: 1.4%	N: 7.5%	S: -----	As: -----	F: -----

3.4.2. Crystal Growth of [PhCNSNS][AsF_6]

[PhCNSNS][AsF_6] (0.08g) was placed in one leg of a two-limbed reaction vessel and CH_2Cl_2 (5ml) was syringed in. The solution was taken to reflux and maintained for 20 min. before filtering off undissolved [PhCNSNS][AsF_6]. The solution was then returned to reflux before being allowed to cool slowly to room temperature and then to -20°C. During this time small lime-green needle-like plates formed. The solution was decanted off and the crystals were picked in the open atmosphere (significant degradation started to occur only after ca. 1 hour. The larger crystals being substantially more air-stable than the crude product).

3.4.3. Preparation of [PhCNSNS][$SbCl_6$]

[SNS][$SbCl_6$] (0.415g, 1mmol) was placed in one leg of a two-limbed reaction vessel and PhCN (2ml) syringed in.. The solution was heated at 100°C for 4 hours; the solution turning olive-green in colour. The reaction vessel was then allowed to cool to produce a dark green microcrystalline precipitate. The crude product was isolated by washing out the unreacted PhCN with CH_2Cl_2.

The olive green precipitate was then transferred to an extractor and briefly extracted with CH_2Cl_2 to yield lime green [PhCNSNS][$SbCl_6$].

Yield : 0.385g,75% F.W.: 515.75

i.r.:v(max): 1597(m), 1410(s),1168(m), 982(w), 932(w), 905(w), 890(w), 795(m), 765(s), 720(w), 680(s), 647(w), 630(s), 585(w), 553(m).

elemental analysis: $C_7H_5N_2S_2SbCl_6$

required:

C: 16.3% H: 1.0% N: 5.4% S: 12.4% Sb: 23.6% Cl:41.3%

observed:

C: 16.4% H: 1.0% N: 5.7% S: 12.1% Sb: 21.1% Cl: 39.9%

mass spectra (E.I.$^+$): 181 (40.2, $PhCN_2S_2$), 135 (4.1, PhCNS), 121 (9.0, PhCS), 104 (15.5, CN_2S_2), 103 (100, PhCN), 92 (1.6, S_2N_2), 78 (55.1, S_2N), 77 (6.4, Ph), 46 (34.1, SN).

^1H n.m.r. (CD_3CN): δ:= 8.968ppm (intensity 1), 8.607ppm (intensity 2), 8.446 ppm (intensity 2)

3.4.4. Reaction of PhCN with [SNS][AlCl4]

On addition of PhCN (1ml) to [SNS][$AlCl_4$] (0.247g, 1mmol) in a two-limbed reaction vessel, a dark brown oil formed. This material was stirred for 2 hours but no change was observed. The viscous oil was washed with CH_2Cl_2 (2x 3ml) to remove unreacted PhCN and then washed with hot CH_2Cl_2 (4x 10ml). The solubles(<15mg) consisted of small colourless microcrystals and some metallic green platelets; provisionally identified as [PhCNSNS][$AlCl_4$] and [S_6N_4][$AlCl_4$]$_2$ respectively by infra-red.

i.r.:v(max): 1595(m), 1405(s), 1345(w), 1325(w), 1297(w), 1260(w), 1215(w), 1190(m), 1170(w), 1160(m)^a, 1100(m), 1070(w), 1050(s)^a, 1025(m)^a, 1000(m), 985(s)^a,933(m)^a, 913(m), 888(m), 840(w), 797(s), 772(vs), 670(s), 645(m)^a, 635(m), 610(w), 583(w), 475(sbr),440(s), 390(m)^a.

a: peaks attributed to [S_6N_4]$^{2+}$; other peaks are attributable to the $PhCNSNS^+$ cation

3.4.5. Preparation of [C_6F_5.CNSNS][AsF_6]

[SNS][AsF_6] (0.267g, 1mmol) was placed in one leg of a two limbed reaction vessel and C_6F_5CN (0.5ml) was syringed in to give an immediate green solution. The mixture was stirred for 3 hours at room temperature before being washed with CH_2Cl_2 to yield colourless, microcrystalline [PhCNSNS][AsF_6] which was then recrystalised from liquid SO_2.

Yield: 0.433g, 94% F.W.: 460

i.r. ν(max): 1655(s), 1620(w), 1530(s), 1500(s), 1390(m), 1295(w), 1173(m), 1162(ms), 1048(m), 1000(s), 956(ms), 900(m), 815(s), 777(m), 700(sbr), 652(m), 581(w), 447(w), 400(s).

elemental analysis: $C_7F_{11}N_2S_2As$

required:	C: 18.3%	N: 6.1%	S: 13.9%	F: 45.4%	As: 16.3%
observed:	C: 18.0%	N: 6.3%	S: -----	F: -----	As: -----

3.4.6. Preparation of [C_6F_5.CNSNS][$SbCl_6$]

[SNS][$SbCl_6$] (0.415g, 1mmol) was placed in one leg of a two-limbed reaction vessel and C_6F_5CN (2ml) syringed in.. The solution was heated at 100°C for 4 hours; during which time the yellow suspension turned into a brown solution. The reaction vessel was then allowed to cool to produce a brown microcrystalline precipitate. The crude product was isolated by washing out the unreacted C_6F_5CN with CH_2Cl_2.

The brown precipitate was then transferred to an extractor and briefly extracted with CH_2Cl_2 to yield yellow-ochre [PhCNSNS][$SbCl_6$] and small quantities of a brown insoluble with an infra-red spectrum identical to the major product.

Yield: 0.460g, 76% F.W.: 605.75

i.r.: ν(max): 1657(s), 1620(m), 1530(m), 1510(s), 1320(w), 1300(w), 1170(m), 1160(m), 1050(m), 1010(s), 953(s), 900(s), 813(s), 777(m), 742(m), 650(m), 580(m), 440(s).

elemental analysis: $C_7F_5Cl_6SbN_2S_2$

required:

C: 13.9%	N: 4.6%	F: 15.7%	Sb: 20.1%	S: 10.6%	Cl: 35.1%

observed:

C: 13.8%	N: 4.4%	F: -----	Sb: 19.8%	S: -----	Cl: -----

mass spectra (E.I.$^+$): 271 (3.0, $C_6F_5CN_2S_2$), 239 (1.4, $C_6F_5CN_2S$), 225 (7.7, C_6F_5CNS), 193 (24.0, C_6F_5CN), 167 (0.2, C_6F_5), 78 (4.1, S_2N).

^{19}F n.m.r. (CD_3CN): δ:= -132.192 (intensity 2), -140.243 (intensity 1), -159.681 (intensity 2).

3.4.7. Reaction of C_6F_5CN with [SNS][$AlCl_4$]

On addition of C_6F_5CN (1ml) to [SNS][$AlCl_4$] (0.247g, 1mmol) in a two-limbed reaction vessel, a dark brown oil formed. This material was stirred for 2 hours but no change was observed. The viscous oil was washed with CH_2Cl_2 (2x 3ml) to remove unreacted C_6F_5CN and then washed with hot CH_2Cl_2 (4x 10ml). The solubles(<10mg) consisted of small colourless microcrystals and some metallic green platelets; provisionally identified as [C_6F_5CNSNS][$AlCl_4$] and [S_6N_4][$AlCl_4$]$_2$ respectively by analogy to the reaction with PhCN.

3.4.8. Reduction of [PhCNSNS][AsF_6]

[PhCNSNS][AsF_6] (ca. 3mg) was placed in an e.s.r. tube with excess [Bu_4N]Br (ca. 10mg) and Ph_3Sb (ca. 5 mg). Toluene was then syringed in and the mixture agitated using ultrasound to yield a brown solution (3 line e.s.r. signal) which on standing for several hours turned purple due to the conversion of $C_6H_5CNSNS^{\bullet}$ to $C_6H_5CNSSN^{\bullet}$ (broad e.s.r. signal).

3.4.9. Reduction of [C_6F_5.CNSNS][AsF_6]

[C6F5CNSNS][AsF_6] (ca. 4mg) was placed in an e.s.r. tube with excess [Bu_4N]Br (ca. 10mg) and Ph_3Sb (ca. 5 mg). Toluene was then syringed in and the mixture agitated using ultrasound to yield a brown solution (3 line e.s.r. signal) which on standing for several hours turned purple due to the conversion of $C_6F_5CNSNS^{\bullet}$ to $C_6F_5CNSSN^{\bullet}$ (broad e.s.r. signal).

3.4.10. Cyclic Voltammogram of [PhCNSNS][AsF_6]

[PhCNSNS][AsF_6] (6 mg) was placed in a three limbed cell with [Bu_4N][BF_4] (0.5g) and CH_3CN (13ml) syringed in. Cyclic voltammograms were run at -11°C using a Ag/Ag$^+$ reference electrode (calibrated at + 0.32(8)V w.r.t. standard calomel electrode prior to use) and Pt working and auxiliary electrodes.

Scan rate ca. 200 mV/s, sensitivity 10μA/V
Plotter sensitivity: X, 0.2 V/cm Y, 0.1 V/cm.

Half-wave reduction potentials: +0.222V, +1.812V
Half-wave oxidation potentials: +0.252V

3.4.11. Cyclic Voltammogram of [C_6F_5.CNSNS][AsF_6]

[C_6F_5CNSNS][AsF_6] (8 mg) was placed in a three limbed cell with [Bu_4N][BF_4] (0.5g) and CH_3CN (13ml) syringed in. Cyclic voltammograms were run at -11°C using a Ag/Ag^+ reference electrode (calibrated at + 0.32(5)V w.r.t. standard calomel electrode prior to use) and Pt working and auxiliary electrodes.
Scan rate ca. 200 mV/s, sensitivity 20μA/V
Plotter sensitivity: X, 0.2 V/cm Y, 0.1 V/cm.

Half-wave reduction potentials: +0.115V, +1.295V
Half-wave oxidation potentials: +0.155V

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CHAPTER FOUR

THE PREPARATION OF SOME BIS- AND TRIS-DITHIADIAZOLIUM SALTS

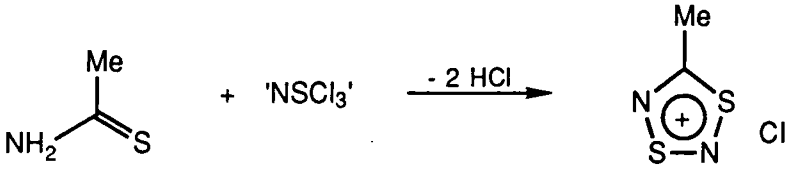
4.1 Introduction

The generation of materials containing one dithiadiazolium ring has been known for many years; reaction[1] of $(NSCl)_3$ with various nitriles, RCN (R:= CCl_3, ^tBu, Ph) gave the 1,2,3,5-dithiadiazolium chlorides (fig. 4.1.1a). However other routes are also available, including the reaction of SCl_2 with N-cyanosulphur difluoride imide ($NCNSF_2$) or $Me_3SiNCNSiMe_3$[2], the reaction of sodium azide with $RCN(NSCl)_2$[3] and thermolysis of $RCN_3S_2Cl_2$[4].

Figure 4.1.1: The two known isomers of the dithiadiazolium ring:
a) 1,2,3,5-dithiadiazolium salts
b) 1,3,2,4-dithiadiazolium salts

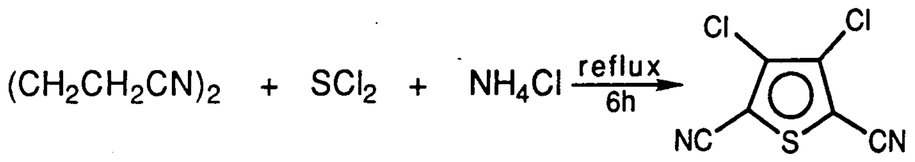
Very few examples of the 1,3,2,4-isomer (fig 4.1.1b) were reported until the advent of the SNS^+ synthon[5-7,15]. However a few examples of this isomer have also been prepared by more esoteric routes[8] and more recently by the reaction[9] of thioacetamides with "$NSCl_3$" in SO_2Cl_2; see equation 4.1.2:

Eqn.4.1.2.



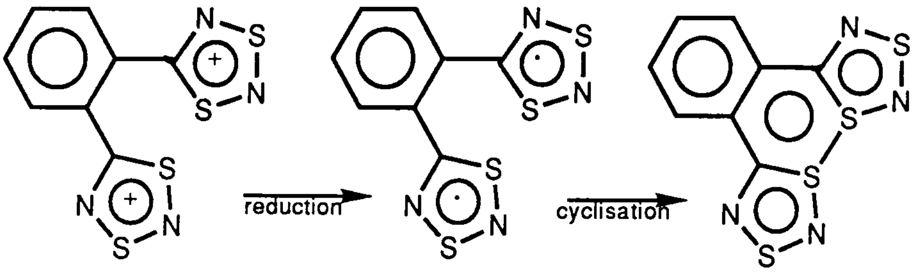
However, the generation of materials containing two dithiadiazolium rings has been elusive; reaction of 1,4-dicyanobenzene with SCl_2 and NH_4Cl (used to prepare NSCl *in situ*) produced only a small quantity of the monosubstituted product[10] whereas a similar reaction with dicyanobutane surprisingly produced a fully substituted thiophene[11](see equation 4.1.3):

Eqn. 4.1.3.



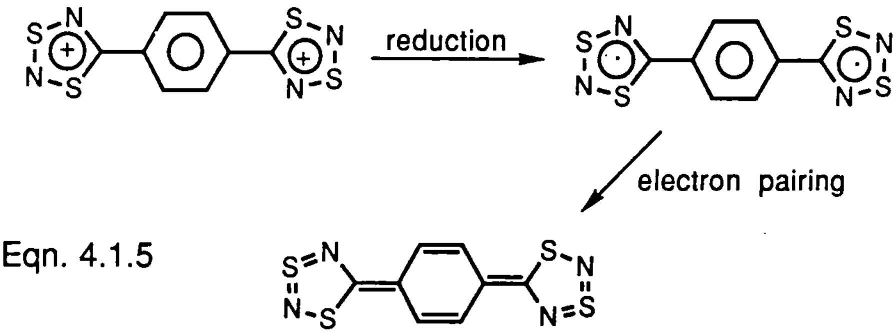
Consequently the synthesis of poly(dithiadiazolium) cations seemed a suitable area in which to examine the reactivity of these SNS$^+$ reagents. Moreover the structure of , for example, bis(dithiadiazoles) may be of interest because of the possibility of intra- as well as inter-molecular dimerisation i.e. intramolecular stabilisation of the radical ring. For example reduction of *ortho*-bis(dithiadiazolium) cations may lead to structures with SS bonding between rings to give a tetracyclic system as shown below (fig 4.1.4):

Eqn. 4.1.4



In the case of the *ortho*- and *para* -analogues intramolecular radical pairing may occur (see equation 4.1.5) whilst in the *meta*-bis(dithiadiazole) a diradical structure may well be expected.

Eqn. 4.1.5



The results of reactions of [SNS][AsF$_6$] and [SNS][SbCl$_6$] with a variety of aryl nitriles are now discussed and compared with other work carried out independently in other laboratories[12,13] at about the same time.

4.2 Results and Discussion

4.2.1 Reaction of 1,4-dicyanobenzene with [SNS][SbCl$_6$]

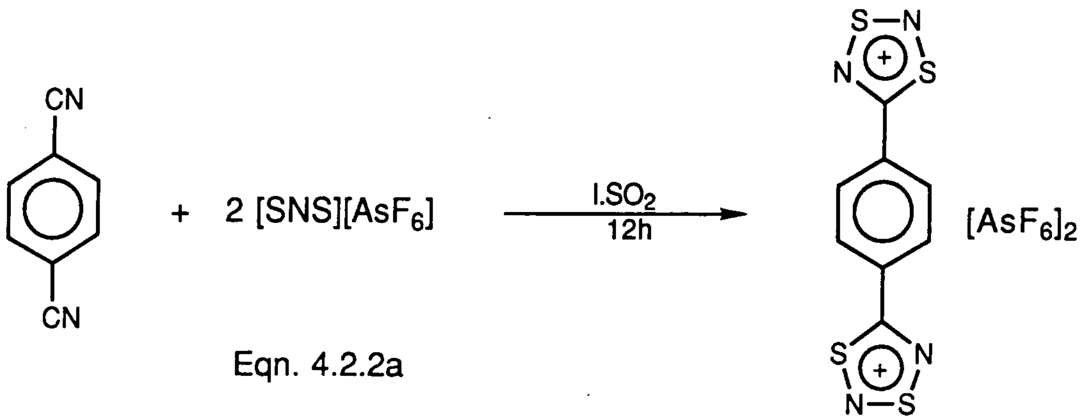
Due to the low solubility of [SNS][SbCl$_6$] in unreactive organic solvents, the reaction between [SNS][SbCl$_6$] and 1,4-dicyanobenzene was slow and unpromising. Indeed after 8-10 hours refluxing in CH_2Cl_2, only starting material and quantities of red-brown intractable products were observed.

It is to be anticipated that similar mixtures of products would be obtained from [SNS][SbCl$_6$] and other solid nitriles. However reaction in neat liquid poly-cyano organics may provide more benficial results (see chapter 3.2.3 and 3.2.6).

Having seen that [SNS][AsF$_6$] is more soluble than its SbCl$_6^-$ counterpart and that its reactions tend to occur in high yield at ambient temperature[15,18-22] (chapter 3.2.1 and 3.2.5), [SNS][AsF$_6$] was examined as a more useful reagent.

4.2.2. Reaction of 1,4-dicyanobenzene with [SNS][AsF$_6$]

A stirred SO_2 solution of [SNS][AsF$_6$] and 1,4-dicyanobenzene in a 2:1 ratio slowly yielded an off-white precipitate of 1,4-[$C_6H_4(CNSNS)_2$][AsF$_6$]$_2$ under a rose-red solution over a period of 18 hours. Filtration and light washing with SO_2 yielded the pure dication in 92% recoverable yield, see equation 4.2.2a:



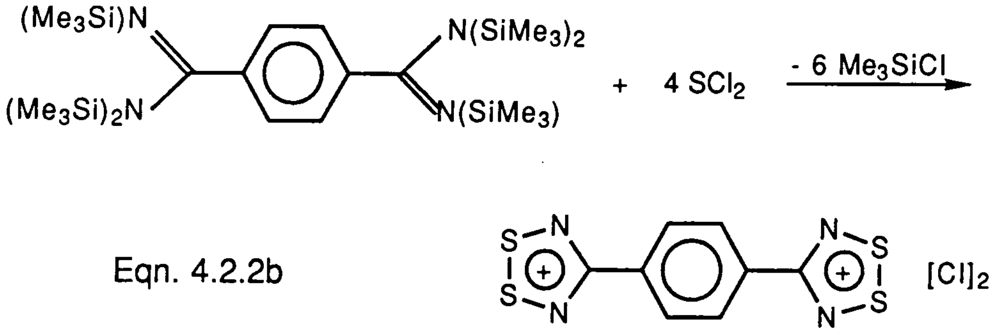
Eqn. 4.2.2a

Reaction of [SNS][AsF$_6$] with 1,4-dicyanobenzene in a 1:1 ratio failed to yield the monosubstituted product but rather the same dicationic species and unreacted 1,4-

dicyanobenzene, indicating that the first dithiadiazolium ring had activated the second cyano group w.r.t. that in neutral dicyanobenzene.

The highly insoluble dication salt proved difficult to crystallise, although lime-green microcrystals were readily obtained by slow exhaustive extraction with SO_2, CH_3CN or CH_2Cl_2 in a sealed extractor over a period of 24-72 hours. Unfortunately none of these crystals were suitable for X-ray analysis. Attempted crystal growth by slow diffusion of $NC.C_6H_4.CN$ onto $[SNS][AsF_6]$ in CH_2Cl_2 also failed to provide crystals of the dication but did produce a few small orange crystallites presumably of the 1:1 product; $[NC.C_6H_4.CNSNS][AsF_6]$.

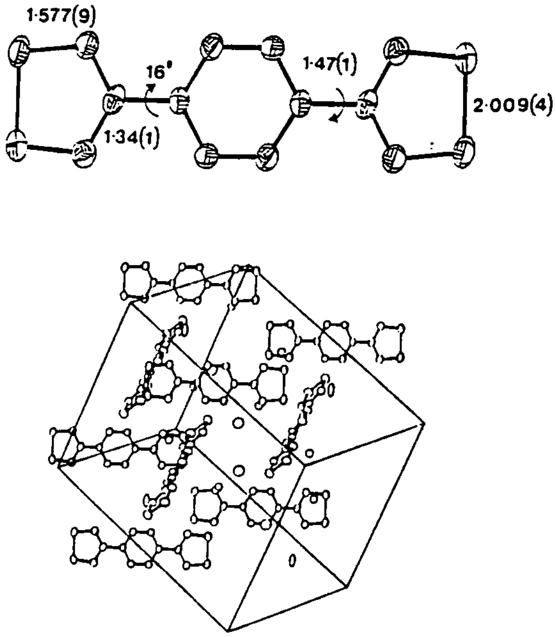
Work at the University of Guelph[13] carried out at the same time, however, produced the isomeric 1,4-benzo(1',2',3',5'-dithiadiazolium) dication, as the SbF_6^- salt, from the reaction of SCl_2 with persilylated amidines, see equation 4.2.2b:



Eqn. 4.2.2b

These bisulphur bridged species were also remarkably difficult to crystallise and the final structure obtained (figure 4.2.2c) show a deviation from planarity in the molecule, possibly as a result of the solvent of crystallisation, PhCN.

Table 4.2.2c X-ray Crystal Structure of *p*-$[C_6H_4(CNSSN)_2][SbF_6]_2.2PhCN$, showing the non-planar cation and molecular packing.



Due to the failure to produce crystals of *para*-$[C_6H_4(CNSNS)_2][AsF_6]_2$, a variety of other salts were prepared in an attempt to improve solubility and obtain more suitable crystals.

4.2.3. Preparation of *para*-$[C_6H_4(CNSNS)_2][Cl]_2$

Reaction of $[^nBu_4N][Cl]$ with *para*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ in CH_2Cl_2 produced an immediate lemon yellow precipitate of *para*-$[C_6H_4(CNSNS)_2][Cl]_2$, isolated in 85% yield.

Eqn. 4.2.3a
$$p\text{-}[C_6H_4(CNSNS)_2][AsF_6]_2 + 2[^tBu_4N]Cl \longrightarrow p\text{-}[C_6H_4(CNSNS)_2]Cl_2 + 2[^tBu_4N][AsF_6]$$

On ageing a slight darkening of colour was observed, although no chemical change was detectable by infra-red.

4.2.4. Preparation of *para*-$[C_6H_4(CNSNS)_2][SbCl_6]_2$

Reaction of *para*-$[C_6H_4(CNSNS)_2][Cl]_2$ with $SbCl_5$ in CH_2Cl_2 provided an off-white precipitate of *para*-$[C_6H_4(CNSNS)_2][SbCl_6]_2$ in 95% recoverable yield; see equation 4.2.4a:

Eqn. 4.2.4a $$p\text{-}[C_6H_4(CNSNS)_2][Cl]_2 + 2SbCl_5 \longrightarrow p\text{-}[C_6H_4(CNSNS)_2][SbCl_6]_2$$

This type of addition reaction should also be possible with other metal halides such as $FeCl_3$, $AlCl_3$ and $SeCl_4$.

4.2.5. Preparation of *para*-$[C_6H_4(CNSNS)_2][Br]_2$

Reaction of *para*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ with two equivalents of $[Et_4N][Br]$ in CH_2Cl_2 yielded (90%) *para*-$[C_6H_4(CNSNS)_2][Br]_2$ as an insoluble crimson precipitate:

Eqn. 4.2.5a $$p\text{-}[C_6H_4(CNSNS)_2][AsF_6]_2 + 2[Et_4N]Br \longrightarrow p\text{-}[C_6H_4(CNSNS)_2]Br_2 + 2[Et_4N][AsF_6]$$

This compound was also prepared by direct bromination of neutral *para*-$[C_6H_4(CNSNS)_2]$ (chapter 4.2.10).

4.2.6. Preparation of *para*-$[C_6H_4(CNSNS)_2][S_3N_3]_2$

Reaction of $[PhCNSSN][AsF_6]$ with $[Pr_4N][S_3N_3]$[14] had yielded large crystals of $[PhCNSSN][S_3N_3]$ which showed novel SS secondary interactions with a planar structure. Consequently the preparation of the dicationic analogue; *para*-$[C_6H_4(CNSNS)_2][S_3N_3]_2$; was attempted by a similar route, the desired compound being isolated in 80% yield as a black-purple micrcrystalline precipitate:

Eqn 4.2.6a $$p\text{-}[C_6H_4(CNSNS)_2][AsF_6]_2 + 2\,[Pr_4N][S_3N_3] \longrightarrow p\text{-}[C_6H_4(CNSNS)_2][S_3N_3]_2 + 2\,[Pr_4N][AsF_6]$$

However attempts at crystal growth by a slow diffusion method were unsuccessful.

4.2.7. Preparation of [*para*-$C_6H_4(CNSNS)_2][Pt(mnt)_2]$

Small needles of $[PhCNSSN]_2[Pt(mnt)_2]$ had been prepared by a simple metathesis reaction between $[PhCNSSN][AsF_6]$ and $[Et_4N]_2[Pt(mnt)_2]$ (see chapter 5.2.1) and in order to attempt to examine these charge-transfer salts further the preparation and crystal growth of the dicationic species was attempted:

$$\text{Eqn. 4.2.7a} \quad p\text{-}[C_6H_4(CNSNS)_2][AsF_6]_2 + [Et_4N]_2[Pt(mnt)_2] \longrightarrow p\text{-}[C_6H_4(CNSNS)_2][Pt(mnt)_2] + 2[Et_4N][AsF_6]$$

Reaction of *para*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ with $[Et_4N]_2[Pt(mnt)_2]$ yielded a microcrystalline, black, highly insoluble product (75% recovered yield) identified by elemental analysis and infra-red data as the desired *para*-$[C_6H_4(CNSNS)_2][Pt(mnt)_2]$ salt. However, attempted crystal growth by a variety of methods (ripple-tank methods, slow diffusion and attempted recrystallisation) failed to produce size-able crystals for X-ray structure determination.

4.2.8. Cyclic voltammetry study of *para*-$[C_6H_4(CNSNS)_2][AsF_6]_2$

The electrochemistry of 1,2,3,5- and 1,3,2,4-dithiadiazolium salts has previously been studied[15,16] and the 1,3,2,4-dithiadiazolium cation has a typical reduction peak in the region $0.11 < E_{p/2}(\text{red}) < 0.27$ V (see also chapter 3.2.10 and 3.2.11). It was of little surprise therefore to find the half-wave reduction potential at 0.224V.(figure 4.2.8a).

Closer examination (inset) showed ,not one reduction peak, but two; indicative of a radical cation intermediate and where both reduction and oxidation processes appear to be reversible:

Figure 4.2.8a:Cyclic Voltammogram of p-[C6H4(CNSNS)$_2$][AsF$_6$]$_2$ in CH$_3$CN using [^{t}Bu$_4$N][AsF$_6$] as supporting electrolyte.

Perhaps more importantly this shows communication between the two dithiadiazolium rings; if there were no communication between the rings then we would expect to observe only one reduction peak for two non-interacting equivalent heterocycles.

Having seen that electrochemical reduction to the neutral molecule was possible, the process was scaled up and reduction was attempted chemically:

4.2.9. Chemical reduction of *para*-[C_6H_4(CNSNS)$_2$][Cl]$_2$

A mixture of *para*-[C_6H_4(CNSNS)$_2$][Cl]$_2$ and Ph_3Sb were stirred in CH_2Cl_2 for 12 hours to produce a blue-black microcrystalline precipitate of *para*-[C_6H_4(CNSNS)$_2$] under a light blue solution.

Eqn. 4.2.9a $$\begin{array}{ccc} p\text{-}[C_6H_4(CNSNS)_2][Cl]_2 & \longrightarrow & p\text{-}[C_6H_4(CNSNS)_2] \\ +\ Ph_3Sb & & +\ Ph_3SbCl_2 \end{array}$$

Interestingly, in comparison; work at the University of New Brunswick[12] has shown that the bis(dithiadiazolium) species, [SNSNC.CNSNS]$^{2+}$ can also be prepared but its reduction tends to lead to mostly polymeric materials, and the neutral [SNSNC.CNSNS] moiety would appear elusive.

The neutral species was isolated in 90% yield and because of the microcrystalline state of the product, as well as its low solubility, crystal growth of the neutral bis(dithiadiazole) was attempted:

4.2.10. Crystal Growth and Structure of [*para*-$C_6H_4(CNSNS)_2$].

Crystals of a suitable size for X-ray analysis were grown by allowing a saturated solution of Ph_3Sb, in CH_2Cl_2, to slowly diffuse through a No.3 glass sinter into a saturated solution of [*para*-$C_6H_4(CNSNS)_2$][Cl]$_2$ over excess [*para*-$C_6H_4(CNSNS)_2$][Cl]$_2$. In this way the number of nucleation sites were reduced and consequently there would be fewer crystallites but of a larger size. These conditions were achieved by the use of an inverted "dog" (see Appendix 1). Over a period of 2-3 days black crystals of [*para*-$C_6H_4(CNSNS)_2$] appeared in the compartment containing [*para*-$C_6H_4(CNSNS)_2$][Cl]$_2$.

These platelets were found to be remarkably air-stable (decomposing on the surface only after several days in the open atmosphere) and a crystal suitable for X-ray diffraction studies was picked and mounted in a 0.3mm glass Lindemann capillary in the open air. The crystal (0.24 x 0.28 x <0.01mm) was shown by an X-ray oscillation photograph to be a single crystal and was submitted for full X-ray structure determination; the results of this analysis are shown in Tables 4.2.10 a-d and Figures 4.2.10 e-g.

The crystal structure shows a single molecule per unit cell, with molecular stacking in the solid state.

Table 4.2.10a
Crystal Data and Atomic Coordinates (x 10^4)

Formula $C_8H_4N_4S_4$ Formula Weight = 284.39

Crystal System: Triclinic Space Group: $P\bar{1}$

Unit Cell Parameters: a= 5.772(1) b= 6.382(1) c= 7.491(1) Å

α= 79.21(1) β= 82.86(1) γ= 70.25(1) °

Unit Cell Volume: 254.57 $Å^3$ Number of Formulae per unit cell(Z)= 1

R= 0.077 for 678 observed reflections with $F > 4\sigma_c(F)$ and $30 < 2\theta < 60°$.

Atom	x	y	z
S(1)	3132(2)	13136(2)	1203(1)
N(1)	6176(6)	12373(6)	829(5)
S(2)	7458(2)	9743(2)	1702(1)
C(1)	4746(7)	9285(7)	2845(5)
N(2)	2754(6)	10933(6)	2591(5)
C(2)	4875(7)	7087(6)	3962(5)
C(3)	2768(6)	6741(6)	4926(5)
C(4)	7132(6)	5259(8)	4055(5)

Table 4.2.10b
Bond Lengths(Å) and Angles (°)

S(1)-N(1)	1.659(4)	S(1)-N(2)	1.646(4)
N(1)-S(2)	1.632(4)	S(2)-C(1)	1.775(4)
C(1)-N(2)	1.276(4)	C(1)-C(2)	1.476(5)
C(2)-C(3)	1.397(5)	C(2)-C(4)	1.424(5)
C(3)-C(4a)	1.346(6)	C(4)-C(3a)	1.346(6)
N(1)-S(1)-N(2)	102.2(2)	S(1)-N(1)-S(2)	110.8(2)
N(1)-S(2)-C(1)	97.0(2)	S(2)-C(1)-N(2)	115.7(3)
S(2)-C(1)-C(2)	120.2(3)	N(2)-C(1)-C(2)	124.1(4)
S(1)-N(2)-C(1)	113.7(3)	C(1)-C(2)-C(3)	120.6(3)
C(1)-C(2)-C(4)	120.9(3)	C(3)-C(2)-C(4)	118.5(3)
C(2)-C(3)-C(4a)	121.0(3)	H(3)-C(3)-C(4a)	119.5(2)
C(2)-C(4)-C(3a)	120.5(3)	H(4)-C(4)-C(3a)	119.8(2)

Table 4.2.10c
Anisotropic Thermal Parameters ($Å^2x10^3$)

The anisotropic temperature factor exponent takes the form:
$-2\pi^2(\underline{h}^2\underline{a}^*\underline{U}_{11}+......+\ 2\underline{hka}^*\underline{b}^*\underline{U}_{12})$

Atom	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{23}$	$\underline{U}_{13}$	$\underline{U}_{12}$
S(1)	67(1)	50(1)	59(1)	5(1)	5(1)	-15(1)
N(1)	67(2)	51(2)	59(2)	4(2)	-2(2)	-27(2)
S(2)	54(1)	61(1)	65(1)	5(1)	0(1)	-23(1)
C(1)	59(2)	55(2)	39(2)	-2(2)	3(2)	-26(2)
N(2)	54(2)	52(2)	57(2)	-4(2)	9(1)	-10(2)
C(2)	56(2)	39(2)	40(2)	6(1)	-3(1)	-19(2)
C(3)	53(3)	42(3)	69(3)	0(2)	-6(2)	- 8(2)
C(4)	42(2)	56(2)	43(2)	5(2)	5(1)	-14(2)

Table 4.2.10d
H atoms: atomic coordinates ($x10^4$) and isotropic thermal parameters ($Å^2$ x 10^3)

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{U}$
H(3)	1227	7949	4860	65
H(4)	8594	5455	3385	59

Figure 4.2.10e: p-$C_6H_4(CNSNS)_2$, the unit cell.

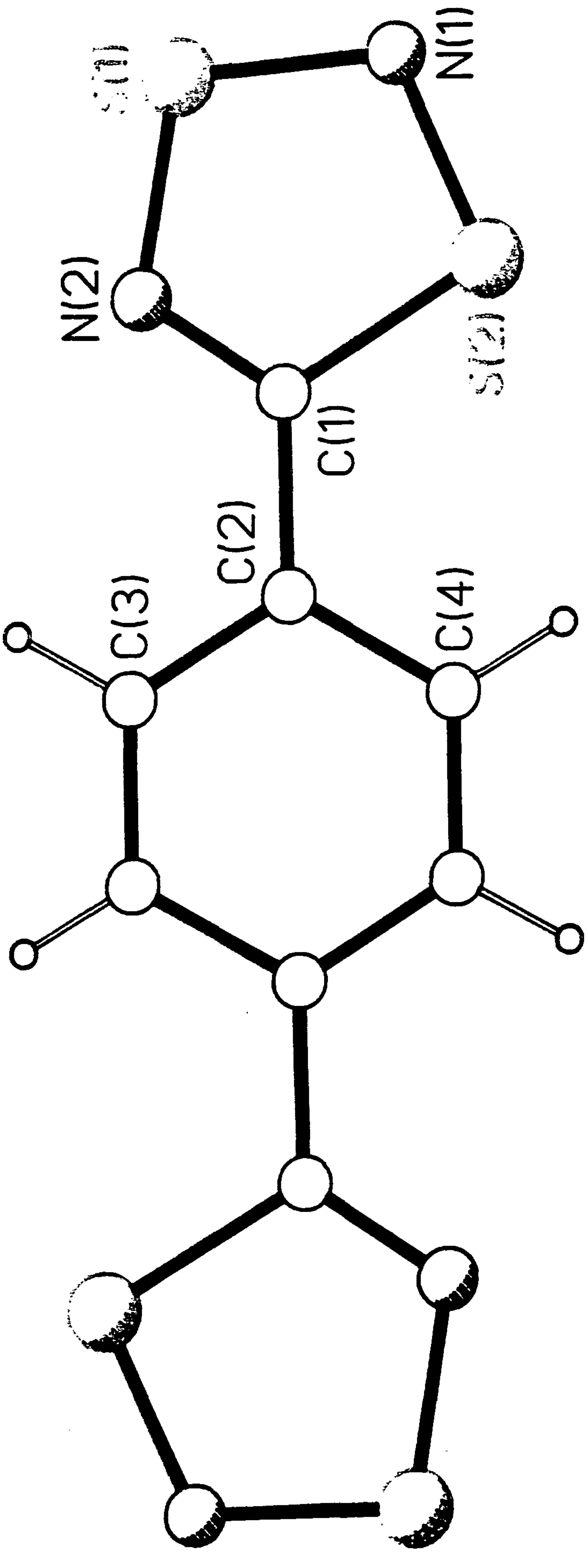


Figure 4.2.10f: Solid State Packing, highlighting the segregated but slipped stacking of *p*-$C_6H_4(CNSNS)_2$.

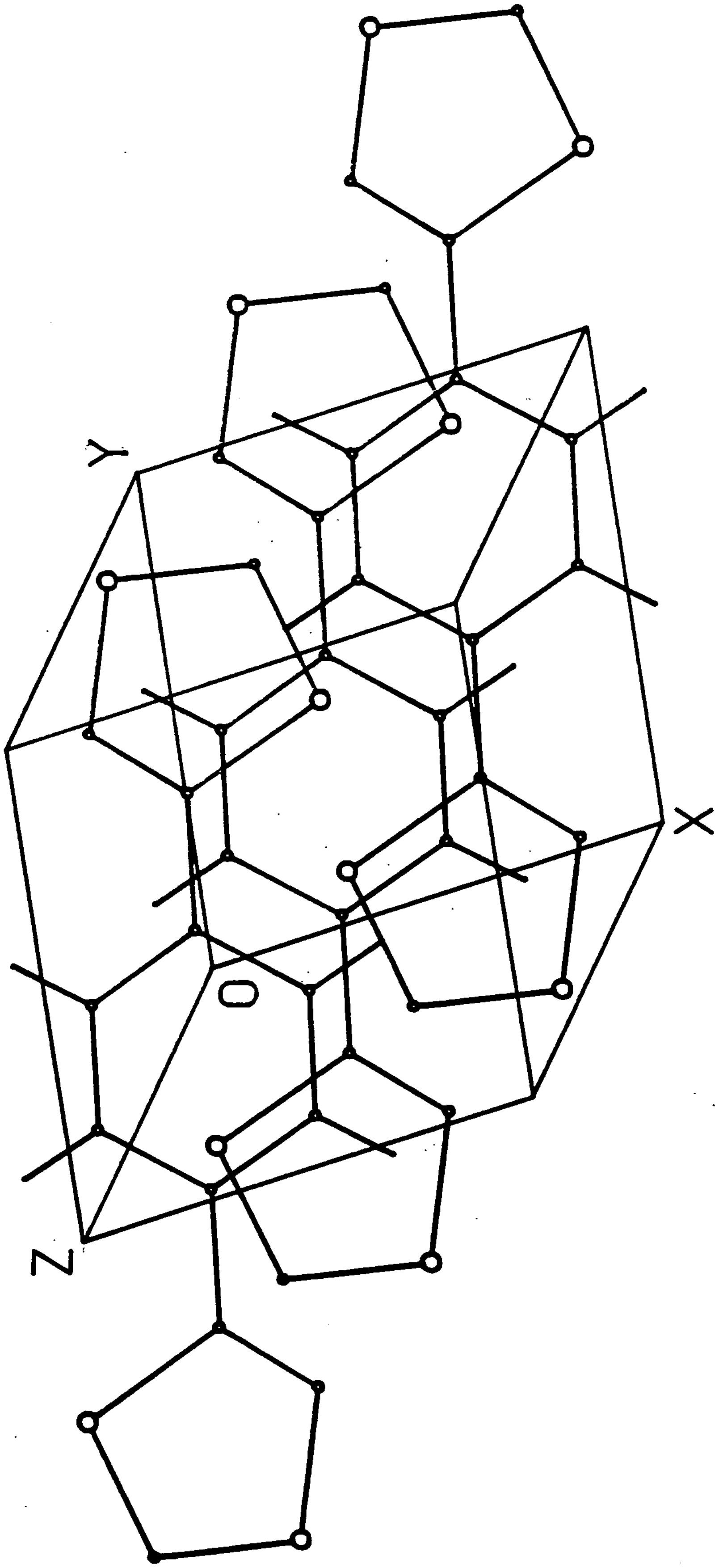
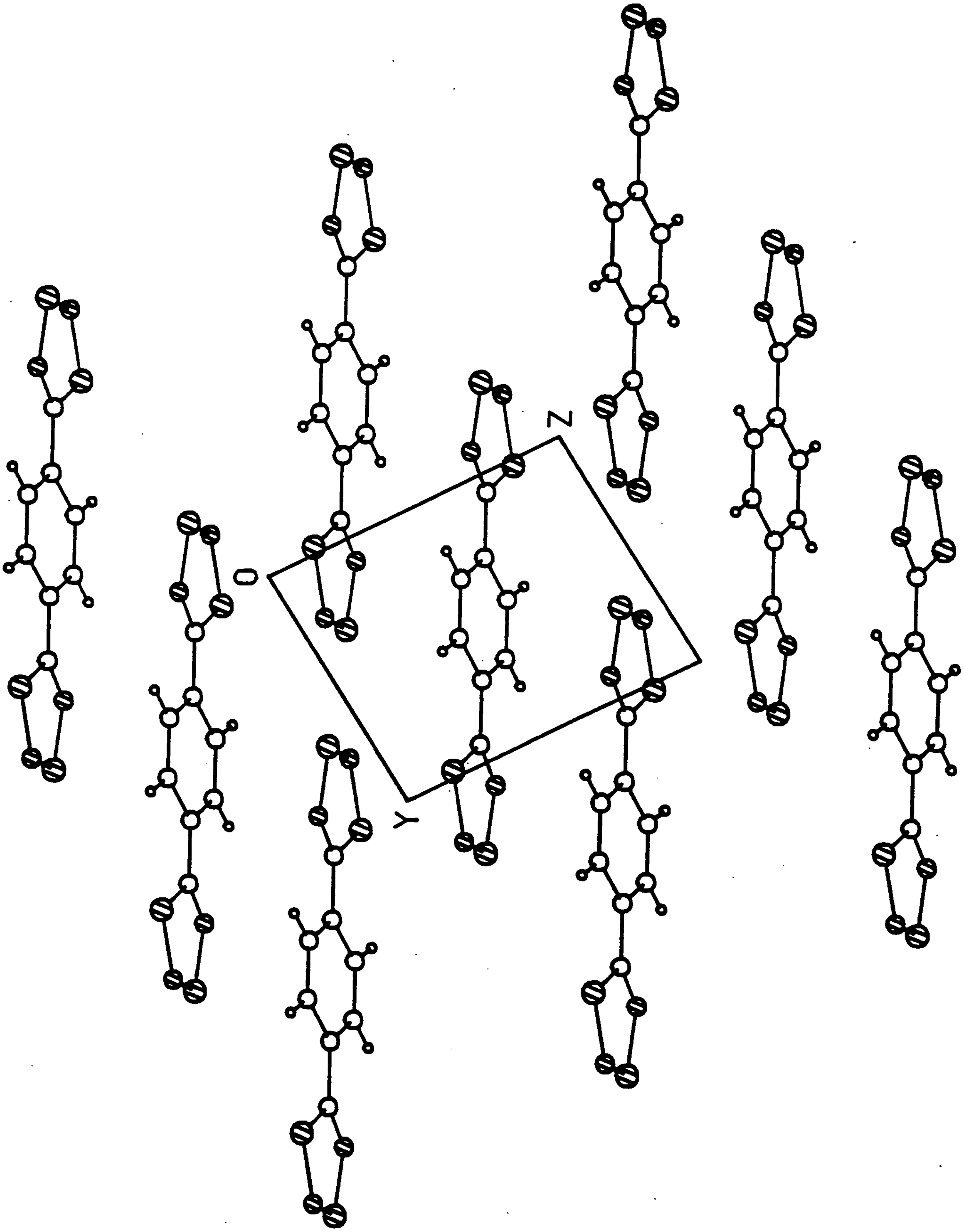


Figure 4.2.10g: Solid State Molecular Packing of *p*-$C_6H_4(CNSNS)_2$, showing a polymeric array of molecules held together through intermolecular interactions.



The X-ray crystal structure reveals a remarkable herring-bone packing of parallel molecules which do not lie over one another but which are slipped along the long axis so that each molecule overlaps several others (Fig.4.2.10g). The secondary interactions, between the outmost SN bonds of adjacent molecules ($d_{N..S}$ = 3.11Å $d_{S..S}$ = 3.21Å) though weak appear to be responsible for holding the molecules in their polymeric array. This can be deduced using data produced by Nyburg and Faerman[31]. Although their paper deals exclusively with atoms terminally bonded to carbon by multiple bonds, we can use its ideas (principally that the van der Waals radius of an atom is not spherically constant, but is probably rather smaller along the line of bonds to that atom). If we take the values proposed in this paper, significant contact distances will be less than 3.20Å for N...N and the limits for N...S and S...S will be between 3.20 and 3.63Å (N...S), and between 3.20 and 4.06Å (S...S), depending on the orientation of the contact vector relative to the bonds.

In the light of this , the shortest N...N, N...S and S...S distances in *p*-[$C_6H_4(CNSNS)_2$] fall into two classes. First there are those interactions which are approximately coplanar with the molecules. The shortest of these distances are N...N 3.227, N...S 3.111 and S...S 3.702Å and judging by the above criteria, it would appear that these are probably very weak interactions.

Secondly, by contrast, there are short contacts between parallel CN_2S_2 rings, particularly S...S at 3.214 and S...N at 3.346Å. In Figure 4.2.10g, there are , for example, interactions between the two rings on either side of the letter Y. These appear to be definitely significant, and they link molecules together into one-dimensional polymeric chains, the "right hand end" of each molecule overlapping with the "left hand end" of the next one (in Figure 4.2.10g, consider the interactions through the letters Y and Z, linking three molecules together in this way to form part of such a chain). Thus the packing and secondary interactions are such as to produce an evenly spaced , though slipped, molecular stack with one molecule per unit cell.

Nevertheless if we consider a single unit, i.e. p-[C6H4(CNSNS)2], we can see that it is possible to have delocalisation of the radical electrons onto the phenylene ring and consequent electron pairing to give a neutral system. Indeed this would appear to play an important part in the structure of this bis(dithiadiazole) and the neutral canonical structures are shown in Diagram 4.2.10h:

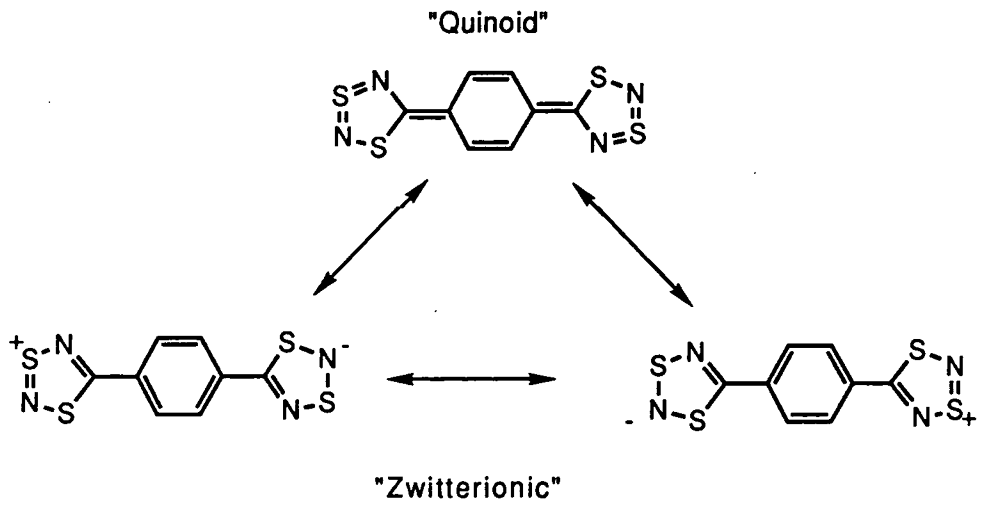


Diagram 4.2.10h: Possible electron distributions in paraphenylene bis (1,3,2,4-dithiadiazole) according to resonance canonical forms.

A comparision of the bond lengths from the crystal data and other known bond lengths shows an essentially quinoid composition as shown in Table 4.2.10i, in accordance with the electron-paired formulism:

Table 4.2.10i

CC, CN and CS Bond Lengths in typical organic and inorganic systems compared to those found in p-[$C_6H_4(CNSNS)_2$].

C-C (alkane)	C=C (ethene)	C=C (aromatic)	C(3)-C(4) (p-[$C_6H_4(CNSNS)_2$])
1.54	1.34	1.39	1.346(6)
C-N	C=N	C=N (aromatic)	C(1)-N(2) (p-[$C_6H_4(CNSNS)_2$])
1.47	1.27	1.35	1.276(4)
C-S	C=S	C=S(thiophene)	C(1)-S(2) (p-[$C_6H_4(CNSNS)_2$])
1.82	1.70	1.72	1.775(4)

It would therefore appear that the free electrons have been delocalised off the ring to give a large degree of quinoid character in the benzene ring and little radical characteristics in the heterocyclic portions. However initial Hückel calculations show that although the Frontier Orbitals have significant quinoid bonding characteristics, (9), there are also two essentially degenerate orbitals (10) and (11) in Figure 4.2.10k.

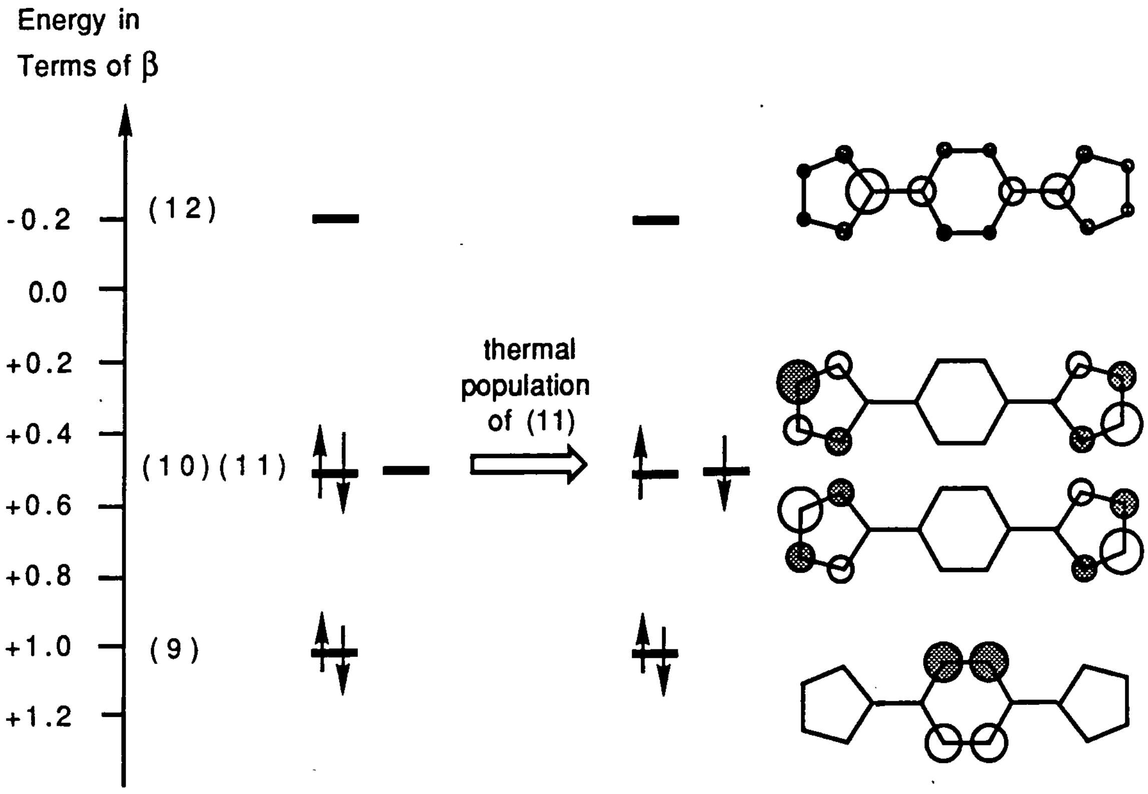
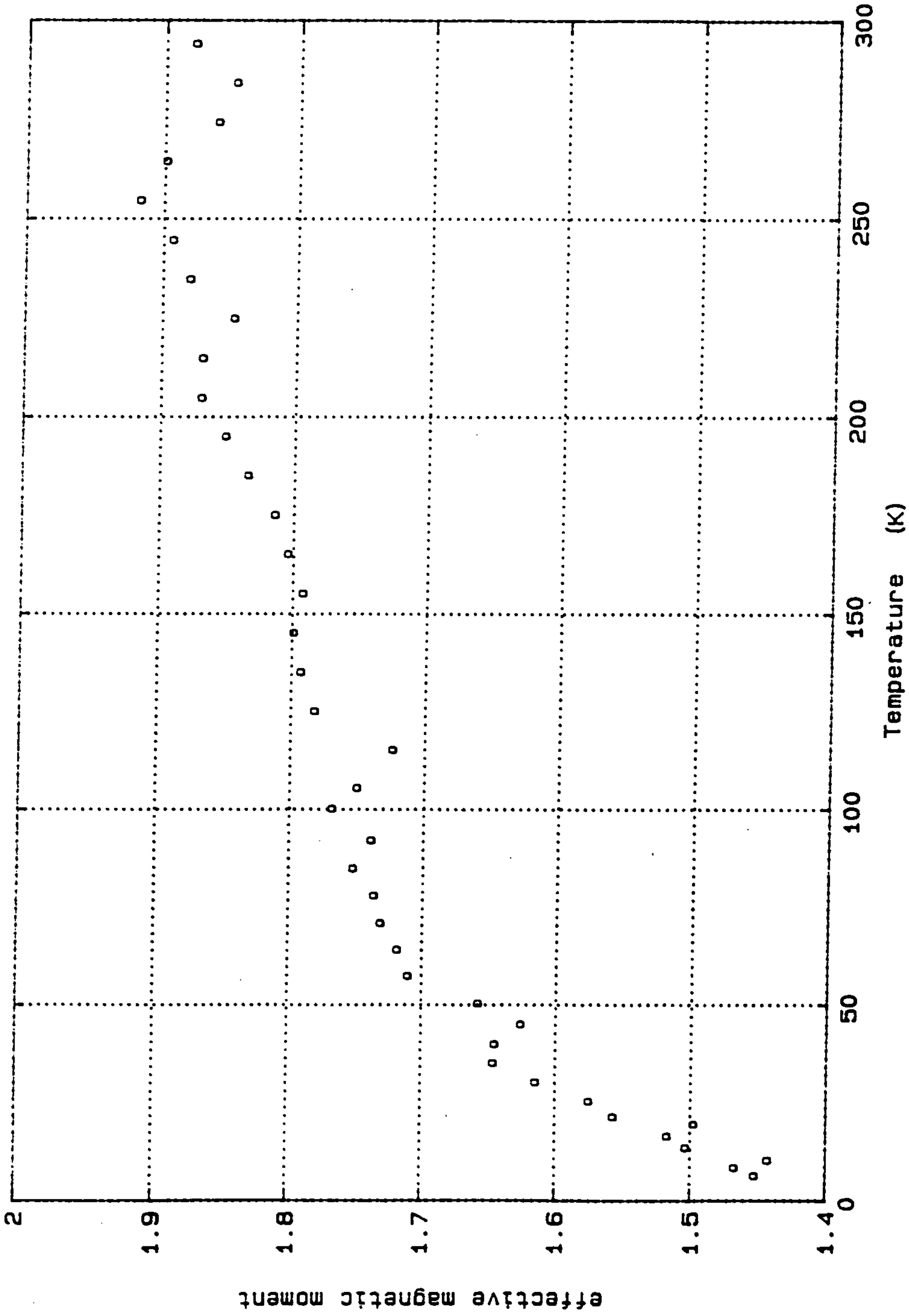


Diagram 4.2.10k: Hückel Molecular Orbitals of *p*-[$C_6H_4(CNSNS)_2$], showing the essentially degenerate nature of the Frontier Orbitals i.e. (10) and (11).

These two orbitals thus allow a thermal population of a diradical state which could be either of singlet or triplet character. Solid state magnetisation measurements show the neutral molecule to be paramagnetic at room temperature but on coling a significant decrease in radical character is observed (Figure 4.2.10l), in agreement with such a thermal population of a low-lying orbital. This material also produces an e.s.r. spectrum in both the solid state and in solution:

Figure 4.2.10I: Variable temperature magnetisation plot for $C_6H_4(CNSNS)_2$ between T=4 and T=300K, using the Faraday Balance method.



4.2.11 Electron Spin Resonance Spectra of p-$[C_6H_4(CNSNS)_2]$

Both 1,2 and 1,3- dithiadiazoles have been studied [18-23] extensively by e.s.r. both in solution and the solid state. In the solution, 1,3-dithiadiazoles are well known to produce a simple 3 line spectrum due to localisation on $N^{14}(I=1)$, with hyperfine coupling to other non-zero spin nuclei observable at low temperature. 1,2-dithiadiazoles, however, produce a 5 line spectrum. The p-$[C_6H_4(CNSNS)_2]$ species shows a strong solution esr spectra (figure 4.11a) typical of a 1,3-dithiadiazole .

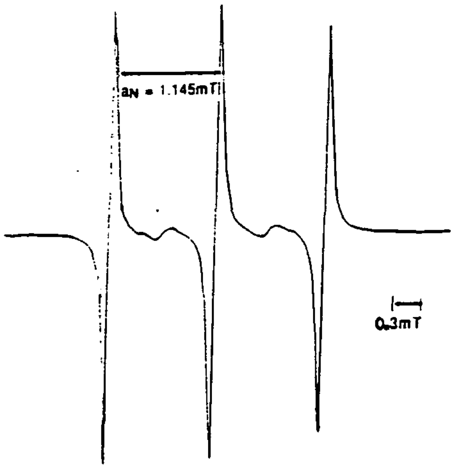


Figure 4.2.11a: Electron Spin Resonance Spectra of p-$[C_6H_4(CNSNS)_2]$

In the solid state an esr spectrum was also observed. Consequently the electron paired formulism of the bis(dithiadiazole) is something of a compromise; the true structure lying somewhere between electron-paired and diradical in nature.

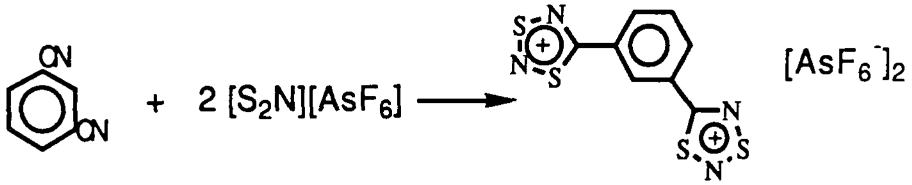
4.2.12 Partial Reduction of p-$[C_6H_4(CNSNS)_2][AsF_6]_2$

Reduction of p-$[C_6H_4(CNSNS)_2][AsF_6]_2$ with $[Bu_4N]Cl/Ph_3Sb$ or Ag in an attempt to prepare the intermediate radical cation was unsuccessful as was the reaction of p-$[C_6H_4(CNSNS)_2]$ with p-$[C_6H_4(CNSNS)_2][AsF_6]_2$. This implies a certain instability to disproportionation, perhaps produced because of the special stability of the neutral molecule caused by its electron paired characteristics.

4.2.13. Reaction of $[SNS][AsF_6]$ with 1,3-dicyanobenzene

Having seen the ease of reaction (12h, ambient temp) of 1,4-dicyanobenzene with 2 equivalents of $[SNS][AsF_6]$ and knowing the isomeric bis(1,2,3,5-dithiadiazolium) dication could also be formed[13] the preparation of *m*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ seemed a suitable synthetic target. Indeed *m*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ was isolated in a similar manner to the para analogue in 85% yield see eqn 4.2.13a:

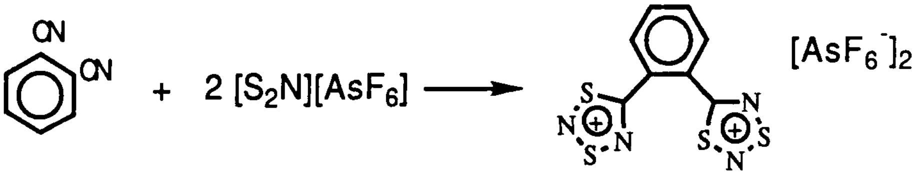
Eqn. 4.2.13a



4.2.14. Reaction of $[SNS][AsF_6]$ with 1,2-dicyanobenzene

The *ortho* analogue of *p*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ was also obtained in high yield (75%) over a period of 12 hours from the reaction of two equivalents of $[SNS][AsF_6]$ with *ortho*-dicyanobenzene:

Eqn. 4.2.14a

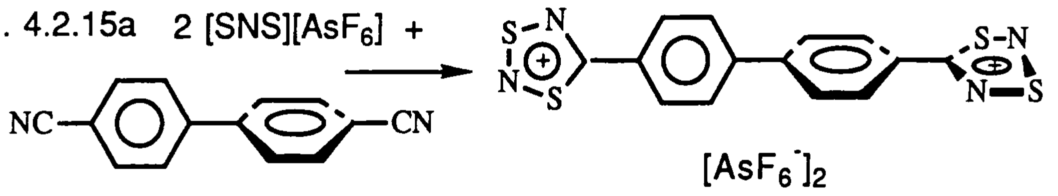


The para-dication is expected to have a negligible permanent dipole moment whereas both *meta* and particularly *ortho*-materials should have larger dipole moments. This increasingly polar nature of *meta* and *ortho* analogues will induce a stronger attraction of polar solvent molecules including water. Consequently both the *ortho* and *meta* dications have an appreciably higher solubility in polar organic and inorganic solvents (e.g. CH_3CN, CH_2Cl_2 and SO_2) but are also much more air-sensitive; *p*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ was only slightly hydrolysed even after several days in the open atmosphere whereas the *ortho* and *meta* dications (also as the AsF_6 salt) were largely decomposed over a period of minutes.

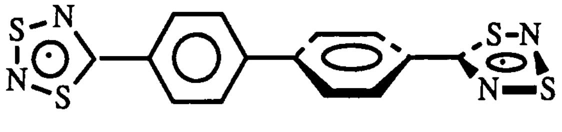
4.2.15 Reaction of $[SNS][AsF_6]$ with 4,4'-dicyanobiphenyl.

The reaction of 4,4'-dicyanobiphenyl[27], $NC.C_6H_4.C_6H_4.CN$, again yielded the required dication in high yield as an orange microcrystalline material:

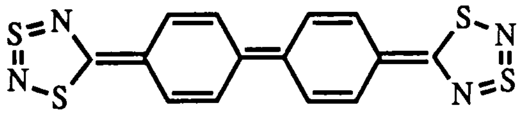
Eqn. 4.2.15a



Reduction of this material will prove interesting as the two phenyl groups in the starting material are mutually perpendicular and reduction should lead to either a totally diradical material or a purely diamagnetic species, depending on the relative orientation of the phenylene rings; see diagram 4.2.15b and 4.2.15c:



4.2.15b



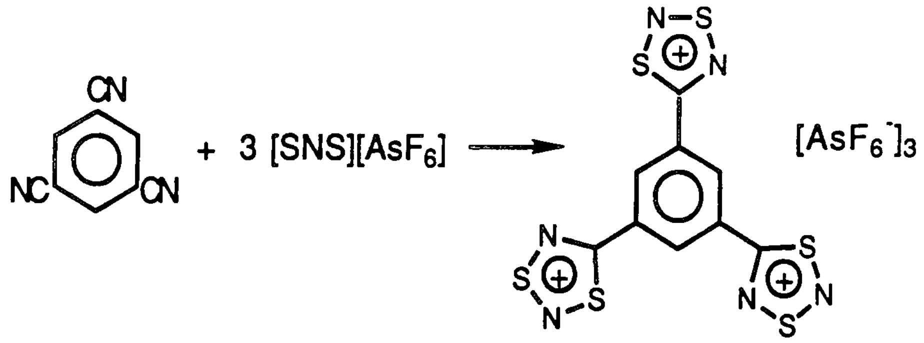
4.2.15c

Electron pairing in the reduced species may produce a planar diamagnetic tetracyclic system whereas a diradical system should allow retention of the mutually perpendicular rings. In the case of p-[$C_6H_4(CNSNS)_2$], we observe electron pairing in the solid state producing a strong quinoid/zwitterionic contribution to the material. However, as the radical dithiadiazole rings become more and more distant the electron pairing energy will become smaller w.r.t. the conformational energy and we will observe a change from electron-paired to diradical structure. It remains to be seen at what separation distance this process takes place but the electrical and/or magnetic properties in such a molecule should prove interesting.

4.2.16 Reaction of [SNS][AsF_6] with 1,3,5-tricyanobenzene

Having seen that [SNS][AsF_6] readily reacts with a variety of dicyano-substituted derivatives to produce 1,3,2,4-dithiadiazolium salts in high yield, the synthesis of materials containing three dithiadiazolium rings appeared highly likely by a similar method. Indeed this was the case, with 1,3,5-$C_6H_3(CN)_3$ reacting with three equivalents of [SNS][AsF_6] over a period of ca. 2 days in liquid SO_2 to produce the trication ; 1,3,5-[$C_6H_3(CNSNS)_3$][AsF_6]$_3$, in high yield; 70% recovery:

Eqn. 4.2.16a



There has been much interest recently[28] in the formation of triradical systems with three-fold centres of symmetry as a basis for organic ferromagnetism. For instance, the preparation of the tri-(nitronyl nitroxide) molecule (4.2.16b) below was recently published[29] and shows novel magnetic behaviour at a variety of temperatures which cannot be readily attributed to ferromagnetic impurities.

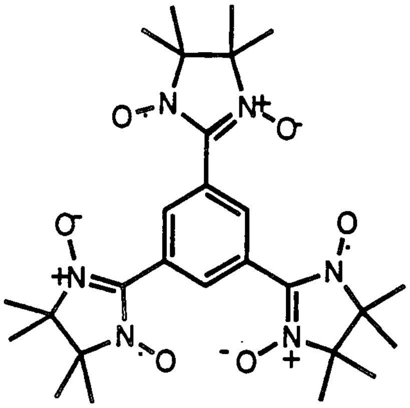


Figure 4.2.16b:
This nitronyl nitroxide triradical exhibits unusual magnetic characteristics.

Consequently the preparation of the reduced, tris(dithiadiazole) species will prove of great interest and an examination of the solid state properties of this neutral species should also be carried out.

4.3.Conclusion

The use of [SNS][AsF_6] as a synthon for di- and tri-functional dithiadiazolium salts as well as their reduced dithiadiazole analogues has been effectively demonstrated. The high yields and ease of reaction at room temperature would suggest that the formation of tetra- , oligo- and poly-dithiadiazolium salts should also be possible. The possibility of a polymeric chain with pendant dithiadiazole radicals would be an attractive target as an inorganic conducting polymer

Meanwhile the ready availability of bis- and tris-dithiadiazolium salts should allow a new insight into the well established chemistry of the monocationic dithiadiazole/ium salts; illustrated here by simple anion metathesis reactions of the p-$[C_6H_4(CNSNS)_2]^{2+}$ dication; showing the versatility and ease of purification now becoming apparent in this area of chemistry.

The novel solid state properties of these bis- and tris-dithiadiazoles should also prove fruitful, with polymeric molecular stacks being formed in preference to dimeric materials. The isolation and full characterisation of the first solid state bis(1,3,2,4- dithiadiazole) illustrates the enhanced stability of these diradicals through intramolecular rather than intermolecular electron pairing. It will be of interest to see whether other poly-dithiadiazoles also have a comparable air stability.

4.4 Experimental

4.4.1: Reaction of 1,4-dicyanobenzene with [SNS][SbCl$_6$]

para-$C_6H_4(CN)_2$ (0.128g,1mmol) was refluxed with a slight excess of [S_2N][$SbCl_6$] (0.826g, 2 mmol) in CH_2Cl_2 in a two-limbed reaction vessel for 18h to yield a yellow precipitate under a red-brown solution. On cooling and washing with CH_2Cl_2 only unreacted $C_6H_4(CN)_2$ and [SNS][$SbCl_6$] were observed plus a small quantity of an intractable red material.

4.4.2: Reaction of 1,4-dicyanobenzene with [SNS][AsF$_6$]

para-$C_6H_4(CN)_2$ (0.128g,1mmol) was stirred with a slight excess of [S_2N][AsF_6] (0.534g, 2 mmol) in l. SO_2 in a two-limbed reaction vessel for 18h to yield an off-white precipitate under a rose solution. The volume was reduced and the crude product washed with minimal amounts of SO_2 and CH_2Cl_2 to remove coloured impurities. The product showed no ν(CN) i.r. absorption at ca. 2200cm^{-1}.

Yield: 0.609g,92%

i.r.: ν(max): 1517(s), 1435(s), 1380(s), 1350(w), 1320(w), 1297(m), 1258(w), 1227(w), 1208(w), 1170(w), 1135(mw), 1115(w), 1030(w), 1020(w), 988(s), 910(m), 888(w), 842(ms), 820(w), 803(s), 770(w), 700(s,br), 670(m), 635(s), 593(m), 572(m), 443(ms), 400(s).

elemental analysis:$C_8H_4N_4S_4As_2F_{12}$ F.W.:662

required:					
C: 14.5%	H: 0.6%	N: 8.5%	S: 19.4%	As: 22.6%	F:34.4%
observed:					
C: 14.6%	H: 0.6%	N: 8.2%	S: 19.7%	As: -----	F: 34.6%

^1H n.m.r.(*p*-dication, CD_3CN): 8.60 (s).

m/e (EI+): 206 (3.98, NC.C_6H_4.CNSNS), 128 (3.56, NC.C_6H_4.CN), 104 (1.54, CNSNS), 102 (1.14, C_6H_4.CN), 76 (8.32, C_6H_4).

4.4.3: Preparation of *p*-[C$_6$H$_4$(CNSNS)$_2$]Cl$_2$

para-[$C_6H_4(CNSNS)_2$][AsF_6]$_2$ (0.662g, 1mmol) and a slight molar excess of [$^nBu_4N$]Cl (0.555g, 2mmol) were stirred in CH_3CN to produce an instant lemon precipitate of *p*-[$C_6H_4(CNSNS)_2$]Cl_2. The product was filtered and then extracted with CH_2Cl_2 in a sealed extractor^{30}.

Yield: 0.302g, 85%

i.r.: ν(max): 1510(w), 1430(m) 1293(m), 1220(w), 1110(m,br),
1020(w), 970(s), 910(m), 860(s), 840(s), 805(m), 777(s),
720(w), 660(m), 630(m), 575(s), 420(s), 405(m).

elemental analysis:$C_8H_4N_4S_4Cl_2$ F.W. 355

required:	C: 27.0%	H: 1.1%	N: 15.8%	S: 36.1%	Cl: 20.0%
observed:	C: 27.1%	H: 1.0%	N: 15.7%	S: -----	Cl: -----

m/e (EI+): 284 (11.3, SNSNC.C_6H_4.CNSNS), 206 (37.8, NC.C_6H_4.CNSNS), 160 (11.4, NC.C_6H_4.CNS), 128 (83.0, NC.C_6H_4.CN).

4.4.4: Preparation of *p*-[$C_6H_4(CNSNS)_2$][$SbCl_6$]$_2$

An excess of $SbCl_5$ (1ml) was added to a suspension of *p*-[$C_6H_4(CNSNS)_2$]Cl_2 (0.335g, 1mmol) in CH_2Cl_2 at room temperature. On agitation this soon yielded a fine white precipitate of *p*-[$C_6H_4(CNSNS)_2$][$SbCl_6$]$_2$ which was filtered and washed with CH_2Cl_2 to remove unreacted $SbCl_5$.

Yield: 0.906g, 95%

i.r.: ν(max): 1503(m), 1430(s), 1390(s), 1292(m), 1242(w), 1222(w),
1207(w), 1132(m), 1013(w), 970(s), 897(m), 881(s),
836(s), 788(s), 720(m), 658(m), 625(m), 580(m), 550(s).

elemental analysis:$C_8H_4N_4S_4Sb_2Cl_{12}$ F.W. 953.5

required:

C: 10.1%	H: 0.4%	N: 5.9%	S: 13.4%	Sb: 25.5%	Cl: 44.7%

observed:

C: 10.0%	H: 0.4%	N: 5.8%	S: -----	Sb: -----	Cl: -----

4.4.5: Preparation of *p*-[$C_6H_4(CNSNS)_2$]Br_2

para-[$C_6H_4(CNSNS)_2$][AsF_6]$_2$ (0.662g, 1mmol) and a slight molar excess of [Et_4N]Br (0.60g, 2mmol) were stirred in CH_3CN to produce an instant crimson precipitate of *p*-[$C_6H_4(CNSNS)_2$]Br_2. The product was filtered and then extracted with CH_2Cl_2 in a sealed extractor.

Yield:0.400g, 90%

i.r.: ν(max): 1505(w), 1427(m), 1396(m), 1290(m), 1245(w), 1222(w),
1150(m), 1005(w), 964(s), 910(m), 855(m), 838(s),
767(s), 720(m), 697(s), 660(m), 628(m), 580(s), 552(s).

elemental analysis:$C_8H_4N_4S_4Br_2$ F.W. 444
required: C: 21.6% H: 0.9% N: 12.6% S: 28.8% Br: 36.0%
observed: C: 21.4% H: 1.0% N: 12.3% S: ----- Br: -----

This salt was also prepared by condensation of excess liquid bromine onto a frozen solution of *p*-$[C_6H_4(CNSNS)_2]$ in CH_2Cl_2. On allowing to warm to room temperature the black precipitate was replaced by a deep red precipitate of *p*-$[C_6H_4(CNSNS)_2]Br_2$. The material was isolated by pumping to dryness and had the same analysis and infra-red spectrum as by the above preparation.

4.4.6: Preparation of *p*-$[C_6H_4(CNSNS)_2][S_3N_3]_2$

para-$[C_6H_4(CNSNS)_2][AsF_6]_2$ (0.662g, 1mmol) and a slight molar excess of $[Pr_4N][S_3N_3]$ (0.648g, 2mmol) were stirred in CH_2Cl_2 to produce an instant black-green precipitate of *p*-$[C_6H_4(CNSNS)_2][S_3N_3]_2$. The product was filtered and then extracted with CH_2Cl_2 in a sealed extractor[30].

Yield: 0.448g, 80%

i.r.: ν(max): 1510(w), 1400(s), 1310(w), 1235(m), 1120(m), 1015(w),
892(m), 852(w), 838(s), 730(s), 692(s), 665(s), 640(s),
600(s), 566(m).

elemental analysis:$C_8H_4N_{10}S_{10}$
required: C: 17.1% H: 0.7% N: 25.1% S: 57.1%
observed: C: 17.5% H: 0.7% N: 24.0% S: -----

4.4.7: Preparation of *p*-$[C_6H_4(CNSNS)_2][Pt(mnt)_2]$

para-$[C_6H_4(CNSNS)_2][AsF_6]_2$ (0.132g, 0.2mmol) and a slight molar excess of $[Et_4N]_2[Pt(mnt)_2]$ (0.147g, 0.2mmol) were stirred in CH_3CN to produce an instant purple-black precipitate of *p*-$[C_6H_4(CNSNS)_2][Pt(mnt)_2]$. The product was filtered and then extracted with CH_2Cl_2 in a sealed extractor[30].

Yield: 0.120g, 79%

i.r.: ν(max): 2200(m),1510(w), 1432(s), 1380(m), 1310(w), 1230(w),
1155(m), 1020(w), 965(s), 900(m), 850(ms,br), 838(m),
777(m), 720(mw), 660(m), 620(m), 605(m), 580(s),
505(m), 404(s), 390 (s), 350(m), 325(m).

elemental analysis:$C_{16}H_4N_8S_8Pt$

required:	C: 25.3%	H: 0.5%	N: 14.7%	S: 33.7%	Pt: 25.7%
observed:	C: 25.5%	H: 0.5%	N: 14.9%	S: -----	Pt: -----

4.4.8: Cyclic Voltammogram of *p*-$[C_6H_4(CNSNS)_2][AsF_6]_2$

para-$[C_6H_4(CNSNS)_2][AsF_6]_2$ (0.012g) and $[Bu_4N]BF_4$ (0.428g, supporting electrolyte) were placed in a three limbed cell (see Appendix2) with a small magnetic follower and dissolved in CH_3CN. A series of cyclic voltammograms were taken at -20°C (temperature controlled using a Haake isotherm bath and circulator unit). The following half-wave reduction and oxidation potentials w.r.t. Ag/Ag^+ were observed at this temperature:

4.4.9 Preparation of *p*-$[C_6H_4(CNSNS)_2]$

para-$[C_6H_4(CNSNS)_2][Cl]_2$ (0.355g, 1mmol) and a slight molar excess of Ph_3Sb (0.355g, 1mmol) were stirred in CH_2Cl_2 to produce a blue-black precipitate of *p*-$[C_6H_4(CNSNS)_2]$ over a period of 1hr. The product was filtered and then washed with CH_2Cl_2 (5x5ml).

Yield: 0.256g, 90%

i.r.: ν(max): 1405(m), 1380(m), 1225(m,br), 1110(mw,br), 1010(s),
925(s), 827(s), 792(m), 775(m), 703(s), 655(w), 640(m),
595(s), 560(w), 540(m), 465(w,br), 400(w), 325(m),
310(s).

elemental analysis:$C_8H_4N_4S_4$ F.W. 284

required:	C: 33.8%	H: 1.4%	N: 19.7%	S: 45.1%
observed:	C: 34.0%	H: 1.5%	N: 19.8%	S: -----

4.4.10: Crystal Growth of *p*-$[C_6H_4(CNSNS)_2]$

A solution of Ph_3Sb (0.070g,1mmol) in CH_2Cl_2 (7ml) was allowed to diffuse through a grade 3 porosity glass sinter into a solution of *para*-

$[C_6H_4(CNSNS)_2][Cl]_2$ (7ml) over excess *para*-$[C_6H_4(CNSNS)_2][Cl]_2$ (0.070g,) in an inverted "dog"[16] . Small clumps of black needles of *para*-$[C_6H_4(CNSNS)_2]$ were formed at the sinter and on the J. Young tap over a period of ca. 36h. From these samples suitable needles for X-ray study (0.24 x 0.28 x <0.01 mm) were cut in the open air and mounted in glass Lindemann capillaries.

4.4.11: Electron Spin Resonance Study of *p*-$[C_6H_4(CNSNS)_2]$

Small samples of *para*-$[C_6H_4(CNSNS)_2]$ were prepared for e.s.r. spectroscopy studies in quartz e.s.r. tubes; one solid state sample (20mg) and a T.H.F. solution sample (ca.2-3mg). Solution samples were run at room temperature and produced a three line spectrum with an a_N value of 1.15mT.

4.4.12: Attempted Preparation of *p*-$[C_6H_4(CNSNS)_2][AsF_6]$

When *para*-$[C_6H_4(CNSNS)_2][AsF_6]_2$ (0.662g, 1mmol) and a molar equivalent of *para*-$[C_6H_4(CNSNS)_2]$ were stirred in CH_3CN or SO_2,in a "dog",a purple-black solution was formed over unreacted *para*-$[C_6H_4(CNSNS)_2]$ and *para*-$[C_6H_4(CNSNS)_2][AsF_6]_2$.

On filtering off this solution and evaporating it to dryness a purple intractable oil was formed which contained a few small black needles.

A similar set of results were obtained using *para*-$[C_6H_4(CNSNS)_2]Cl_2$ instead of the AsF_6 salt.

4.4.13: Reaction of 1,3-dicyanobenzene with [SNS][AsF$_6$]

meta-$C_6H_4(CN)_2$ (0.128g,1mmol) was stirred with a slight excess of $[S_2N][AsF_6]$ (0.534g, 2 mmol) in l. SO_2 in a two-limbed reaction vessel for 18h to yield an off-white precipitate under a rose solution. The volume was reduced and the crude product washed with minimal amounts of SO_2 and CH_2Cl_2 to remove coloured impurities. The product showed no ν(CN) i.r. absorption at ca. 2200cm^{-1}.

Yield: 0.563g, 85%

i.r.: ν(max): 1600(s), 1490(m), 1420(s), 1405(s), 1340(s), 1290(m), 1250(w), 1230(w), 1195(m), 1180(m), 1150(w), 1125(w), 1045(m), 1035(s), 986(s), 940(m), 905(m), 895(s), 870(m), 805(m), 802(s), 790(m), 700(s,br), 635(m), 620(s), 590(s), 575(m), 525(w).

elemental analysis:$C_8H_4N_4S_4As_2F_{12}$ F.W.:662

required:

C: 14.5% H: 0.6% N: 8.5% S: 19.4% As: 22.6% F:34.4%

observed:

C: 14.6% H: 0.6% N: 8.4% S: ----- As: ----- F: -----

^{1}H n.m.r.(*m*-dication, CD_3CN,): 9.07 (t), 8.74 (q), 8.16 (t).

4.4.14: Reaction of 1,2-dicyanobenzene with [SNS][AsF_6]

ortho-$C_6H_4(CN)_2$ (0.128g,1mmol) was stirred with a slight excess of [S_2N][AsF_6] (0.534g, 2 mmol) in l. SO_2 in a two-limbed reaction vessel for 18h to yield an off-white precipitate under a rose solution. The volume was reduced and the crude product washed with minimal amounts of SO_2 and CH_2Cl_2 to remove coloured impurities. The product showed no ν(CN) i.r. absorption at ca. 2200cm^{-1}.

Yield: 0.497g, 75%

i.r.: ν(max): 1585(m), 1420(s), 1405(s), 1330(s), 1220(w), 1195(m), 1170(w), 1145(s), 986(s), 925(m), 905(m),870(m),785(s), 700(s,br), 585(s), 570(s), 530(m), 450(m), 400(s).

elemental analysis:$C_8H_4N_4S_4As_2F_{12}$ F.W.:662

required:

C: 14.5% H: 0.6% N: 8.5% S: 19.4% As: 22.6% F:34.4%

observed:

C: 14.6% H: 0.7% N: 8.5% S: ----- As: ----- F: -----

4.4.15: Reaction of 4,4'-dicyanobiphenyl with [SNS][AsF_6]

4,4'-NC.C_6H_4.C_6H_4.CN[27] (0.204g,1mmol) was stirred with a slight excess of [S_2N][AsF_6] (0.534g, 2 mmol) in l. SO_2 in a two-limbed reaction vessel for 18h to yield an orange solution. On reduction of the volume an orange precipitate of [SNSNC.C_6H_4.C_6H_4.CNSNS][AsF_6]$_2$ was formed which was washed with cold SO_2 at -70°C. The product showed no ν(CN) i.r. absorption at ca. 2200cm^{-1}.

Yield: 0.723g, 98%

elemental analysis:$C_{14}H_8N_4S_4As_2F_{12}$ F.W.: 738

required:

C: 22.8% H: 1.1% N: 7.6% S: 17.3% As: 20.3% F: 30.9%

observed:

C: 22.8% H: 1.0% N: 7.5% S: ----- As: ----- F: -----

4.4.16: Reaction of 1,3,5-tricyanobenzene with [SNS][AsF_6]

1,3,5-$C_6H_3(CN)_3$ (0.153g,1mmol) was stirred with a slight excess of [S_2N][AsF_6] (0.801g, 3 mmol) in l. SO_2 in a two-limbed reaction vessel for 36h to yield a yellow solution over an off-white precipitate. The solvent was removed and washed with CH_2Cl_2 and a trace of SO_2 to remove slightly coloured impurities.. The product showed no ν(CN) i.r. absorption at ca. 2200cm^{-1}.

Yield: 0.668g, 70%

i.r.: ν(max): 1605(m), 1405(s), 1330(w), 1280(w), 1265(m), 1200(s), 1195(m), 1153(m), 1062(m), 1022(w), 950(s), 900(s), 850(m), 800(s), 700(s,br), 610(m), 585(s), 575(m), 560(w), 540(w), 440(s), 400(s).

elemental analysis:$C_9H_3N_6S_6As_3F_{18}$ F.W.: 954

required:

C: 11.3% H: 0.3% N: 8.8% S: 20.1% As: 23.6% F: 35.9%

observed:

C: 11.4% H: 0.3% N: 8.7% S: ----- As: ----- F: -----

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CHAPTER FIVE

SOME NOVEL DITHIADIAZOLIUM SALTS AND A DITHIADIAZOLE COMPLEX CONTAINING GROUP VIII (Pt,Pd) METAL CENTRES

5.1 Introduction

For some time the solid state association of a variety of heterocyclic radicals has been the topic of particular interest in the synthesis of low dimensional conducting materials[1,2]. In particular, it has been hoped that perpendicular stacks of uniform radicals (see fig.5.1.1) such as $R_2C_2N_3S$, RCN_2S_2 or RCN_3S_2 may have extended S...S interactions; mixing singly occupied molecular orbitals to produce a conduction band.

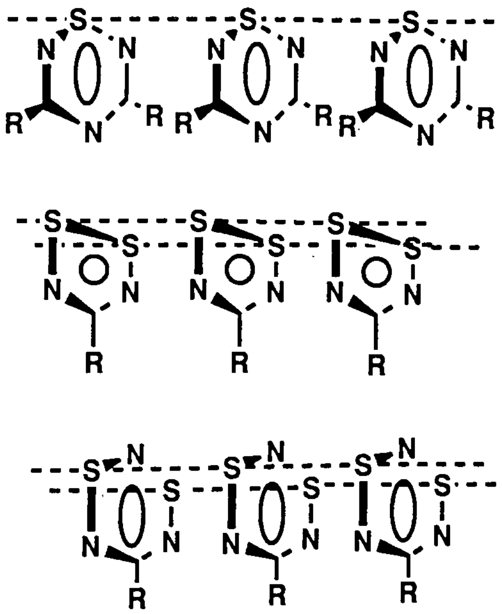

Figure 5.1.1
Interactions of monomeric heterocyclic radicals in the solid state may lead to extended molecular stacks, forming a conduction band.

The solid state structure of *p*-[$C_6H_4(CNSNS)_2$] (see chapter 4.2.10) shows essentially perpendicular stacks of molecules with equal spacing as well as some secondary S...S and S...N interactions* . However these stacks are slipped and are therefore unlikely to act as conducting materials. In all other known dithiadiazoles[3,4-6], thiatriazinyls[7] and dithiatriazines[1] there are also intermolecular interactions but these materials are dimeric in nature with weaker secondary interactions between dimeric species and these materials do not show any useful electrical properties.

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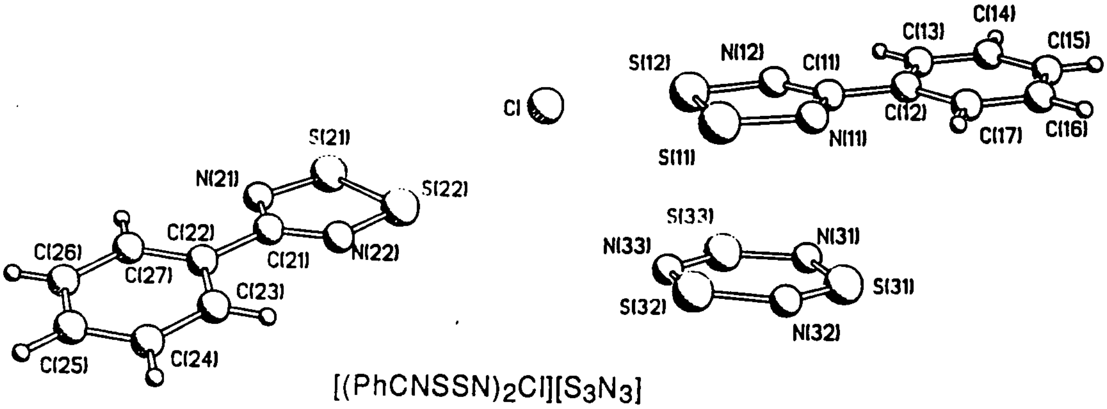
* Single crystals of suitable dimensions for conductivity measurements have not yet been obtained.

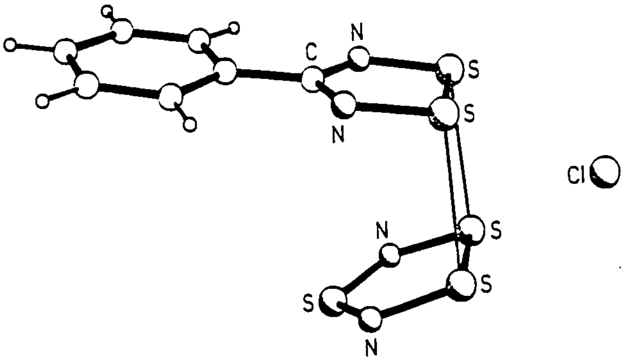
Nevertheless it has been proposed[8] that calculations on dimeric materials may be used "as a basis for the rational choice of donors and acceptors in new conducting materials". Consequently we have examined a variety of materials containing dithiadiazolium derivatives in mixed valence states where the RCN2S2 rings are involved in different interacting pseudo-planar structures[9-11]:

The reaction of 4-phenyl-1,2,3,5-dithiadiazole with S_5N_5Cl and S_4N_3Cl was examined by S.T. Wait[9-12] and led to four novel dithiadiazolium salts; $[PhCNSSN]_2Cl$, $[PhCNSSN][S_3N_3]$, $[(PhCNSSN)_2Cl][S3N3]$ and $[PhCNSSN][S_3N_2]Cl$; the third of these materials possessing a metallic golden lustre. These materials are remarkably air stable and this has been attributed to their layered structures which hinder hydrolysis of the PhCNSSN ring. The structures of the latter three materials are shown in Figure 5.1.2 and show strong S...S interactions and in the case of $[PhCNSSN][S_3N_2]Cl$ and $[(PhCNSSN)_2Cl][S_3N_3]$ S...Cl interactions as well.

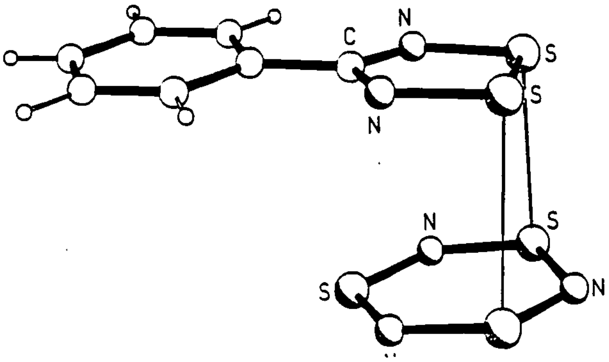
Figure 5.1.2: Quasi-planar stacking arrangements are observed in a variety of $PhCN_2S_2$ salts with S...S and S...Cl interactions observable.



$[(PhCNSSN)_2Cl][S_3N_3]$



$[PhCNSSN][S_3N_2]Cl$



$[PhCNSSN][S_3N_3]$

In examining these materials, it is convenient to measure the degree of charge-transfer by a comparison of S-S bond distances in the PhCNSSN ring [12] (Table 5.1.3).:

Table 5.1.3. S...S bond distances in some phenyl dithiadiazole/ium species

Compound	dss(Å)	ref
[PhCNSSN]Cl	1.991	13
[PhCNSSN][AsF_6]	2.017	10
[PhCNSSN][S_3N_2]Cl	2.055	9,10
[PhCNSSN][S_3N_3]	2.064	10,11
$[PhCNSSN]_2$	2.089	3
[$(PhCNSSN)_2Cl$][S_3N_3]	2.193	9,10
Cp_2Ni_2[PhCNSSN]	2.905	16
Fe_2CO_6[PhCNSSN]	2.930	14
Sum of van der Waals radii	3.2-4.0	15

In the transition metal complexes, Fe_2CO_6[PhCNSSN] and Cp_2Ni_2[PhCNSSN], there would appear to be negligable S...S bonding.

Out of plane interactions lead to changes of electron density in the RCNSSN a_2 orbital which is anti-bonding w.r.t. S-S ; electron donation from out of plane anions leads to an increase in the S-S bond length.

In plane interactions, meanwhile, lead to electron density changes in the RCNSSN b_1 orbital which is bonding w.r.t. S-S (see Figure 5.1.4):

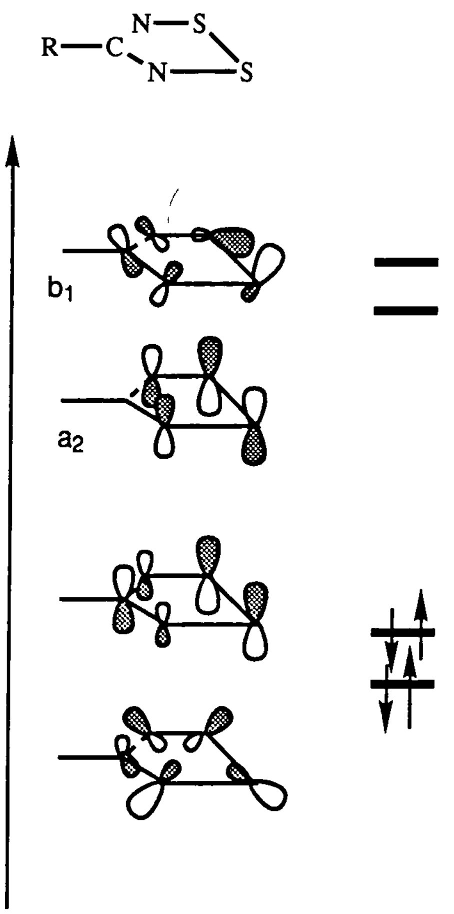


Figure 5.1.4.
Frontier Orbitals of the RCN2S2+ cation.

In plane interactions between cation and anion lead to bond shortening via the b_1 orbital whilst out of plane interactions occur via the a_2 orbital and lead to bond lengthening.

Group VIII metals (Ni, Pt, Pd) are well known to form stable planar complexes[17] of varying oxidation states (particularly 0, +2 and +3) some of which are known to form conducting salts[18] via extended conjugation bands. Therefore the possibility of forming dithiadiazolium complexes with these metal centres appeared to be a profitable area of research in the synthesis of organic metals.

The preliminary results of reactions between the dithiadiazolium cation and planar $Pt(mnt)_2^-$ and $Pt(mnt)_2^{2-}$ are now discussed and compared with the reaction of phenyl dithiadiazole with $Pd(PPh_3)_4$. I am indebted to Dr. S.T. Wait for his expert help and guidance through the Pt work and to Dr. I.B. Gorrell for his experimental details on the Pd complex reaction.

5.2 Results and Discussion

5.2.1 Reaction of [PhCNSSN][AsF_6] with $[Et_4N]_2[Pt(mnt)_2]$

Reaction of two equivalents of [PhCNSSN][AsF_6] with $[Et_4N]_2[Pt(mnt)_2]$ in CH_3CN produced a black microcrystalline precipitate of $[PhCNSSN]_2[Pt(mnt)_2]$ under a red-green dichroic solution. The insoluble product was isolated in 90% yield by careful washing with CH_2Cl_2 and liquid SO_2.

5.2.2 Crystal Growth and Structure of $[PhCNSSN]_2[Pt(mnt)_2]$

Small, black, lustrous rhombs of $[PhCNSSN]_2[Pt(mnt)_2]$ were grown in methylene chloride by allowing a saturated solution of $[Et_4N]_2[Pt(mnt)_2]$ to diffuse through a glass sinter (porosity grade 3) into a saturated solution of [PhCNSSN][AsF_6] over excess [PhCNSSN][AsF_6].

The crystals were air stable over a period of several weeks and a suitable crystal (0.6 x0.05 x <0.01 mm) was picked and mounted in a Lindemann capillary on the bench. This crystal was shown to be single by an oscillation photograph and submitted for a full X-ray structure determination. This analysis was carried out using a synchrotron radiation source at the Daresbury laboratories by Dr. W. Clegg (Newcastle University) for whose time and efforrt I am deeply indebted. The results of this analysis are shown in Tables 5.2.2a-c and Figures 5.2.2d-f.

Figure 5.2.2d shows a single cation-anion pair with some S...S interactions (i.e. S(2)...S(3) @ 3.00Å and S(1)...S(4) @ 3.71Å) between the dithiadiazolium cation and the mnt ligand of the anion. This interaction produces a slight deviation (ca. 5^o) of the ion pair from planarity, as well as the expected dithiadiazolium SS bond expansion; the S(3)-S(4) bond distance increasing slightly from 2.017 Å in [PhCNSSN][AsF_6] to 2.044Å in $[PhCNSSN]_2[Pt(mnt)_2]$. This increase in bond distance is only small and may be attributed to the fact that the $Pt(mnt)_2$ centre is interacting with two [PhCNSSN] rings and not one as seen previously (e.g. [PhCNSSN][S_3N_3], [PhCNSSN][S_3N_2]Cl etc.).

Figure 5.2.2e shows molecular packing in a stacked arrangement, where the stack has mixed cation anion character and an [ABA'] stacking system; the PhCNSSN rings alternating in their arrangement so as to allow SS interactions with different sulphur atoms in the $Pt(mnt)_2$ anion. This solid state arrangement precludes extensive delocalisation down the stack, leading only to small sections of interaction in each unit cell.

Table 5.2.2a: Crystal Data

Crystal System: triclinic — Space Group: $P\bar{1}$

Formula: $C_{20}H_{10}S_8N_8Pt$ — Formula Weight: 837

Unit Cell Parameters: a= 6.6240Å b= 10.1650Å c= 10.5490Å

α= 85.21° β= 76.84° γ= 79.73°

Table 5.2.2b: Atomic Coordinates

Atom Type	x	y	z
Pt(1)	0.00000	0.00000	0.00000
S(1)	0.25245	0.12983	-0.00570
S(2)	-0.19404	0.17115	-0.09675
C(1)	0.14345	0.27485	-0.07399
C(2)	-0.04440	0.29656	-0.11791
C(3)	0.25645	0.38837	-0.09316
C(4)	-0.10200	0.41487	-0.18832
N(1)	0.33995	0.47562	-0.10392
N(2)	-0.14983	0.51228	-0.24813
S(3)	-0.45252	0.25265	0.16609
S(4)	-0.20537	0.27961	0.24519
N(3)	-0.47218	0.11023	0.23480
N(4)	-0.18336	0.13522	0.31286
C(5)	-0.32450	0.05962	0.30512
C(6)	-0.32439	-0.07650	0.36530
C(7)	-0.47945	-0.14870	0.35411
C(8)	-0.47981	-0.27778	0.41053
C(9)	-0.32510	-0.33467	0.47815
C(10)	-0.17003	-0.26247	0.48934
C(11)	-0.16968	-0.13339	0.43291
S(1A)	-0.25245	-0.12983	0.00570
S(2A)	0.19404	-0.17115	0.09675
C(1A)	-0.14345	-0.27485	0.07399
C(2A)	0.04440	-0.29656	0.11791
C(3A)	-0.25645	-0.38837	0.09136
C(4A)	0.10200	-0.41487	0.18832
N(1A)	-0.33995	-0.47562	0.10392
N(2A)	0.14983	-0.51228	0.24813

Table 5.2.2c: Bond lengths(Å) and angles(°)

Pt(1)-S(1)	2.296	Pt(1)-S(2)	2.286	Pt(1)-S(1A)	2.296
Pt(1)-S(2A)	2.286	S(1)-C(1)	1.701	S(2)-C(2)	1.720
C(1)-C(2)	1.400	C(1)-C(3)	1.461	C(2)-C(4)	1.400
C(3)-N(1)	1.110	C(4)-N(2)	1.164	S(3)-S(4)	2.044
S(3)-N(3)	1.577	S(4)-N(4)	1.591	N(3)-C(5)	1.363
N(4)-C(5)	1.331	C(5)-C(6)	1.473	C(6)-C(7)	1.395
C(6)-C(11)	1.395	C(7)-C(8)	1.395	C(8)-C(9)	1.395
C(9)-C(10)	1.395	C(10)-C(11)	1.395	S(1A)-C(1A)	1.701
S(2A)-C(2A)	1.720	C(1A)-C(2A)	1.400	C(1A)-C(3A)	1.461
C(2A)-C(4A)	1.400	C(3A)-N(1A)	1.110	C(4A)-N(2A)	1.164

S(1)-Pt(1)-S(2)	90.7	S(1)-Pt(1)-S(1A)	180.0
S(2)-Pt(1)-S(1A)	89.3	S(1)-Pt(1)-S(2A)	89.3
S(2)-Pt(1)-S(2A)	179.9	S(1A)-Pt(1)-S(2A)	90.7
Pt(1)-S(1)-C(1)	100.3	Pt(1)-S(2)-C(2)	102.9
S(1)-C(1)-C(2)	126.4	S(1)-C(1)-C(3)	117.7
C(2)-C(1)-C(3)	115.9	S(2)-C(2)-C(1)	119.5
S(2)-C(2)-C(4)	119.8	C(1)-C(2)-C(4)	120.4
C(1)-C(3)-N(1)	179.1	C(2)-C(4)-N(2)	179.2
S(4)-S(3)-N(3)	95.2	S(3)-S(4)-N(4)	94.2
S(3)-N(3)-C(5)	115.7	S(4)-N(4)-C(5)	116.8
N(3)-C(5)-N(4)	117.9	N(3)-C(5)-C(6)	118.9
N(4)-C(5)-C(6)	123.2	C(5)-C(6)-C(7)	119.7
C(5)-C(6)-C(11)	120.3	C(7)-C(6)-C(11)	120.0
C(6)-C(7)-C(8)	120.0	C(7)-C(8)-C(9)	120.0
C(8)C(9)-C(10)	120.0	C(9)-C(10)-C(11)	120.0
C(6)-C(11)-C(10)	120.0	Pt(1)-S(1A)-C(1A)	100.3
Pt(1)-S(2A)-C(2A)	102.9	S(1A)-C(1A)-C(2A)	126.4
S(1A)-C(1A)-C(3A)	117.7	C(2A)-C(1A)-C(3A)	115.9
S(2A)-C(2A)-C(1A)	119.5	S(2A)-C(2A)-C(4A)	119.8
C(1A)-C(2A)-C(4A)	120.4	C(1A)-C(3A)-N(1A)	179.1
C(2A)-C(4A)-N(2A)	179.2		

Figure 5.2.2d: A cation-anion pair in $[PhCNSSN]_2[Pt(mnt)_2]$.

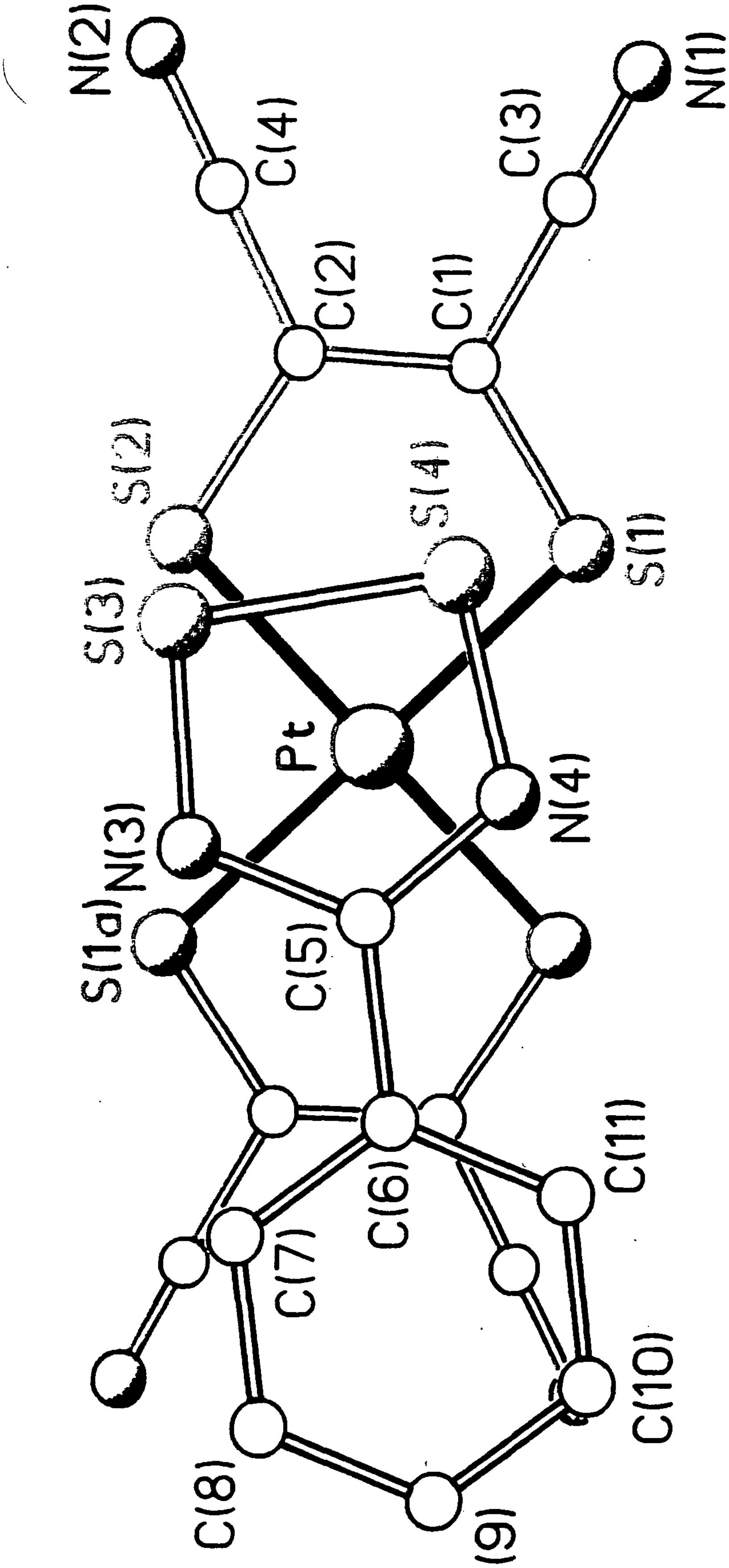


Figure 5.2.2e: Molecular Stacking in $[PhCNSSN]_2[Pt(mnt)_2]$.

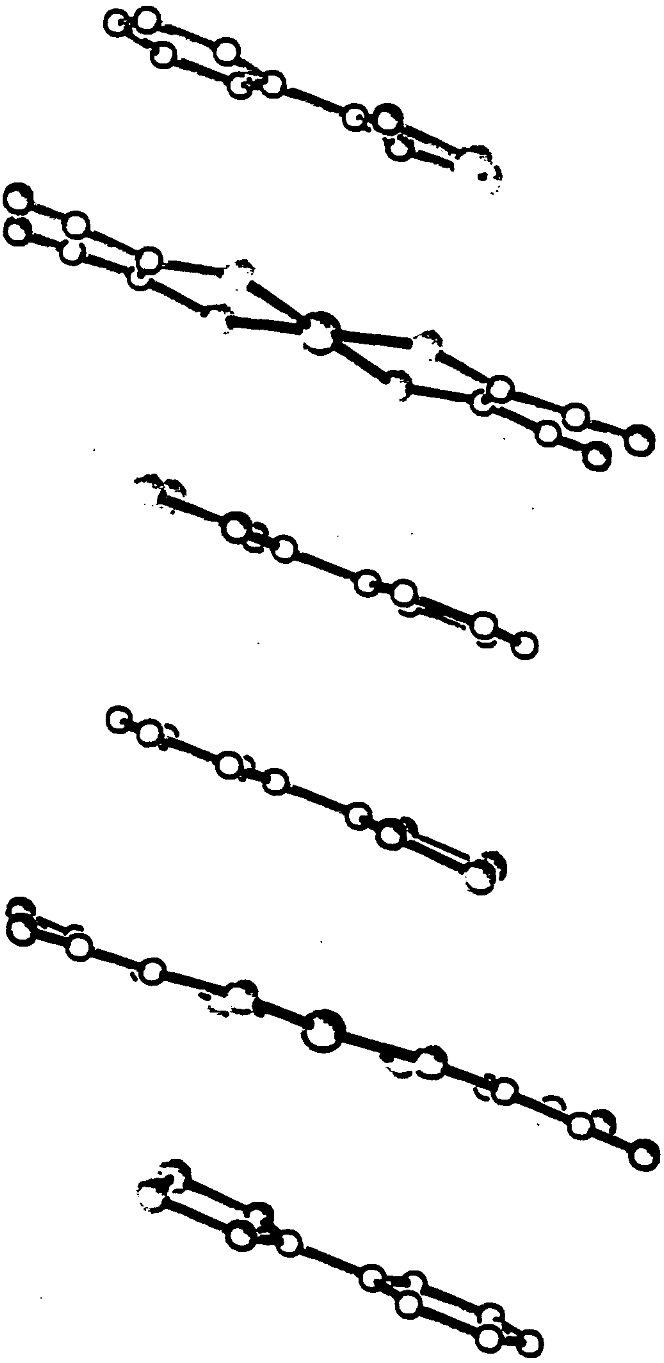
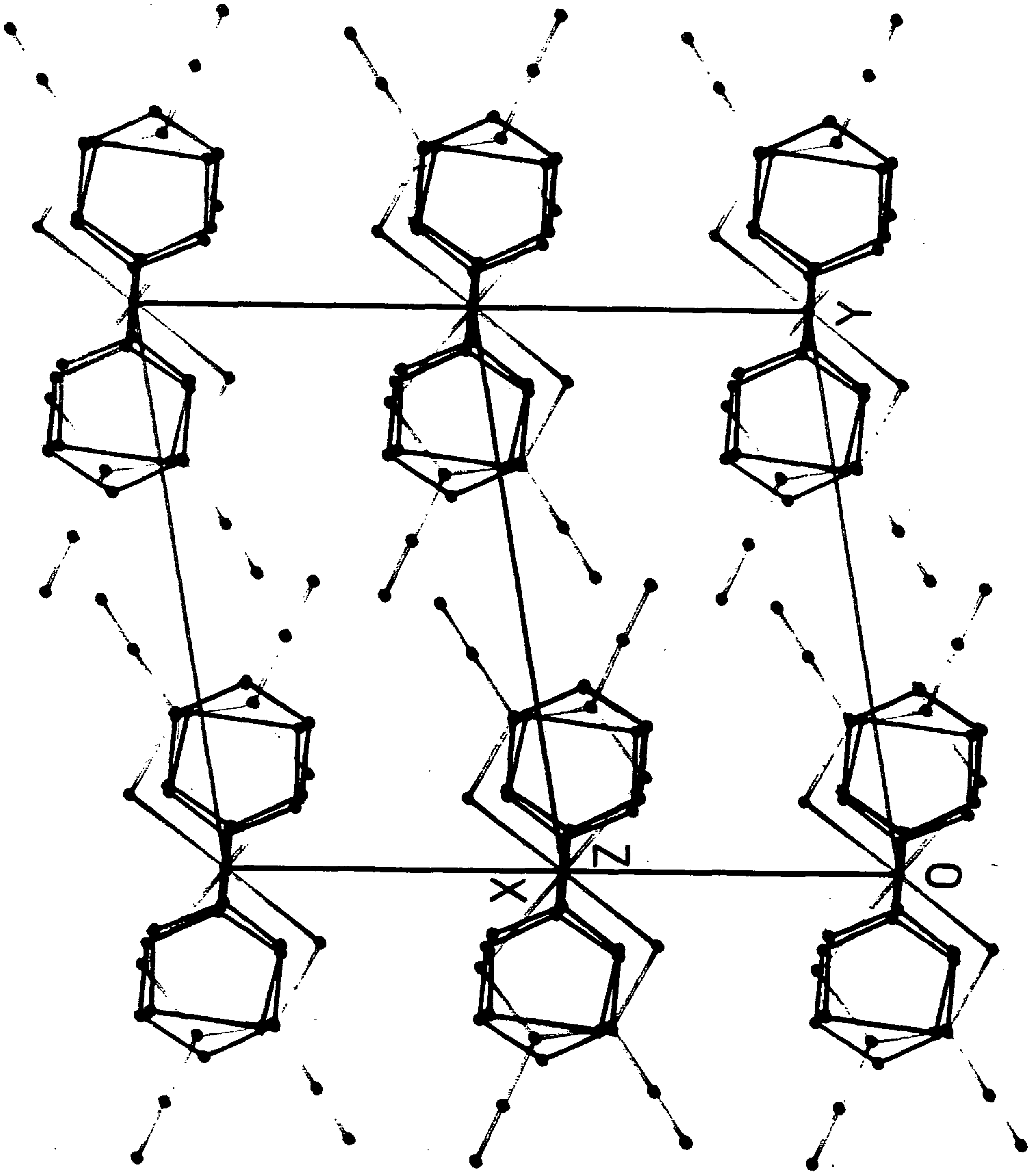


Figure 5.2.2f: View of $[PhCNSSN]_2[Pt(mnt)_2]$ perpendicular to the z axis.



Many $Pt(mnt)_2$ salts have been shown to form segregated stacks of cations and anions which have high conductivities and can be thought of as low dimensional conducting materials. However as the cations become larger there is a tendancy to form mixed stacks which tend not to have such interesting solid state properties. Indeed, this is the case in $[PhCNSSN]_2[Pt(mnt)_2]$, where there are mixed stacks with no apparent interaction between stacks, as shown in Figure 5.2.2f.
In the case of the PhCNSSN rings observed here, these secondary interactions within stacks are particularly noticeable. This ability of sulphur to form weak S...S interactions can be assigned to the unusual electronic attributes of conjugated thiazyl linkages i.e. high electron affinity coupled with a low ionisation potential (e.g. the low energy of dimerisation of dithiadiazoles, typically 30-35 kJ/mol[19-21]).

By "removing" one dithiadiazolium ring from the structure, however, it should be possible to produce a mixed stack of the type [ABA'B] which would allow extended conjugation down the stack. Consequently the synthesis of $[PhCNSSN][Pt(mnt)_2]$ was attempted.

5.2.3. Preparation of $[PhCNSSN][Pt(mnt)_2]$

A 1:1 mixture of $[PhCNSSN][AsF_6]$ and $[Et_4N][Pt(mnt)_2]$ in acetonitrile produced an instant black precipitate of $[PhCNSSN][Pt(mnt)_2]$ under a red-green solution, analogous to the reaction with $[Et_4N]_2[Pt(mnt)_2]$ (see chapter 5.2.1). However similar attempts at crystal growth in a variety of solvents (CH_3CN, CH_2Cl_2, SO_2, hexane and mixed solvent systems) were unsuccessful; all reactions produced only microcrystalline powders.

5.2.4. Preparation of $[p\text{-}Cl\text{-}C_6H_4.CNSSN][Pt(mnt)_2]$

It was suggested[22] that the use of substituted aromatics may be beneficial to the crystallisation of these highly insoluble salts, as the lowering of symmetry and/or solid state interactions help aid crystal growth in many cases. Cosequently the readily available $[p\text{-}Cl\text{-}C_6H_4.CNSSN][AsF_6]$ salt was used. The *para*-chloro derivative has very similar physical properties to the simple phenyldithiadiazolium cation (e.g. the reduction potential of $p\text{-}Cl\text{-}C_6H_4.CNSSN^+$ is V and that of $PhCNSSN^+$ is reduced at V) and we may consequently observe a similar physical and structural material but with a greater degree of crystallinity.

Indeed [*p*-Cl-C_6H_4.CNSSN][Pt(mnt)$_2$] was readily formed as a microcrystalline precipitate from the reaction of [*p*-Cl-C_6H_4.CNSSN][AsF_6] with [Et_4N][Pt(mnt)$_2$] in either CH_2Cl_2 or CH_3CN.

Crystal growth, however, was again unsuccessful; the reaction occuring too rapidly even by "slow" diffusion methods through a glass sinter. In order to further slow down the metathesis reaction, the less soluble [*p*-Cl-C_6H_4.CNSSN]Cl salt was used; a bulk scale reaction producing the desired [*p*-Cl-C_6H_4.CNSSN][Pt(mnt)$_2$]. However a crystal growth experiment surprisingly produced black needles of [(*p*-Cl-C_6H_4.CNSSN)$_2$Cl][Pt(mnt)$_2$]:

5.2.5.Structure of [(*p*-Cl-C_6H_4.CNSSN)$_2$Cl][Pt(mnt)$_2$]

Slow diffusion of a solution of [Et_4N][Pt(mnt)$_2$] in CH_3CN, containing "a breath of SO_2", through a glass sinter (porosity grade 3) into a solution of [*p*-Cl-C_6H_4.CNSSN]Cl over excess [*p*-Cl-C_6H_4.CNSSN]Cl produced long black needles (up to 1cm long) of [(*p*-Cl-C_6H_4.CNSSN)$_2$Cl][Pt(mnt)$_2$] over a period of 24 hours.

The crystals were found to be air stable (up to one week without tarnishing) and were picked in the open air and mounted in 0.2mm Lindemann capillaries. An X-ray oscillation photograph of one of these crystals (0.12 x 0.20 x 0.68mm) showed it to be single and it was submitted for a full X-ray structure determination. The results of this analysis are shown in Tables 5.2.5a-e and Figures 5.2.5f-k.

The unit cell is composed of only [(*p*-Cl-C_6H_4.CNSSN)$_2$Cl]$^+$ and Pt(mnt)$_2^-$ ions (Figures 5.2.5f and g). However due to the slightly asymmetric nature of the [(*p*-Cl-C_6H_4.CNSSN)$_2$Cl]$^+$ cation there are 8 formulae per unit cell, giving it unusually large dimensions (a= 13.545Å, b= 33.147Å and c= 13.751Å) and a volume of some 6137.4Å^3.

Table 5.2.5a Crystal Data

Formula: $C_{22}H_8N_8S_8Cl_3Pt$ Formula Weight: 942.3

Crystal System: monoclinic Space Group: $\underline{P}2_1/c$

Unit Cell Parameters: a= 13.545(2) b=33.147(4) c=13.756(1) Å

α= 90.00 β= 96.42(1) γ= 90.00°

Unit Cell Volume: 6137.4 Å^3 Number of Formulae per unit cell (Z)=8

R= 0.063 for 5666 observed reflections with $\underline{F}$> 4σ_c($\underline{F}$) and 30<2θ<35

Table 5.2.5b Atomic Coordinates

Atom	x	y	z
Pt(1)	2336(1)	761(1)	2883(1)
S(11)	3952(2)	940(1)	3134(2)
S(12)	1902(2)	1410(1)	3130(2)
S(13)	723(2)	574(1)	2700(2)
S(14)	2779(2)	120(1)	2581(3)
C(11)	3905(7)	1445(3)	3336(8)
C(12)	3024(6)	1654(3)	3339(8)
C(13)	773(6)	73(3)	2485(7)
C(14)	1648(7)	-121(3)	2382(8)
C(15)	4809(8)	1657(4)	3592(10)
C(16)	3025(8)	2069(4)	3467(9)
C(17)	-130(8)	-154(3)	2359(8)
C(18)	1713(7)	-523(3)	2168(10)
N(15)	5590(7)	1816(3)	3771(8)
N(16)	3024(8)	2417(3)	3545(9)
N(17)	-897(6)	-331(3)	2256(7)
N(18)	1772(8)	-879(4)	1992(11)
Pt(2)	5000	0	0
S(21)	6586(2)	204(1)	-46(2)
S(22)	4639(2)	599(1)	670(2)
C(21)	6574(7)	658(3)	434(8)
C(22)	5761(6)	850(3)	767(7)
C(23)	7533(7)	900(3)	575(9)
C(24)	5766(7)	1264(3)	1112(8)
N(23)	8262(7)	1061(3)	696(10)
N(24)	5792(6)	1580(3)	1368(8)
Pt(3)	0	0	5000
S(31)	-1622(2)	-174(1)	4677(2)
S(32)	437(2)	-657(1)	4897(2)
C(31)	-1584(6)	-663(3)	4605(7)
C(32)	-712(8)	-899(3)	4643(8)
C(33)	-2488(8)	-891(1)	4355(8)
C(34)	-643(8)	-1331(4)	4592(9)
N(33)	-3261(6)	-1053(3)	4164(8)
N(34)	-625(8)	-1680(3)	4575(9)
S(41)	1574(2)	603(1)	44(2)

Table 5.2.5b continued: Atomic Coordinates

Atom	x	y	z
S(42)	277(2)	845(1)	296(2)
N(41)	2188(6)	1015(2)	227(7)
N(42)	680(6)	1289(2)	474(7)
C(41)	1659(7)	1333(3)	451(7)
C(42)	2109(7)	1724(3)	590(8)
C(43)	1554(8)	2061(3)	615(8)
C(44)	1993(9)	2435(4)	765(10)
C(45)	2997(10)	2470(3)	892(10)
C(46)	3575(9)	2135(3)	914(10)
C(47)	3157(8)	1755(3)	748(9)
Cl(4)	3560(3)	2944(1)	1090(3)
S(51)	5728(2)	94(1)	2816(2)
S(52)	7053(2)	-72(1)	2398(2)
N(51)	5188(6)	-325(2)	2540(6)
N(52)	6700(6)	-508(2)	2059(7)
C(51)	5744(7)	-596(3)	2157(8)
C(52)	5339(8)	-1002(3)	1878(8)
C(53)	5941(9)	-1325(3)	1709(9)
C(54)	5540(9)	-1706(3)	1497(9)
C(55)	4527(9)	-1737(3)	1442(9)
C(56)	3923(9)	-1434(3)	1614(9)
C(57)	4330(7)	-1061(3)	1815(8)
Cl(5)	4053(3)	-2222(1)	1216(3)
S(61)	8800(2)	1324(1)	3103(2)
S(62)	7521(2)	1601(1)	3311(2)
N(61)	9442(6)	1723(2)	3122(7)
N(62)	7962(6)	2037(2)	3338(7)
C(61)	8919(7)	2063(3)	3257(7)
C(62)	9417(8)	2455(3)	3236(8)
C(63)	8914(9)	2805(3)	3424(8)
C(64)	9354(10)	3184(3)	3330(9)
C(65)	10329(10)	3208(3)	3106(9)
C(66)	10835(8)	2869(3)	2938(10)
C(67)	10415(7)	2483(3)	3026(9)
Cl(6)	10830(3)	3674(1)	2975(2)
S(71)	6614(2)	599(1)	5439(3)
S(72)	5290(2)	840(1)	5538(3)
N(71)	7211(6)	1011(3)	5648(8)
N(72)	5705(6)	1282(3)	5778(7)
C(71)	6662(7)	1331(3)	5815(7)
C(72)	7117(7)	1732(3)	5923(8)
C(73)	7117(7)	1732(3)	5923(8)
C(74)	6932(9)	2444(4)	6069(10)
C(75)	7923(9)	2488(3)	5961(10)
C(76)	8542(9)	2155(3)	5836(9)
C(77)	8137(8)	1771(3)	5865(9)
Cl(7)	8409(3)	2973(1)	5889(3)
Cl(8)	5000	0	5000
Cl(9)	0	0	0
Cl(10)	7152(2)	744(1)	3185(3)

Table 5.2.5c: **Bond Lengths (Å)**

Pt(1)-S(11)	2.257(3)	Pt(1)-S(12)	2.267(3)
Pt(1)-S(13)	2.258(3)	Pt(1)-S(14)	2.260(3)
S(11)-C(11)	1.700(11)	S(12)-C(12)	1.717(9)
S(13)-C(13)	1.688(10)	S(14)-C(14)	1.721(10)
C(11)-C(12)	1.381(13)	C(11)-C(15)	1.422(14)
C(12)-C(16)	1.385(16)	C(13)-C(14)	1.370(14)
C(13)-C(17)	1.430(14)	C(14)-C(18)	1.370(16)
C(15)-N(15)	1.182(15)	C(16)-N(16)	1.160(16)
C(17)-N(17)	1.187(14)	C(18)-N(18)	1.210(18)
Pt(2)-S(21)	2.261(3)	Pt(2)-S(22)	2.266(3)
S(21)-C(21)	1.644(11)	S(22)-C(22)	1.723(9)
C(21)-C(22)	1.392(14)	C(21)-C(23)	1.520(14)
C(22)-C(24)	1.454(15)	C(23)-N(23)	1.118(14)
C(24)-N(24)	1.102(14)	Pt(3)-S(31)	2.267(3)
Pt(3)-S(32)	2.265(3)	S(31)-C(31)	1.625(10)
S(32)-C(32)	1.752(11)	C(31)-C(32)	1.413(14)
C(31)-C(33)	1.447(14)	C(32)-C(34)	1.438(16)
C(33)-N(33)	1.179(14)	C(34)-N(34)	1.155(17)
S(41)-S(42)	1.996(4)	S(41)-N(41)	1.604(8)
S(42)-N(42)	1.578(8)	N(41)-C(41)	1.328(12)
N(42)-C(41)	1.339(12)	C(41)-C(42)	1.436(14)
C(42)-C(43)	1.349(15)	C(42)-C(47)	1.416(15)
C(43)-C(44)	1.382(16)	C(44)-C(45)	1.355(18)
C(45)-C(46)	1.358(17)	C(45)-Cl(4)	1.753(12)
C(46)-C(47)	1.390(15)	S(51)-S(52)	2.022(4)
S(51)-N(51)	1.598(8)	S(52)-N(52)	1.576(9)
N(51)-C(51)	1.317(13)	N(52)-C(51)	1.349(13)
C(51)-C(52)	1.488(14)	C(52)-C(53)	1.382(15)
C(52)-C(57)	1.373(14)	C(53)-C(54)	1.392(16)
C(54)-C(55)	1.369(18)	C(55)-C(56)	1.334(16)
C(55)-Cl(5)	1.745(11)	C(56)-C(57)	1.369(15)
S(61)-S(62)	2.009(4)	S(61)-N(61)	1.582(9)
S(62)-N(62)	1.565(9)	N(61)-C(61)	1.355(12)
N(62)-C(61)	1.316(13)	C(61)-C(62)	1.466(14)
C(62)-C(63)	1.383(16)	C(62)-C(67)	1.416(16)
C(63)-C(64)	1.403(16)	C(64)-C(65)	1.390(19)
C(65)-C(66)	1.349(16)	C(65)-Cl(6)	1.707(12)
C(66)-C(67)	1.410(16)	S(71)-S(72)	1.982(4)
S(71)-N(71)	1.599(10)	S(72)-N(72)	1.592(9)
N(71)-C(71)	1.329(14)	N(72)-C(71)	1.301(13)
C(71)-C(72)	1.467(14)	C(72)-C(73)	1.396(15)
C(72)-C(77)	1.399(15)	C(73)-C(74)	1.371(17)
C(74)-C(75)	1.375(18)	C(75)-C(76)	1.410(17)
C(75)-Cl(7)	1.743(12)	C(76)-C(77)	1.388(16)

Table 5.2.5d:Bond Angles (^{o})

S(11)-Pt(1)-S(12)	89.5(1)	S(11)-Pt(1)-S(13)	177.5(1)
S(12)-Pt(1)-S(13)	90.8(1)	S(11)-Pt(1)-S(14)	90.1(1)
S(12)-Pt(1)-S(14)	178.0(1)	S(13)-Pt(1)-S(14)	89.6(1)
Pt(1)-S(11)-C(11)	103.3(3)	Pt(1)-S(12)-C(12)	103.4(4)
Pt(1)-S(13)-C(13)	103.5(3)	Pt(1)-S(14)-C(14)	102.4(4)
S(11)-C(11)-C(12)	122.9(8)	S(11)-C(11)-C(15)	118.7(8)
C(12)-C(11)-C(15)	118.1(10)	S(12)-C(12)-C(11)	120.8(8)
S(12)-C(12)-C(16)	118.5(7)	C(11)-C(12)-C(16)	120.7(9)
S(13)-C(13)-C(14)	122.0(7)	S(13)-C(13)-C(17)	119.3(7)
C(14)-C(13)-C(17)	118.6(9)	S(14)-C(14)-C(13)	122.1(8)
S(14)-C(14)-C(18)	114.1(8)	C(13)-C(14)-C(18)	123.7(9)
C(11)-C(15)-N(15)	175.7(12)	C(12)-C(16)-N(16)	178.0(13)
C(13)-C(17)-N(17)	177.8(12)	C(14)-C(18)-N(18)	179.1(15)
S(21)-Pt(2)-S(22)	89.8(1)	Pt(2)-S(21)-C(21)	102.2(4)
Pt(2)-S(22)-C(22)	103.0(4)	S(21)-C(21)-C(22)	126.4(8)
S(21)-C(21)-C(23)	119.1(8)	C(22)-C(21)-C(23)	114.5(9)
S(22)-C(22)-C(21)	118.6(8)	S(22)-C(22)-C(24)	116.9(7)
C(21)-C(22)-C(24)	124.3(9)	C(21)-C(23)-N(23)	176.5(12)
C(22)-C(24)-N(24)	178.3(11)	S(31)-Pt(3)-S(32)	89.8(1)
Pt(3)-S(31)-C(31)	103.3(3)	Pt(3)-S(32)-C(32)	102.7(4)
S(31)-C(31)-C(32)	125.6(7)	S(31)-C(31)-C(33)	120.3(7)
C(32)-C(31)-C(33)	113.6(9)	S(32)-C(32)-C(31)	118.3(8)
S(32)-C(32)-C(34)	113.9(8)	C(31)-C(32)-C(34)	127.5(9)
C(31)-C(33)-N(33)	175.2(12)	C(32)-C(34)-N(34)	179.9(13)
S(42)-S(41)-N(41)	94.6(3)	S(41)-S(42)-N(42)	96.1(3)
S(41)-N(41)-C(41)	115.3(7)	S(42)-N(42)-C(41)	115.0(7)
N(41)-C(41)-N(42)	118.8(8)	N(41)-C(41)-C(42)	121.0(9)
N(42)-C(41)-C(42)	120.0(9)	C(41)-C(42)-C(43)	121.5(9)
C(41)-C(42)-C(47)	119.2(9)	C(43)-C(42)-C(47)	119.2(10)
C(42)-C(43)-C(44)	121.0(10)	C(43)-C(44)-C(45)	120.3(11)
C(44)-C(45)-C(46)	120.1(11)	C(44)-C(45)-Cl(4)	120.6(10)
C(46)-C(45)-Cl(4)	119.3(10)	C(45)-C(46)-C(47)	120.9(11)
C(42)-C(47)-C(46)	118.3(10)	S(52)-S(51)-N(51)	95.3(3)
S(51)-S(52)-N(52)	94.9(3)	S(51)-N(51)-C(51)	114.8(7)
S(52)-N(52)-C(51)	115.4(7)	N(51)-C(51)-N(52)	119.5(9)
N(51)-C(51)-C(52)	120.5(9)	N(52)-C(51)-C(52)	119.9(9)
C(51)-C(52)-C(53)	122.5(9)	C(51)-C(52)-C(57)	118.7(9)
C(53)-C(52)-C(57)	118.7(9)	C(52)-C(53)-C(54)	121.0(11)
C(53)-C(54)-C(55)	116.4(11)	C(54)-C(55)-C(56)	124.3(11)
C(54)-C(55)-Cl(5)	115.2(9)	C(56)-C(55)-Cl(5)	120.3(10)
C(55)-C(56)-C(57)	118.4(11)	C(52)-C(57)-C(56)	121.1(10)
S(62)-S(61)-N(61)	95.6(3)	S(61)-S(62)-N(62)	95.3(3)
S(61)-N(61)-C(61)	113.8(7)	S(62)-N(62)-C(61)	115.8(7)
N(61)-C(61)-N(62)	119.4(8)	N(61)-C(61)-C(62)	119.1(9)
N(62)-C(61)-C(62)	121.3(8)	C(61)-C(62)-C(63)	120.1(10)
C(61)-C(62)-C(67)	120.9(10)	C(63)-C(62)-C(67)	119.0(10)
C(62)-C(63)-C(64)	120.7(11)	C(63)-C(64)-C(65)	119.6(11)
C(64)-C(65)-C(66)	120.3(10)	C(64)-C(65)-Cl(6)	118.2(9)
C(66)-C(65)-Cl(6)	121.3(10)	C(65)-C(66)-C(67)	121.5(11)
C(62)-C(67)-C(66)	118.7(10)	S(72)-S(71)-N(71)	94.9(4)

Table 5.2.5d continued: Bond Angles (°)

S(71)-S(72)-N(72)	94.8(3)	S(71)-N(71)-C(71)	115.6(7)
S(72)-N(72)-C(71)	116.8(8)	N(71)-C(71)-N(72)	117.9(9)
N(71)-C(71)-C(72)	120.3(9)	N(72)-C(71)-C(72)	121.4(9)
C(71)-C(72)-C(73)	119.4(9)	C(71)-C(72)-C(77)	118.9(9)
C(73)-C(72)-C(77)	121.7(10)	C(72)-C(73)-C(74)	118.8(11)
C(73)-C(74)-C(75)	120.0(11)	C(74)-C(75)-C(76)	122.0(11)
C(74)-C(75)-Cl(7)	119.0(9)	C(76)-C(75)-Cl(7)	118.8(10)
C(75)-C(76)-C(77)	118.2(11)	C(72)-C(77)-C(76)	118.8(10)

Table 5.2.5e: Anisotropic thermal parameters (Å^2 x 10^3)

The anisotropic temperature factor exponent takes the form:
$-2\pi 2(h^2a^{*2}\underline{U}_{11}+...........+2hka^{*}b^{*}\underline{U}_{12})$

Atom	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{23}$	$\underline{U}_{13}$	$\underline{U}_{12}$
Pt(1)	50(1)	72(1)	72(1)	-5(1)	6(1)	1(1)
S(11)	59(2)	79(2)	103(3)	-14(2)	9(2)	-3(1)
S(12)	56(1)	76(2)	90(2)	-5(2)	8(1)	8(1)
S(13)	59(1)	82(2)	79(2)	-2(2)	11(1)	-8(1)
S(14)	55(2)	72(2)	111(3)	-14(2)	5(2)	9(1)
C(11)	50(6)	84(8)	69(7)	23(6)	4(5)	-7(5)
C(12)	37(5)	66(7)	77(8)	-10(6)	9(5)	4(5)
C(13)	38(5)	86(7)	46(6)	7(5)	10(4)	-5(5)
C(14)	55(6)	83(8)	66(8)	-7(6)	-4(5)	0(6)
C(15)	61(7)	88(8)	118(11)	0(7)	0(7)	8(6)
C(16)	64(7)	100(10)	71(8)	-6(7)	5(6)	-13(7)
C(17)	80(8)	81(8)	69(8)	1(6)	31(6)	18(6)
C(18)	52(6)	75(8)	135(12)	-31(8)	-6(7)	9(6)
N(15)	87(7)	101(8)	111(9)	-6(6)	7(6)	17(6)
N(16)	101(8)	86(7)	120(9)	-2(6)	10(7)	-4(6)
N(17)	60(5)	114(8)	99(8)	-2(6)	24(5)	-10(5)
N(18)	75(7)	163(12)	174(14)	-69(10)	12(8)	-4(7)
Pt(2)	48(1)	65(1)	67(1)	-2(1)	1(1)	2(1)
S(21)	60(2)	68(2)	86(2)	-4(2)	4(1)	-6(1)
S(22)	51(1)	69(2)	91(2)	-13(2)	8(1)	6(1)
C(21)	64(6)	83(8)	58(7)	20(6)	2(5)	10(6)
C(22)	26(4)	98(8)	63(7)	2(6)	-5(4)	7(5)
C(23)	57(6)	99(9)	83(9)	-18(7)	23(6)	-4(6)
C(24)	54(6)	67(7)	94(9)	-20(6)	9(6)	7(5)
N(23)	63(6)	104(8)	183(12)	-32(8)	37(7)	-22(6)
N(24)	74(6)	75(6)	110(8)	-23(5)	5(6)	5(5)
Pt(3)	49(1)	66(1)	69(1)	2(1)	5(1)	3(1)
S(31)	59(2)	71(2)	78(2)	-2(1)	5(1)	-3(1)
S(32)	50(1)	76(2)	97(2)	-2(2)	3(1)	10(1)
C(31)	31(5)	90(8)	58(7)	16(6)	-6(4)	5(5)
C(32)	70(7)	84(8)	55(7)	11(6)	-6(5)	-12(6)
C(33)	83(7)	85(8)	63(8)	7(6)	5(6)	21(6)
C(34)	60(7)	91(9)	72(8)	-4(7)	3(6)	4(7)
N(33)	44(5)	118(8)	128(9)	-10(7)	-20(5)	2(5)
N(34)	101(8)	73(7)	113(9)	-11(7)	17(7)	20(7)
S(41)	73(2)	66(2)	101(2)	-6(2)	5(2)	7(1)
S(42)	66(2)	68(2)	103(2)	-2(2)	11(2)	1(1)
N(41)	61(5)	58(5)	84(7)	-3(5)	2(5)	8(5)
N(42)	70(5)	65(6)	75(6)	1(5)	17(5)	2(5)
C(41)	53(5)	48(6)	65(7)	-2(5)	3(5)	4(5)
C(42)	69(6)	73(7)	61(7)	-1(6)	15(6)	21(6)
C(43)	68(7)	62(7)	85(8)	-5(6)	8(6)	2(6)
C(44)	88(9)	88(9)	98(10)	1(7)	1(7)	30(7)
C(45)	99(10)	76(8)	92(10)	-22(7)	4(8)	-2(7)

Table 5.2.5e continued: Anisotropic thermal parameters (Å^2 x 10^3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(46)	70(7)	79(8)	129(12)	-6(8)	1(7)	1(6)
C(47)	75(7)	66(7)	88(9)	0(6)	0(6)	7(6)
Cl(4)	142(3)	84(2)	149(4)	-12(2)	11(3)	-35(2)
S(51)	71(2)	66(2)	86(2)	-6(1)	8(2)	5(1)
S(52)	60(1)	66(2)	93(2)	0(2)	3(1)	-4(1)
N(51)	72(5)	55(5)	73(6)	-10(4)	4(5)	-18(4)
N(52)	59(5)	60(6)	117(8)	-1(5)	12(5)	18(4)
C(51)	57(6)	68(7)	66(7)	-15(5)	-3(5)	16(5)
C(52)	80(7)	52(6)	73(8)	12(5)	4(6)	5(5)
C(53)	77(7)	75(8)	96(9)	3(7)	2(7)	18(6)
C(54)	112(9)	60(7)	94(10)	-6(7)	14(8)	-5(7)
C(55)	109(9)	53(7)	94(9)	-4(6)	1(8)	-22(6)
C(56)	82(8)	70(8)	96(10)	-10(7)	-11(7)	5(7)
C(57)	59(6)	70(8)	85(9)	-5(6)	-5(6)	0(6)
Cl(5)	139(3)	82(2)	147(4)	-17(2)	2(3)	-29(2)
S(61)	65(2)	62(2)	106(2)	-1(2)	-4(2)	4(1)
S(62)	61(2)	67(2)	105(2)	-3(2)	7(2)	-3(1)
N(61)	77(6)	48(5)	99(7)	-2(5)	3(5)	1(4)
N(62)	62(5)	60(6)	105(7)	-10(5)	8(5)	3(4)
C(61)	67(6)	40(6)	60(7)	0(5)	-15(5)	5(5)
C(62)	75(7)	76(7)	71(8)	-8(6)	1(6)	5(6)
C(63)	76(7)	100(9)	71(8)	-20(7)	-3(6)	5(7)
C(64)	119(10)	52(7)	103(10)	-4(6)	-8(8)	-7(7)
C(65)	111(9)	53(7)	81(9)	-17(6)	1(7)	-13(7)
C(66)	59(7)	75(8)	134(12)	3(8)	-2(7)	-8(6)
C(67)	58(6)	81(8)	99(10)	9(7)	4(6)	7(6)
Cl(6)	122(3)	75(2)	97(2)	-3(2)	12(2)	-28(2)
S(71)	68(2)	82(2)	138(3)	-27(2)	17(2)	7(2)
S(72)	66(2)	74(2)	115(3)	10(2)	19(2)	-3(1)
N(71)	71(6)	82(7)	114(9)	-38(6)	-2(6)	6(5)
N(72)	70(6)	73(6)	104(8)	7(5)	9(5)	11(5)
C(71)	52(6)	83(7)	57(7)	-6(5)	4(5)	14(5)
C(72)	68(7)	61(7)	63(7)	-6(5)	-8(6)	-11(6)
C(73)	74(7)	56(8)	118(11)	-1(7)	-4(7)	4(6)
C(74)	89(9)	77(9)	106(11)	6(7)	-3(8)	-1(7)
C(75)	99(9)	73(8)	88(9)	-7(7)	5(7)	-17(7)
C(76)	76(8)	80(9)	101(10)	-25(7)	-2(7)	1(7)
C(77)	69(7)	76(8)	89(9)	-16(7)	13(6)	-2(6)
Cl(7)	136(3)	89(2)	93(2)	-6(2)	12(2)	-34(2)
Cl(8)	123(4)	85(3)	97(3)	-17(3)	26(3)	-27(3)
Cl(9)	156(5)	82(3)	92(3)	-5(3)	-1(3)	-42(3)
Cl(10)	104(2)	76(2)	114(3)	5(2)	-7(2)	-17(2)

Figure 5.2.5f: Structure of the $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Cl}]^+$ cation in $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Cl}][\text{Pt(mnt)2}]$

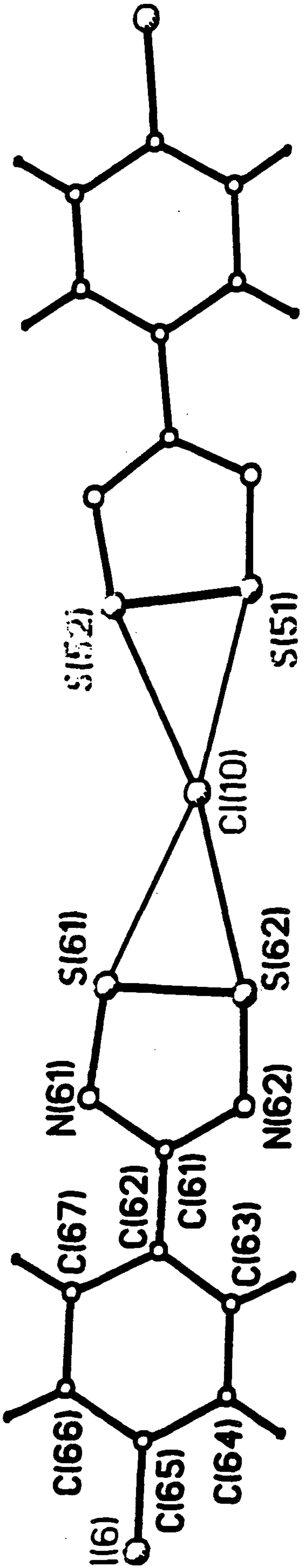


Figure 5.2.5g: Structure of the $Pt(mnt)_2^-$ anion in $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl][Pt(mnt)2]$

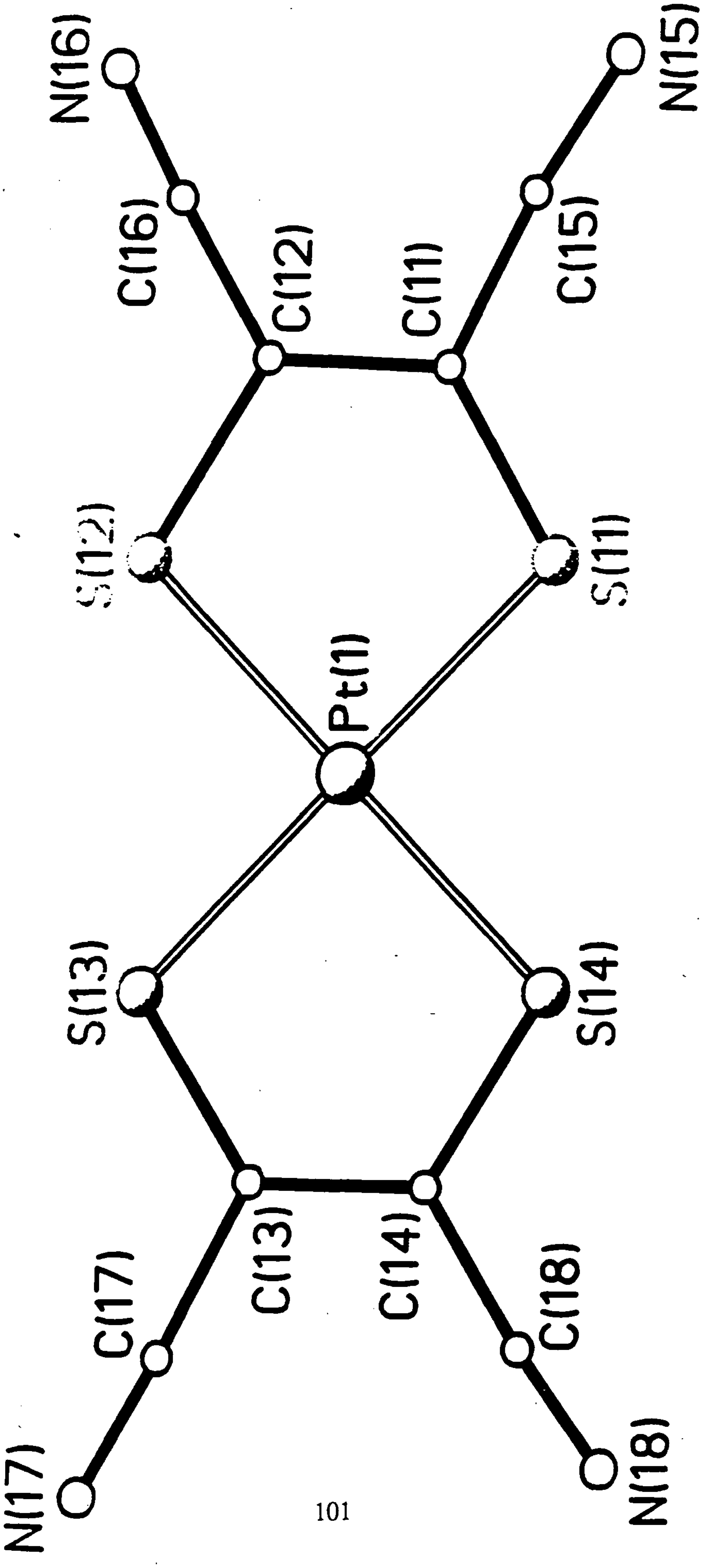


Figure 5.2.5h: A single molecular plane of cations and anions

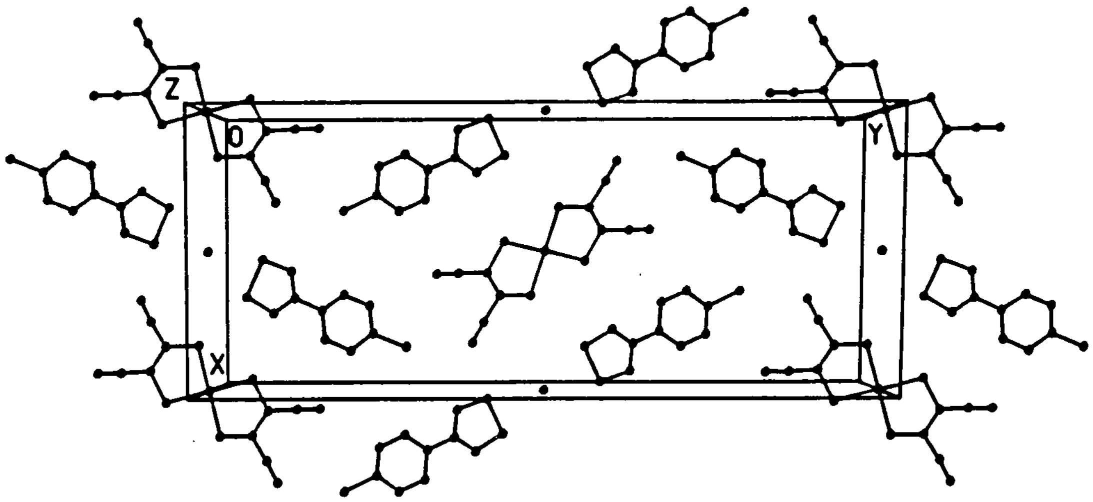


Figure 5.2.5i: A view of two molecular planes showing the slipped stacking of molecules between planes.

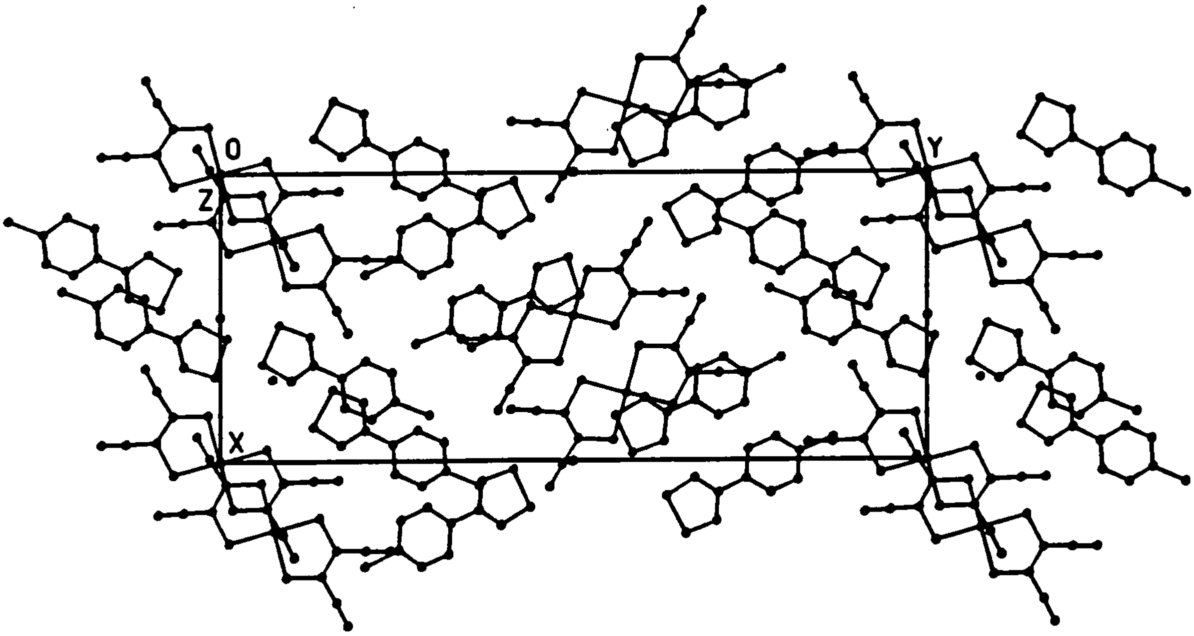
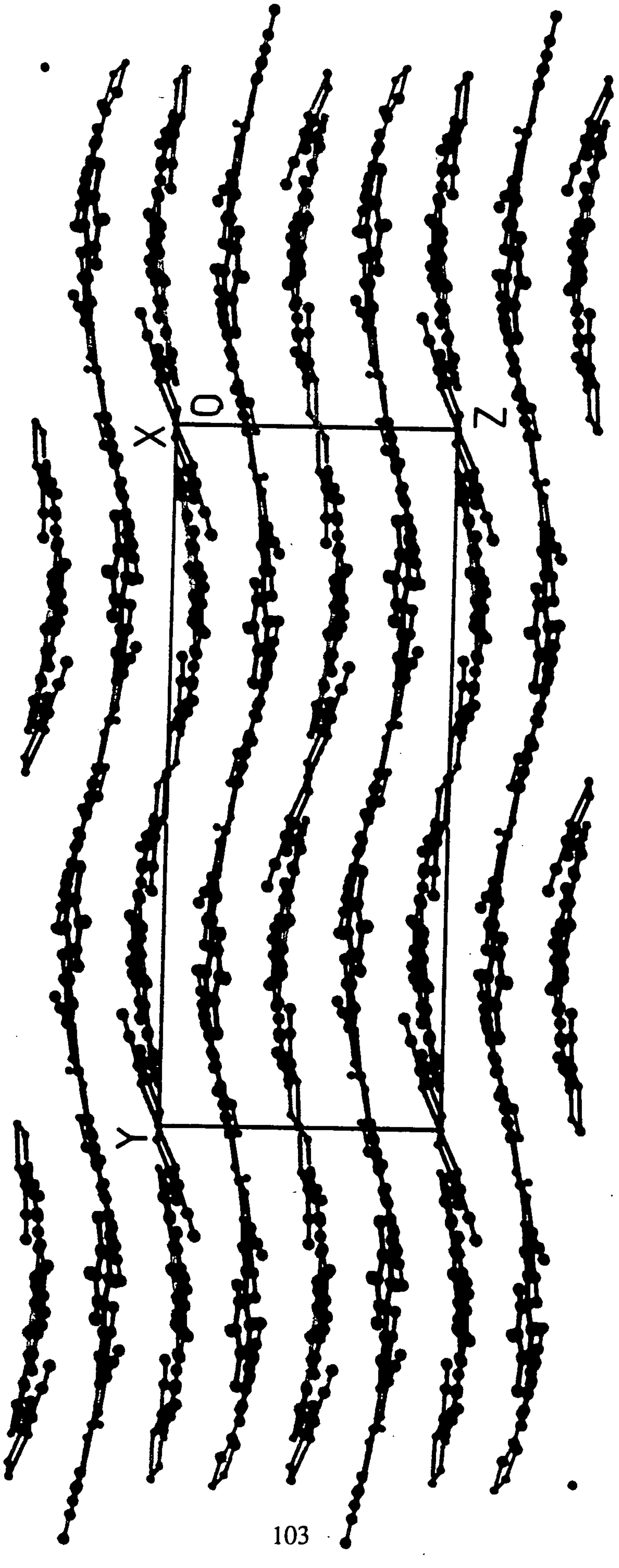


Figure 5.2.5k: View perpendicular to the x axis, showing the wave-like nature of $[(p\text{-Cl.C}_6\text{H}_4\text{.CNSSN})_2\text{Cl}][\text{Pt(mnt)}_2]$



The structures of the cation and anion are shown in Figures 5.2.5f and g respectively. The cation, $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl]^+$, is similar to its previously reported[9,10] phenyl analogue, $[(PhCNSSN)_2Cl]^+$, in that it is planar with the chloride centre taking up an asymmetric environment between the two dithiadiazolium rings which are slightly bent w.r.t. one another. This chlorine centre is weakly bonded to all four sulphur atoms of the CNSSN ring systems by way of interactions with the RCNSSN b_1 orbitals (see figure 5.2.5f) in a similar manner to that in [PhCNSSN]Cl. However the Cl^- anion is interacting with four sulphur atoms in $[(p\text{-}Cl.C_6H_4CNSSN)_2Cl]^+$, rather than the two in [PhCNSSN]Cl. Consequently the SS bond lengths in $[(p\text{-}Cl.C_6H_4CNSSN)_2Cl]^+$ (2.009Å and 2.022Å) are somewhat longer than those in [PhCNSSN]Cl (1.991Å) but shorter than those in $[PhCNSN]AsF_6$ (2.017Å), where there is minimal cation-anion interaction.

The solid state structure of this compound can be considered to be built up of "planes", in which each plane contains an equal number of $[(p\text{-}Cl.C_6H_4.CNSSN)_2Cl]^+$ cations and $Pt(mnt)_2^-$ anions; see figure 5.2.5h . The ions in each plane are, in fact, inclined w.r.t. the xy plane leading to a buckled effect in each layer. There would appear to be negligible in plane interactions between ions.

When a second 'plane' is superimposed on the first (Figure 5.2.5i), some 3.459Å above it, we can see that each layer of ions is staggered w.r.t. the previous layer such that we have segregated, but slipped, stacks of both cations and anions; the distance between layers making secondary interactions negligible.

Figure 5.2.5j shows the molecular packing as observed perpendicular to the x axis and highlights the layered nature of this compound. Moreover it shows the essentially segregated though buckled nature of this material. It is interesting to note the wave-like characteristics observed in this view and that the unit cell dimension b (33.147Å) along the x axis is equivalent to one wavelength! The physical properties of this type of compound may prove to be intersting!

5.2.6. Preparation of [(*p*-Cl.C6H4.CNSSN)$_2$Cl][Pt(mnt)$_2$]

The bulk preparation of this compound could be achieved by two routes as illustrated in equations 5.2.6a and 5.2.6b:

Eqn. 5.2.6a: $$2\,[p\text{-Cl.C}_6\text{H}_4\text{CNSSN}]\text{Cl} + [\text{Bu}_4\text{N}][\text{Pt(mnt)}_2] \longrightarrow [\text{Bu}_4\text{N}]\text{Cl} + [(p\text{-Cl.C}_6\text{H}_4\text{CNSSN})_2\text{Cl}][\text{Pt(mnt)}_2]$$

Eqn. 5.2.6b: $$3\,[p\text{-Cl.C}_6\text{H}_4\text{CNSSN}]\text{Cl} + [\text{Bu}_4\text{N}]_2[\text{Pt(mnt)}_2] \longrightarrow 3\,[\text{Bu}_4\text{N}]\text{Cl} + p\text{-Cl.C}_6\text{H}_4\text{CNSSN} + [(p\text{-Cl.C}_6\text{H}_4\text{CNSSN})_2\text{Cl}][\text{Pt(mnt)}_2$$

Both synthetic routes were attempted successfully although the first was more direct and purification was moderately easier as indicated by the differing isolated yields (75% to 65% respectively).

5.2.7 Preparation of [(PhCN$_2$S$_2$)$_2$Cl][Pt(mnt)$_2$]

This was prepared in a similar manner to the para-chloro analogue as shown above (see 5.2.6) using [Et$_4$N][Pt(mnt)$_2$] and [PhCNSSN]Cl. This material was isolated in 85% yield.

5.2.8 Reaction of [PhCNSSN]$_2$ with Pd(PPh$_3$)$_4$

Previous work[12] has shown that reaction of both Pd(PPh$_3$)$_4$ and Pt(PPh$_3$)$_4$ with [PhCNSSN]$_2$ has led to the formation of new materials, deep red in colouration, which were not fully characterised, but were provisionally proposed as M(PPh3)$_2$(PhCN$_2$S$_2$). However the analysis was inconclusive and it was thought possible that some sort of salt may be formed of the type [PhCNSSN]$_x$[M(PPh$_3$)$_4$]$_y$, with either mixed or segregated stacks of anions and cations.

Consequently the reaction was repeated under slightly differing conditions; i.e. at ambient temperature rather than 80+°C in toluene for several days.

On stirring [PhCNSSN]$_2$ with Pd(PPh$_3$)$_4$ in CH$_2$Cl$_2$ for 2 days a deep red solution formed which on cooling (-20°C) or evaporation readily yielded a red-brown precipitate. This was then exhaustively extracted with hexane to remove [PhCNSSN]$_2$ and triphenylphosphine. The remaining red product had the same infra-red spectral data as the previously described preparation.

However due to its ease of reaction at room temperature and its low solubility in CH$_2$Cl$_2$, a crystal growth experiment was carried out.

5.2.9 Crystal Growth and Structure of $Pd_3(PPh_3)_4(PhCNSSN)_2.2CH_2Cl_2$

Slow diffusion of $[PhCNSSN]_2$ in CH_2Cl_2 through a grade 3 porosity sinter into a concentrated solution of $Pd(PPh_3)_4$ over excess $Pd(PPh_3)_4$ slowly produced red diamonds of $Pd_3(PPh_3)_4(PhCNSSN)_2.2CH_2Cl_2$ over a period of 12 hours.

The crystals were found to be air stable and were readily picked and mounted in 0.2 and 0.3mm Lindemann capillaries. An oscillation photograph showed the crystal to be single and it was consequently submitted for a full X-ray analysis.

Due to the solvent of crystallisation, and the high numbers of atoms a variety of restraints were used (all phenyl groups were considered to be identical with C_{2v} symmetry. One of the CH_2Cl_2 solvent molecules also appeared to be disordered and a further restraint was needed). Due to the problems in solving the structure the R value was high (ca. 0.14) but the structure is "fine and correct beyond any doubt"[13].

Figure 5.2.9a shows the complete structure and atom labelling. However the structure is highly crowded and therefore Figure 5.2.9b shows the molecule with the dithiadiazole ring illustrated by just the sulphur atoms and Figure 5.2.9c illustrates the relationship between the Pd centres and the dithiadiazole rings, as well as providing some selected bond distances.

From Figure 5.2.9c (showing selected bond lengths) we can see that all the S-S bonds in the PhCNSSN unit have been broken with the former S-S bonds in the CN_2S_2 rings are now 3.0 Å (c.f. $[PhCNSSN]_2$: 2.089 Å) and the ones that used to link the dimeric structure together (i.e. S(1)-S(4) and S(2)-S(3)) are now some 3.5Å (c.f. $[PhCNSSN]_2$: 3.088Å and 3.115 Å). These S-S bond lengths are similar to those found in the two other dithiadiazole-metal complexes[14,15]; that in $Cp_2Ni_2(PhCNSSN)$ being 2.905Å whilst that in $Fe_2(CO)_6(PhCNSSN)$ is 2.930Å.

Each Pd centre has, however, managed to retain a planar geometry and we can imagine the structure as a set of Pd centres with bridging dithiadiazole units and terminal PPh_3 units. Interestingly this is the first structure ,of this type, which contains three metal centres and two bridging dithiadiazole units; previous structures ($Cp_2Ni_2(PhCNSSN)$ and $Fe_2(CO)_6(PhCNSSN)$) have shown only two metal centres and one dithiadiazole bridge.

Figure 5.2.9a:

The Crystal Structure of $Pd_3(PPh_3)_4(PhCNSSN)_2.2CH_2Cl_2$

Solvent of crystallisation has been removed for clarity

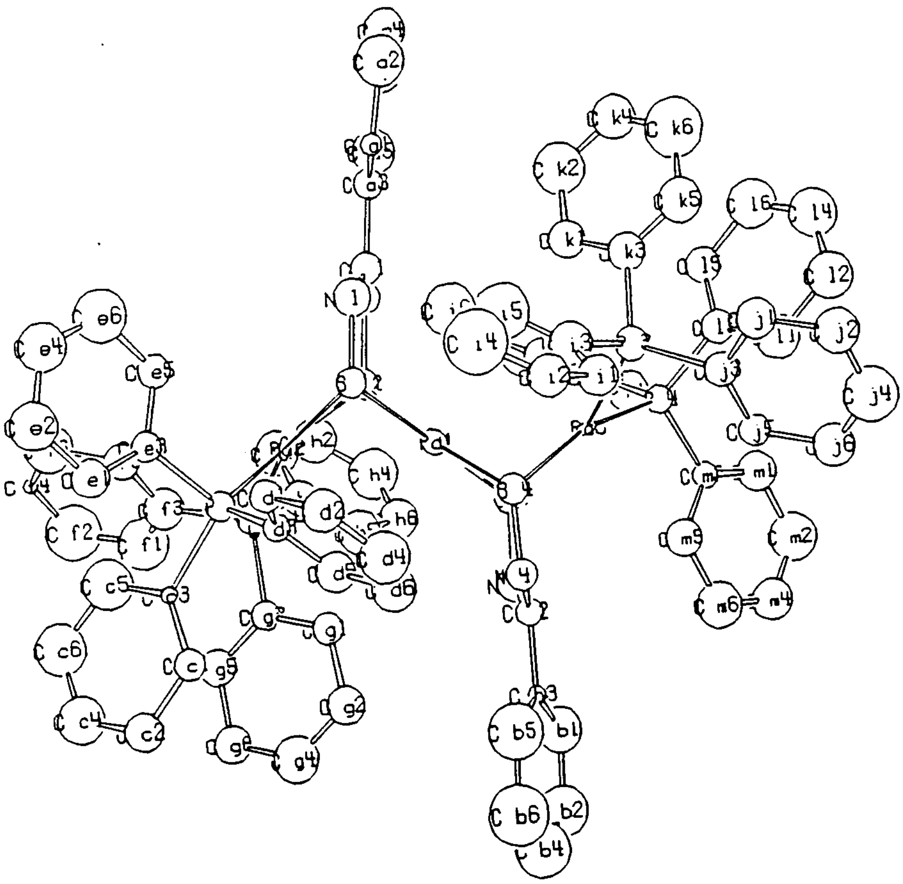


Figure 5.2.9b:

The Crystal Structure of $Pd_3(PPh_3)_4(PhCNSSN)_2.2CH_2Cl_2$

Only showing the S atoms of the PhCNSSN rings for clarity

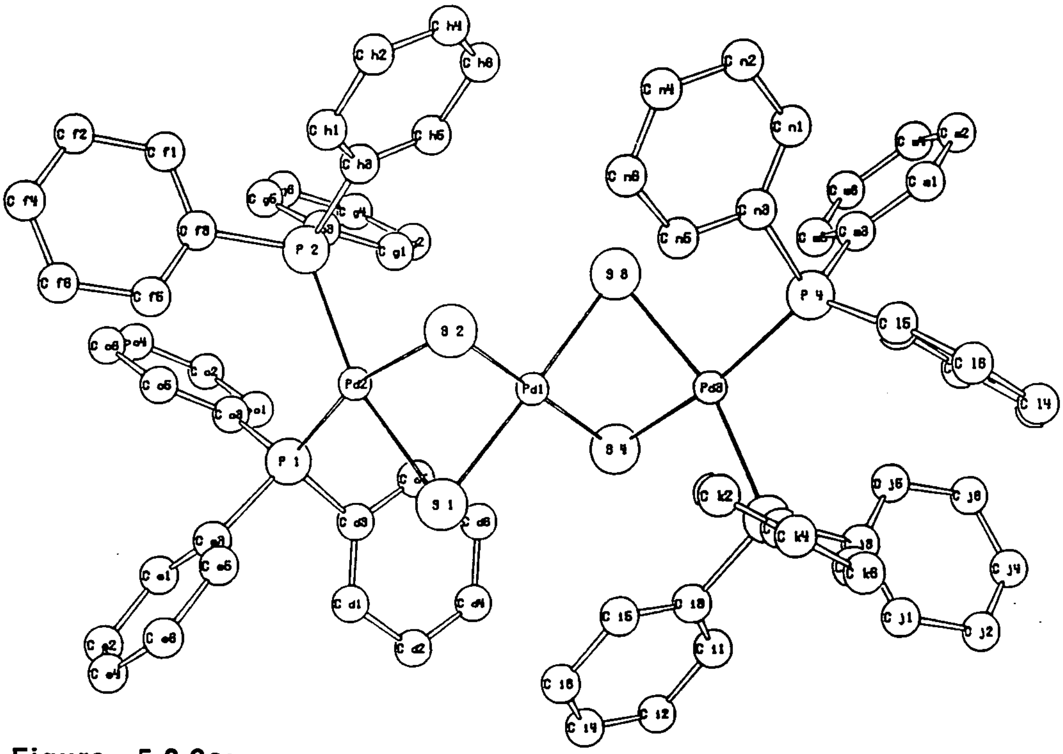
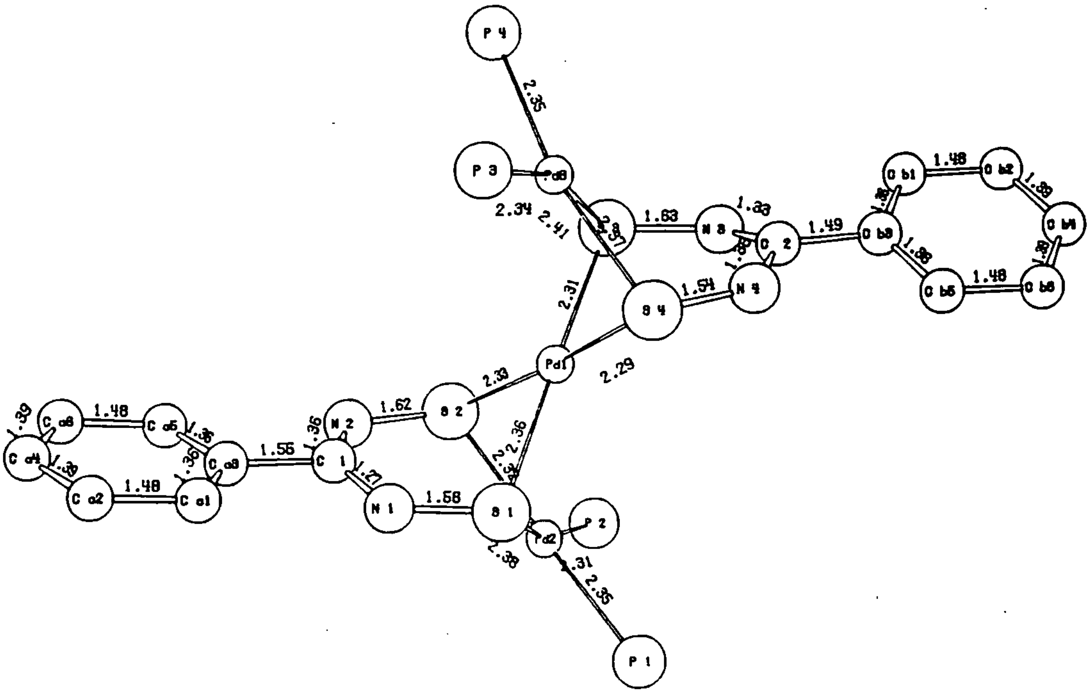


Figure 5.2.9c:

The Crystal Structure of $Pd_3(PPh_3)_4(PhCNSSN)_2.2CH_2Cl_2$

Indicating the triphenylphosphine groups by P, allowing an examination of the phenyl dithiadiazole rings and the planarity of the Pd environment.

Selected bond distances and angles are also shown.



Nevertheless a variety of other dithiadiazole complexes have been found which are highly insoluble and possibly polymeric in nature e.g. $[(PhCNSSN)CuCl]_x$. We can therefore suggest that these materials are composed of metal chains with bridging dithiadiazole ligands, as shown in Figure 5.2.9d:

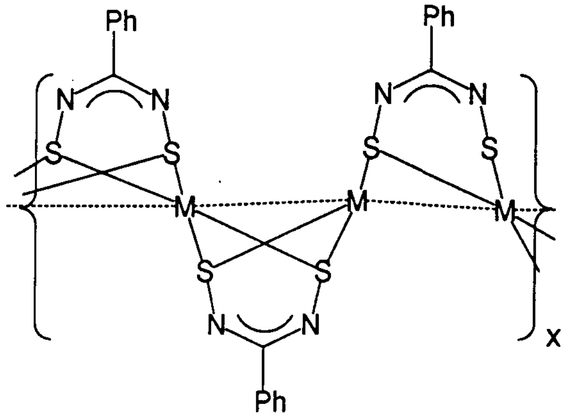


Figure 5.2.9d: Possible structure of a polymeric metal- dithiadiazole complex, found in a variety of reactions of zero-valent metals with phenyl dithiadiazole.

Indeed, in the case of the reaction $Pt(PPh_3)_4$ with $(PhCNSSN)_2$, a green intermediate is observed before the formation of an analagous red-orange precipitate, and this has been postulated as the monomeric $(PhCNSSN)Pt(PPh_3)_2$. By using bulky substituents such as PPh_3 the metal centre becomes shielded from attack by the PhCNSSN radical and smaller chains are formed. By using different substituents it should be possible to control the process so that oligomeric chains of well defined length may be formed, producing metal ladders with alternate bridging PhCNSSN units. Of interest for future work would be the analagous reactions of the recently prepared bis (dithiadiazoles); *p*-$[C_6H_4(CNSNS)_2]$ and *p*-$[C_6H_4(CNSSN)_2]$. These should then allow a further degree of dimensionality to the structures.

5.3 Conclusions

The dithiadiazolium cation forms a wide variety of charge-transfer complexes with the $Pt(mnt)_2$ anion. These materials show some novel solid state structures in which S...S interactions once again play an important role.

By reducing these interactions (e.g. by using $Pt(oxalate)_2$ anions etc. to minimise S..S interactions between cation and anion) then different stacking arrangements may result which may lead to novel electrical or magnetic properties.

By using materials such as the bis dithiadiazolium cations then the dimensionality of these materials may be increased and these too should have interesting solid state properties.

Reaction of $[PhCNSSN]_2$ with $Fe_3(CO)_{12}$ or $[CpNi(CO)]_2$ has previously been shown to produce materials with a bridging dithiadiazole unit between two metal centres, whereas other reactions have led to the formation of polymeric materials. The isolation of $Pd_3(PhCNSSN)_2(PPh_3)_4$ from a similar reaction with *zero-valent* transition metal complexes would suggest that these polymeric structures are composed of chains of metal centres linked through bridging dithiadiazole units.

The reaction of bis (dithiadiazoles) may provide an interesting possibility for cross linking between these metal chains.

5.4 Experimental

5.4.1. Preparation of $[PhCNSSN]_2[Pt(mnt)_2]$

$[Et_4N]_2[Pt(mnt)_2]$ (0.655g, 1mmol) and $[PhCNSSN][AsF_6]$ (0.74g, 2mmol) were placed in one limb of a two limbed reaction vessel and CH_3CN syringed in to yield an immediate black-green precipitate under a red-green dichroic solution. The mixture was stirred for 2 hours before filtration and evaporation to dryness. The crude product was transferred to a sealed extractor and extracted with CH_2Cl_2 for 10 hours.

Yield: 0.59g, 90% F.W.: 656.1

i.r..:ν(max): 2215(m), 1600(w), 1440(m), 1395(s), 1300(w), 1167(m), 1153(w), 1100(w), 1025(w), 922(mw), 905(m), 845(m), 783(m), 720(ms), 695(vs), 550(w), 520(w), 500(w).

elemental analysis: $C_{22}H_{10}S_8N_8Pt$

	C	H	N	S	Pt
required:	C: 31.5%	H: 1.2%	N: 13.8%	S: 30.6%	Pt: 23.3%
observed:	C: 31.2%	H: 1.3%	N: 13.6%	S: -----	Pt: -----

5.4.2 Crystal growth of $[PhCNSSN]_2[Pt(mnt)_2]$

$[Et_4N]_2[[Pt(mnt)_2]$ (0.075g) was placed in one leg of a dog and $[PhCNSSN][AsF_6]$ (0.06g) placed in the second limb. CH_3CN (10ml) was syringed into both legs and the vessel inverted so as to allow slow diffusion through the glass sinter (porosity grade3). Over a period of several hours small microcrystals of $[PhCNSSN]_2[Pt(mnt)_2]$ formed at the interface. The solution was decanted off and the crystals remaining were found to be suitable for X-ray analysis.

5.4.3. Preparation of $[PhCNSSN][Pt(mnt)_2]$

$[Et_4N][Pt(mnt)_2]$ (0.525g, 1mmol) and $[PhCNSSN][AsF_6]$ (0.370g, 1 mmol) were placed in one leg of a two limbed reaction vessel and CH_3CN syringed in. A deep black-brown precipitate of $[PhCNSSN][Pt(mnt)_2]$ soon formed and this was stirred for a further two hours to ensure complete reaction. The solubles were filtered off and the dark precipitate pumped to dryness before being transfered to a sealed extractor and washed with CH_2Cl_2 for 4 hours.

Yield:0.558g, 85% F.W. 656.1

i.r.: ν(max): 2218(m), 1600(w), 1395(s), 1300(w), 1175(w), 1165(m), 1100(w), 1053(m), 1030(w), 1000(w), 922(mw), 905(mw), 845(mw), 780(m), 770(w), 720(m), 695(vs), 680(s), 672(m), 550(w), 520(w), 500(mw).

elemental analysis: $C_{15}H_5N_6S_6Pt$

required: C: 27.4% H: 0.8% N: 12.9% S: 29.3% Pt: 29.7%

observed: C: 27.0% H: 0.7% N: 12.7% S: ----- Pt: -----

5.4.4 Preparation of [*p*-Cl.C_6H_4.CNSSN][Pt(mnt)$_2$]

[Bu_4N][Pt(mnt)$_2$] (0.717g, 1mmol) and [*p*-Cl.C_6H_4.CNSSN]Cl (0.405g, 1mmol) were placed in one limb of a two limbed reaction vessel and CH_3CN syringed in. A black precipitate was formed immediately. The material was filtered after 1 hour stirring and then pumped to dryness. The crude product was then extracted with CH_2Cl_2.

Yield:0.601g, 87% F.W. 690.6

i.r.:ν(max): 2200(m), 1585(m), 1410(mw), 1390(s), 1165(m), 1095(s), 1010(w), 920(mw), 840(m), 730(s), 725(m), 720(w), 680(mw), 555(m), 520(w), 500(mw).

elemental analysis:$C_{15}H_4N_6S_6PtCl$

required:

C: 26.1% H: 0.6% N: 12.2% S: 27.8% Pt: 28.25 Cl:5.14%

observed:

C: 26.4% H: 0.7% N: 12.4% S: ----- Pt: ----- Cl:----

5.4.5. Crystal Growth of [(*p*-Cl-C_6H_4.CNSSN)$_2$Cl][Pt(mnt)$_2$]

[Bu_4N][[Pt(mnt)$_2$] (0.075g) was placed in one leg of a dog and [*p*-Cl.C_6H_4.CNSSN]Cl (0.06g) placed in the second limb. CH_3CN (10ml) was syringed into both legs and the vessel inverted so as to allow slow diffusion through the glass sinter (porosity grade3). Over a period of several days large needles of [(*p*-Cl.C_6H_4.CNSSN)$_2$Cl][Pt(mnt)$_2$] formed in the [*p*-Cl.C_6H_4.CNSSN]Cl compartment . The solution was decanted off and the crystals remaining were found to be suitable for X-ray analysis.

5.4.6 Preparation of [(*p*-Cl-C_6H_4.CNSSN)$_2$Cl][Pt(mnt)$_2$]

[Bu_4N][Pt(mnt)$_2$] (0.36g, 0.5mmol) and [*p*-Cl.C_6H_4.CNSSN]Cl (0.405g, 1mmol) were placed in one limb of a two limbed reaction vessel and CH_3CN syringed in. A black precipitate was formed immediately. The material was filtered after 1 hour of stirring and then pumped to dryness. The crude product was then extracted with CH_2Cl_2 for four hours.

Yield: 0.353g, 75% F.W. 941.6

elemental analysis: $C_{22}H_8N_8S_8Cl_3Pt$

required:

C: 28.0% H: 0.9% N: 11.9% S: 27.2% Pt: 20.7% Cl: 11.3%

observed:

C: 28.0% H: 0.9% N: 11.8% S: ----- Pt: ----- Cl: -----

5.4.7 Preparation of $[(PhCNSSN)_2Cl][Pt(mnt)_2]$

$[Bu_4N][Pt(mnt)_2]$ (0.31g, 0.5mmol) and [PhCNSSN]Cl (0.217g, 1mmol) were placed in one limb of a two limbed reaction vessel and CH_3CN syringed in. A black precipitate was formed immediately. The material was filtered after 1 hour of stirring and then pumped to dryness. The crude product was then extracted with CH_2Cl_2 for four hours.

Yield: 0.371g, 85% F.W. 872.6

elemental analysis: $C_{22}H_{10}N_8S_8ClPt$

required:

C: 30.3% H: 1.2% N: 12.8% S: 29.3% Pt: 22.3% Cl: 4.1%

observed:

C: 29.1% H: 1.1% N: 12.4% S: ----- Pt: ----- Cl: -----

5.4.8. Reaction of $[PhCNSSN]_2$ with $Pd(PPh_3)_4$

$[PhCNSSN]_2$ (0.181g, 0.5mmol) and $Pd(PPh_3)_4$ (0.25g) were stirred at room temperature in CH_2Cl_2 (15ml) for 48 hours to yield a deep red-brown solution. The material was then pumped to dryness and transfered to a sealed extractor and extracted with hexane for 48 hours to remove unreacted $[PhCNSSN]_2$ and PPh_3. The deep orange-red product had i.r. data identical with that previously reported[12].

5.4.9. Crystal Growth of $Pd_3(PhCNSSN)_2(PPh_3)_4.2CH_2Cl_2$

$Pd(PPh_3)_4$ (0.080g) was placed in one leg of a dog and $[PhCNSSN]_2$ (0.080g) placed in the second limb. CH_2Cl_2 (10ml) was syringed into both legs and the vessel inverted so as to allow slow diffusion through the glass sinter (porosity grade3). Over a period of several hours large red diamonds of $Pd_3(PhCNSSN)_2(PPh_3)_4$ formed in the $Pd(PPh_3)_4$ compartment . The solution was decanted off and the crystals remaining were found to be suitable for X-ray analysis.

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CHAPTER SIX

THE ATTEMPTED FORMATION OF PHOSPHORUS CONTAINING SULPHUR-NITROGEN HETEROCYCLES

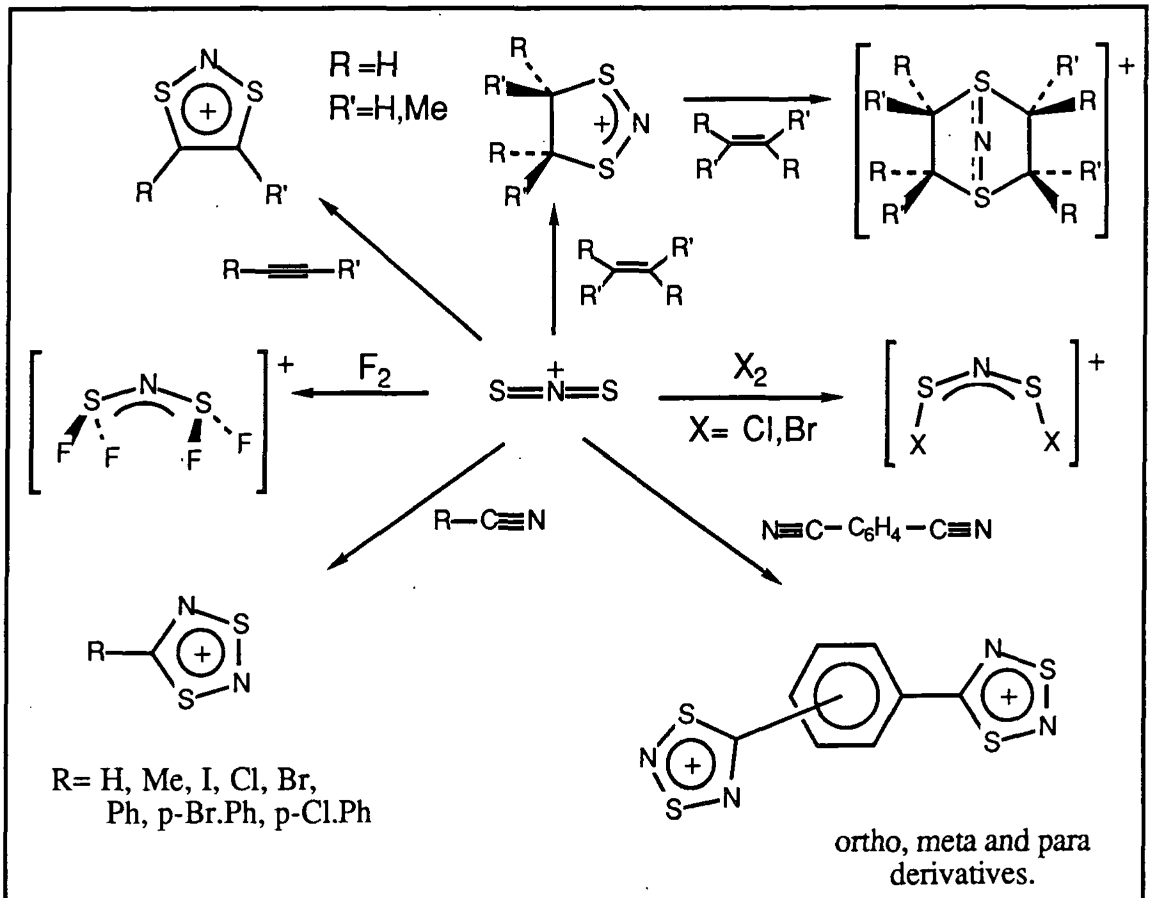
6.1 Introduction

The chemistries of both S/N and P/N rings have been extensively studied[1,2] but the formation and reactivity of small P/S/N containing rings is lesser known[3] although the chemistry of 6-membered P/S/N heterocycles is somewhat better characterised[1]. Therefore as part of some exploratory work into this area two lines of approach were taken:-

A:To synthesise a five membered P/S/N ring from acyclic reagents.

In order to form such a five membered ring two synthetic approaches were used; the [4+2] cycloaddition reaction of SNS^+ with a P=P bond, and a cyclisation route via a condensation reaction:

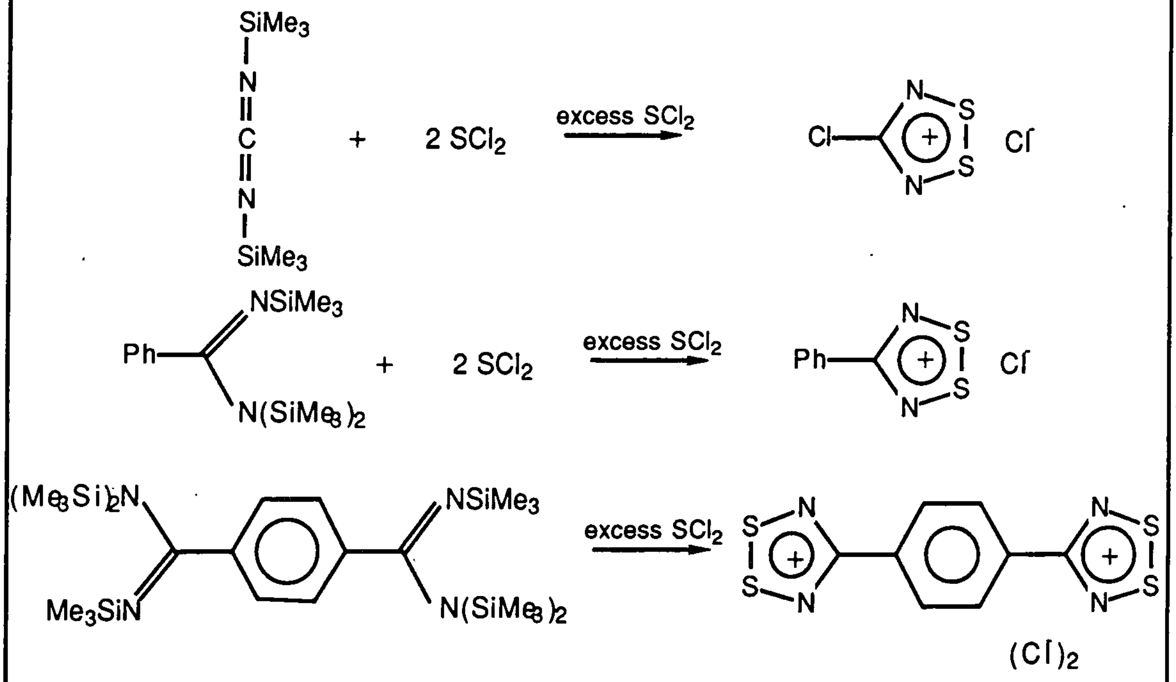
$[SNS][AsF_6]$ has been shown to undergo a variety of cyclisation reactions in high yield; it reacts with a variety of simple alkynes[4], alkenes[5] and nitriles[6], as well as halogens[7] and S=N bonds[8]:



Scheme 1: Some reactions of the SNS^+ reagent.

The reactions occur readily at ambient temperature and the yields are generally high (>75%). However the reactions of the [SNS][AsF_6] synthon with more complex organics,e.g. alkynes with reactive functional group substituents, or with other functional groups (such as R-P=P-R, R-C≡P or R-N=C) have not been studied. Consequently the reaction of [SNS][AsF_6] with ArP=PAr was examined in order to study the reactivity of this 4π reagent further.

The reaction of SCl_2 with molecules containing trimethylsilyl groups has been shown to be a useful route to sulphur-containing heterocycles, as shown below[9-11].



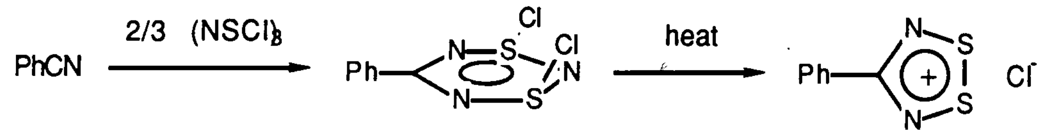
Cyclisation reactions between SCl_2 and trimethylsilyl-containing groups are well known in the formation of CN_2S_2 rings.

Not only will these silyl reagents react with SCl2 but they will also react with metal halides to give some unusual metallocycles[12]. In a similar manner $SeCl_2$, prepared *in situ* from stoichiometric quantities of $SeCl_4$ and Ph_3Sb, can be used to make the analagous selenium derivatives[11].

Consequently the reactions of some simple sulphur systems were carried out with readily available $(Me_3Si)_2NPN(SiMe_3)$ as a potential route to some new P/S/N heterocycles.

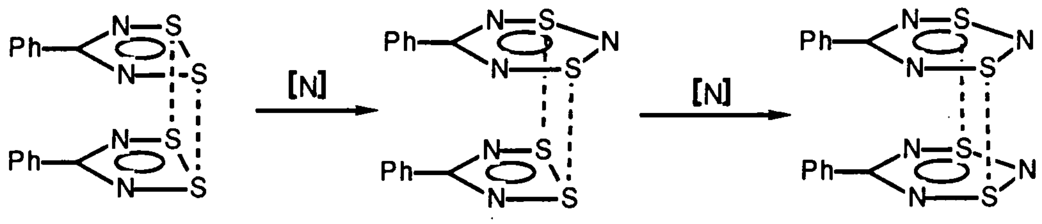
B:To attempt the insertion of a heteroatom into the RCN_2S_2 heterocycle.

$[PhCN_2S_2]Cl$ is formed from the reaction[13] of PhCN with $(NSCl)_3$, conveniently formed *in situ* from NH_4Cl and SCl_2. The reaction has been shown to proceed via a 6-membered $RCN_3S_2Cl_2$ ring[14] which is thermally unstable w.r.t. loss of dinitrogen as shown in the reaction scheme below:



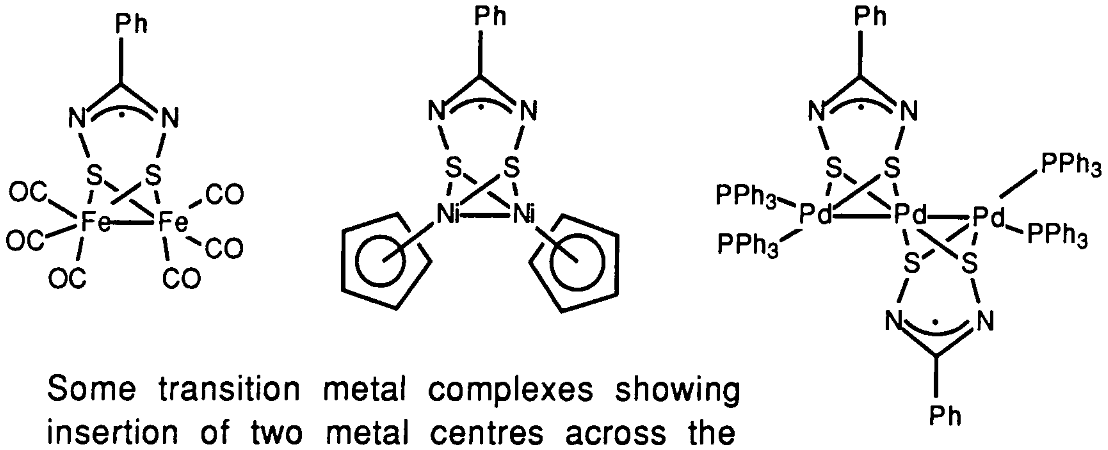
Preparation of 1,2,3,5-dithiadiazolium chloride.

However, $[PhCN_2S_2]Cl$ and its reduced analog, $(PhCN_2S_2)_2$, have been shown to undergo nitrogen insertion, in a low temperature nitrogen D.C. plasma, to give the 6-membered $PhCN_3S_2$ species[15]; a material which can also be prepared by chemical reduction of $PhCN_3S_2Cl_2$. Obviously this removal or insertion of an atom into the SS bond is a reversible process.



Insertion of N into the S-S bond of dithiadiazoles in a nitrogen D.C. plasma also occurs in the associated dithiadiazolium salts.

Phenyl-dithiadiazole, $(PhCN_2S_2)_2$, has also been shown to undergo a variety of reactions with zero-valent transition metals[16-18], with insertion of two metal centres across the S-S bond. A few of these complexes have been identified by single-crystal X-ray analysis and some examples are given over:



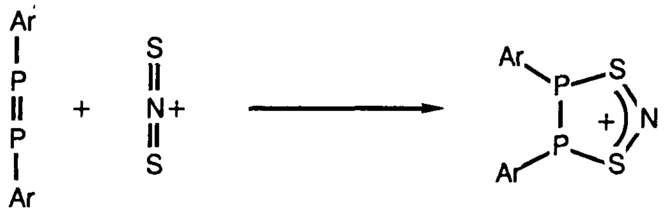
Some transition metal complexes showing insertion of two metal centres across the S-S bond.

The susceptibility of the S-S bond to ring insertion is evident and the reaction of [$PhCN_2S_2$]Cl with some simple phosphorus or nitrogen based systems would be of interest in the synthesis of some 6-membered CN_2S_2P or CN_3S_2 structures.

6.2 Results and Discussion

6.2.1 Reaction of [SNS][AsF_6] with ArP=PAr (Ar= 2,4,6-(^{t}Bu)$_3C_6H_2$-)

The chemistries of both S/N and P/N rings have been studied extensively but P/S/N containing rings are little known. Consequently the [4+2] cycloaddition reaction of ArP=PAr with [SNS][AsF_6] seemed to be a novel approach to the synthesis of a P/S/N heterocycle:



A 1:1 mixture of these two materials in liquid SO_2 produced only an orange, air-sensitive, intractable oil and a white precipitate (identified by i.r. as a hydrolysis product) over a period of 3-4 hours.

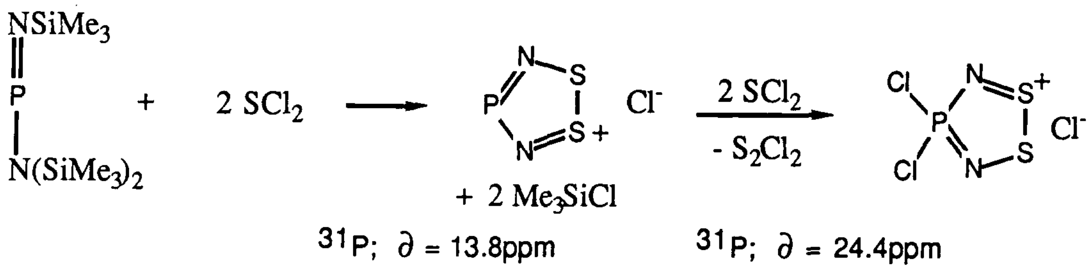
The possibility of oxidation of P^{III} to P^V in the starting material by SO_2 was examined but no observable reaction took place over a similar time period under similar conditions.

^{31}P n.m.r. of the oil showed a variety of products and again none were isolated by agitation with pentane or toluene.

In this reaction, the use of [SNS][AsF_6] was required. This material is highly air-sensitive and was readily hydrolysed under the humid atmosphere of Toulouse. During the course of these experiments samples of [SNS][AsF_6] were observed to deteriorate in a matter of minutes both inside and outside the glove-box. Consequently little emphasis can be placed on these preliminary results and they should be repeated under more rigorous conditions before any conclusions can be made.

6.2.2. Reaction of $(SiMe_3)_2NPN(SiMe_3)$ with SCl_2

This reaction looked to be a convenient route to the proposed[19] PN_2S_2 cations; the phosphorus analogs of the well characterised CN_2S_2, dithiadiazolium, ring systems. A synthetic pathway is laid out in the scheme below:



Slow addition of a dilute solution (typically ca. 10% in CH_2Cl_2) of $(SiMe_3)_2NPN(SiMe_3)$ to an excess of SCl_2 in CH_2Cl_2 at 0°C produced three major products (^{31}P n.m.r., ∂ = 24.4, 13.8, -2.6ppm). Subsequent heating at 50°C for 3 hours and evaporating to an oil yielded one major product, (^{31}P n.m.r., ∂ = 24.6 ppm, c.f. $(NPCl_2)_3$; ^{31}P n.m.r., ∂ = 20ppm.) with no ^{1}H n.m.r.spectrum.

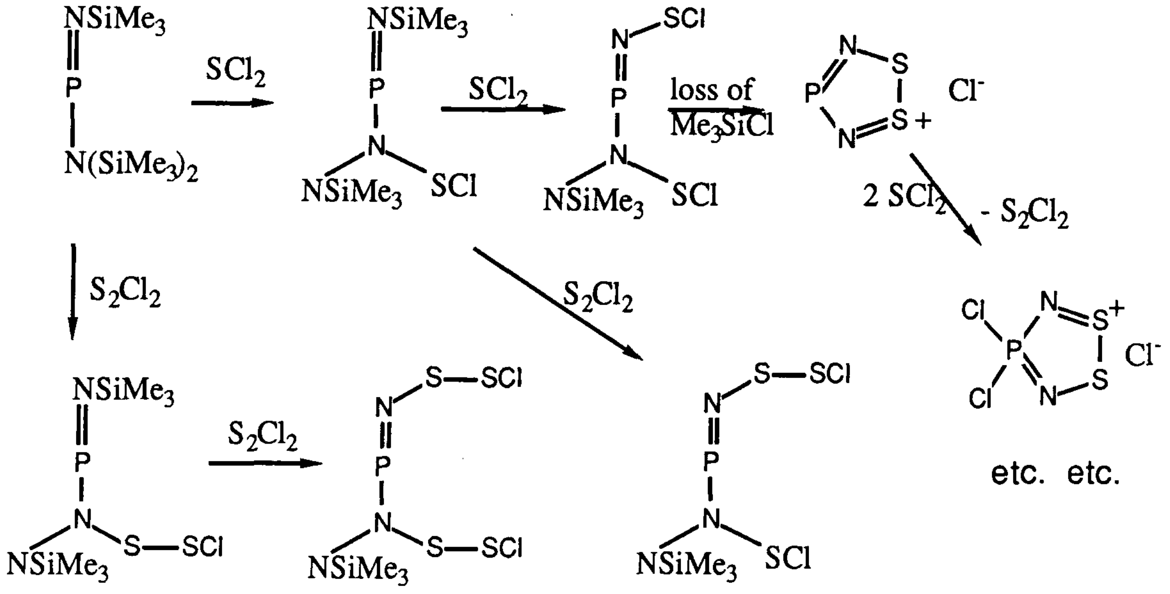
The particularly noticeable reduction in the peak at 13.8 ppm has lead to the tentative suggestion that this may be attributed to the $PN_2S_2^+$ cation. Indeed on either standing in SCl_2 or upon chlorination this peak was seen to be reduced whilst that at ∂=24.4 ppm increased.

The third major product (^{31}P; ∂= -2.6ppm) was unassigned but may be a hydrolysis or oxidation product .

The use of other reaction solvents such as acetonitrile or pentane produced an increase in the minor side products.

On standing or briefly extracting with acetonitrile, small quantities of a highly air-sensitive orange precipitate could be recovered from the crude material which had i.r. and analytical data consistent with the proposed structure; $[Cl_2PN_2S_2]Cl$.

Minor products can be attributed to side reactions involving reaction of S_2Cl_2, always found in SCl_2, with $(Me_3Si)_2NPN(SiMe_3)$ and other similar structures as outlined below:



The vast variety of possible side reactions available produce a number of minor products, but thermolysis would appear to favour the formation of the required $Cl_2PN_2S_2^+Cl^-$ ring.

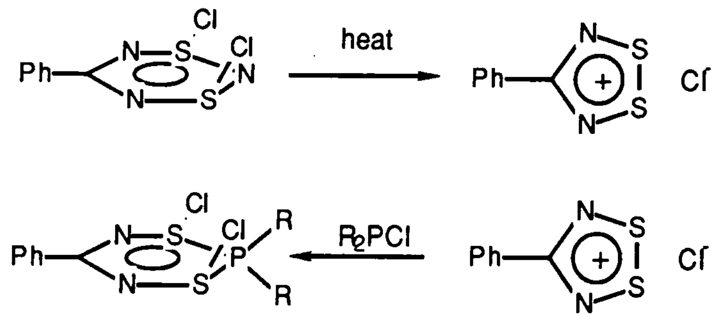
Further heating should allow fragmentation of these materials via S-S bond cleavage to the desired $[Cl_2PN_2S_2]Cl$.

The presence of S_2Cl_2 (b.p. ca. 180°C) ,however, continued to hinder the isolation of the major product (ca. 80% by n.m.r.) but this may perhaps be alleviated in future by fresh distillation of SCl_2 before use.

Interestingly reaction of the crude product with KPF_6 did not appear to yield the desired hexafluorophosphate anion of the phosphorus-containing heterocycle.

6.2.3 Reaction of $[PhCN_2S_2]Cl^-$ with Ph_2PCl and $(^iPr_2N)_2PCl$

Insertion of an R_2P unit into the 5-membered dithiadiazole ring was attempted using both Ph_2PCl and $(^iPr_2N)_2PCl$; chlorination of the two sulphur atoms was assumed to take place along with ring insertion of the phosphorus centre. The reaction being similar to the thermal decomposition[14] of $PhCN_3S_2Cl_2$:



The proposed reaction of R_2PCl with $PhCN_2S_2^+Cl^-$ is similar to the thermal decomposition of $PhCN_3S_2Cl_2$.

In both cases the orange colouration of $[PhCN_2S_2]Cl$ was replaced over a period of ca. 3 h; by either a yellow solution (Ph_2PCl) or a deep red solution ($(^iPr_2N)_2PCl$) on addition of Ph_2PCl or $(^iPr_2N)_2PCl$ respectively.

In the case of $(^iPr_2N)_2PCl$, slow evaporation of the solvent yielded some small red crystalline needles. These needles (^{31}P n.m.r., ∂ =68.59ppm) were highly air sensitive decomposing to a white powder (^{31}P n.m.r., ∂ = 19.46ppm) in a period of minutes in the open atmosphere. A variety of other peaks of weaker intensity were also observed in the ^{31}P n.m.r. spectra.

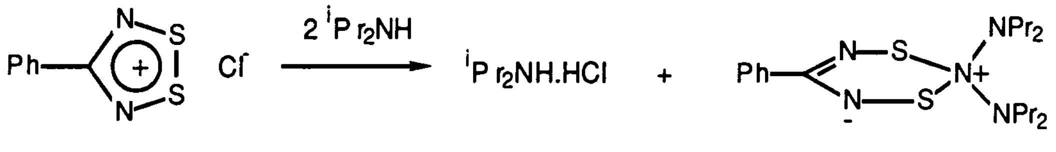
A similar set of ^{31}P n.m.r. signals were observed for the reaction with Ph_2PCl; a major product (^{31}P n.m.r., ∂ = 82.16ppm) decomposing over a period of days with an increase in a second signal (^{31}P n.m.r., ∂= 34.37ppm) . However in this case removal of the solvent yielded only a viscous oil (presumably due to excess Ph_2PCl) from which only small quantities of the white hydrolysis product could be precipitated with toluene. From the colour of the residual solution, it would appear that the initial product is yellow.

The air-sensitivity and highly coloured nature of the $[PhCN_2S_2]Cl/(^iPr_2N)_2PCl$ product is consistent with a $PhCN_2S_2Cl_2PR_2$ structure although further analysis is necessary to determine inequivocably the exact nature of this species.

Addition of KBr to the reaction mixture did not seem to affect the reaction products but did increase the rate of reaction, presumably due to the greater solubility of the bromide salt w.r.t. the chloride starting material.

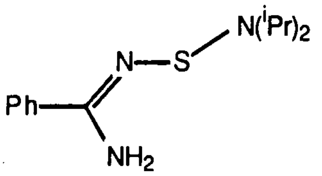
6.2.4 Reaction of $^{i}Pr_2NH$ with $[PhCN_2S_2]Cl$

It was hoped that this reaction may produce the $PhCN_2S_2N(^{i}Pr)_2$ species by elimination of HCl as the $iPr_2NH.HCl$ adduct:



Indeed reaction readily occured in CH_2Cl_2 at room temperature with the evolution of HCl and the formation of a yellow solution. Uncharacteristically, there was no precipitate of the adduct, $^{i}Pr_2NH.HCl$, but evaporation of the solution to dryness,followed by extraction with pentane, yielded insoluble $^{i}Pr_2NH.HCl$ and a soluble yellow microcrystalline product plus trace quantities of $(PhCN_2S_2)_2$ (identified by observation).

The structure of the major, yellow, component is proposed as 6.2.4b below on the basis of ^{1}H n.m.r. and infra-red data:



The reaction mechanism would appear to proceed via chloride abstraction in the first instance (to yield intermediate $(PhCN_2S_2)_2$) followed by attack of further $^{i}Pr_2NH$ and ring opening of the CN_2S_2 ring. In the presence of a slight excess $^{i}Pr_2NH$ negligable quantities of $(PhCN_2S_2)_2$ are observed.

6.3 Conclusions

The reaction of SCl_2 with $Me_3SiNPN(SiMe_3)_2$ would appear to yield the five membered PN_2S_2 heterocycle; initially as $[PN_2S_2]Cl$ and then as the P^V system, $[Cl_2PN_2S_2]Cl$. However further work is required to maximise the yield of this material before it can be fully characterised.

Ph_2PCl , $(^iPr_2N)_2PCl$ and $^iPr_2NH$ all react with [PhCNSSN]Cl. However the reactions are complex and the products incompletely characterised. Initial indications would ,however ,suggest that ring insertion does not take place but rather a ring opening reaction causes the variety of products.

Further work is necessary to determine the reaction pathway(s) in these reactions and this will require more rigorous conditions than those which were available during my enjoyable stay in France.

6.4 EXPERIMENTAL

6.4.1.Reaction of $SNS^+AsF_6^-$ with ArPPAr ($Ar=2,4,6\text{-tri}(^tBu)C_6H_2$-)

Equimolar amounts of $[SNS][AsF_6]$ (0.134g,0.5mmol) and ArPPAr (0.277g, 0.5mmol) were stirred over a period of up to 18 hours in liquid SO_2. During this time there was no observable reaction. Reduction of the volume produced an orange oil over a white precipitate. The white precipitate was isolated by washing with CH_2Cl_2 and identified by infra-red spectroscopy as a hydrolysis product.

white precipitate:

ν(max):3210(s),3051(s),3005(s),2747(s),2647(s),661(s),1598(s),1481(s),1435(s),1354(m),1199(s), 1152(s),1127(s), 1104(w), 1070(w),1026(w), 1000(w), 959(m), 931(w), 860(w), 819(m), 798(m), 783(m), 768(m), 748(m), 729(s), 689(s) , 631(m), 552(m), 533(s), 495(m) , 436(m), 399(w).

^{31}P n.m.r. showed the orange oil to be composed of a mixture of unidentifiable products.

^{31}P n.m.r. (CH_2Cl_2):	142.45 singlet	70.72 multiplet
	110.05 singlet	66.96 multiplet

6.4.2a.Reaction of $[PhCN_2S_2]Cl$ with Ph_2PCl

$[PhCN_2S_2]Cl$ (0.22g, 1mmol) was stirred in CH_2Cl_2 (10ml) at room temperature and an excess of Ph_2PCl (1ml) was added slowly over a period of 5 minutes.Stirring was continued for 1 hour during which time a change in colouration from orange to pale yellow was observed. ^{31}P n.m.r. of the mixture showed unreacted Ph_2PCl and two other major products:

^{31}P n.m.r. (CH_2Cl_2):	**82.16**	**broad**	43.39	Ph_2POCl
	80.43	Ph_2PCl	**34.37**	**singlet**
	47.84	weak	26.93	weak

Reduction of the volume produced a yellow oil and a small quantity of a white precipitate which increased on standing. This material (^{31}P; ∂ = 34.61, 34.46) was identified as a hydrolysis product by ^1H n.m.r. and infra-red:

^1H n.m.r. ($CDCl_3$):	7.334 ppm broad Ph	4.909 ppm broad NH

7.216 ppm broad Ph

infra-red: 3200br (N-H), 2460s (P-O) etc.

The major product (^{31}P, ∂ =82.16) could not be readily isolated, even by heating under vacuum in an attempt to remove Ph_2PCl.

The reaction rate was increased in the presence of KBr which increased the solubility of the $PhCN_2S_2^+$ salt and was increased further in more polar solvents such as acetonitrile.

6.4.2b.Reaction of $[PhCN_2S_2]Cl$ with $(^iPr_2N)PCl$

$[PhCN_2S_2]Cl$ (0.22g, 1 mmol) was stirred in CH_2Cl_2 (10ml) at room temperature and a solution of $(^iPr_2N)_2PCl$ (4 mmol in 10ml CH_2Cl_2) was added over a period of 10 minutes. The system was stirred for a further 4 hours during which time a deep red colouration appeared and the unreacted sparingly soluble $[PhCN_2S_2]Cl$ was observed to disappear. A variety of products were observed by ^{31}P n.m.r. including a small quantity of $(^iPr_2N)_2PCl$ and its oxidation product:

$^{31}P(CH_2Cl_2)$:	169.24	weak	29.33	weak
	136.20	$(^iPr_2N)_2PCl$	**19.46**	**singlet**
	88.67	weak		
	68.59	**singlet**		

Reduction of the volume yielded small crystalline highly air-sensitive needles, which on hydrolysis yielded a white product; analagous to that observed in the $Ph_2PCl/[PhCN_2S_2]Cl$ reaction.

On that basis (and with a slight reduction in the intensity of the 68.59 ppm peak in the ^{31}P n.m.r. and an associated increase in the 19.46ppm peak) the red product was assigned at ^{31}P, ∂ = 68.59 and its hydrolysis product at ^{31}P, ∂ = 19.46ppm.

Again the rate of reaction could be increased by the addition of KBr or by using more polar reaction solvents.

6.4.3. Reaction of $[PhCN_2S_2]Cl$ with iPr_2NH

$[PhCN_2S_2]Cl$ (0.22g,1 mmol) was stirred in CH_2Cl_2 and $^iPr_2NH$ (4mmol in a 10% solution with CH_2Cl_2) was added at room temperature. There was an evolution of dense white fumes but no precipitate of the expected $^iPr_2NH.HCl$ adduct was observed at ambient temperature. However on cooling to -20°C a precipitate formed and the product was filtered off and evaporated to dryness before extraction with pentane.

Pentane extraction yielded a yellow microcrystaline solid plus trace quantities of some red needle-like material which was highly air-sensitive and optical examination showed it to be $(PhCN_2S_2)_2$.

The yellow solid was provisionally identified as $PhC(NH_2)NSN^iPr_2$ by ^1H n.m.r. and infra-red:

^1H n.m.r.($CDCl_3$):	8.055 ppm intensity 2		NH
	7.330 ppm intensity 4	**?**	Ph
	3.009 ppm intensity 2		CH
	1.15 ppm intensity 12		CH_3

i.r. 3289s (N-H) etc.

1201m , 1183m, 1152m (S-N) etc.

6.4.4.Reaction of $Me_3SiNPN(SiMe_3)_2$ with SCl_2

In a typical reaction $Me_3SiNPN(SiMe_3)_2$ (1ml in 9ml of CH_2Cl_2) was added slowly over 1-2 hours to a stirred solution of SCl_2 (4ml) in CH_2Cl_2 (10ml) at -10°C. A dark colouration would form and rapidly disappear again after each dropwise addition to give a final orange solution.

^{31}P n.m.r. showed three major products in the crude material plus a variety of minor imputities:

^{31}P n.m.r. (CH_2Cl_2)	30.41 ppm weak	5.47 ppm weak
crude	**24.14 ppm strong**	**-2.64 ppm strong**
	13.78 ppm strong	-10.17 ppm weak
	8.60 ppm weak	-12.15 ppm weak

After evaporation to an oil no peaks were observed in the proton n.m.r. showing the absence of trimethylsilyl groups.On heating or standing for several days; two major peaks were observed; the other species presumably being reaction intermediates.

^{31}P n.m.r. (CH_2Cl_2)	**24.26 strong**
after heating	**-2.07 strong**

On direct chlorination only one major peak was observed;^{31}P n.m.r.; ∂= + 24.5ppm.

The peaks are therefore assigned as follows:

^{31}P n.m.r. (CH_2Cl_2)	24.26 ppm	$Cl_2PN_2S_2^+Cl^-$
	-2.07 ppm	$PN_2S_2^+Cl^-$

On evaporating the crude reaction mixture a viscous oil was obtained which yielded on standing (or preferably by precipitation with pentane from CH_2Cl_2) small quantities of an orange powder. This powder was extremely air-sensitive but samples suitable for elemental analysis and infra-red were prepared:

elemental analysis: $Cl_3PN_2S_2$

required:

C:----- H: ----- N: 12.1% P: 13.9% S: 27.8% Cl: 46.2

observed:

C:----- H:----- N: 12.04% P: ----- S: ----- Cl: -----

infra-red:

3131s (N-H), 1565m, 1406s, 1250s, 1103m, 971w, 842m, 600w, 559ms, 505s.

Reactions carried out in CH_3CN or pentane produced more by-products under similar conditions. Reaction of excess KPF_6 with the crude product in CH_2Cl_2 appeared to have no effect; no PF_6^- septet was observed in the ^{31}P n.m.r. even after 2 days agitation at ambient temperature.

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APPENDICES

APPENDIX 1

Experimental Techniques

A1.1 General Experimental Techniques.

The dry-box.

Many sulphur-nitrogen containing materials are susceptable to oxidation and/or hydrolysis. Consequently it is necessary for many manipulations to be carried out under an atmosphere of dry nitrogen.

A pressure-regulated Vacuum-Atmospheres glove-box (Type HE43-2) fitted with an HE-493 Dri-Train was used for this purpose.

Bench Manipulations.

All manipulations of moisture- and oxygen-sensitive compounds, hygroscopic materials and solvent distillations were carried out *in vacuo* or under an atmosphere of departmental nitrogen (dried by passing through a P_4O_{10} tower)

Infra-Red Spectra.

These were recorded as nujol mulls between KBr or CsI plates on a Perkin-Elmer 477 or 577 grating spectrophotometer.

Mass Spectra.

Mass spectra were recorded using a VG Analytical 7070E spectrometer using either the electron impact (E.I.) method or the chemical ionisation (C.I.) technique.

Nuclear Magnetic Resonance Spectra.

n.m.r. of ^{19}F, ^{1}H were recorded using a Brüker AC250 machine by Dr. R. Matthews (University of Durham).

Elemental Analysis.

C, H and N analyses were carried out on a Carlo-Erba 1106 Elemental Analyser by Mrs. M. Cocks (University of Durham Chemistry Department).

Sulphur was determined as sulphate and chlorine as chloride, following oxygen flask combustion, by titration against barium perchlorate and silver nitrate respectively.

Platinum, arsenic, aluminium, iron and antimony were determined by decomposition in acid and the concentration measured by atomic absorption spectrophotometry by Mrs. J. Dostal (University Of Durham Chemistry Department).

Glassware.

All glassware was oven-dried at ca.130 ^{o}C for a minimum of 30 minutes and preferably in excess of 4 hours for reaction vessels.

Metal Vacuum Line.

A metal vacuum line was used for the manipulation of SO_2 and AsF_5.

Temperature Regulation.

Low temperatures, in the region -40 ^{o}C to +20 ^{o}C, could be maintained by the use of a Haake F3 digital bath circulator filled with alcohol. Temperatures above 20 ^{o}C were obtained using a waterbath or oilbath.

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 Phillips X-ray generator (type PW1009 130) fitted with an X-ray tube (Cu anode, Ni filter) at 42kV and 16mA.

Providing the image (recorded on Agfa-Gevaert Osray X-ray film) showed the crystal to be single then this was then submitted for a full X-ray structure determination. This was carried out at Newcastle University by Dr. W. Clegg on a Siemens AED2 diffractometer with a graphite monochromator using MoK_α radiation (l=0.71073Å). $\omega-\theta$ scan mode was used for data collection with appropriately chosen scan width and time. Programs (SHELTXL and local software) were run on a Data General Model 30 computer.

Differential Scanning Calorimetry.

Samples for DSC were hermetically seated in aluminium capsules by cold welding. The DSC traces were recorded using a Mettler FP80 control unit coupled to a Mettler FP85 thermal analysis cell and a Fisons y-t chart recorder.

A1.2 More Specialised Techniques.

"The Dog".

This is a two-limbed reaction vessel where each limb is surmounted by a J.Young tap and the two limbs are separated by a medium porosity (grade 3) glass sinter.
See Diagram A1.2.1

The Closed Extractor.

This is based on the soxhlet extraction system where the solvent is heated in the lower bulb and condensed by means of a water-jacket above the medium porosity (grade 3) glass sinter.
See Diagram A1.2.2

Diagram A1.2.1

"The Dog"

1. Reaction Bulb.
2. Glass sinter (usually porosity grade 3).
3. J. Young teflon tap.
4. $^1/4$" ground glass connector.

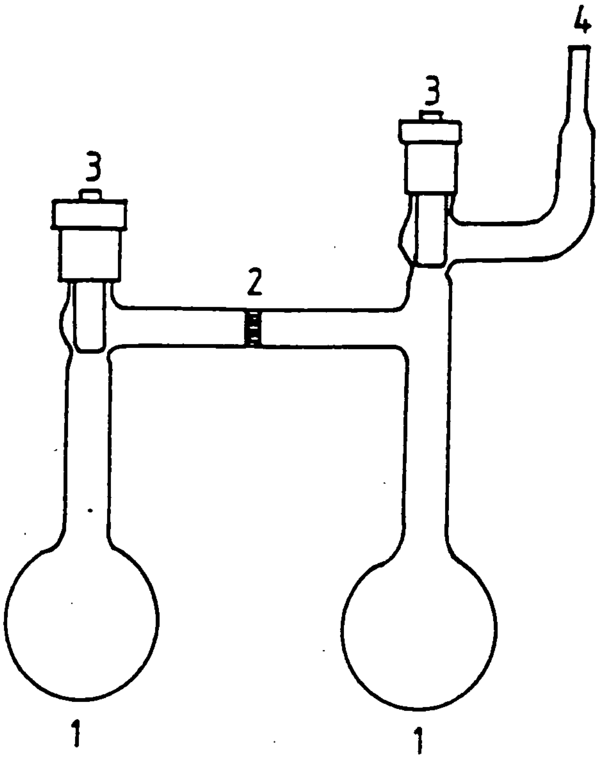
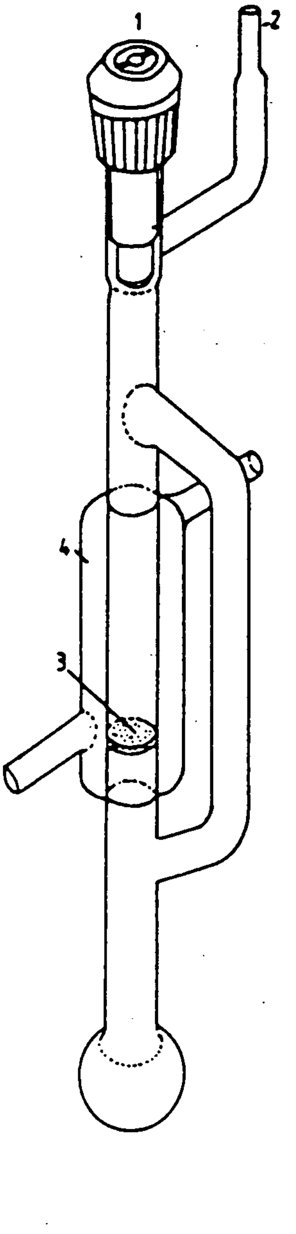


Diagram A1.2.2

The Closed Extractor.

1. J. Young teflon tap.
2. $^1/4$" ground glass connector.
3. Glass sinter (usually porosity grade 3).
4. Cooling jacket.



A1.3 Elecrochemistry.

Cyclic Voltammetry.

This was carried out in a 3-limbed undivided cell with a bulb volume of ca.15ml, designed by Dr. Z.V. Hauptman (University of Durham Chemistry Department). Each limb allowed the use of an electrode via modified Swagelok connectors which also provided an air-tight system. The three probes used were:

A reference electrode
A working electrode
An auxiliary electrode.
See Diagram A1.3.1

The Reference Electrode.

This was designed by Dr. Z.V. Hauptman (University of Durham Chemistry Department) and is of the Ag/Ag$^+$ type previously reported[1]. This electrode maintains a constant potential for many months and is dependant on room temperature and not the temperature of the solution it is in. It can also be used under pressure, e.g. in an SO_2 solution.

See Diagram A1.3.2

The Working Electrode.

The working electrode was designed by Dr. Z.V. Hauptman (University of Durham Chemistry Department) and consists of a polished platinum disk mounted in FEP tubing and connected to a 1/4" steel bar.

The Auxiliary Electrode.

The auxiliary electrode, also designed by Dr. Z.V. Hauptman (University of Durham Chemistry Department) consists of a Platinum coil connected to a monel bar by means of two holes which allow the bar to be slotted through the sheet.

Other Instrumentation.

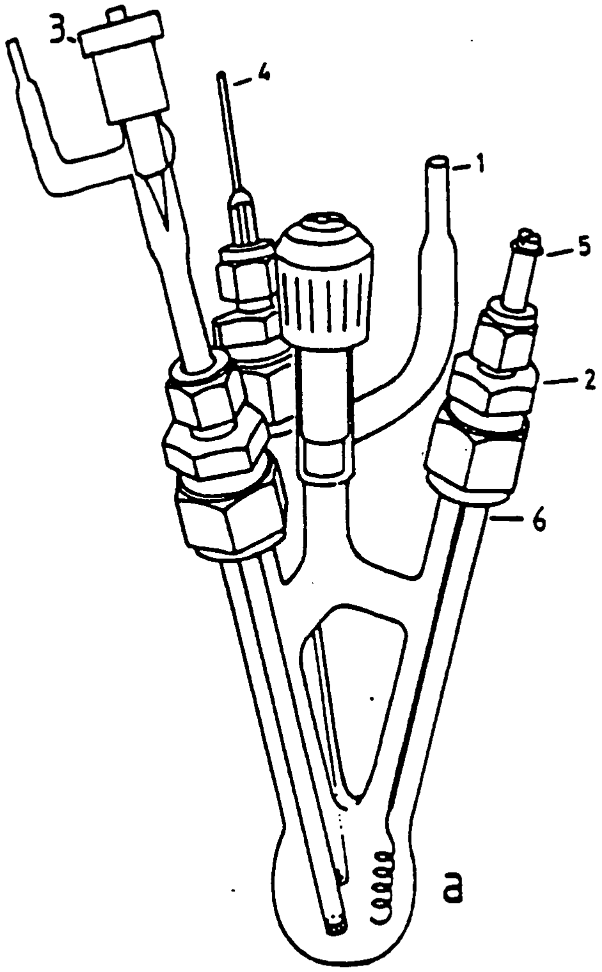
A constant current was maintained by a Ministat precision potentiostat supplied by H.G. Thompson Associates (Newcastle Upon Tyne).

The cyclic voltammograms were recorded using a BioAnalytical Systems potential wave generator (type CV-113) and a Linseis x-y recorder (type LY1710Q).

Diagram A1.3.1

A 3-limbed undivided cell for cyclic voltammetry
(Modified glass to metal Swagelok connectors inset).

1. 1/4" ground glass.
2. Swagelok 1/2" to 1/4" reducing union.
3. Reference Electrode.
4. Working Electrode.
5. Auxiliary Electrode.
6. 1/2" ground glass connector.
7. 1/2" ground glass connector.
8. Compression Nut.
9. Front ferrule.
10. Back ferrule (reversed).
11. PTFE "O" ring.



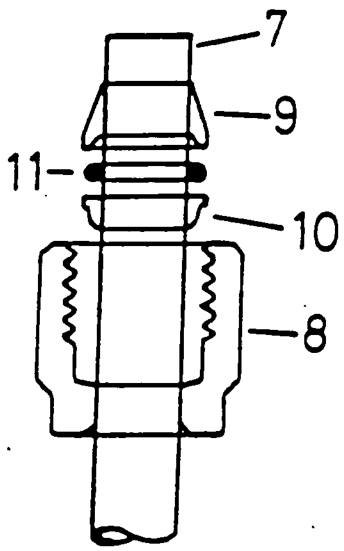
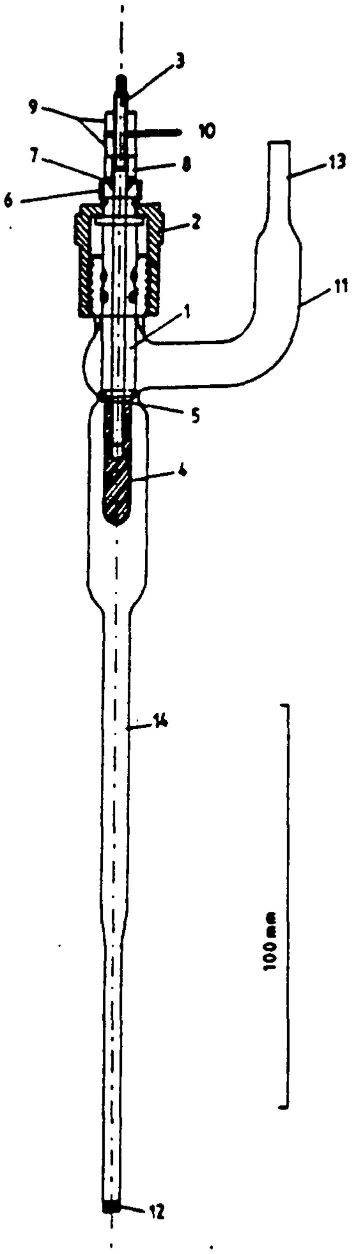


Diagram A1.3.2

Ag/Ag$^+$ reference electrode

1. PTFE stem of J. Young tap.
2. Turning knob of J. Young tap.
3. 1/8" diameter Monel with 5BA thread on both ends, tightly fitting into the central bore of the PTFE stem.
4. Silver Electrode 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.
12. Pyrex sinter (porosity grade 4).
13. 1/4" glass connector.
14. 1/4" o.d. section for air-tight mounting in the cell.



APPENDIX 2
Preparation of Starting Materials.

A2.1 Preparation of Sulphur-Nitrogen Starting Materials.

S_4N_4.

This was prepared by the reaction of S_2Cl_2 and NH_3 according to the literature method[1]. Samples prepared by Dr. S.T. Wait were readily available.

$S_3N_2Cl_2$.

This was prepared from the reaction between NH_4Cl, SCl_2 and S according to the literature method[2].

$(NSCl)_3$.

This was prepared according to the method of Jolly and Maguire[2], by the direct chlorination of $S_3N_2Cl_2$.

1,2-$[PhCN_2S_2]Cl$.

This was prepared from the rection between NH_4Cl, SCl_2 and PhCN according to the literature method[3].

1,2-$[PhCN_2S_2]AsF_6$.

This was prepared [4] from the reaction between $AgAsF_6$ and 1,2-$[PhCN_2S_2]Cl$.

$(1,2\text{-}PhCN_2S_2)_2$.

This was prepared according to the literature method[3] by reduction of 1,2-$[PhCN_2S_2]Cl$ with Zn/Cu couple in THF.

$[SNS][AsF_6]$.

This was prepared according to the literature method[5] from the reaction between S_4N_4, S and AsF_5.

$[SNS][SbCl_6]$.

This was prepared from the reaction between $(NSCl)_3$, S and $SbCl_5$ according to the literature method[6].

$[N(SCl)_2][X]$ where X= $AlCl_4$, $SbCl_6$ or $FeCl_4$.

These salts were prepared according to the literature method[7], from the reaction of $(NSCl)_3$ with SCl_2 and the appropriate Lewis base i.e. $AlCl_3$, $SbCl_5$ and $FeCl_3$ respectively.

$[Pr_4N][S_3N_3]$.

This was prepared according to the literature method[8] but with slight modifications, as previously reported[9].

A2.2 Preparation of Other Starting Materials.

$C_6F_4(CN)_2$

Samples of this material were kindly provided by Dr G.M. Brooke (University of Durham).

C_6F_5CN

Samples were kindly provided by Dr. T. Holmes (University of Durham).

$SbCl_5$

$SbCl_5$ (Aldrich) was distilled and stored under nitrogen before use.

$AgAsF_6$

This was prepared by reacting Ag (powder) with AsF_5 in liquid SO_2. Samples were kindly provided by Dr. Z.V. Hauptman (University of Durham).

4,4'-$NC.C_6H_4.C_6H_4.CN$

Samples of this compound were prepared by R. Plumb (University of Durham).

$[R_4N]_2[Pt(mnt)_2]$

Samples of this material were kindly donated by Dr. S.T. Wait, and also prepared by R. Plumb (University of Durham).

$[R_4N][Pt(mnt)_2]$

Samples of this material were kindly prepared by Dr. S.T. Wait (University of Durham).

***ortho-*, *meta-* and *para-* dicyanobenzene.**

These materials (Aldrich) were recrystallised three times from acetone (or sublimed *in vacuo* by A.W. Luke) before use.

1,3,5,- tricyanobenzene

Initial samples were produced by R. Plumb (University of Durham), later samples were used as provided (Aldrich).

CH_3CN

CH_3CN (HPLC grade, Aldrich) was distilled off CaH_2, passed through a *g*- alumina column and stored under nitrogen before use.

SO_2

SO_2 (BDH) was dried over CaH_2 and then distilled onto P_4O_{10} before use.

CH_2Cl_2

CH_2Cl_2 (BDH) was distilled off CaH_2 and stored under nitrogen before use.

Toluene

This was distilled off lump sodium and stored under nitrogen before use.

Hexane

This was degassed and stored over sodium wire before use.

All other reagents (Aldrich) were used without further purification .

References

1. M. Villena-Blanco and W.L. Jolly, *Inorg. Synth.*, 1977, 9, 98.

2. W.L.Jolly and K.D. Maguire, *Inorg. Synth.*, 1967, 9, 102.

3. A.J.Banister, N.R.M.Smith and R.G.Hey, *J. Chem. Soc. Perkin Trans. I*, 1983,1181.

4. Z.V. Hauptman, unpublished results.

5. A.J. Banister, R.G. Hey, G.K. MacLean and J. Passmore; *Inorg. Chem.*, 1982, 21, 1679.

6. A.J. Banister and A.G. Kendrick; *J. Chem. Soc., Dalton Trans.*, 1987, 1565.

7. G.G. Alange, A.J. Banister and P.J. Dainty; *Inorg. Nucl. Chem. Lett.*, 1979, 15, 175.

8. J.Bojes and T. Chivers, *Inorg. Chem.*, 1978, 17, 318.

9. Simon Wait, Ph.D. Thesis, University of Durham, 1989.

APPENDIX 3

First Year Induction Courses: October 1987

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

Research Colloquia, Seminars and Lectures Organised By the Department of Chemistry

* - Indicates Colloquia attended by the author

During the Period: 1987-1988

BIRCHALL, Prof. D. (I.C.I. Advanced Materials) 25th April 1988
Enviromental Chemistry of Aluminium

*BORER, Dr. K.(U.D.I.R.L.) 18th February 1988
The Brighton Bomb- A Forensic Science View

BOSSONS, L. (Durham Chemistry Teacher's Centre) 16th March 1988
GCSE Practical Assessment

BUTLER, Dr. A.R. (University of St. Andrews) 5th November 1987
Chinese Alchemy

CAIRNS-SMITH, Dr. A. (Glasgow University) 28th January 1988
Clay Minerals and the Origin of Life

DAVIDSON, Dr. J. (Herriot-Watt University) November 1987
Metal Promoted Oligomerisation of Alkynes

* GRADUATE CHEMISTS (N.E. Polytechnics and Universities) 19th April 1988
R.S.C. Graduate Symposium

* GRAHAM, Prof. W.A.G. (University of Alberta, Canada) 3rd March 1988
Rhodium and Iridium Complexes in the Activation of
Carbon-Hydrogen Bonds

* GRAY, Prof. G.W. (University of Hull) 22nd October 1987
Liguid Crystals and their Applications

HARTSHORN, Prof. M.P. (Canterbury Univ., New Zealand) 7th April 1988
Aspects of Ipso-Nitration

*HOWARD, Dr. J. (I.C.I. Wilton) 3rd December 1987
Chemistry of Non-Equilibrium Processess

* LUDMAN, Dr. C.J. (University of Durham) 10th December 1987
Explosives

McDONALD, Dr. W.A. (I.C.I. Wilton) 11th May 1988
Liguid Crystal Polymers

*MAJORAL, Prof. J.-P. (Universite' Paul Sabatier) 8th June 1988
Stabilisation by Complexation of Short-Lived
Phosphorus Species

MAPLETOFT, Mrs. M. (Durham Chem. Teacher's Centre) 4th November 1987
Salter's Chemistry

NIETO DE CASTRO, Prof. C.A. (University of Lisbon) 18th April 1988
Transport Properties of Non-Polar Fluids

OLAH, Prof. G.A. (University of Southern California) 29th June 1988
New Aspects of Hydrocarbon Chemistry

*PALMER, Dr. F. (University of Nottingham) 21st January 1988
Luminescence (Demonstration Lecture)

* PINES, Prof. A. (University of California, Berkeley, U.S.A.) 28th April 1988
Some Magnetic Moments

RICHARDSON, Dr. R. (University of Bristol) 27th April 1988
X-Ray Diffraction from Spread Monolayers

ROBERTS, Mrs. E. (SATRO Officer for Sunderland) 13th April 1988
Talk-Durham Chemistry Teacher's Centre - "Links
Between Industry and Schools

ROBINSON, Dr. J.A. (University of Southampton) Aspects of Antibiotic BioSynthesis	27th April 1988
* ROSE van Mrs. S. (Geological Museum) Chemistry of Volcanoes	29th October 1987
*SAMMES, Prof. P.G. (Smith, Kline and French) Chemical Aspects of Drug Development	19th December 1987
SEEBACH, Prof. D. (E.T.H. Zurich) From Synthetic Methods to Mechanistic Insight	12th November 1987
*SODEAU, Dr. J. (University of East Anglia) Durham Chemistry Teacher's Centre Lecture: "Spray Cans, Smog and Society"	11th May 1988
SWART, Mr. R. M. (I.C.I.) The Interaction of Chemicals with Lipid Bilayers	16th December 1987
* TURNER, Prof. J.J. (University of Nottingham) Catching Organometallic Intermediates	11th February 1988
UNDERHILL, Prof. A. (University of Bangor) Molecular Electronics	25th February 1988
*WILLIAMS, Dr. D.H. (University of Cambridge) Molecular Recognition	26th November 1987
* WINTER, Dr. M.J. (University of Sheffield) Pyrotechnics (Demonstration Lecture)	15th October 1987

During the Period: 1988-1989

ASHMAN, Mr. A. (Durham Chemistry Teacher's Centre) 3rd May 1989
The Chemical Aspects of the National Curriculum

AVEYARD, Dr. R. (University of Hull) 15th March 1989
Surfactants at your Surface

*AYLETT, Prof. B.J. (Queen Mary College, London) 16th February 1989
Silicon-Based Chips: - The Chemist's Contribution

* BALDWIN, Prof. J.E. (University of Oxford) 9th February 1989
Recent Advances in the Bioorganic Chemistry of
Penicillin Biosynthesis

* BALDWIN & WALKER, Drs. R.R. & R.W. (Hull Univ.) 24thNovember 1988
Combustion: Some Burning Problems

BOLLEN, Mr. F. (Durham Chemistry Teacher's Centre) 18th October 1988
Lecture about the use of SATIS in the classroom

BUTLER, Dr. A.R. (St. Andrews University) 15th February 1989
Cancer in Linxiam: The Chemical Dimension

* CADOGAN, Prof. J.I.G. (British Petroleum) 10th November 1988
From Pure Science to Profit

CASEY, Dr. M. (University of Salford) 20th April 1989
Sulphoxides in Stereoselective Synthesis

WATERS & CRESSEY, Mr. D. & T. (Durham Chemistry Teacher's Centre) 1st February 1989
GCSE Chemistry 1988: "A Coroners Report"

CRICH, Dr. D. (University College London) 27th April 1989
Some Novel Uses of Free Radicals in Organic Synthesis

DINGWALL, Dr. J. (Ciba Geigy) 18th October 1988
Phosphorus-containing Amino Acids: Biologically
Active Natural and Unnatural Products

* ERRINGTON, Dr. R.J. (University of Newcastle-upon-Tyne) 1st March 1989
Polymetalate Assembly in Organic Solvents

FREY, Dr. J. (Southampton University) 11th May 1989
Spectroscopy of the Reaction Path: Photodissociation
Raman Spectra of NOCl

*GRADUATE CHEMISTS, (Polytechs and Universities in North East England) 12th April 1989
R.S.C. Symposium for presentation of papers by
postgraduate students.

*HALL, Prof. L.D. (Addenbrooke's Hospital Cambridge) 2nd February 1989
NMR - A Window to the Human Body

HARDGROVE, Dr. G. (St. Olaf College U.S.A.) December 1988
Polymers in the Physical Chemistry Laboratory

HARWOOD, Dr. L.(Oxford University) 25th January 1988
Synthetic Approaches to Phorbols Via Intramolecular
Furan Diels-Alder Reactions: Chemistry under Pressure

JAGER, Dr. C. (Friedrich-Schiller University GDR) 9th December 1988
NMR Investigations of Fast Ion Conductors of the
NASICON Type

* JENNINGS, Prof. R.R. (Warwick University) 26th January 1989
Chemistry of the Masses

*JOHNSON, Dr. B.F.G. (Cambridge University) 23rd February 1989
The Binary Carbonyls

JONES, Dr. M.E. (Durham Chemistry Teacher's Centre) 14th June 1989
Discussion Session on the National Curriculum

JONES, Dr. M.E. (Durham Chemistry Teacher's Centre) 28th June 1989
GCSE and A Level Chemistry 1989

* LUDMAN, Dr. C.J. (Durham University) 18th October 1988
The Energetics of Explosives

MACDOUGALL, Dr. G. (Edingburgh University) 22nd February 1989
Vibrational Spectroscopy of Model Catalytic Systems

MARKO, Dr. I. (Sheffield University) 9th March 1989
Catalytic Asymmetric Osmylation of Olefins

McLAUCHLAN, Dr. K.A. (University of Oxford) 16th November 1988
The Effect of Magnetic Fields on Chemical Reactions

MOODY, Dr. C.J. (Imperial College) 17th May 1989
Reactive Intermediates in Heterocyclic Synthesis

* MORTIMER, Dr. C. (Durham Chemistry Teacher's Centre)14th December 1988
The Hindenberg Disaster - an Excuse for Some Experiments

NICHOLLS, Dr. D. (Durham Chemistry Teacher's Centre) 11th July 1989
Demo. "Liquid Air"

PAETZOLD, Prof. P. (Aachen) 23rd May 1989
Iminoboranes XB=NR: Inorganic Acetylenes

PAGE, Dr. P.C.B. (University of Liverpool) 3rd May 1989
Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides

POLA, Prof. J. (Czechoslovak Academy of Science) 15th June 1989
Carbon Dioxide Laser Induced Chemical Reactions
New Pathwats in Gas-Phase Chemistry

*REES, Prof. C.W. (Imperial College London) 27th October 1988
Some Very Heterocyclic Compounds

REVELL, Mr. P. (Durham Chemistry Teacher's Centre) 14th March 1989
Implementing Broad and Balanced Science 11-16

*SCHMUTZLER, Prof. R. (Techn. Univ. Braunschweig) 6th October 1988
Fluorophosphines Revisited - New Contributions to an Old Theme

* SCHROCK, Prof. R.R. (M.I.T.) 13th February 1989
Recent Advances in Living Metathesis

SINGH, Dr. G. (Teesside Polytechnic) 9th November 1988
Towards Third Generation Anti-Leukaemics

* SNAITH, Dr. R. (Cambridge University) 1st December 1988
Egyptian Mummies: What, Where, Why and How

STIBR, Dr. R. (Czechoslovak Academy of Sciences) 16th May 1989
Recent Developments in the Chemistry of Intermediate-Sited Carboranes

*VON RAGUE SCHLEYER, Prof. P. (Univ. Erlangen Nurnberg) 21st October 1988
The Fruitful Interplay Between Calculational and Experimental Chemistry

* WELLS, Prof. P.B. (Hull University) 10th May 1989
Catalyst Characterisation and Reactivity

During the Period 1989-1990

ASHMAN, Mr.A. (Durham Chemistry Teachers' Centre) 11th October,1989
The National Curriculum - an update

BADYAL, Dr J.P.S. (Durham University) 1st November 1989
Breakthroughs in Heterogeneous Catalysis

BECHER, Dr.J. (Odense University) 13th November 1989
Synthesis of New Macrocyclic Systems using
Heterocyclic Building Blocks.

BERCAW, Prof. J.E. (California Institute of Technology) 10th November 1989
Synthetic and Mechanistic Approaches to
Zieger-Natta Polymerisation of Olefins

BLEASDALE, Dr. C. (Newcastle University) 21st February 1990
The Mode of Action of some anti-tumour Agents

BOLLEN, Mr.F. (Formerly Science Advisor, Newcastle LEA) 27th March 1990
Whats New in Satis, 16-19.

BOWMAN, Prof. J.M. (Emory University) 23rd March 1990
Fitting Experiment with Theory in Ar-OH

BUTLER, Dr. A. (St. Andrews University) 7th December 1989
The Discovery of Penicillin: Facts anf Fancies

CAMPBELL, Mr. W.A. (Durham Chemistry 12th September 1989
Teachers Centre)

Industrial Catalysis- some ideas for the
National Curriculum.

CHADWICK, Dr. P. (Dept. Physics, Durham University) 24th January 1990.
Recent Theories of the Universe (with reference
to National Curriculum Attainment Target 16)

CHEETHAM, Dr.A.K. (Oxford University) 8th March 1990
Chemistry of Zeolite Cages

CLARK, Prof. D.T. (ICI Wilton) 22nd February 1990
Spatially Resolved Chemistry (using Nature's
Paradigm in the Advanced Materials Arena).

COLE-HAMILTON, Prof. D.J. (St. Andrews University) 29th November 1989
New Polymers from Homogeneous Catalysis

*CROMBIE, Prof. L. (Nottingham University) 15th February 1990
The Chemistry of Cannabis and Khat

DYER, Dr. U. (Glaxo) 31st January 1990
Synthesis and Conformation of C-Glycosides

FLORIANI, Prof. C. (Lausanne Univ., Switzerland) 25th October 1989
Molecular Aggregates- A Bridge Between
Homogeneous and Heterogeneous Systems

GERMAN, Prof. L.S. (USSR Academy of Sciences, Moscow) 9th July 1990
New Syntheses in Fluoroaliphatic Chemistry:
Recent Advances in the Chemistry of Fluorinated Oxiranes.

GRAHAM, Dr.D. (B.P. Research Centre) 4th December 1989
How Proteins Absorb to Interfaces

*GREENWOOD, Prof. N.N. (University of Leeds) 9th November 1989
Novel Cluster Geometries in Metalloborane
Chemistry

HOLLOWAY, Prof. J.H. (University of Leicester) 1st February 1990
Noble Gas Chemistry

HUGHES, Dr.M.N. (King's College, London) 30th November 1989
A Bug's Eye View of the Periodic Table

HUISGEN, Prof. R. (Universität München) 15th December 1989
Recent Mechanistic Studies of [2+2] Additions

IDDON, Dr.B. (University of Salford) 15th December 1989
Schools' Christmas Lecture-
The Magic of Chemistry

JONES, Dr.M.E. (Durham University Teachers Centre) 3rd July 1990
The Chemistry A Level 1990

JONES, Dr. M.E. (Durham University Teachers Centre) 21st November 1989
GCSE and Dual Award Science as a Starting Point
for A level Chemistry- How Suitable are They?

JOHNSON, Dr. G.A.L. (Durham University Teachers Centre) 8th February 1990
Some Aspects of Local Geology in the National Science
Curriculum (Attainment Target 9)

KLINOWSKI, Dr.J. (Cambridge University) 13th December 1989
Solid State NMR Studies of Zeolite Catalysts

LANCASTER, Rev. R. (Kimbolton Fireworks) 8th February 1990
Fireworks - Principles and Practice.

LUNAZZI, Prof. L. (University of Bologna) 12th February 1990
Application of Dynamic NMR to the Study of
Conformational Enantiomerism

PALMER, Dr. F. (Nottingham University) 17th October 1989
Thunder and Lightning

PARKER, Dr. D. (Durham University) 16th November 1989
Macrocycles, Drugs and Rock'N'Roll

PERUTZ, Dr. R.N. (York University) 24th January 1990
Plotting the Course of C-H Activations with
Organometallics.

PLATONOV, Prof. V.E. (USSR Academy of Sciences, Novorsibirsk)9th July 1990
Polyfluoroindanes: Synthesis and Transformation

POWELL, Dr.R.L. (ICI) 6th December 1989
The Development of CFC Replacements

POWIS, Dr. I. (Nottingham University) 21st March 1990
Spinning off in a Huff: Photodissociation
of Methyl Iodide

RICHARDS, Mr. C. (Health and Safety Exec., Newcastle) 28th February 1990
Safety in School Science Laboratories and COSHH

ROZHKOV, Prof. I.N. (USSR Academy of Sciences, Moscow) 9th July 1990
Reactivity of Perfluoroalkyl Bromides

STODDART, Dr.J.F. (Sheffield University) 1st March 1990
Molecular Lego

SUTTON, Prof. D. (Simon Fraser Univ., Vancouver B.C.) 14th February 1990
Synthesis and Applications of Dinitrogen and Diazo
Compounds of Rhenium and Iridium.

THOMAS, Dr.R.K. (Oxford University) 28th February 1990
Neutron Reflectometry from Surfaces

THOMPSON, Dr. D.P. (Newcastle University) 7th February 1990
The Role of Nitrogen in Extending Silicate
Crystal Chemistry.

APPENDIX 5

The Crystal Structure of [PhCNSNS][AsF_6]

A5.1 Crystal Growth

Crystals of [PhCNSNS][AsF_6] were grown by slow exhaustive extraction of purified [PhCNSNS][AsF_6] with CH_2Cl_2 in a sealed extractor. Crystals suitable for a full X-ray analysis were picked in the open atmosphere and mounted in 0.2 and 0.3 mm Lindeman capillaries.

A5.2 Crystal Structure

An oscillation photograph showed the crystal to be single and it was analysed by Dr. C.E.F. Rickard (Queen Mary and Westfield College). The results of this analysis are shown in Tables A5.2.1-4 and Figures A5.2.5-6:

A5.2.1 Crystal Data

Stoichiometry		$C_7H_5AsF_6N_2S_2$		Mol.Wt.	370.17
Crystal System		Monoclinic		Space Group	$P2_1/a$
a	10.824(5)	b	8.287(2)	c	13.599(3)Å
α	90	β	106.32(4)	γ	90°
Z	4				
V	1170.66 Å^3				
D	2.10 g/cm^3				
R	0.05				

A5.2.2 Bond Lengths (Å) in [PhCNSNS][AsF_6]

F(1)-As	1.705(7)	F(2)-As	1.699(6)	F(3)-As	1.683(7)
F(4)-As	1.673(7)	F(5)-As	1.669(7)	F(6)-As	1.670(8)
N(1)-S(1)	1.576(7)	N(2)-S(1)	1.561(8)	N(2)-S(2)	1.596(8)
C(1)-S(2)	1.732(8)	C(1)-N(1)	1.336(9)	C(2)-C(1)	1.445(9)
C(3)-C(2)	1.386(9)	C(7)-C(2)	1.370(10)	C(4)-C(3)	1.378(10)
C(5)-C(4)	1.362(11)	C(6)-C(5)	1.387(12)	C(7)-C(6)	1.399(11)

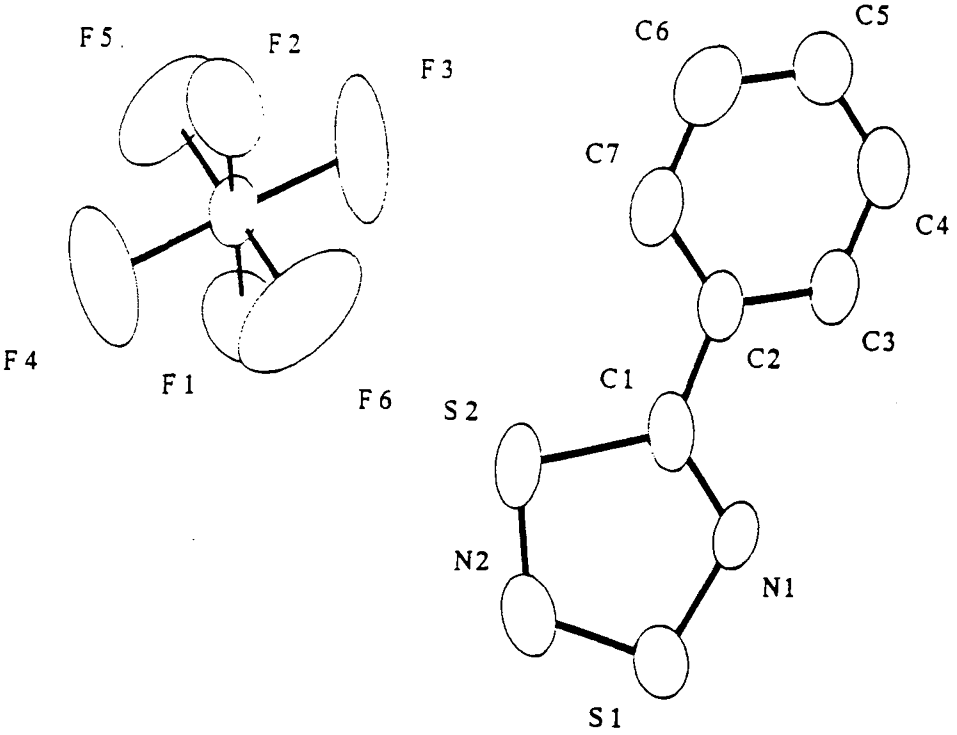
A5.2.3 Bond Angles (°) in [PhCNSNS][AsF_6]

F(2)-As-F(1)	178.7(3)	F(3)-As-F(1)	88.7(4)
F(3)-As-F(2)	90.8(4)	F(4)-As-F(1)	90.4(4)
F(4)-As-F(2)	90.1(4)	F(4)-As-F(3)	178.5(4)
F(5)-As-F(1)	89.1(4)	F(5)-As-F(2)	92.0(4)
F(5)-As-F(3)	88.5(5)	F(5)-As-F(4)	92.6(5)
F(6)-As-F(1)	90.6(4)	F(6)-As-F(2)	88.3(4)
F(6)-As-F(3)	90.1(5)	F(6)-As-F(4)	88.8(5)
F(6)-As-F(5)	178.5(4)	N(2)-S(1)-N(1)	103.3(4)
C(1)-S(2)-N(2)	97.4(4)	C(1)-S(1)-N(1)	114.3(5)
S(2)-N(2)-S(1)	113.1(4)	N(1)-C(1)-S(2)	111.9(6)
C(2)-C(1)-S(2)	124.0(6)	C(2)-C(1)-N(1)	124.1(6)
C(3)-C(2)-C(1)	118.4(7)	C(7)-C(2)-C(1)	120.9(7)
C(7)-C(2)-C(3)	120.8(7)	C(4)-C(3)-C(2)	118.7(8)
C(5)-C(4)-C(3)	121.6(8)	C(6)-C(5)-C(4)	119.9(8)
C(7)-C(6)-C(5)	119.2(8)	C(6)-C(7)-C(2)	119.8(8)

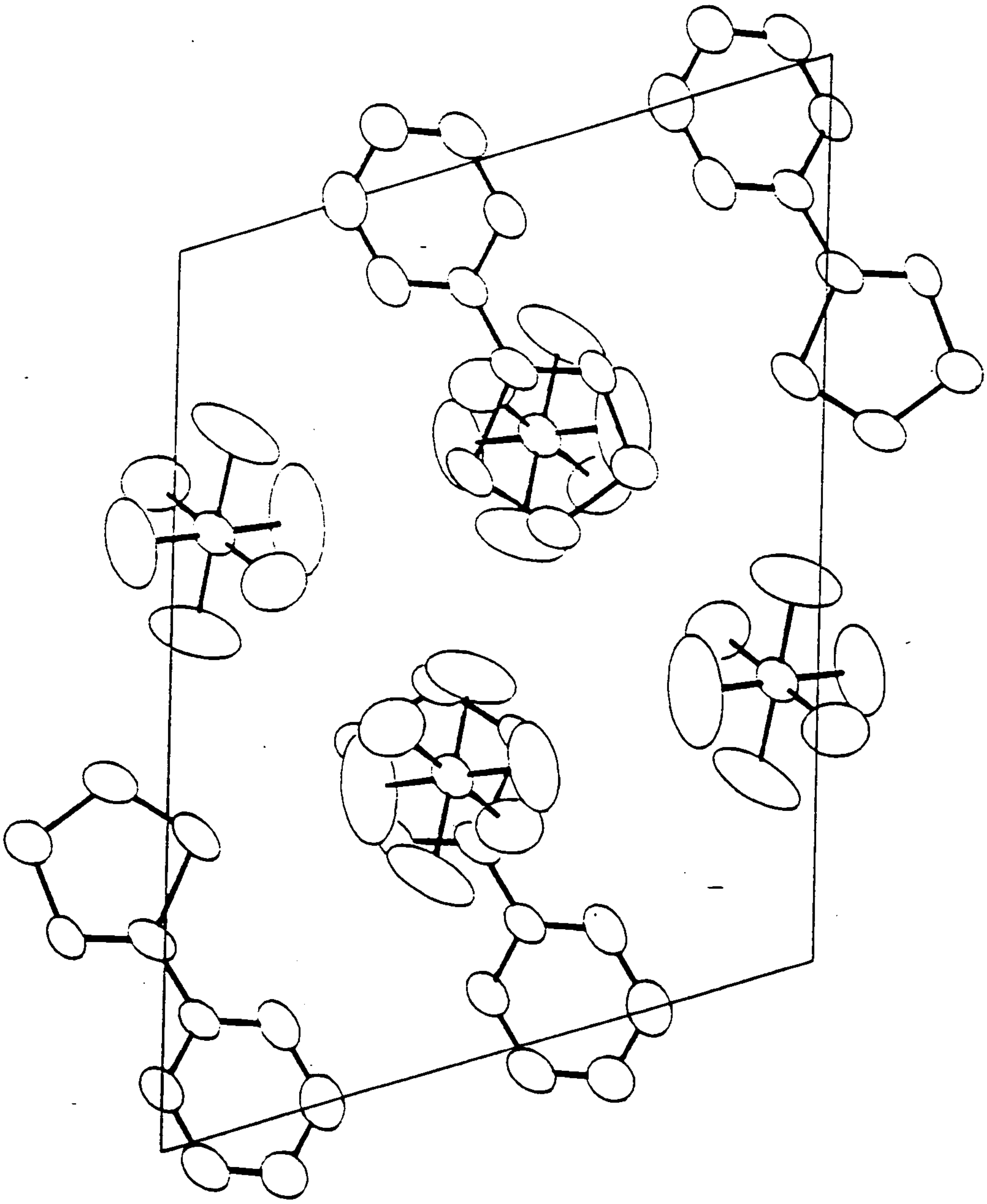
A5.2.4 Intermolecular Contacts (Å) in [PhCNSNS][AsF$_6$]

S(1)-F(1a)	3.020
S(2)-F(1b)	3.710
S(2)-F(2c)	3.131
S(1)-F(4a)	3.221
S(1)-F(5d)	3.000
C(1)-F(5b)	3.318
N(2)-F(1a)	3.211
N(1)-F(1b)	3.269
C(1)-F(2c)	3.135
S(2)-F(4c)	3.560
N(1)-F(5d)	3.050
S(1)-F(6a)	3.667
S(1)-F(1b)	3.078
N(2)-F(1b)	3.318
C(3)-F(3b)	3.228
N(2)-F(4c)	3.262
S(2)-F(5b)	3.263
S(1)-F(6c)	3.154

A5.2.5 [PhCNSNS][AsF$_6$]; Cation-Anion Pair.



A5.2.6 [PhCNSNS][AsF_6]; Molecular Packing.



" ...I put the dusty volume back on the library shelf and went home very late, not optimistic about the world our children will inherit but with a renewed conviction that science could solve many of the problems facing us, if only those who control the purse strings would relax their vice-like grip"

New Scientist (24.6.89).