Bis- and Tris-(1,2,3,4-Dithiadiazolium) salts and related radicals

Luke, Anthony W.

Bis- and Tris-(1,3,2,4-Dithiadiazolium) Salts and Related Radicals

Anthony W. Luke

Graduate Society

University of Durham

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Nitrogen is nitrogen, it passes miraculously from the air into plants, from these into animals, and from animals into us; when its function in our body is exhausted, we eliminate it, but it still remains nitrogen, aseptic, innocent.

...maybe the priest was right too, when he said that in Hell there is a smell of sulphur; after all, even the dogs don't like it, everyone knows that.

Primo Levi, *The Periodic Table*

Clean this mess up 'else we'll all end up in jail,

Those test-tubes and the scale,

Just get it all outa here...

Is there gas in the car....?

Steely Dan, *Kid Charlemagne* (ABC Records)

ABSTRACT

Using the cycloaddition of [SNS][AsF_6] to nitriles a variety of 5-substituted-1,3,2,4-dithiadiazolium salts (salts containing the -CNSNS cationic ring) were prepared : *mono*-(1,3,2,4-dithiadiazolium) salts from mononitriles, *bis*-(1,3,2,4-dithiadiazolium) salts from dinitriles and 1,3,5-*tris*-(1,3,2,4-dithiadiazolium) salts from 1,3,5-tricyanobenzene.

salts of these dithiadiazolium cations with other anions were prepared by simple anion metathesis reactions.

Bis- and *tris*-(1,3,2,4-dithiadiazolium) salts were reduced to give stable *bis*- and *tris*-(1,3,2,4-dithiadiazolyl) radicals which were studied by electron spin resonance spectroscopy (ESR). These multiradicals were formed as dark, sparingly soluble powders upon reduction of a dithiadiazolium salt.

Bis- and *tris*-(1,3,2,4-dithiadiazolyl)s were shown by ESR to undergo rearrangement in solution to the more stable 1,2,3,5-dithiadiazolyl isomer (containing the -CNSSN ring).

Preparation of the 1,3,5-*tris*-(1,3,2,4-dithiadiazolium) iodide [C_6H_3-1,3,5-$(CNSNS)_3$][$I]_3$ in an ESR tube gave a series of ESR spectra similar to those observed for dithiadiazolyl radicals.

Reduction of the 1,3,5-*tris*-(1,3,2,4-dithiadiazolium) cation [C_6H_3-1,3,5-$(CNSNS)_3]^{3+}$ gave a material identified by elemental analysis as 1,3,5-*tris*-(dithiadiazolyl). Reoxidation of this material with bromine gave a *tris*-(tribromide) salt [C_6H_3-1,3,5-$(CN_2S_2)_3$][$Br_3]_3$. In the same way, reoxidation of the *bis*-(dithiadiazolyl) [C_6H_4-1,3-$(CN_2S_2)_2$] gave a *bis*-(tribromide) [C_6H_4-1,3-$(CN_2S)_2$][$Br_3]_2$.

1,3,2,4-dithiadiazolium cations were found to initiate the cationic ring-opening polymerization of tetrahydrofuran, and samples of high molecular weight *poly*(THF) with low polydispersity initiated by [PhCNSNS][AsF_6] and [C_6H_3-1,3,5-$(CNSNS)_3$][$AsF_6]_3$ were prepared and studied.

The reaction of 1,3,2,4-dithiadiazolium salts with water was studied, and it was shown by infrared and NMR spectroscopy that one dithiadiazolium ring reacts with two equivalents of water, with a 1:1 reaction compound not being formed.

The 1,2,3,5-dithiadiazolyl dimer $(PhCNSSN)_2$ was found to dechlorinate the activated quinone o-chloranil to give [PhCNSSN]Cl and a quinone coupling product.

ACKNOWLEDGEMENTS

This thesis would not have been possible without the support of the following people. My sincere and heartfelt thanks go to all of them.

My supervisor, Dr. Arthur J. Banister, for his guidance, encouragement, boundless enthusiasm and friendship.

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MEMORANDUM

The work described in this thesis was carried out by me, in the Department of Chemistry at the University of Durham between October 1988 and July 1991. I declare that this work has not been submitted previously for a degree at this or any other University. This thesis is a report of my own original work, except where acknowledged by reference. The copyright of this thesis rests with the author. No quotation should be published without his written consent, and information derived from it should be acknowledged. Material from this thesis has been or will be included in the following publications:

"Dithiadiazolium Salts as Initiators for the Cationic Ring-Opening Polymerization of Tetrahydrofuran" : Banister, A.J. and Luke, A.W., *J. Polym. Sci., A : Polym. Chem.*, **30**, 2653 (1992)

"Solid-State Rearrangements of Some 1,3,2,4-Dithiadiazoles to their 1,2,3,5-Analogues" : Aherne, C., Banister, A.J., Luke, A.W., Rawson, J.M., and Whitehead, R.J., *J. Chem. Soc., Dalton Trans.*, 1277 (1992)

"Some Electrochemical Studies of Dithiadiazolylium Cations : Evidence for the Dithiadiazolide Anion " : Aherne, C.M., Banister, A.J., Gorrell, I.B., Luke, A.W., Hansford, M.I., Hauptman, Z.V. and Rawson, J.M., *J. Chem. Soc., Dalton Trans.*, accepted for publication in 1993

"The Crystal Structure of [*p*-Cl-C_6H_4-CNSSN][AsF_6]" : Hursthouse, M.B., Rickard, C.E.F., Banister, A.J., Luke, A.W. and Rawson, J.M., *Acta Crystallogr., C,* submitted for publication

"Spin-Spin Exchange Phenomena in Multi-Dithiadiazolyl Radicals : Evidence for Intermolecular Exchange" : Banister, A.J., Luke, A.W., Rawson, J.M., Whitehead, R.J. and Singer, R., manuscript in preparation.

"1,3,5-Benzene-*tris*-(1,3,2,4-Dithiadiazolylium) Cations and The Analogous 1,3,5-Benzene-*tris*-(1,3,2,4-Dithiadiazolyl) Radical" : Banister, A.J., Luke, A.W. and Whitehead, R.J., manuscript in preparation.

"Intramolecular Through-Space N-F Coupling in Fluorinated 1,3,2,4-Dithiadiazolyl Radicals" : Banister, A.J., Luke, A.W., Rawson, J.M., Whitehead, R.J. and Singer, R.J., manuscript in preparation

"The Use of Phenyl Dithiadiazole as a Coupling Agent in the formation of C-C, Si-Si and P-P Bonds via Halogen Abstraction" : Banister, A.J., Gorrell, I.B. and Luke, A.W., manuscript in preparation

"Some Synthetic and Structural Aspects of Dithiadiazoles, RCN_2S_2, and Related Compounds" : A review of the work of A.J. Banister's Group, including a number of pieces of work from this thesis.
Banister, A.J. and Rawson, J.M., in "The Chemistry of Inorganic Ring Systems", Steudel, R. (Ed.), Studies in Inorganic Chemistry, Vol. 14, Elsevier (1992)

This thesis is dedicated to my Mam, and to the memory

of my Dad, Adrian Luke.

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CHAPTER 1 : INTRODUCTION.

CN_2S_2 HETEROCYCLES : A REVIEW

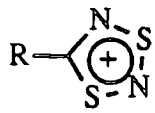
1.1 Background

This chapter is a brief review of the literature since 1977 on the subject of CN_2S_2 heterocycles. These ring systems are a relatively new area of study, but an area of increasing interest because of their potential as new synthetic reagents, pharmaceuticals, polymerization initiators and precursors to novel low - dimensional materials.

Compounds analogous to CN_2S_2 heterocycles, but containing selenium in place of sulphur, have recently been synthesised and are of great interest. These compounds are included in the scope of this review.

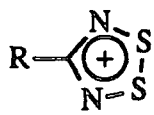
There is currently no universally accepted nomenclature system for the heterocyclic ring systems described in this work. The nomenclature system used in this review and throughout this work is as follows : cationic species are termed **dithiadiazolium** compounds, neutral closed shell (*ie* non-radical) compounds are termed **dithiadiazoles**, and free radicals containing the CN_2S_2 ring are termed **dithiadiazolyls**.

The most common occurrence of the CN_2S_2 ring is the family of dithiadiazolium salts $[RCN_2S_2]^+$, and these are known in two isomeric forms ; 5-substituted-1,3,2,4-dithiadiazolium salts **1**, and 4-substituted-1,2,3,5-dithiadiazolium salts **2**.



5-substituted 1,3,2,4-dithiadiazolium salt

1



4-substituted 1,2,3,5 dithiadiazolium salt

2

In the following section the syntheses of these salts are discussed. 4-Substituted-1,2,3,5-dithiadiazolium salts **2** will be dealt with first, since they were the first of the two isomers to be reported.

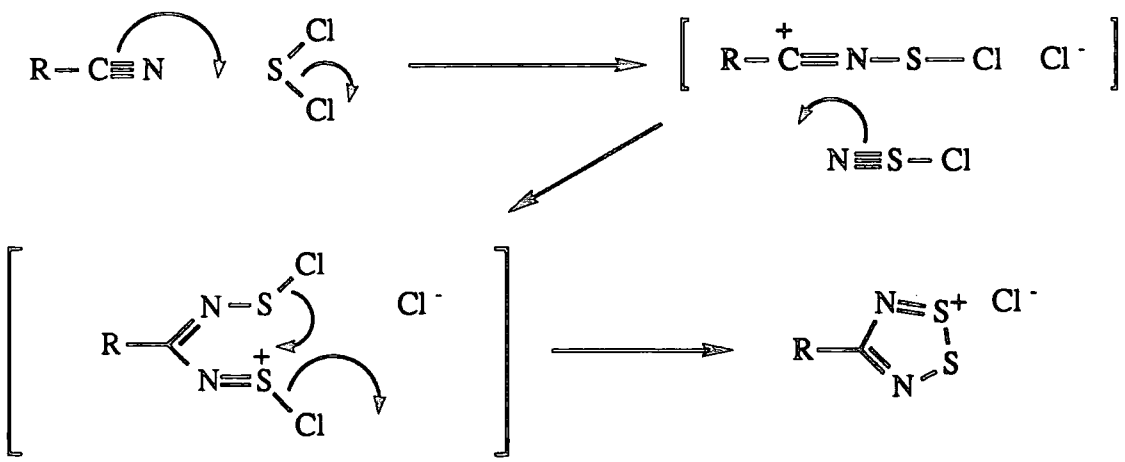
1.2 Synthesis

1.2.1. 4-Substituted-1,2,3,5-Dithiadiazolium Salts

1.2.1.a). From $(NSCl)_3$ and nitriles

The reaction of *cyclo*-trichlorotrithiatriazine $(NSCl)_3$ and nitriles was the first reported[1,2] synthesis of the 1,2,3,5-dithiadiazolium cation, in 1977. (A synthesis dating back to 1969 was reported[3] in a paper published in 1982[4]). Dithiadiazolium chlorides are produced in low to moderate yield.

A variation on this method involves the *in situ* generation of monomeric NSCl from NH_4Cl and SCl_2[2], and the synthesis may be further improved[5] by carrying out the reaction under an atmosphere of chlorine to minimise the formation of the side product $S_3N_2Cl_2$. The mechanism of the reaction involves the dissociation of $(NSCl)_3$ into the monomer NSCl on warming[6]. The monomer is then attacked by the more nucleophilic nitrile group. This is shown in Scheme 1.2.1.



Scheme 1.2.1

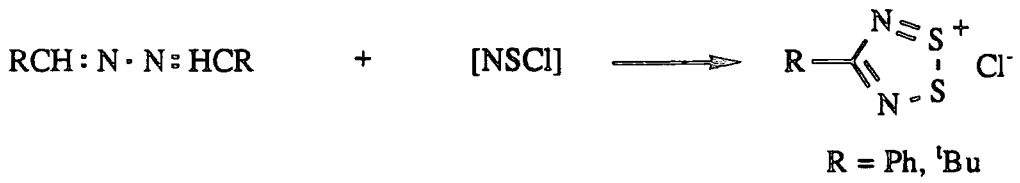
Preparation of 1,2,3,5-dithiadiazolium salts from NH_4Cl, SCl_2 and nitriles

This method is a good medium scale (5 - 35g) synthesis of dithiadiazolium chlorides. Salts of other anions are accessible by metathesis, with for example $AgAsF_6$ to yield hexafluoroarsenates, which are generally more soluble and hence synthetically useful.

1,2,3,5-Dithiadiazolium salts have also been prepared from $(NSCl)_3$ and olefins[2], for example tetrachloroethylene to give 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride.

1.2.1.b). From $(NSCl)_3$ and RCH=N-N=CHR

Cyclo-trichlorotrithiatriazene reacts with aldazines (RCH=N-N=CHR) to give 1,2,3,5-dithiadiazolium chlorides with alkyl or aryl substituents[7] as shown in Scheme 1.2.2 below.



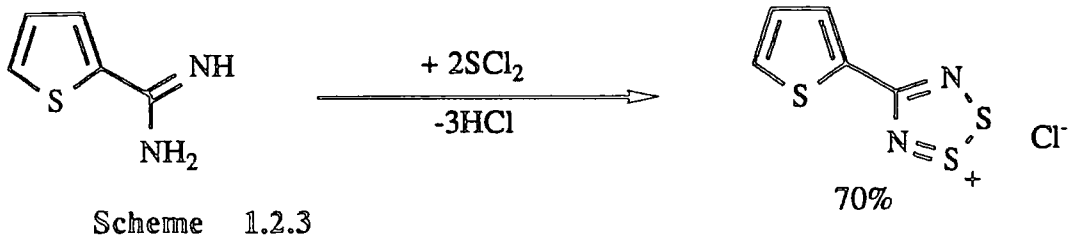
R = Ph, ^{t}Bu

Scheme 1.2.2
Preparation of 1,2,3,5-Dithiadiazolium Salts from Aldazines and $(NSCl)_3$

Cyclo-trichlorotrithiatriazene also reacts with trichloroacetic anhydride, giving a mixture of products including 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride[8].

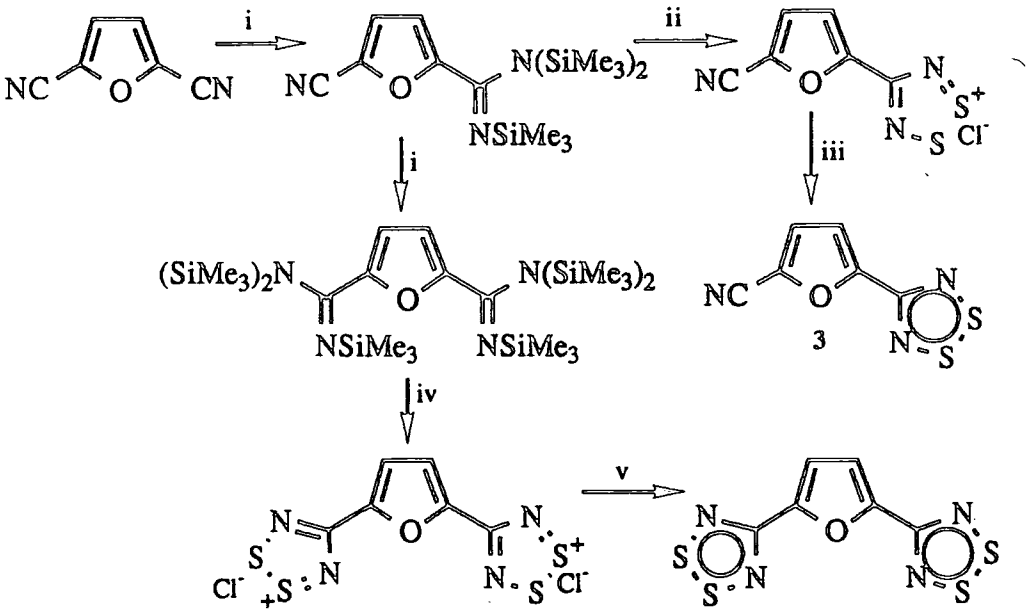
1.2.1.c). From amidines or amidinium salts

Amidines and amidinium salts, including silyl derivatives, have been used in conjunction with a base to effect the high yield synthesis of a variety of 1,2,3,5-dithiadiazolium and diselenadiazolium salts[2,9-15], both *mono*- and *multi*functional . Particularly interesting are the salts with heterocyclic substituents,e.g.2-thienyl[9,10] as shown in Scheme 1.2.3.



Scheme 1.2.3
Preparation of 1,2,3,5-Dithiadiazolium Salts from Amidines and SCl_2

Recent work by Oakley et al. using this synthetic method has resulted in the preparation of stable *mono*- and *bis*-(1,2,3,5-dithiadiazolyl)s with a furanyl central group[16]. These compounds have been studied by X-Ray crystallography following vacuum sublimation and have given some fascinating structural information. Scheme 1.2.4 shows the syntheses of the *mono*- and *bis*-(1,2,3,5-dithiadiazolyl)s based on 2,5-dicyanofuran. The *mono*-dithiadiazolyl radical 3 has been studied by X-Ray crystallography[16], and consists of eclipsed dimer units, as shown in Fig. 1.2.1. The usefulness of this method in preparing dithiadiazolyls with free cyano- substituents is further highlighted by the recent preparation and X-Ray single crystal structure determination of the monoradical 4-(3-cyanophenyl)-1,2,3,5-dithiadiazolyl[17] .



Scheme 1.2.4
Preparation of *mono*- and *bis*-(1,2,3,5-Dithiadiazolyls) from 2,5-Dicyanofuran
i. $Li[N(SiMe_3)_2]$, Me_3SiCl : -LiCl
ii. $2SCl_2$: $-3Me_3SiCl$
iii. $0.5Ph_3Sb$: $-0.5Ph_3SbCl_2$
iv. $4SCl_2$: $-6Me_3SiCl$
v. Ph_3Sb : $-Ph_3SbCl_2$

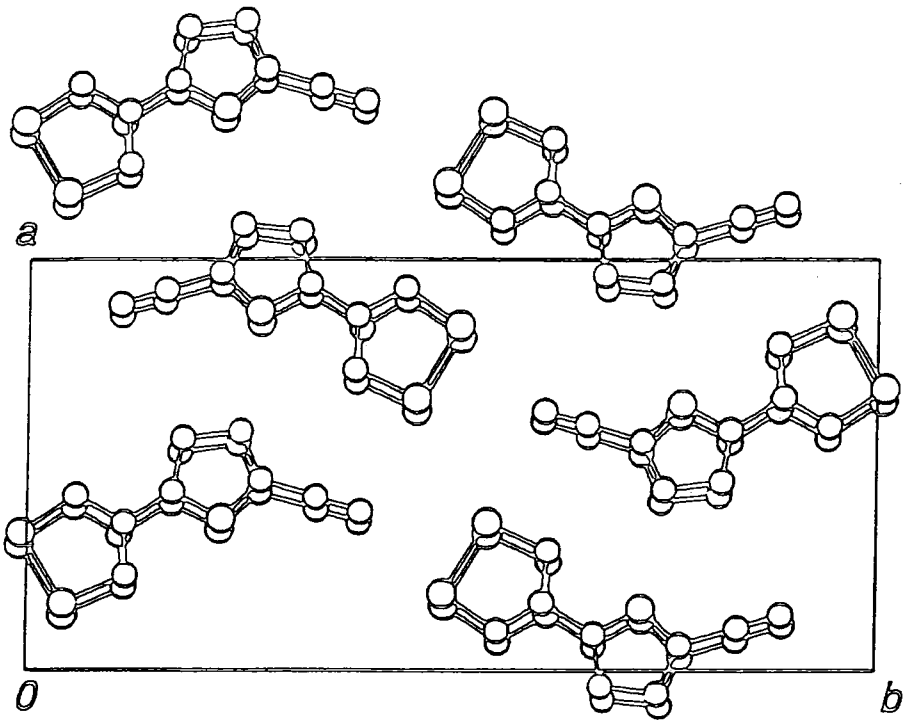
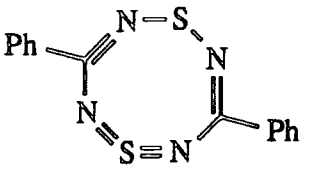


Fig. 1.2.1

Eclipsed dimeric units in the X-Ray crystal structure of 3

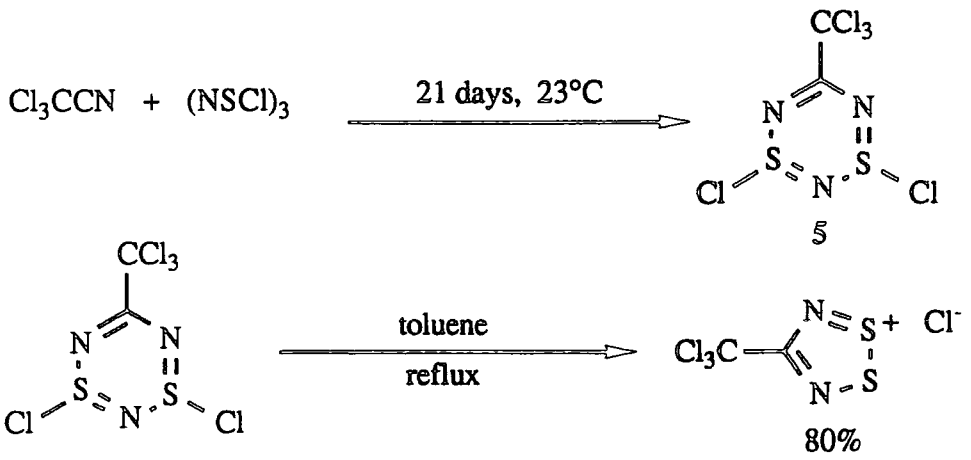
An additional product from this reaction is a dithiatetrazocine 4 (also accessible *via* reaction of $Li[PhCN_2(SiMe_3)_2]$ or $PhCN_2(SiMe_3)_3$ with SCl_2). Reaction of 4.LiCl with $AgAsF_6$ in liquid SO_2 gives the corresponding 1,2,3,5-dithiadiazolium cation as the hexafluoroarsenate[18].



Dithiatetrazocine
4

1.2.1.d). Thermolysis of 1,3-dichloro-1,3,2,4,6-dithiatriazines

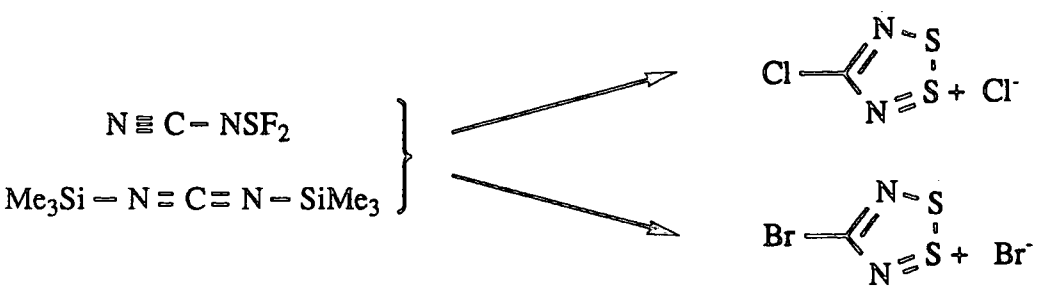
In Section 1.2.1a the preparation of dithiadiazolium chlorides form $(NSCl)_3$ and nitriles was outlined. There, the reaction mixture was heated to effect the dissociation of $(NSCl)_3$ into the free monomer. Carrying out the same reaction at lower temperature gives an intermediate 1,3-dichloro-1,3,2,4,6-dithiatriazine (5), which upon thermolysis e.g. under reflux in toluene, gives a dithiadiazolium chloride in good yield[19,20] as shown in Scheme 1.2.5. The same reaction has also been carried out at lower temperatures using sodium azide[21].



Scheme 1.2.5
Preparation of 1,2,3,5-Dithiadiazolium salts from Nitriles and $(NSCl)_3$ *via* 1,3-Dichloro-1,3,2,4,6-dithiatriazine 5

1.2.1.e). From cyanamides or carbodiimides

Reaction of N-cyanosulphurdifluoride or bis-(trimethylsilyl)carbodiimide with excess SCl_2 gives 4-chloro-1,2,3,5-dithiadiazolium chloride in good yield[22,23], as shown in Scheme 1.2.6. The analogous reaction with S_2Br_2 gives 4-bromo-1,2,3,5-dithiadiazolium bromide. Reaction of [ClCNSSN][Cl] with AgF_2 was found to give the fluoro-substituted analogue [FCNSSN][Cl].



Scheme 1.2.6
4-Halo-1,2,3,5-dithiadiazolium Salts from Sulphur Halides and N-Cyanosulphur-difluoride or *bis*-(Trimethylsilyl)carbodiimide

1.2.2. 5-Substituted-1,3,2,4-Dithiadiazolium Salts

1.2.2.a). From $[SNS]^+$ salts and nitriles

The $[SNS]^+$ cation was first reported as the $[SbCl_6]^-$ salt[24], produced in unspecified yield from the reaction of a variety of sulphur imido species with $SbCl_5$. The more soluble $[AsF_6]^-$ salt[25] is used in the preparation of 1,3,2,4 - dithiadiazolium salts with nitriles.

The reaction is a general, quantitative, symmetry allowed cycloaddition involving electron donation from the H.O.M.O. of the nitrile to the L.U.M.O. of the $[SNS]^+$ cation. This is shown in Fig 1.2.2.

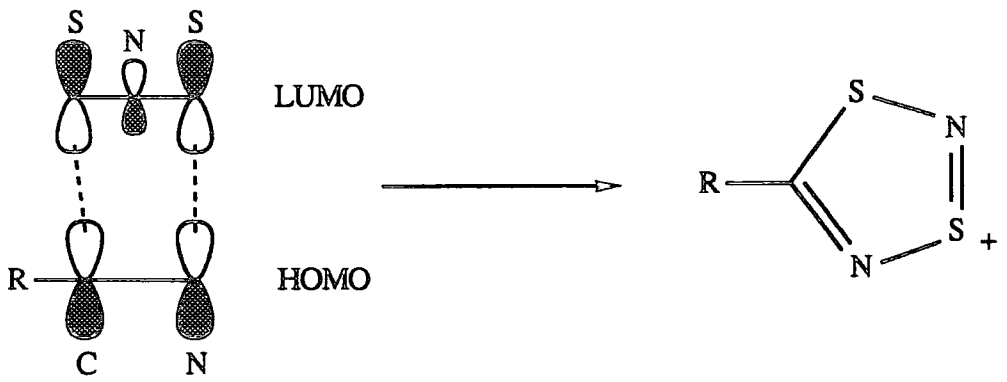


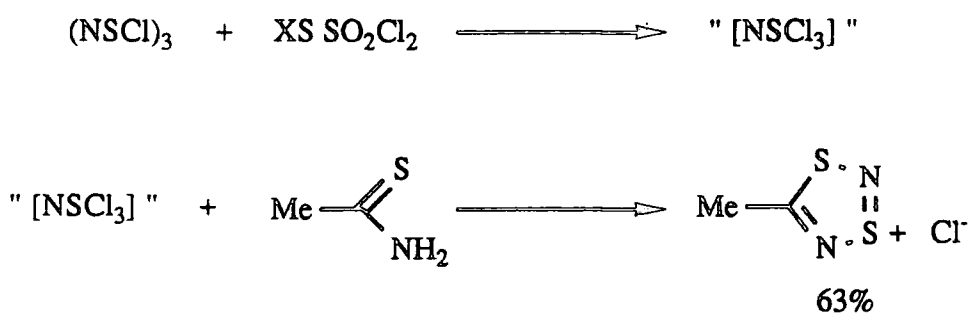
Fig. 1.2.2

Interaction of the HOMO of a nitrile with the LUMO of $[SNS]^+$ in the formation of 1,3,2,4-dithiadiazolium salts

This method has been used to prepare many dithiadiazolium salts, including di- and tri-functional salts[26-32]. The reaction gives products in quantitative or near-quantitative yield, often to analytical purity without further purification.

1.2.2.b). From thioamides and "$NSCl_3$"

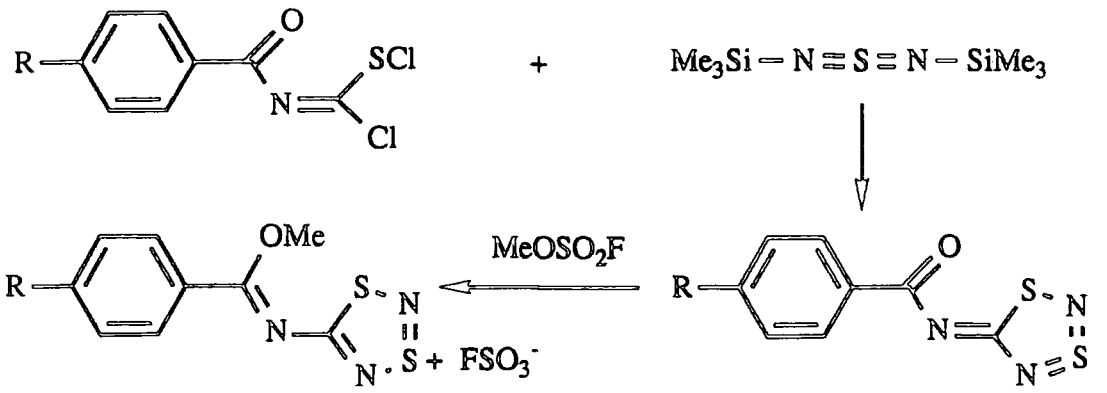
This reaction was first reported in 1987[33], but has been the subject of some dispute[34]. Reaction of $(NSCl)_3$ with excess SO_2Cl_2 was reported to generate "$NSCl_3$" *in situ*, and subsequent reaction with thioamides gave 1,3,2,4-dithiadiazolium chlorides (as shown in Scheme 1.2.7) without having to carry out a metathesis reaction on another salt, e.g. the hexafluoroarsenate.



Scheme 1.2.7
Preparation of 1,3,2,4-Dithiadiazolium Chlorides from $(NSCl)_3$, SO_2Cl_2 and Thioamides

1.2.2.c). From chlorosulphenyl chlorides and silylated sulphur diimides

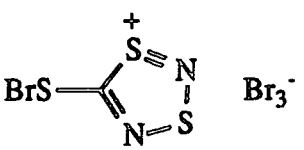
This reaction produces an intermediate neutral 1,3,2,4-dithiadiazole, which upon reaction with $MeOSO_2F$ gives 1,3,2,4-dithiadiazolium salts[35,36] as shown in Scheme 1.2.8.



Scheme 1.2.8
Preparation of 1,3,2,4-Dithiadiazolium Salts from Chlorosulphenyl-chlorides and Silylated Sulphurdiimides

1.2.2.d). From S_4N_4, Bromine and Carbon Tetrachloride

In 1982 Wolmershaüser and co-workers[37,38] reported the synthesis of 5-bromosulphenyl-1,3,2,4-dithiadiazolium tribromide (6) from S_4N_4, elemental bromine and carbon tetrachloride. The monobromide salt and the binary S/N cation $[S_4N_3]^+$ as tribromide and monobromide salts were also produced in the reaction.



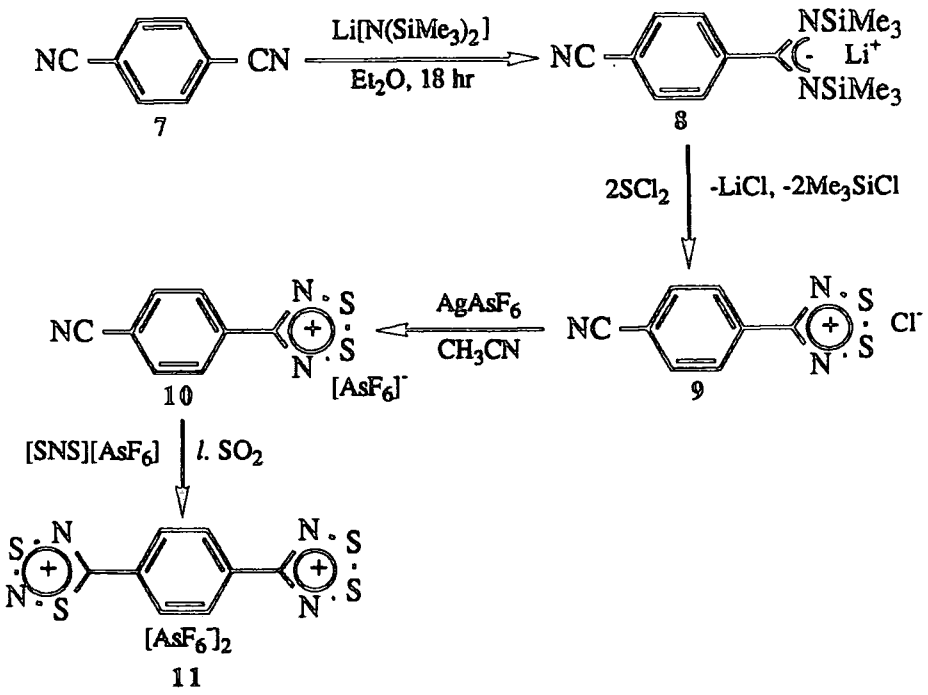
6

1.2.2.e). Mixed Dithiadiazolium Salts

Banister *et al*[39] have recently produced a *bis*-dithiadiazolium salt with one 1,3,2,4-dithiadiazolium ring and one 1,2,3,5-dithiadiazolium ring in the same molecule. As shown in Scheme 1.2.9 the salt **11** was synthesized from 1,4-dicyanobenzene **7**, from which the silyl derivative **8** was prepared by reaction with $Li[(Me_3Si)_2N]$. Reaction of **8** with SCl_2 gave 4-(4-cyanophenyl)-1,2,3,5-dithiadiazolium chloride **9**. For the formation of the 1,3,2,4-dithiadiazolium ring by cycloaddition of $[SNS][AsF_6]$ to **9** it was found necessary to prepare the $[AsF_6]$ salt **10** by metathesis with $AgAsF_6$. Nucleophilic anions such as Cl^- react with $[SNS]^+$, and thus incorporation of an hard anion in **9** was necessary. Reaction of **10** with $[SNS][AsF_6]$ in liquid SO_2 gave **11**, which was characterised by cyclic voltammetry ; two distinct reduction peaks corresponding to the two ring isomers were observed.

1.3 Structure and Bonding

The dithiadiazolium ring in both isomeric forms is planar or very nearly so. Several crystal structures of both isomers have been determined; See Table 1.3.1 below.



Scheme 1.2.9

Preparation of 1,3,2,4-1,2,3,5-
bis-(dithiadiazolium) salt 11 (Ref. 39)

TABLE 1.3.1 Reported X-Ray Crystal Structures of Dithiadiazolium Salts

1,2,3,5-Dithiadiazolium Salts [RCNSSN][X]

R	X	Ref	
CF_3	Cl^-	22	a
CCl_3	Cl^-	40	
Cl	$[AsF_6]^-$	43	
CH_3	Cl^-	44	
CH_3	$[CoCl_4]^{2-}$ / Cl^-	44	b
Ph	$[AsF_6]^-$ / Cl^-	21	c
Ph	$[AsF_6]^-$	21, 23	
Ph	Cl^-	41	d
Ph	Cl^-	45	e
Ph	$[S_3N_3]^-$	45	f
Ph	$[S_3N_3]^-$	46	
Ph	$[Pt^{II}(mnt)_2]^{2-}$	47	g
4-ClC_6H_4	$[AsF_6]^-$	42	
4-ClC_6H_4	$[Pt^{III}(mnt)_2]^-$	47	g
1,4-Phenylene	$[SbF_6]^-$	12	h

1,3,2,4-Dithiadiazolium Salts [RCNSNS][X]

R	X	Ref	
CH3	$[AsF_6]^-$	26, 27	
BrS	$[Br_3]^-$	38	
Ph	$[AsF_6]^-$	47	
Methide	$[AsF_6]^-$	32	i

Notes

a Structure of the mixed oxidation state compound $(CF_3CNSSN)_3Cl$.

b Structure of the multiple salt $[CH_3CNSSN]_5[CoCl_4][Cl]_3$.

c Structure of the triple salt $[PhCNSSN]_3[AsF_6]_2[Cl]$.

d The solid state structure contains toluene of crystallization ; Formula $[PhCNSSN][Cl].1/6\ C_7H_8$.

e This structure contains the cation $[(PhCNSSN)(S_3N_2)]^+$.
f This compound contains the mixed oxidation state cation $[(PhCNSSN)_2Cl]^+$.
g mnt = maleonitriledithiolate dianion $[NCC(S)C(S)CN]^{2-}$.
h Structure of the PhCN solvate of the *bis*-(1,2,3,5-dithiadiazolium) salt $[C_6H_4\text{-}1,4\text{-}(CNSSN)_2][SbF_6]_2.2PhCN$.
i Structure of $[C(CNSNS)_3][AsF_6]_2.SO_2$, prepared from $K[C(CN)_3]$ + $3SNSAsF_6$ in liquid SO_2

Using a model developed by Banister[48] to explain the bonding in binary sulphur-nitrogen cations and anions, the dithiadiazolium ring may be considered to be a 6π Hückel aromatic species, with each sulphur contributing an electron pair to delocalised π-bonding, and the two nitrogens and the carbon contributing one each ; a total of 7 π-electrons. Removing one to account for the positive charge gives a 6π aromatic species.

1.4 Properties of Dithiadiazolium Salts

Dithiadiazolium salts are crystalline solids, stable in dry air but highly sensitive to moisture. They react readily with nucleophiles e.g. water[31], alcohols and amines[49] to give a mixture of products, including precipitated sulphur.

In common with many other compounds of sulphur and nitrogen, dithiadiazolium salts exist in a wide range of colours, dependent both on the anion and on the substituent. For example, 1,3,2,4-dithiadiazolium hexafluoroarsenates are colourless, the chlorides are lemon yellow, the bromides are burgundy red and the iodides are black, the range of colours reflecting the hardness of the anion. In addition, 4-phenyl-1,2,3,5-dithiadiazolium chloride is bright yellow, whereas 4-(diethylamino)-1,2,3,5-dithiadiazolium chloride is purple-black[20].

1.5 Stable Radicals from Dithiadiazolium Salts

1.5.1 Reduction of Dithiadiazolium Salts to Stable Free Radicals

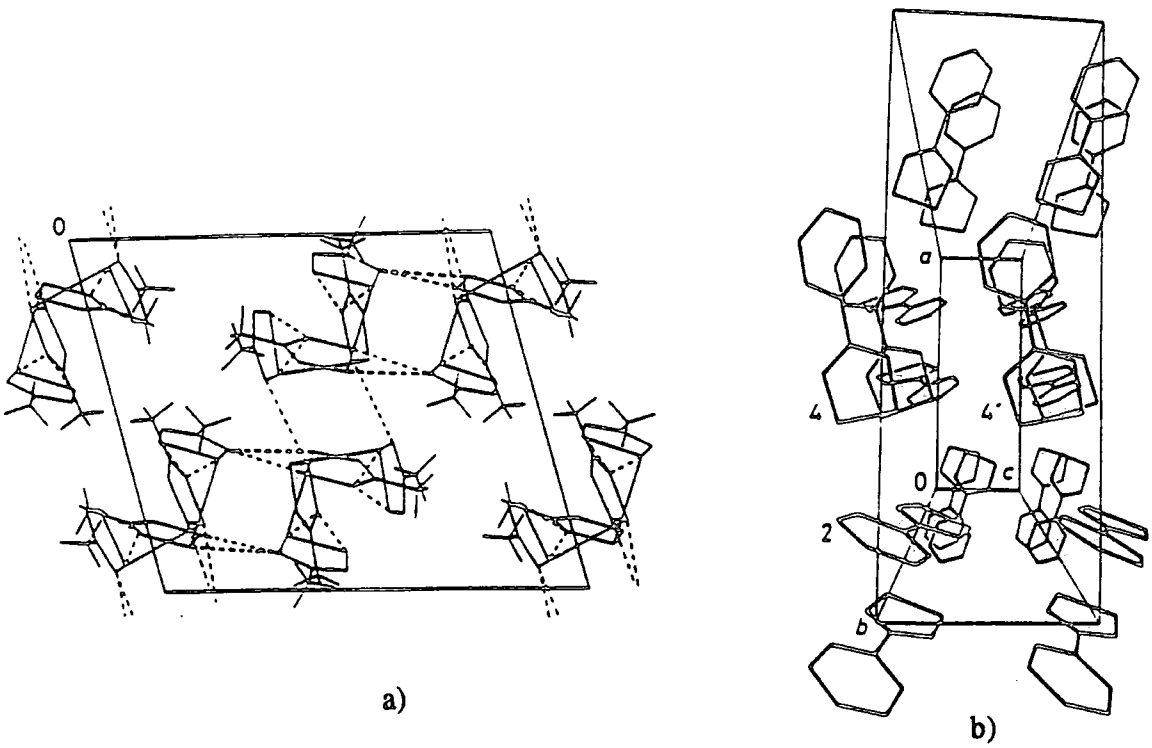
The most striking property of the dithiadiazolium salts and their relatives is their facile reduction to give dithiadiazolyls[4,6,22,31,50-52], free radicals of remarkable stability. The 6π

dithiadiazolium cationic ring accepts one electron from a reducing agent to give 7π neutral radicals. 1,2,3,5-Dithiadiazolyls (RCNSSN)·, derived from 1,2,3,5-dithiadiazolium salts, exist in the solid state as diamagnetic dimers, for example the methyl- and phenyl-substituted dithiadiazolyls shown in Fig 1.5.1, and several crystal structure determinations have been carried out. See Table 1.5.1 below.

Table 1.5.1 : Reported X-Ray Crystal Structures of Dithiadiazolyls

Formula	Ref
1,2,3,5-Dithiadiazolyls (RCNSSN)	
$(F_3CCNSSN)_2$	22
$(PhCNSSN)_2$	53
$(H_3CCNSSN)_2$	54
$(C_6H_4\text{-}1,4\text{-}(CNSSN)_2)_2$	13
$(3\text{-}(CN)\text{-}C_6H_4CNSSN)_2$	19
$(C_6H_4\text{-}1,3\text{-}(CNSSN)_2)_2$	14
$(C_6H_3\text{-}1,3,5\text{-}(CNSSN)_3)\cdots$	15
$2,5\text{-}[(NSSNC)OC_4H_2(CN)]\cdot$	16
$2,5\text{-}[(NSSNC)OC_4H_2(CNSSN)]\cdot\cdot$	16
1,3,2,4-Dithiadiazolyls (RCNSNS)	
$(C_6H_4\text{-}1,4\text{-}(CNSNS)_2)$	28
1,2,3,5-Diselenadiazolyls (RCNSeSeN)	
$(PhCNSeSeN)_2$	11

Reduction of 1,3,2,4-dithiadiazolium salts gives 1,3,2,4-dithiadiazolyls, which undergo a remarkable bimolecular rearrangement to the more stable 1,2,3,5-isomer. This phenomenon, which is easily monitored by ESR spectroscopy, was first studied by Passmore and co-workers[50] on *mono*-dithiadiazolyls in solution. The stable *bis*-(1,3,2,4-



a) b)

Fig. 1.5.1

X-Ray crystal structures of 1,2,3,5-dithiadiazolyl dimers

a) $(MeCNSSN)_2$ (Ref. 54)

b) $(PhCNSSN)_2$ (Ref. 53)

dithiadiazolyl) (C_6H_4-1,4-$(CNSNS)_2$)[28] is particularly interesting in this respect. Rearrangement of this species to the more stable *bis*-(1,2,3,5-dithiadiazolyl) occurs very slowly, and does not reach complete rearrangement even after several weeks in dry benzene[55]. This may be due to resonance stabilisation of the 1,3,2,4-isomer as a non-radical quinoid-type structure as shown in Fig 1.5.2. This closed-shell resonance structure raises questions regarding nomenclature, since it may be classed as a *dithiadiazole* species, whereas the diradical canonical form may be termed a *dithiadiazolyl* species. Thus it could be argued reasonably that the name of the compound has two canonical forms!

Diradical form Quinoid form

Fig.1.5.2

Diradical and quinoid resonance forms for the

bis-(1,3,2,4-dithiadiazolyl) [C_6H_4-1,4-$(CNSNS)_2$]

The mechanism postulated for this rearrangement involves the formation of "head-to-tail" dimers[49], where the Singly-Occupied Molecular Orbitals of each dithiadiazolyl ring are able to interact. This is shown in Fig 1.5.3.

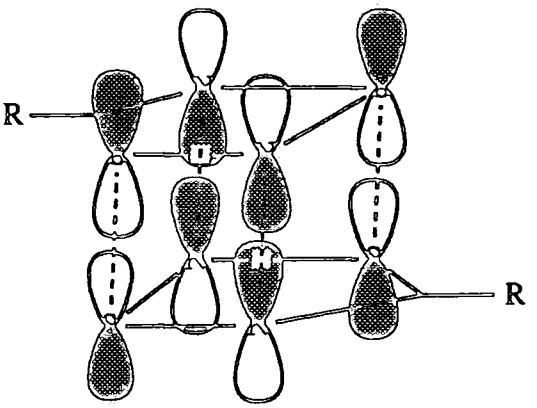


Fig.1.5.3 : Head-to-tail SOMO interaction in the bimolecular rearrangement of 1,3,2,4-dithiadiazolyl radicals to their 1,2,3,5-analogues

Recent work in this laboratory[56] has shown that the rearrangement of the 1,3,2,4-dithiadiazolyls also occurs in the solid state, and can be induced thermally. The rearrangement process is seen by Differential Scanning Calorimetry as a sharp exotherm at elevated temperatures.

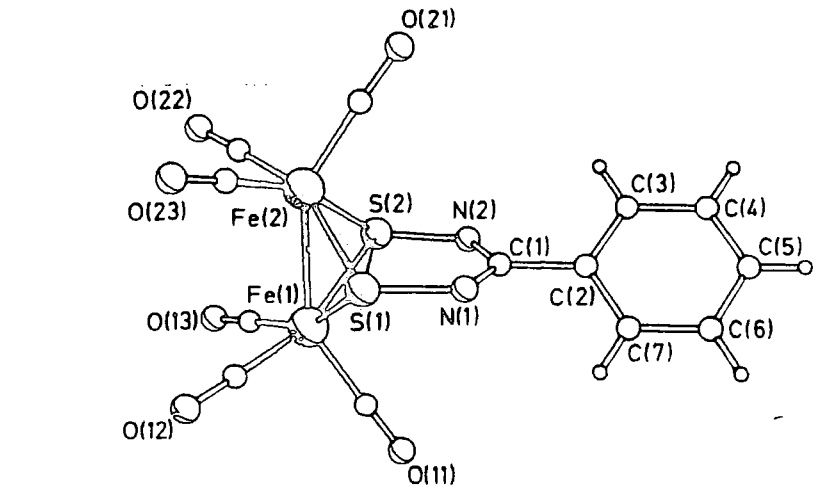
The stable monoradical (5-^{t}BuCNSNS)· has been prepared as a paramagnetic liquid[51] by heating the diamagnetic dimer, the rise in susceptibility upon melting arising from the dissociation of dimer units to give the monomeric radical. Rearrangement to the 1,2,3,5-dithiadiazolyl isomer was effected by UV irradiation.

1.5.2 Some Chemistry of Dithiadiazolyl Radicals

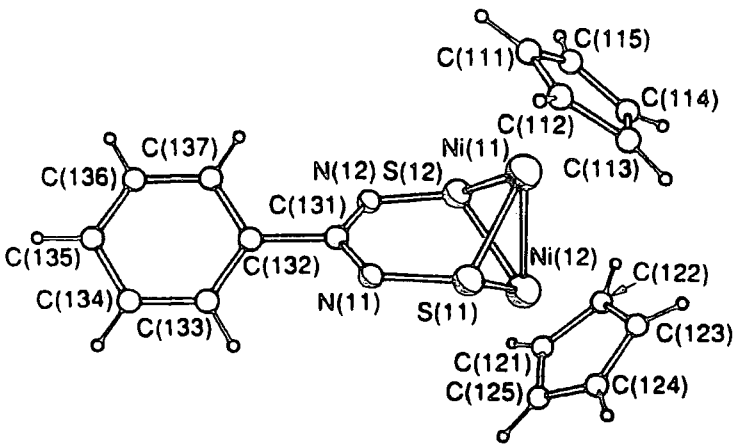
Dithiadiazolyl radicals undergo reoxidation to dithiadiazolium salts with a variety of oxidising agents, for example Cl_2 and SO_2Cl_2 to give chlorides, and Br_2 to give bromides. As part of this work, novel *bis* - and *tris* - (tribromide)s were prepared from the reaction of *bis* - and *tris* - (dithiadiazolyl)s with elemental bromine. Furthermore, it was found that halogen abstraction from activated C-Cl bonds could be effected by dithiadiazolyl radicals. It has already been shown[57] that these radicals will abstract Br from activated C-Br bonds.

4-Phenyl-1,2,3,5-dithiadiazolyl ($PhCN_2S_2$)· has been complexed to a number of low-valent transition metals, and two X-Ray Crystal structures have been reported, *i.e.* $[Fe_2(CO)_6(PhCN_2S_2)]$[58] and $[(C_5H_5)_2Ni_2(PhCN_2S_2)]$[59]. As shown in Fig 1.5.4 the radical acts as a bridging ligand between the two metal centres. There is at present no evidence for a dithiadiazolyl radical complexed to a single metal centre. Further work with triphenylphosphine complexes of palladium and platinum shows a great deal of potential, and a crystal structure of the tris-palladium complex $[Pd_3(PPh_3)_4(PhCNSSN)_2].2CH_2Cl_2$ has been determined[47], although the structure was found to be highly disordered (R = 14%) due to the solvent of crystallisation (CH_2Cl_2).

4-Phenyl-1,2,3,5-dithiadiazolyl dimer was found to undergo an interesting nitrogen atom insertion reaction in a cool nitrogen plasma[54] to give the corresponding dithiatriazine dimer, with insertion of nitrogen atoms into the S-S bond in the dithiadiazolyl ring. In addition, dithiatriazines were formed form a variety of dithiadiazolium salts using this method. The reactions are shown in Scheme 1.5.1.



a)



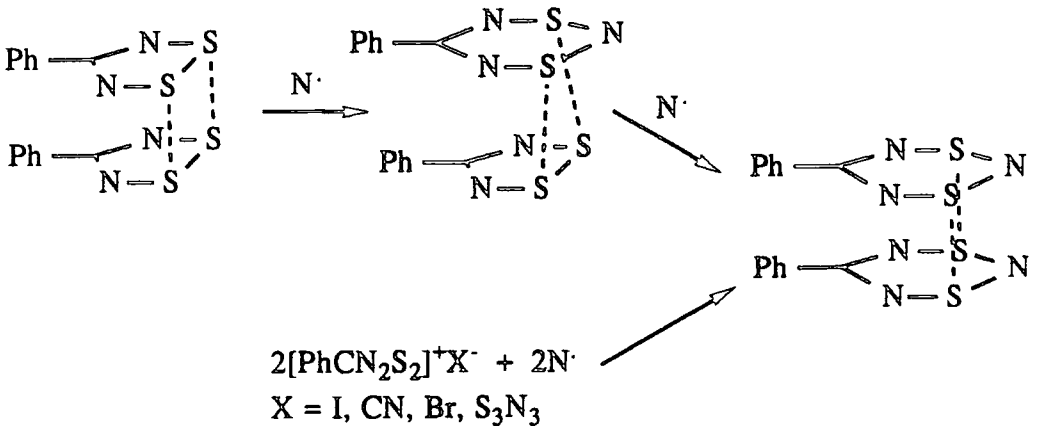
b)

Fig. 1.5.4

X-Ray crystal structures of 1,2,3,5-dithiadiazolyl metal complexes

a) $[Fe_2(CO)_6(PhCN_2S_2)]$ (Ref. 58)

b) $[(C_5H_5)_2Ni_2(PhCN_2S_2)]$ (Ref. 59)

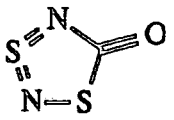


Scheme 1.5.1

Reactions of dithiadiazolyls and dithiadiazolium salts in a cool nitrogen plasma

1.6 Other CN_2S_2 Systems

An example of a well-studied neutral dithiadiazole is the dithiadiazolone 12, first reported in 1975[60,61] by Roesky and Wehner. The compound is accessible by a number of routes[62]. See Scheme 1.6.1



12

$$S_2N_2Sn(CH_3)_2 + COF_2 = S_2N_2CO + 2(CH_3)_2SnF_2 \quad \text{Eq. 1.1}$$

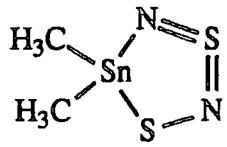
$$ClCOSCl + (CH_3)_3SiN{=}S{=}NSi(CH_3)_3 = S_2N_2CO + 2(CH_3)_3SiCl \quad \text{Eq. 1.2}$$

Scheme 1.6.1 : Synthesis of Dithiadiazolone 12

Crystal structures of the molecule[63] and of its adduct with Lewis acids including AsF_5[64] have been determined. The molecule can coordinate via the exocyclic oxygen to metals, and

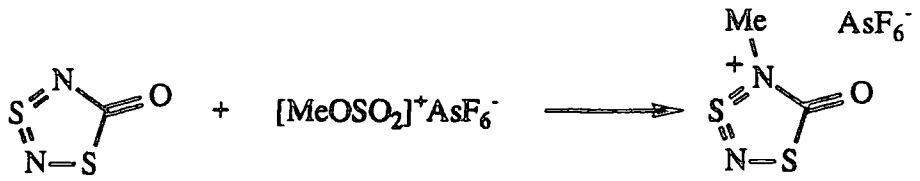
the interesting complex $[Zn(O{=}CNSNS)_6][AsF_6]_2$ has been prepared[65]. The X-Ray structure of the complex[66] is shown in Fig 1.6.1.

As shown in Equation 1.1, the preparation of the dithiadiazolone involves the substitution of C=O for $(CH_3)_2Sn$ in the dithiadiazastannole 13, which was reported[67,68] in 1973.



13

The dithiadiazolone can be methylated at the 4 - position[69] to give a dithiadiazolonium cation as shown in scheme 1.6.2.



12

Scheme 1.6.2
Methylation of dithiadiazolone 12

CN_2S_2 rings with higher degrees of saturation are known, commonly with alkylated nitrogens and / or S=O groups. The neutral 1,3,2,4-dithiadiazoles shown in Fig 1.6.2 are prepared from the reaction of diphenyl sulphur diimide with RC(S)NCO[70] (R = phenyl, 4-chlorophenyl, 4-methoxyphenyl).

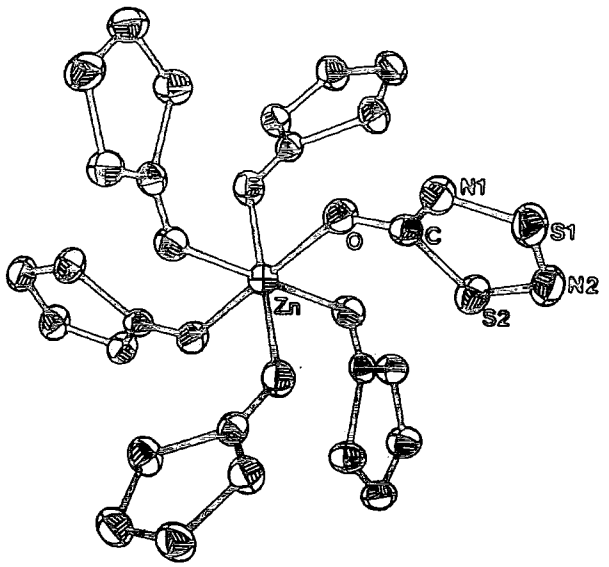
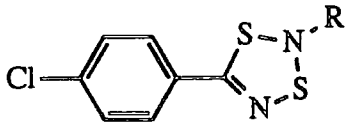


Fig. 1.6.1

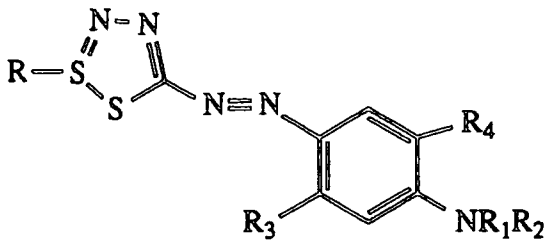
X-Ray crystal structure of the cation in the dithiadiazolone zinc complex $[Zn(O{=}CNSNS)_6][AsF_6]_2$ (Ref. 66)



R = Ph, 4-Chlorophenyl, 4-Methoxyphenyl

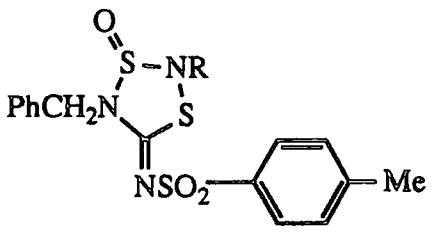
Fig. 1.6.2
Neutral 1,3,2,4-Dithiadiazoles from RC(S)NCO and Diphenylsulphurdiimide

An unusual example of a neutral S-alkylated dithiadiazole is the 1,2,3,4-dithiadiazole ring 14, which finds use in thermal recording systems as an agent for lightfast magenta images[71].



14

Trapping of thiaziridinimines with N-sulphenylimines[72] gives the substituted 1,3,2,4-dithiadiazolidine-3-thione 15 as one of the products, whilst the reaction of ClCOSCl with $SO_2(MeNH)_2$ in the presence of a base[73] leads to the highly saturated dithiadiazolone species 16.



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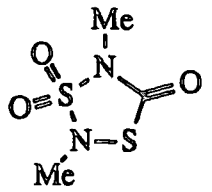

16

1.7 Conclusion

Compounds containing the CN_2S_2 ring with varying degrees of saturation are becoming increasingly studied due to their potential for novel materials, particularly new conductors. The ease of preparation of stable free radicals from unsaturated cationic species, radicals which may be isolated as solids, marks these compounds out as new synthetic reagents with many as yet undiscovered applications. This thesis expands the library of known dithiadiazolium salts and their related radicals, but in addition takes a small step into the uncharted territories of their general reactivity, an area somewhat neglected in this branch of chemistry.

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CHAPTER 2 : EXPERIMENTAL

2.1 General Experimental Procedure

Dithiadiazolium salts are stable in dry air, but very sensitive to moisture. Thus, inert atmosphere techniques were employed throughout this work.

All air- and moisture- sensitive materials were handled under dry nitogen in a Vacuum Atmospheres HE43-2 glove box fitted with a HE493 Dri-Train, a diagram of which is shown in Fig. 2.1.1. All glassware was pre-dried overnight at 180°C prior to use. For handling highly moisture-sensitive materials pre-dried glassware was flamed immediately before loading into the glove box. For most reactions standard vacuum-line methods were used. Liquid sulphur dioxide, elemental bromine and arsenic pentafluoride were handled on a stainless steel vacuum line designed and built by Dr. Z.V. Hauptman.

2.2 Special Apparatus

2.2.1 The "Dog"

This is a twin-bulbed reaction vessel incorporating a glass sinter in the horizontal tube connecting the two legs. Teflon vacuum taps (J. Young Co.) enable this apparatus (shown in Fig. 2.2.1.) to be used for all reactions incorporating liquified gases *eg* SO_2, AsF_5.

2.2.2. The Closed Extractor

This apparatus was designed by Dr. Z.V. Hauptman and is based on the common Soxhlet extractor. The closed design and the Teflon vacuum tap enable the apparatus (shown in Fig. 2.2.2.) to be used for extractions involving liquid sulphur dioxide.

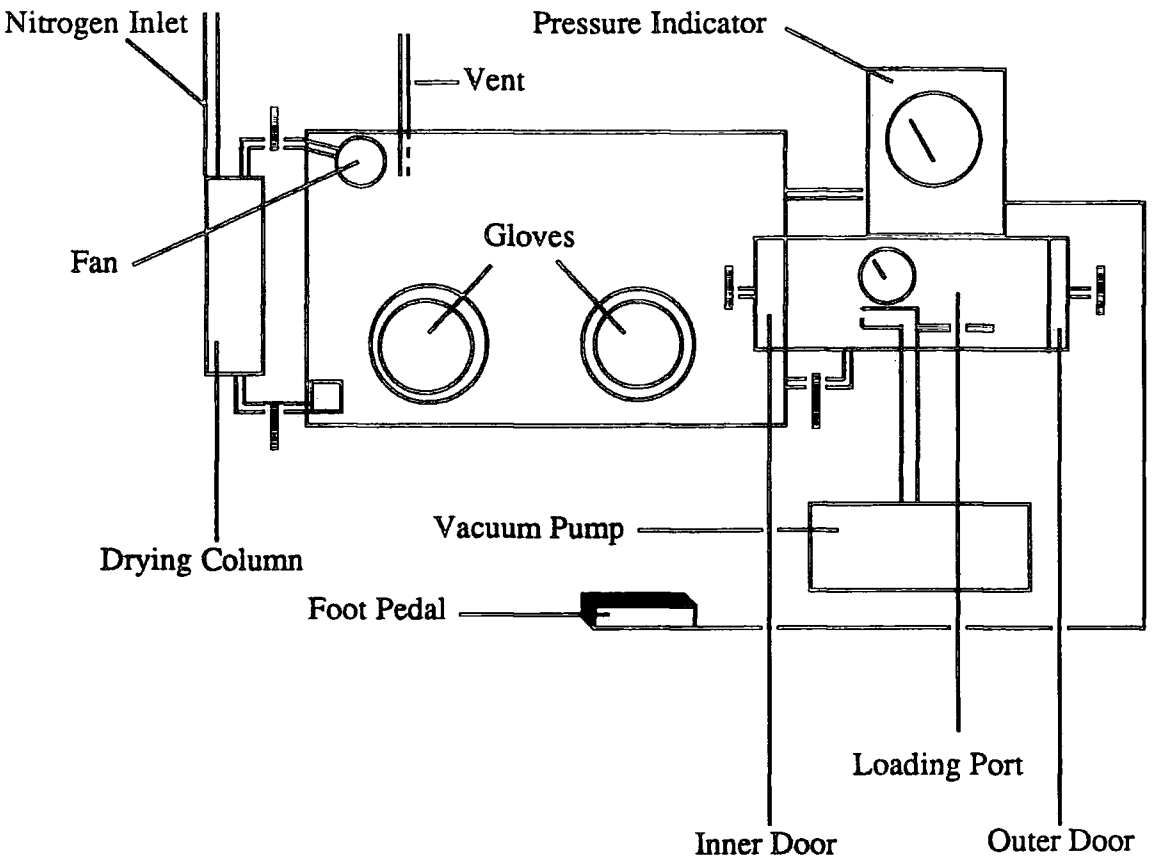


Fig. 2.1.1
The glove box

Fig. 2.2.1 The "Dog"

1. reaction bulb
2. glass sinter (usually porosity Grade 3)
3. J. Young Co. Teflon tap
4. 1/4" ground glass vacuum adaptor

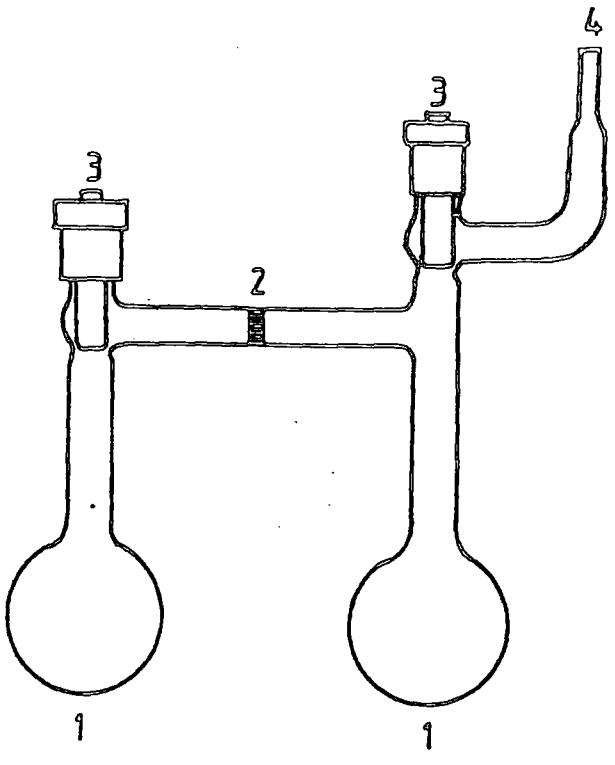
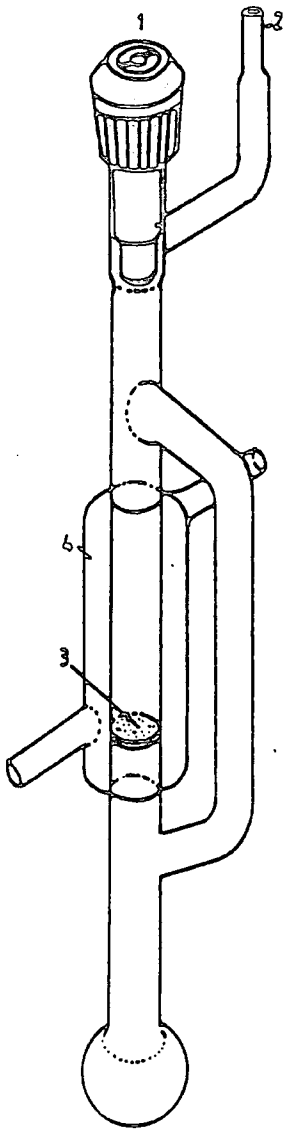


Fig. 2.2.2 The Closed Extractor

1. J. Young Co. Teflon tap
2. 1/4" ground glass vacuum adaptor
3. glass sinter (usually porosity Grade 3)
4. cooling jacket



2.3 Purification of Reagents

2.3.1 Purification of Solvents

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

Dichloromethane was dried by distilling off CaH_2 into clean dry flasks under an atmosphere of dry nitrogen.

Diethyl ether (anhydrous) was poured directly onto fresh sodium wire in a clean dry flask under an atmosphere of dry nitrogen.

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

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

NMR solvents (CD_3CN, CD_2Cl_2, $CDCl_3$, toluene-d_8 : - all Aldrich or Janssen) were used without further purification under an atmosphere of dry nitrogen. For highly sensitive samples nmr solvents were dried by distillation off P_4O_{10}.

2.3.2 Purification of Solid Materials

Ammonium chloride (Aldrich ACS Grade) was oven-dried at 180°C for at least 24 hrs prior to use.

Bu_4NCl, Bu_4NBr and Bu_4NI (Lancaster Synthesis) were purified by precipitation from acetone solution with anhydrous diethyl ether, followed by filtration, with the whole process being repeated. The purified materials were then heated *in vacuo* for several hours, and then transferred into the glove box in tightly stoppered flasks for storage. Dryness was checked by IR spectroscopy.

Triphenylantimony (Aldrich) was recrystallised twice from dry acetonitrile and stored in the glovebox.

4-Bromobenzonitrile, 4-chlorobenzonitrile, 1,2-dicyanobenzene, 1,3-dicyanobenzene, 2,6-dicyanotoluene, tetrafluoro-1,2-dicyanobenzene, tetrafluoro-1,3-dicyanobenzene, and 1,3,5-tricyanobenzene (Aldrich), were purified by sublimation *in vacuo* prior to use.

Tetrachloro-*o*-benzoquinone and tetrafluoro-*p*-benzoquinone (Aldrich) were sublimed *in vacuo* immediately prior to use. Tetrachloro -*p*- benzoquinone was used without prior purification.

Rhenium carbonyl (Aldrich) was sublimed twice *in vacuo* at 75°C prior to use.

Trimethylamine N-oxide (anhydrous) was prepared from the dihydrate (Lancaster Synthesis) by heating under dynamic vacuum at 60°C for 12 hours followed by triple vacuum sublimation with monitoring of water content by IR spectroscopy. The dried material was stored in the glovebox in a tightly - sealed container to prevent uptake of atmospheric moisture.

2.3.3 Purification of Gaseous Reagents

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

Nitrogen (Oxygen - Free, White Spot Grade) was passed through two glass columns packed with P_4O_{10}.

Sulphur dioxide (BDH GPR Grade) was dried by standing over P_4O_{10} for one week, followed by distillation onto CaH_2 at least 24 hrs before use.

2.3.4 Liquid Starting Materials

Bromine (BDH "ARISTAR") was dried by repeated distillation *in vacuo* prior to use, and stored under vacuum.

t - Butyl alcohol was dried over anhydrous magnesium sulphate and distilled through a Vigreux column under an atmosphere of dry nitrogen. The first 10% of the distillate was discarded to remove light - end fractions observed in NMR study of the crude material. The distillate was checked for purity by gas chromatography.

Acryloyl chloride, benzonitrile, benzoyl chloride, 2-fluorobenzonitrile, 2-methylbenzonitrile and oxalyl chloride (Aldrich) were used without further purification.

2.3.5 Preparation of Other Starting Materials

$[S{=}N{=}S]^+AsF_6^-$ was prepared according to the literature route[1], using slightly impure S_4N_4 (which is considerably safer to handle than the praecidigitogenic[2] purified material). Crude product was washed with dry dichloromethane to remove coloured impurities and residual AsF_3.

4-Phenyl-1,2,3,5-dithiadiazolium chloride was prepared from PhCN, SCl_2 and NH_4Cl according to the literature route[3].

4-Phenyl-1,2,3,5-dithiadiazolyl dimer was prepared by reduction of 4-phenyl-1,2,3,5-dithiadiazolium chloride according to the literature route[3], and was purified by sublimation *in vacuo* prior to use. It was found that this material slowly decomposed in storage under dry nitrogen , hence resublimation was found to be necessary immediately prior to use.

2.4 Infrared Spectroscopy

Infrared spectra were recorded as Nujol mulls between KBr plates using a Perkin-Elmer 577 Grating Infrared Spectrophotometer. For all moisture-sensitive samples mulls were made up in the glove box and the plates sealed in a brass holder. This arrangement was found to be satisfactory in preventing degradation of samples by moisture outside the glovebox. Nujol was stored in the glovebox over sodium. Infrared spectra of poly(tetrahydrofuran) were recorded as polymer films cast on KBr plates from dichloromethane/methanol.

Infrared data of compounds are presented as the positions of maxima in wavenumbers (cm^{-1}), with additional information regarding the intensity of absorptions. The abbreviations used throughout this thesis are as follows :

ν_{max}	absorption maximum
s	strong absorption
vs	very strong absorption
m	absorption of intermediate intensity
w	weak absorption
br	broad absorption band
sh	shoulder on the side of a peak

2.5 Electron Spin Resonance Spectroscopy (ESR)

ESR spectra were obtained on a Varian Associates Model EPR Spectrometer. In a typical experiment a flame-dried quartz ESR tube was loaded with a dithiadiazolium salt, tetrabutylammonium chloride and triphenylantimony. Syringing on solvent (commonly toluene) followed by sonication in an ultrasonic cleaning bath generated the radical, and spectra were obtained generally within 10 mins. of radical generation. For ESR studies in liquid SO_2 a modified tube was used, incorporating a Teflon vacuum tap (J. Young Co.) connected to a thick-walled quartz ESR tube. The tube, similar in design to the ^1H NMR tube for SO_2 solutions described below (Section 2.6, Fig. 2.6.1) could then be re-used or flame-sealed. Additional ESR spectra were recorded by Dr. Richard Singer at the University of Cambridge.

2.6 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H, ^{19}F and ^{13}C NMR spectra were recorded on Hitachi Perkin-Elmer R24B 60 MHz (^1H) and Bruker AC250 MHz and AMX 500 MHz (^1H, ^{19}F and ^{13}C) NMR Spectrometers. Spectra of solutions in liquid SO_2 were obtained using special thick - walled NMR tubes ; ^1H NMR spectra were recorded using a tube as shown in Fig. 2.6.1. Solid material was loaded into the tube in the glovebox and the sample was dissolved up by condensing in SO_2 on the steel

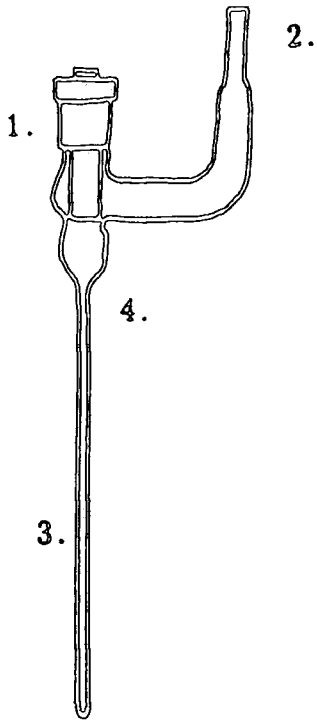


Fig. 2.6.1

^{1}H NMR tube for SO_2 solutions

1. J. Young & Co. Teflon tap
2. 1/4" ground glass vacuum connector
3. thick-walled ^{1}H NMR tube
4. flame-sealed here

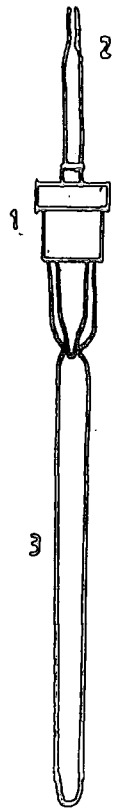


Fig. 2.6.2

^{13}C NMR tube for SO_2 solutions

1. J. Young & Co. Teflon tap
2. 1/4" ground glass vacuum connector
3. thick-walled ^{13}C NMR tube

vacuum - line. The solution was then frozen down to 77K with liquid nitrogen and the tube flame - sealed. These tubes were not reusable. ^{13}C spectra were recorded using a tube asshown in Fig. 2.6.2. The procedure for making up solutions was the same as for ^{1}H samples, but the Teflon vacuum taps (J. Young Co.) allowed the tube to be reused following removal of solvent and solid materials. ^{13}C NMR spectra of polymerizing THF were recorded as gels, with a small amount of $CDCl_3$ added as a spin lock.

2.7 Differential Scanning Calorimetry (DSC)

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

2.8 Elemental Analyses

Carbon, hydrogen and nitrogen analyses were performed by Mrs. M. Cocks on a Carlo Erba 1106 Elemental Analyser. All other analyses were performed by Mr. R. Coult or Mrs. J. Dostal. Bromine analysis was performed by oxygen flask combustion with dissolution of the resultant fumes in aqueous hydrogen peroxide, followed by potentiometric titration against standardised $AgNO_3$ solution. Rhenium analysis was performed by digestion of samples in conc. HNO_3 to solubilise metallic species, and the Re content of the resultant liquor was determined by atomic absorption spectrophotometry.

2.9 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) for determination of the molecular weight of poly(THF) was carried out by Mr. G. Forrest (Dept. of Chemistry, University of Durham) on a Waters 590 GPC apparatus against a polystyrene standard, using THF as solvent.

2.10 General Synthetic Methodology

2.10.1 Preparation of 5-Substituted-1,3,2,4-Dithiadiazolium Salts

In a typical reaction $[S=N=S]^+AsF_6^-$ was weighed into a dry "dog" in the glovebox. In the case of solid nitriles the required amount was weighed into the other leg. For reactions with liquid nitriles an excess was syringed into the other leg outside the glovebox under a counterflow of dry nitrogen. The reaction vessel was then evacuated (with freezing - down when using liquid nitriles) and liquid SO_2 was condensed into both legs sufficient to fully dissolve both reagents. The two solutions were then mixed by cross-filtration and the mixture stirred at room temperature for a period of time depending on the nature of the nitrile. Reactions with mononitriles were stirred for 3 hr, dinitriles for 24-48 hr, and 1,3,5 - tricyanobenzene for 5 days. SO_2 was then removed and highly - coloured impurities were removed by washing repeatedly with dry dichloromethane containing a trace of SO_2.

2.10.2 Metathesis Reactions of 5-Substituted-1,3,2,4-Dithiadiazolium Salts

In a typical reaction a dithiadiazolium AsF_6^- salt was weighed into one leg of a dry "dog" with the stoichiometric amount of the tetrabutylammonium salt of another anion. Addition of dry CH_3CN under a counterflow of dry nitrogen caused instantaneous reaction with precipitation of the dithiadiazolium salt of the other anion. Removal of soluble Bu_4NAsF_6 by filtration followed by repeated washing with back - distilled CH_3CN yielded the purified products. For metathesis reactions with *bis* - and *tris* - (dithiadiazolium) salts the solvent was commonly introduced into a separate leg of the reaction vessel and degassed before adding to the reagent mixture under vacuum. This was done to minimize contact with trace moisture in the nitrogen atmosphere.

2.10.3 Reduction of 1,3,2,4-Dithiadiazolium Salts to Radicals

Preparative scale reductions of 1,3,2,4-dithiadiazolium salts were carried out on the chlorides. An amount of the purified dithiadiazolium chloride was put into one leg of a "dog" with a small excess of a reducing agent, commonly triphenylantimony. The reaction mixture was then sealed off. CH_3CN was intoduced into the other leg and thoroughly degassed. The solvent was then distilled over onto the reaction mixture and the mixture stirred overnight to ensure complete reaction. For monoradicals purification was carried out by removal of solvent on the vacuum line followed by sublimation *in vacuo*. Di- and tri- radicals separated out as dark, sparingly - soluble powders which were purified by washing repeatedly with back - distilled CH_3CN followed by drying *in vacuo*.

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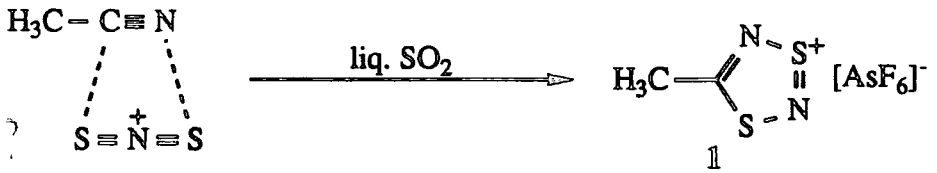
CHAPTER 3

REACTION OF [SNS][AsF_6] WITH MONONITRILES : PREPARATION OF MONO-(1,3,2,4-DITHIADIAZOLIUM) SALTS

3.1 Introduction

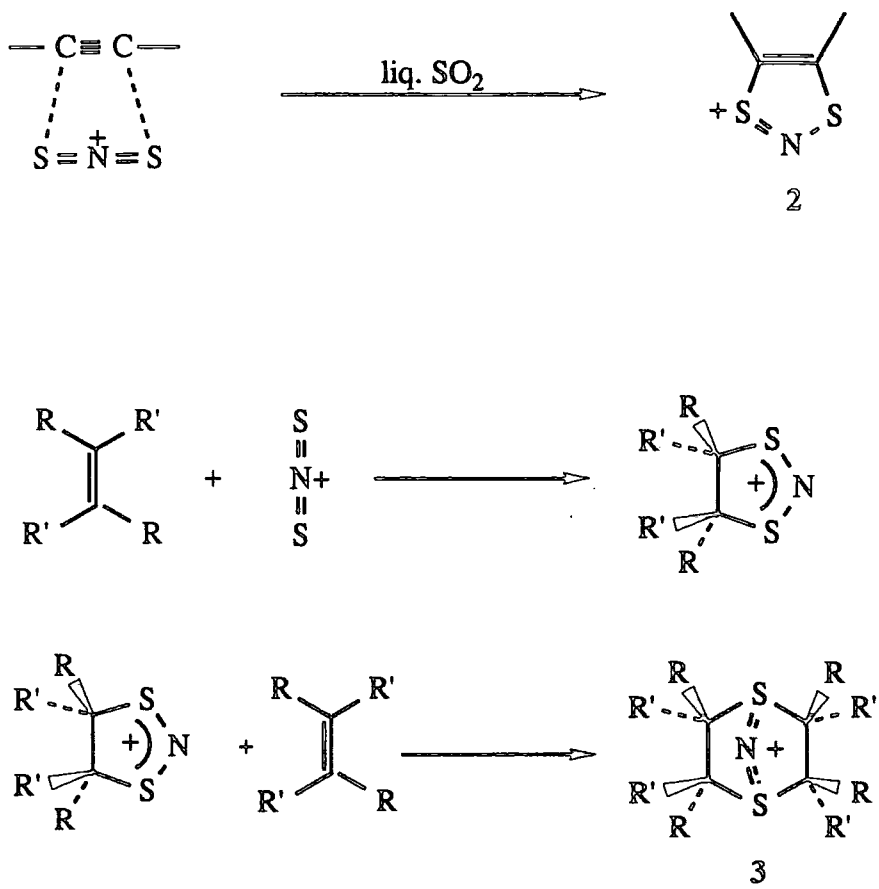
The general, quantitative cycloaddition of [SNS][AsF_6] to nitriles was first reported[1] by Schriver, working in Passmore's laboratory, following a study of the solubility of [SNS][AsF_6] in various solvents. Addition of CH_3CN to pure [SNS][AsF_6] did not give a solution, but rather a chemical reaction occurred, with the release of a considerable amount of heat. Analysis of the reaction products showed that $[SNS]^+$ had added across the CN triple bond of CH_3CN to give the 5-methyl-1,3,2,4-dithiadiazolium cation $[CH_3CNSNS]^+$ **1** as its $[AsF_6]^-$ salt. This is illustrated in Scheme 3.1.1.



Scheme 3.1.1

Cycloaddition of $[SNS]^+$ to CH_3CN

This reaction was found subsequently to be general for nitriles and also for other species containing multiple bonds : [SNS][AsF_6] adds across the C-C triple bond in alkynes to give 1,3,2-dithiazolium salts **2**, and in a very interesting reaction [SNS][AsF_6] reacts with two equivalents of a number of alkenes to give bicyclic cationic species **3**[2] as shown in Scheme 3.1.2.



Scheme 3.1.2

Cycloaddition of $[SNS]^+$ to alkynes and alkenes

1,3,2,4-Dithiadiazolium salts had been previously reported as oxidation products of 1,3,2,4-dithiadiazoles, obtained from the reaction of chlorosulphenyl chlorides with silylated sulphur diimides[3] (see Chapter 1, Section 1.2.2c), but Passmore and Schriver's method using the reaction of $[SNS][AsF_6]$ with nitriles was found to be superior for two main reasons.

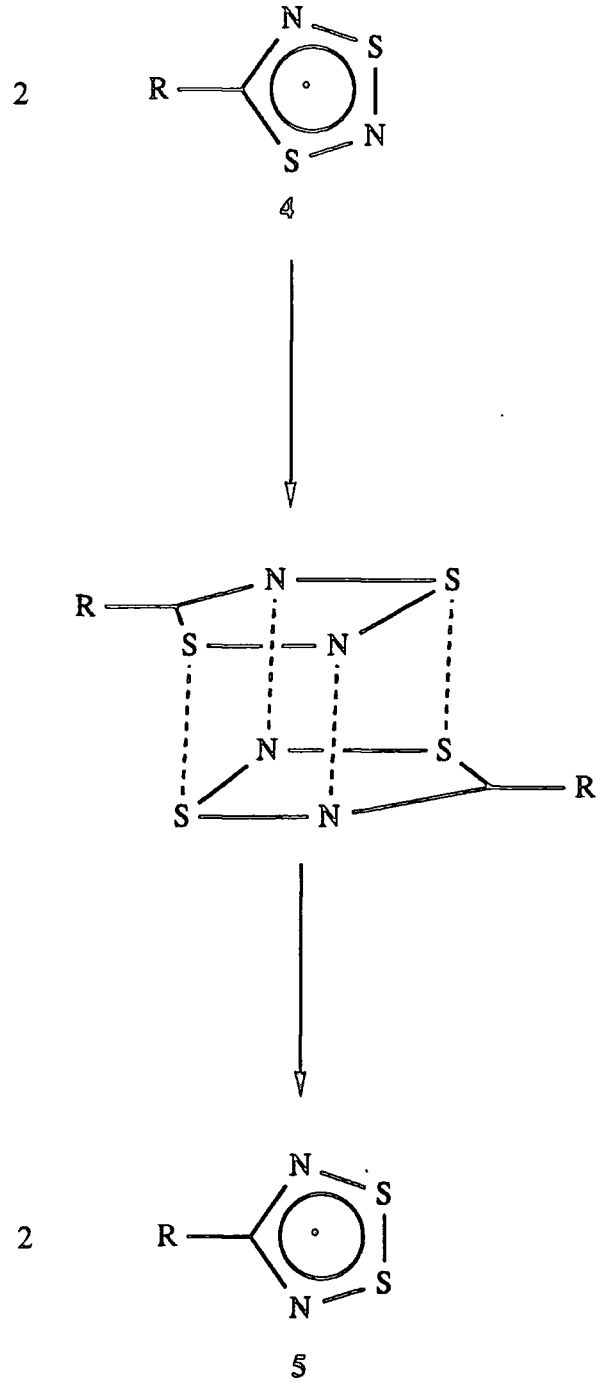
Firstly, the cycloaddition of $[SNS][AsF_6]$ to nitriles was found to be general, and thus a wide variety of nitriles (commonly available in multi-gramme quantities at low prices) could be derivatized in a single step without having to synthesize silylated precursors. Secondly, the reaction was found to be quantitative (or nearly so) for a large number of different

nitriles. 1,3,2,4-Dithiadiazolium salts were commonly obtained as crystalline solids to analytical and spectroscopic purity, thus in many cases obviating the need for further purification.

The preparation of [SNS][AsF_6] itself[4] does involve a number of potentially hazardous reagents (S_4N_4 and AsF_5 with S_8 in the presence of Br_2) and a solvent system (liquid SO_2) which commands a healthy respect and a good deal of care in its use, but the synthesis is a single step, high yield (75+ %) reaction which can be safely carried out on up to a 10 g scale.

As outlined in Chapter 1 (Section 1.5.1,) the 6π 1,3,2,4-dithiadiazolium cationic ring was found to undergo a facile single-electron reduction to give members of a family of persistent free radicals, the 7π 1,3,2,4-dithiadiazolyls **4**, which underwent bimolecular rearrangement[5] in solution to give the more stable 1,2,3,5-dithiadiazolyls **5**, as shown in Scheme 3.1.3.

As an introduction to this novel branch of Main Group chemistry, the author prepared a series of 5-aryl-1,3,2,4-dithiadiazolium salts from functionalized aromatic mononitriles, and this work is described in this chapter.



Scheme 3.1.3

Rearrangement of 1,3,2,4-dithiadiazolyls 4 to 1,2,3,5-dithiadiazolyls 5

3.2 Results and Discussion

3.2.1 Reaction of [SNS][AsF_6] with 2-Fluorobenzonitrile

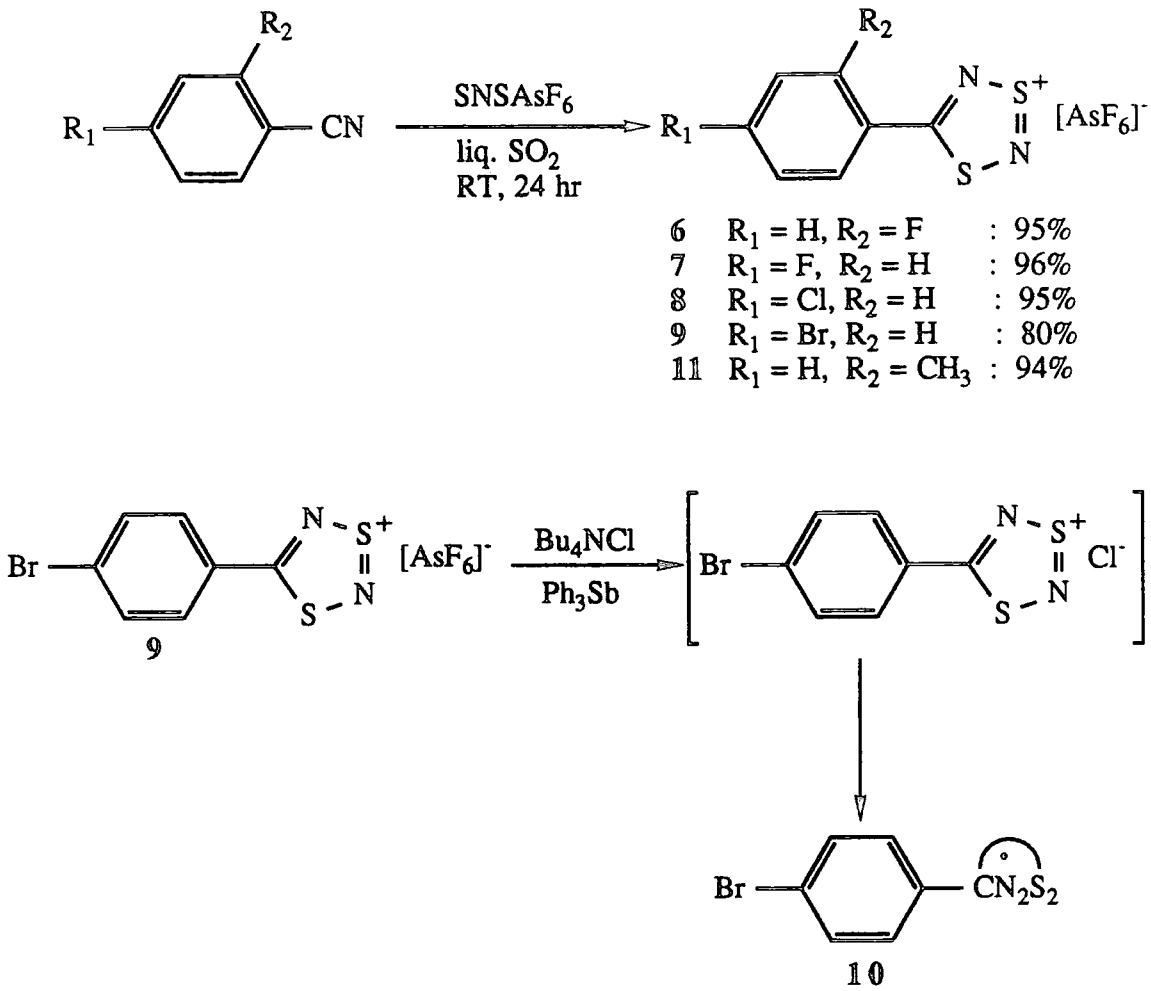
Reaction of [SNS][AsF_6] with 2-fluorobenzonitrile in liquid SO_2 over 24 hours gave 5-(2-fluorophenyl)-1,3,2,4-dithiadiazolium hexafluoroarsenate **6** in 95% yield, as shown in Scheme 3.2.1. The product, a pale yellow solid, was soluble at room temperature in liquid SO_2 and CH_3CN, sparingly soluble in CH_2Cl_2 and insoluble in toluene and hexane. In common with all dithiadiazolium salts the product was highly moisture-sensitive. Infrared analysis of the product showed no CN stretching band (c. 2230 cm^{-1}). The spectrum is shown in Fig. 3.2.1.

3.2.2 Reaction of [SNS][AsF_6] with 4-Fluorobenzonitrile

Reaction of [SNS][AsF_6] with 4-fluorobenzonitrile in liquid SO_2 over 24 hours gave 5-(4-fluorophenyl)-1,3,2,4-dithiadiazolium hexafluoroarsenate **7** in 96% yield, as shown in Scheme 3.2.1. The product, a pale yellow solid, was soluble at room temperature in liquid SO_2 and CH_3CN, sparingly soluble in CH_2Cl_2 and insoluble in toluene and hexane. In common with all dithiadiazolium salts the product was highly moisture-sensitive. Infrared analysis of the product showed no CN stretching band (c. 2230 cm^{-1}). The spectrum is shown in Fig. 3.2.2.

3.2.3 Reaction of [SNS][AsF_6] with 4-Chlorobenzonitrile

Reaction of [SNS][AsF_6] with 4-chlorobenzonitrile in liquid SO_2 over 24 hours gave 5-(4-chlorophenyl)-1,3,2,4-dithiadiazolium hexafluoroarsenate **8** in 95% yield, as shown in Scheme 3.2.1. The product, a yellow powder, was soluble at room temperature in liquid SO_2 and CH_3CN, sparingly soluble in CH_2Cl_2 and insoluble in toluene and hexane. In common with all dithiadiazolium salts the product was highly moisture-sensitive. Infrared analysis of the product showed no CN stretching band (c. 2230 cm^{-1}). The spectrum is shown in Fig. 3.2.3.



Scheme 3.2.1

Preparation of *mono*-(1,3,2,4-dithiadiazolium) salts from substituted benzonitriles ; reduction of 5-(4-bromophenyl)-1,3,2,4-dithiadiazolium salt **9** to dithiadiazolyl **10**

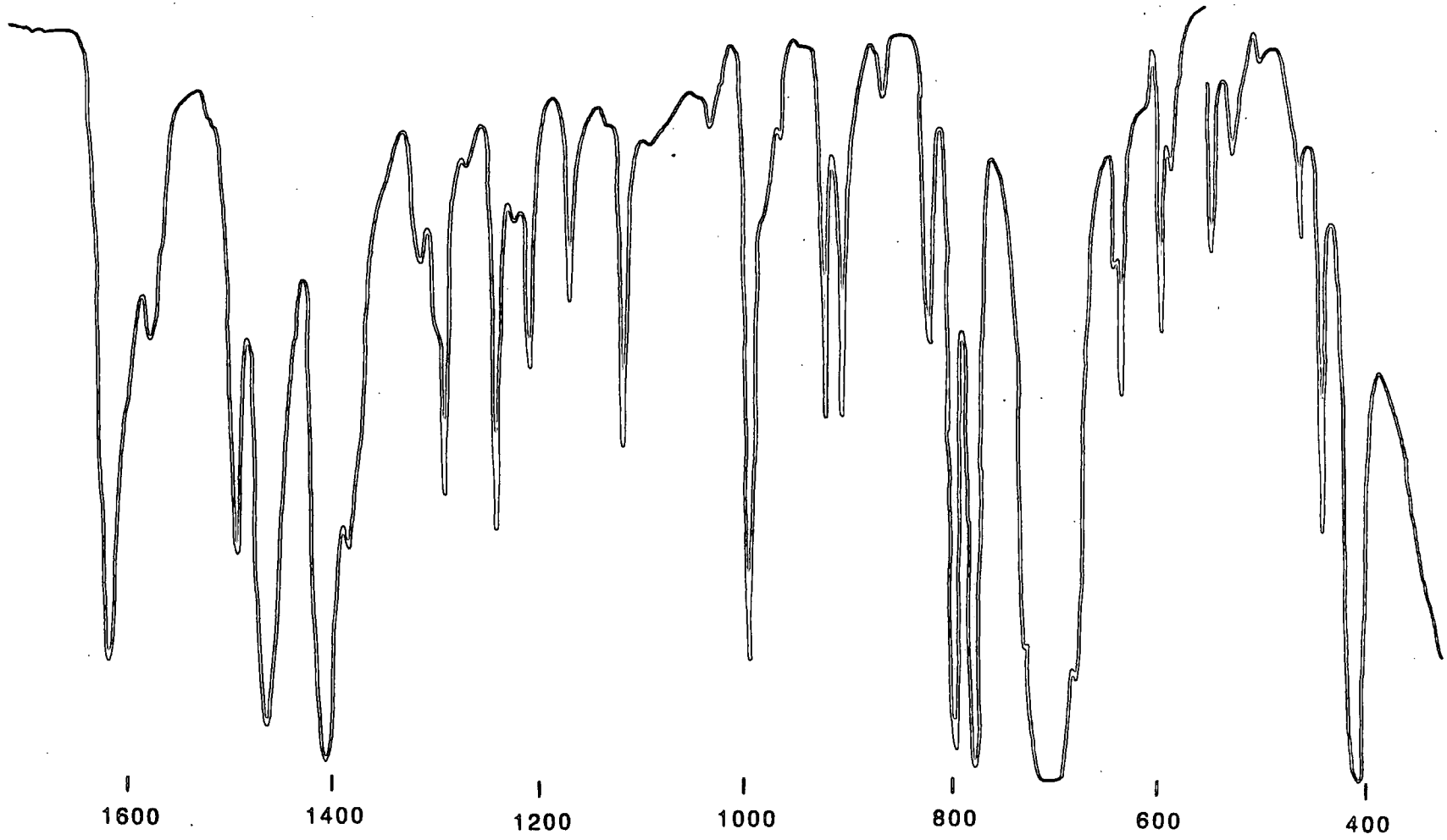


Fig. 3.2.1

IR spectrum (Nujol mull) of

[*o*-F-C_6H_4-CNSNS][AsF_6] 6

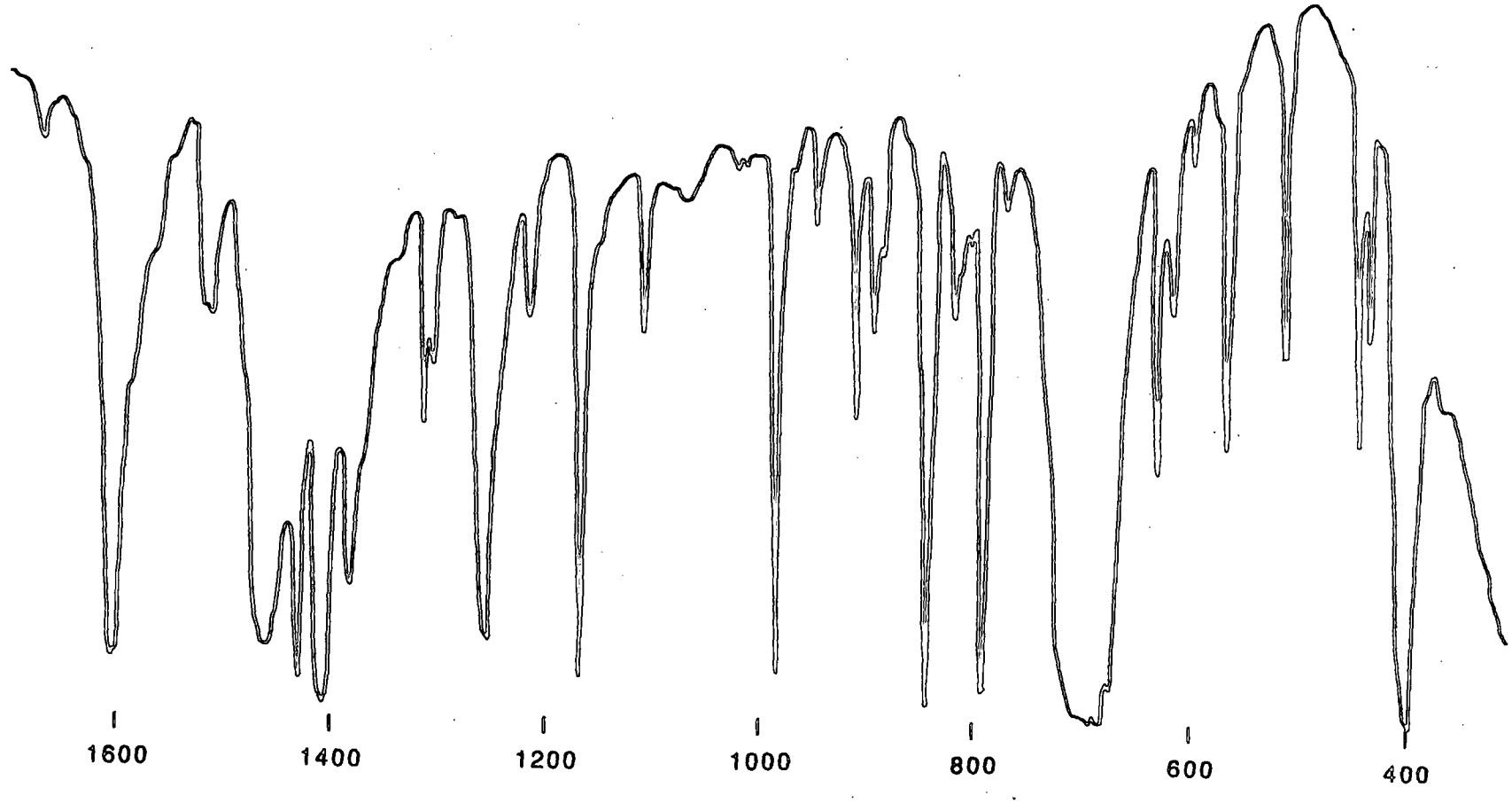


Fig. 3.2.2

IR spectrum (Nujol mull) of

[*p*-F-C_6H_4-CNSNS][AsF_6] 7

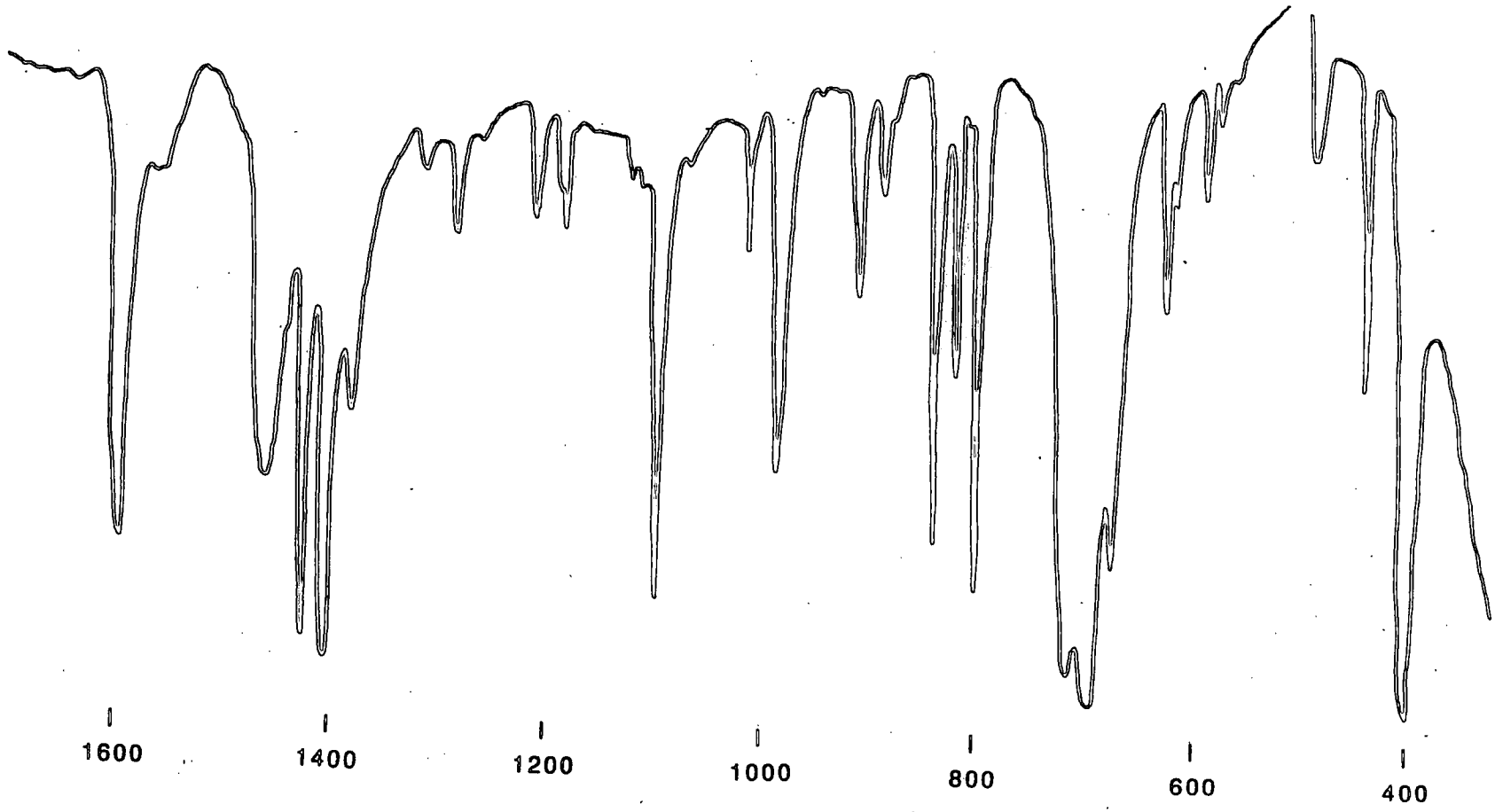


Fig. 3.2.3

IR spectrum (Nujol mull) of

[*p*-Cl-C_6H_4-CNSNS][AsF_6] 8

3.2.4 Reaction of [SNS][AsF_6] with 4-Bromobenzonitrile

Reaction of [SNS][AsF_6] with 4-bromobenzonitrile in liquid SO_2 over 24 hours gave 5-(4-bromophenyl)-1,3,2,4-dithiadiazolium hexafluoroarsenate **9** in 73% yield, as shown in Scheme 3.2.1. The relatively low yield can be attributed to the relatively high solubility of the product in CH_2Cl_2, which was used to wash out coloured impurities. The product, a bright yellow solid, was soluble at room temperature in liquid SO_2 and CH_3CN, moderately soluble in CH_2Cl_2 and insoluble in toluene and hexane. In common with all dithiadiazolium salts the product was highly moisture-sensitive. Infrared analysis of the product showed no CN stretching band (c. 2230 cm^{-1}). The spectrum is shown in Fig. 3.2.4. The purified product was reduced with Ph_3Sb in the presence of Bu_4NCl to give the dithiadiazolyl **10** which was purified by sublimation *in vacuo*. The IR spectrum of **10** is shown in Fig. 3.2.5.

3.2.5 Reaction of [SNS][AsF_6] with 2-Methylbenzonitrile

Reaction of [SNS][AsF_6] with 2-methylbenzonitrile (*o*-tolunitrile) in liquid SO_2 over 24 hours gave 5-(2-methylphenyl)-1,3,2,4-dithiadiazolium hexafluoroarsenate **11** in 94% yield, as shown in Scheme 3.2.1. The product, a bright yellow solid, was soluble at room temperature in liquid SO_2 and CH_3CN, moderately soluble in cold CH_2Cl_2 and insoluble in toluene and hexane. In common with all dithiadiazolium salts the product was highly moisture-sensitive. Infrared analysis of the product (Fig. 3.2.6) showed no CN stretching band (c. 2230 cm^{-1})

3.2.6 NMR Spectra of *mono*-(1,3,2,4-Dithiadiazolium) Salts

Cycloaddition of $[SNS]^+$ across the CN triple bond of substituted benzonitriles to give *mono*-(1,3,2,4-dithiadiazolium) salts does not involve any of the other substituents directly, and thus ^1H NMR spectra of the products have the same form as those of the parent nitriles. However, introduction of a positively-charged substituent (the dithiadiazolium ring) onto the benzene ring causes changes in the shielding of hydrogen

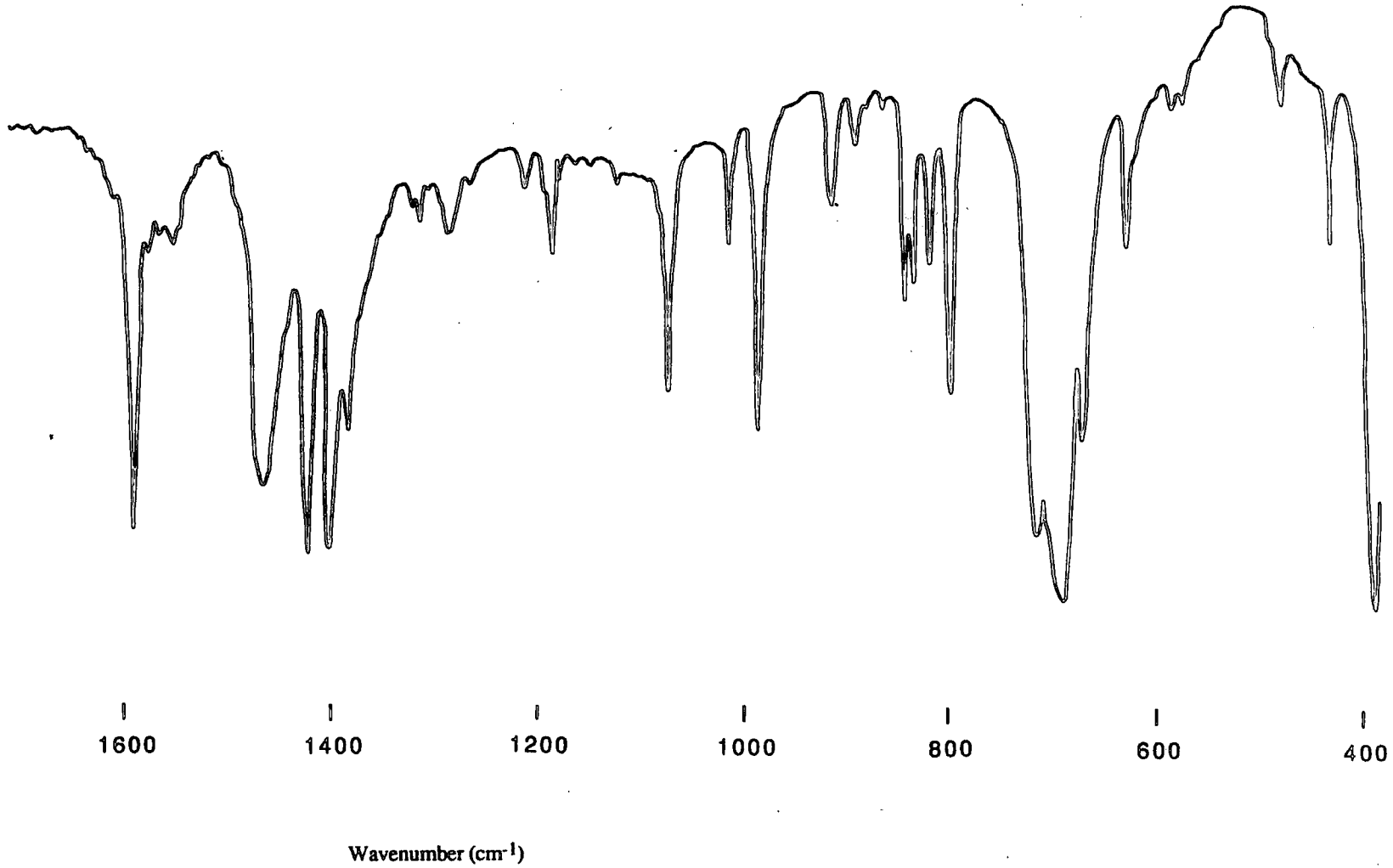


Fig. 3.2.4

IR spectrum (Nujol mull) of

[*p*-Br-C_6H_4-CNSNS][AsF_6] 9

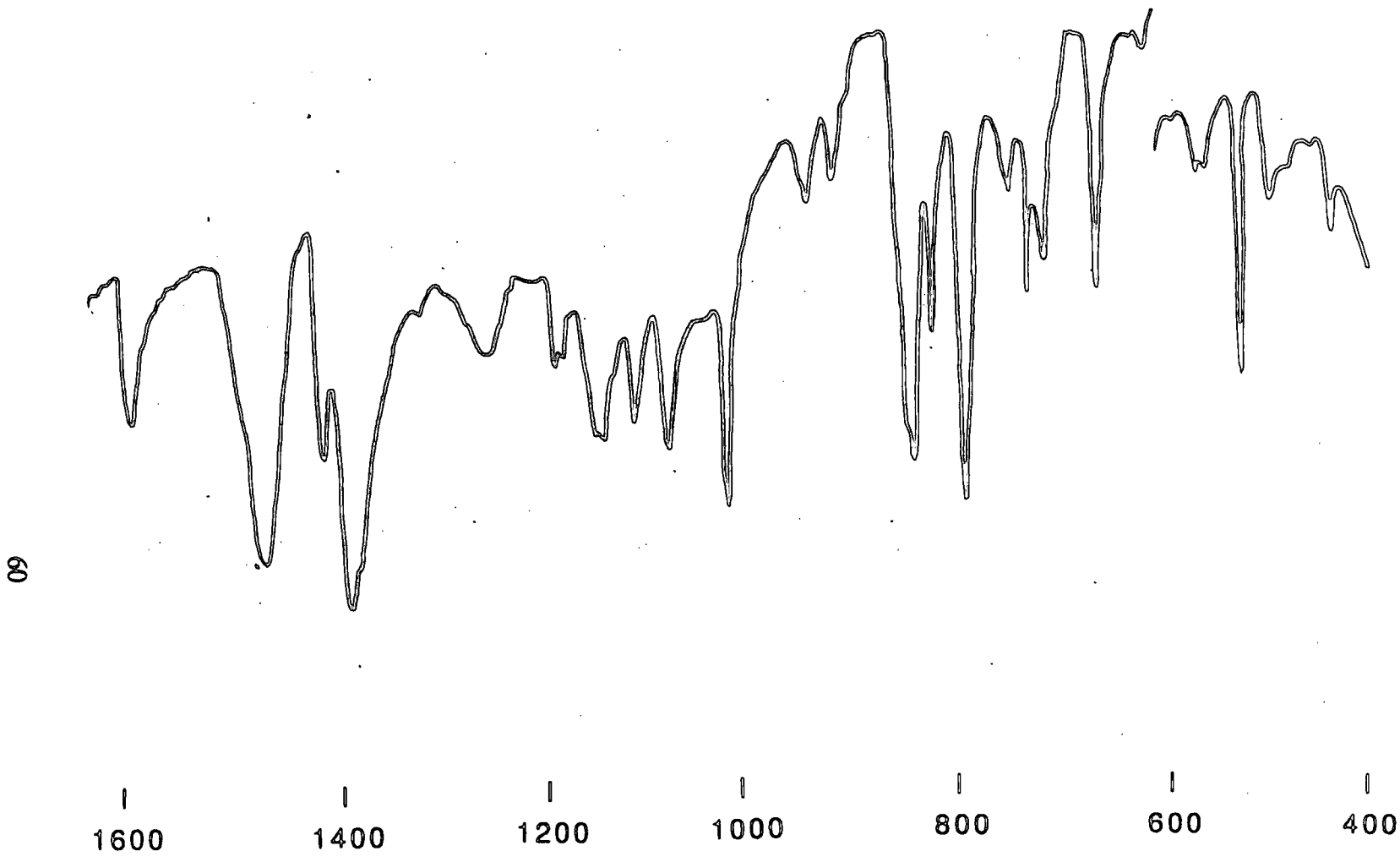


Fig. 3.2.5

IR spectrum (Nujol mull) of

(p-Br-C_6H_4-CN_2S_2)$_2$ 10

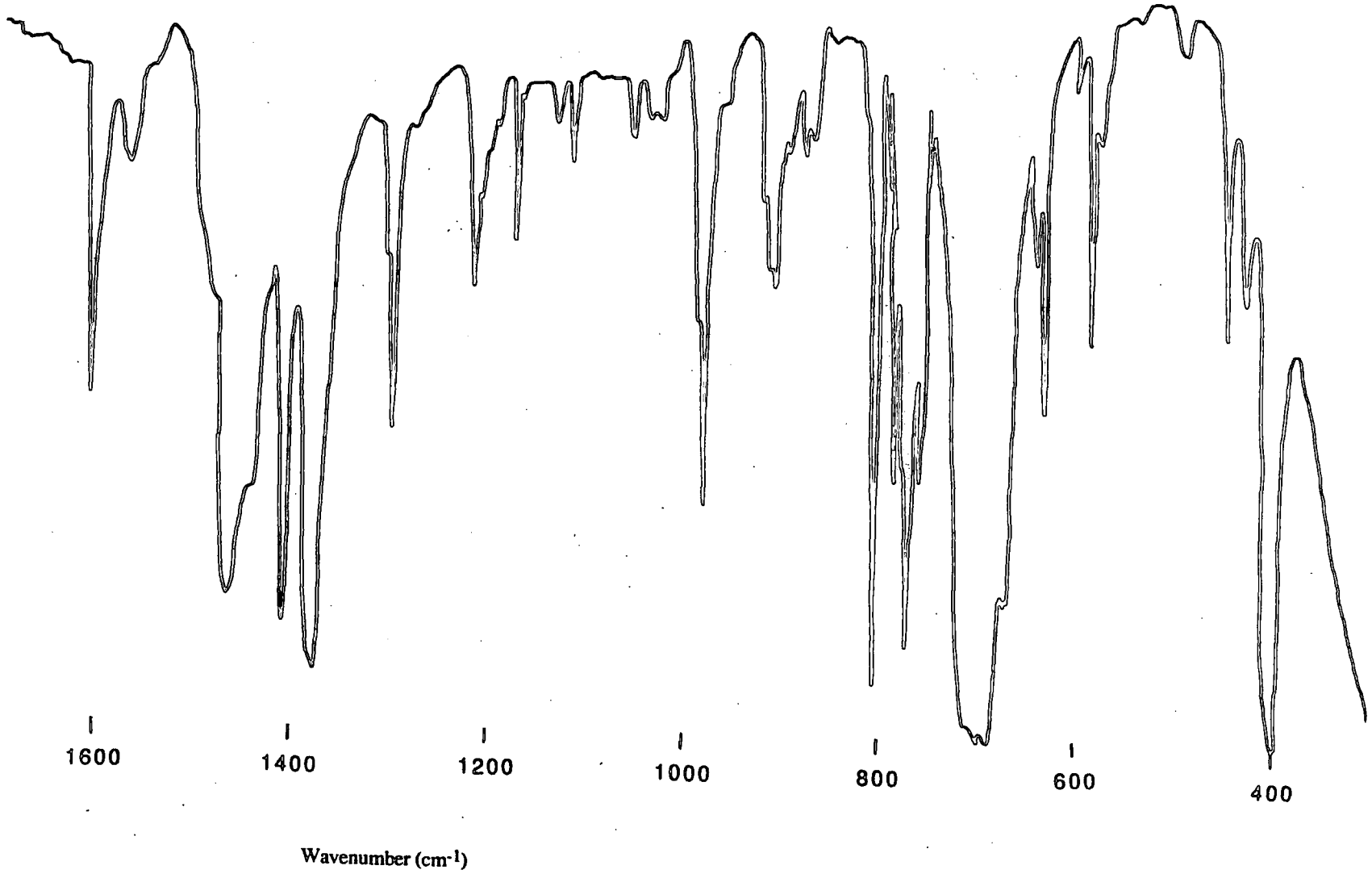


Fig. 3.2.6

IR spectrum (Nujol mull) of

[*o*-(CH_3)-C_6H_4-CNSNS][AsF_6] 11

substituents, and hence differences in chemical shift are observed for a given hydrogen in a dithiadiazolium salt compared to its parent nitrile. The observed effect is a downfield shift of all resonances, with the largest shift increment observed for hydrogens *ortho-* with respect to the carbon bearing the dithiadiazolium ring.

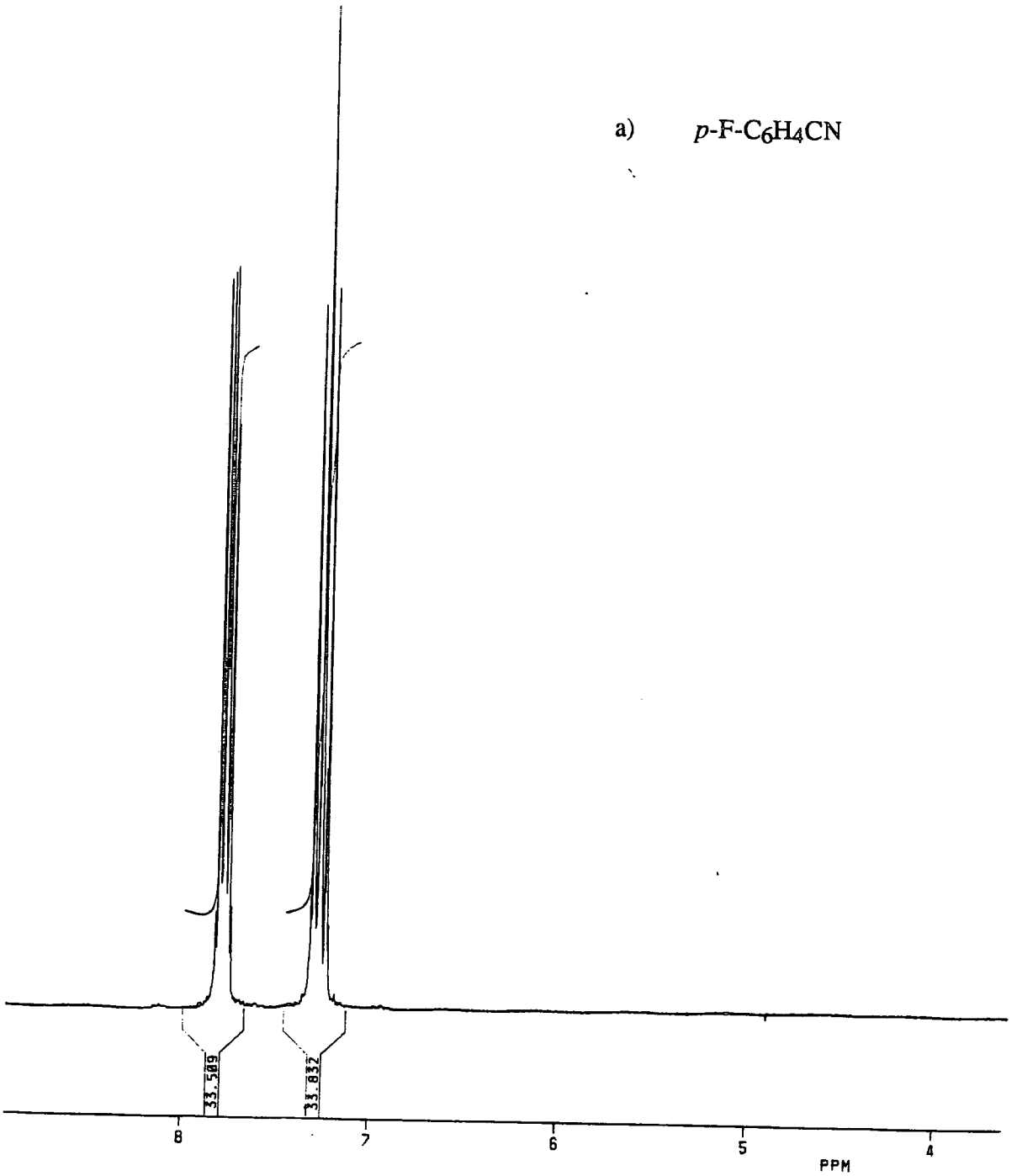
Fig. 3.2.7 shows the ^{1}H NMR spectra of 7,8,9 and 11 alongside those of their parent nitriles. In all cases, resonances are shifted downfield in the salt compared to the nitrile. The spectrum of 11, shown in Fig. 3.2.7h, is particularly interesting in that formation of the dithiadiazolium ring brings about shift differences that cause noticeable resolution of the signals for the four aryl hydrogens. These resonces in 2-methylbenzonitrile, shown in Fig. 3.2.7g occur as two multiplets, and even using a 250MHz spectrometer resolution is difficult. In the spectrum of 11 (Fig. 3.2.7h) the aryl hydrogen signals occur as three multiplets. The doublet at δ 8.2 ppm can be assigned to the hydrogen *ortho-* with respect to the dithiadiazolium ring (C6 in 2-methylbenzonitrile). Tentative assignments for the full spectrum are shown in Fig. 3.2.8.

For the 1,3,2,4-dithiadiazolium salts derived from p-substituted benzonitriles there is no such problem since the aryl hydrogens are distributed about the benzene ring approximately symmetrically and their spectra are therefore symmetrical also, consisting of two doublets of doublets. Further splittings are observed in the spectrum of the 5-(4-fluorophenyl)-1,3,2,4-dithiadiazolium cation because of spin-spin coupling between hydrogen and fluorine. Spectra of this cation and its parent nitrile are shown in Fig. 3.2.7a-b.

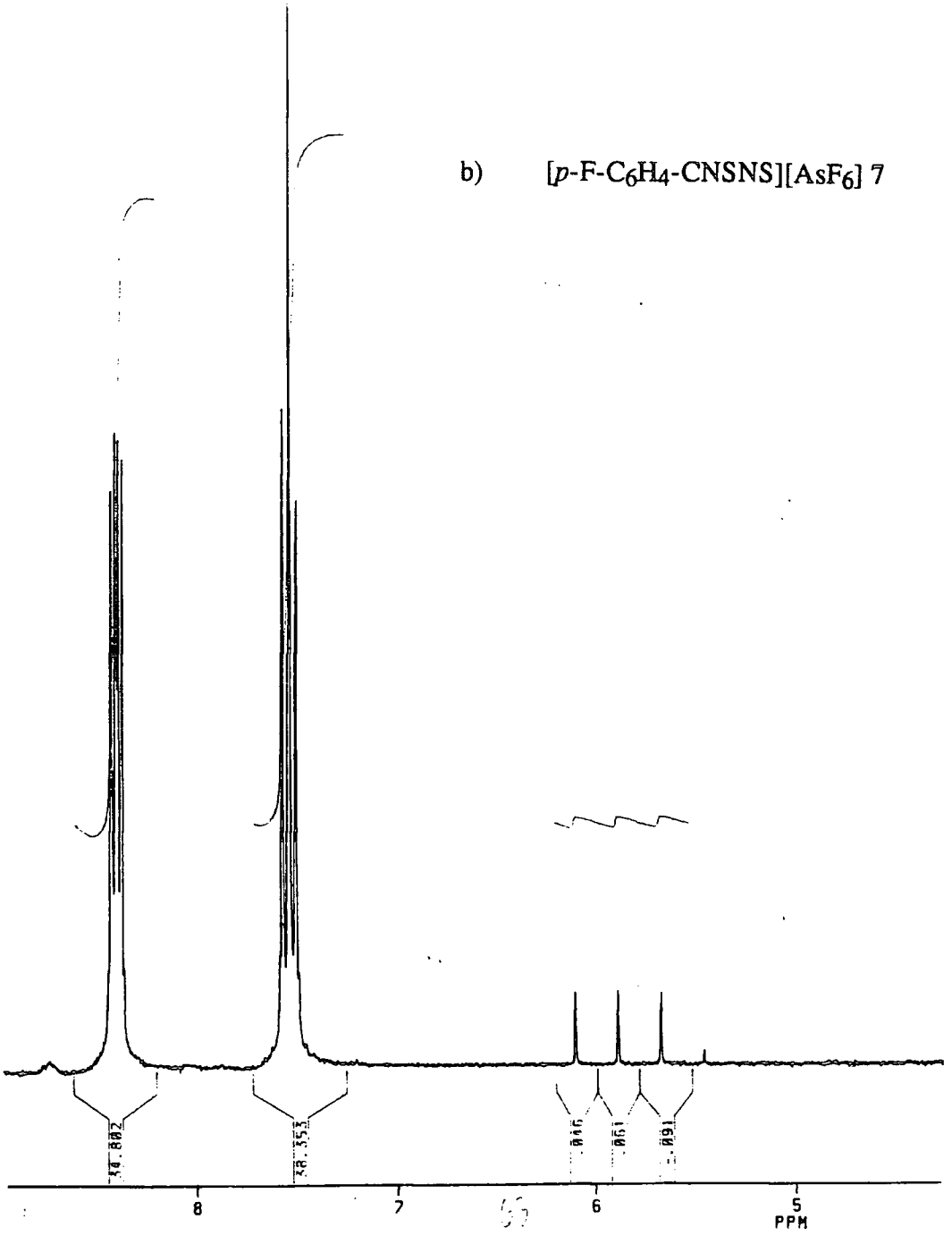
Fig. 3.2.7

^{1}H NMR spectra of *mono*-(1,3,2,4-dithiadiazolium) salts and their parent nitriles

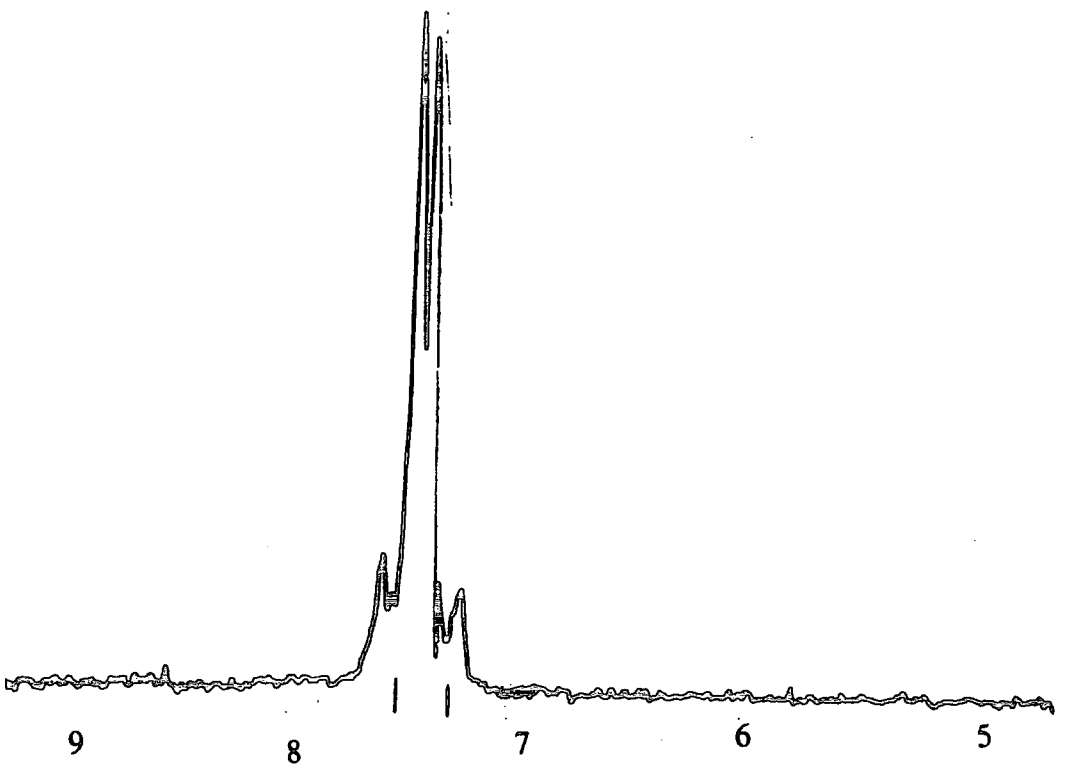
Solvent : CD_3CN Reference : TMS



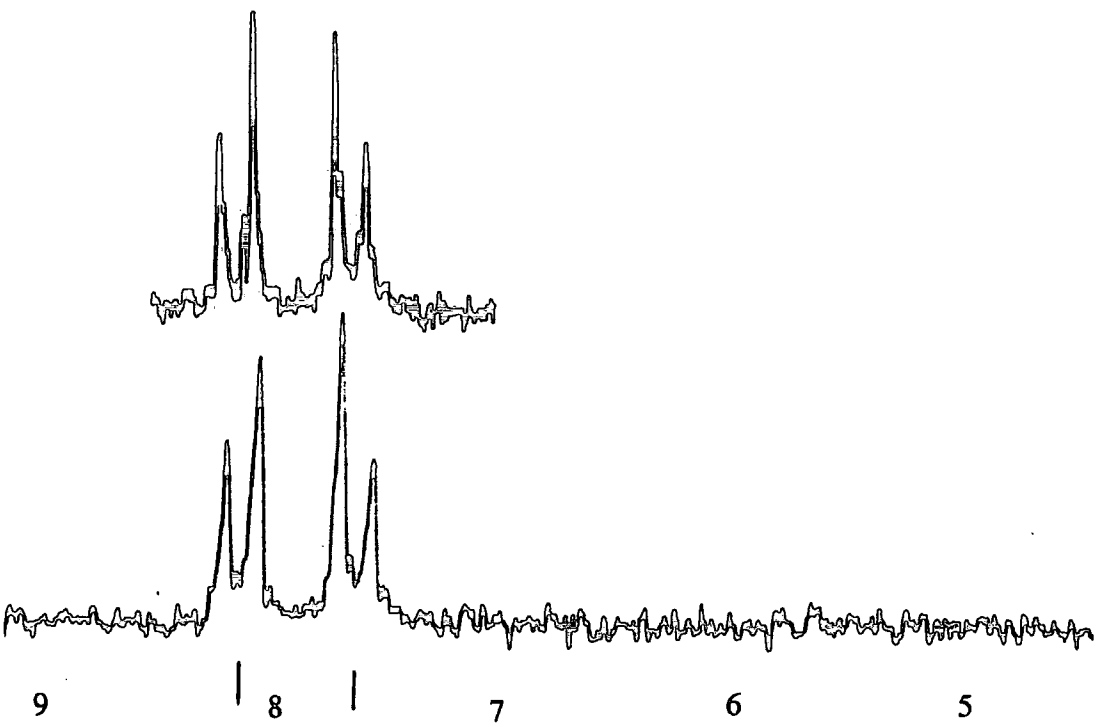
b) [*p*-F-C_6H_4-CNSNS][AsF_6] 7



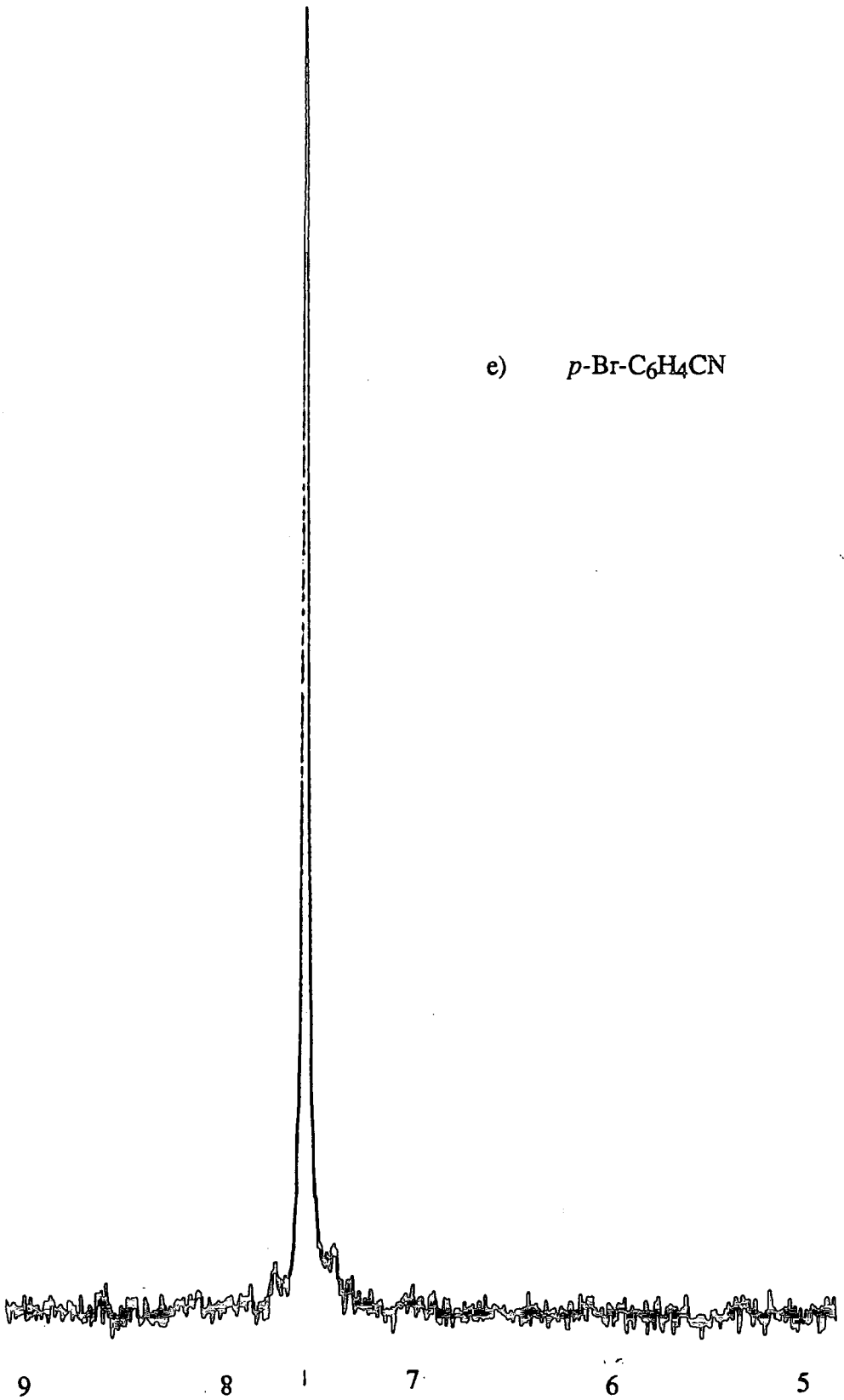
c) p-Cl-C_6H_4CN



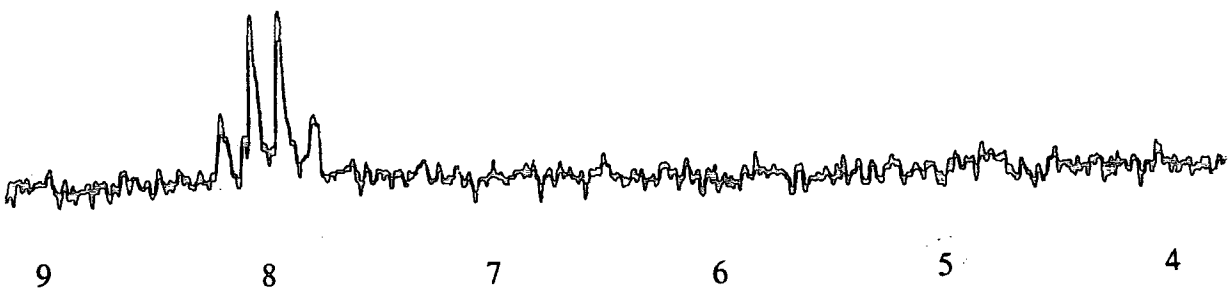
d) [*p*-Cl-C_6H_4-CNSNS][AsF_6] 8



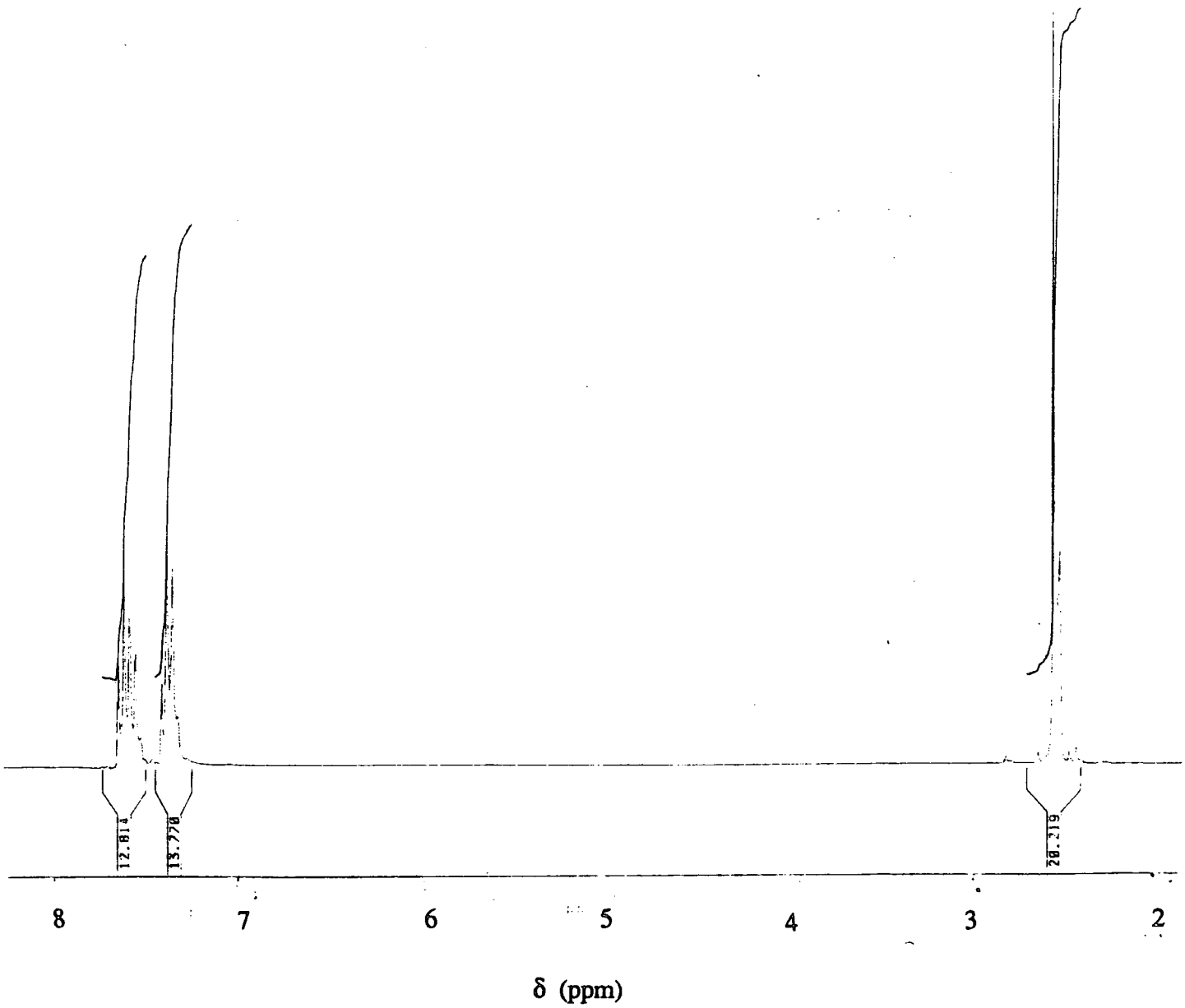
e) *p*-Br-C_6H_4CN



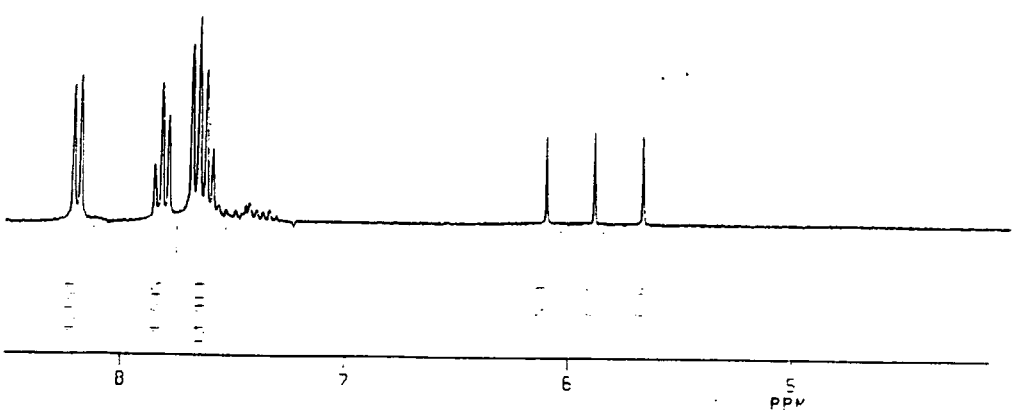
f) [*p*-Br-C_6H_4-CNSNS][AsF_6] 9

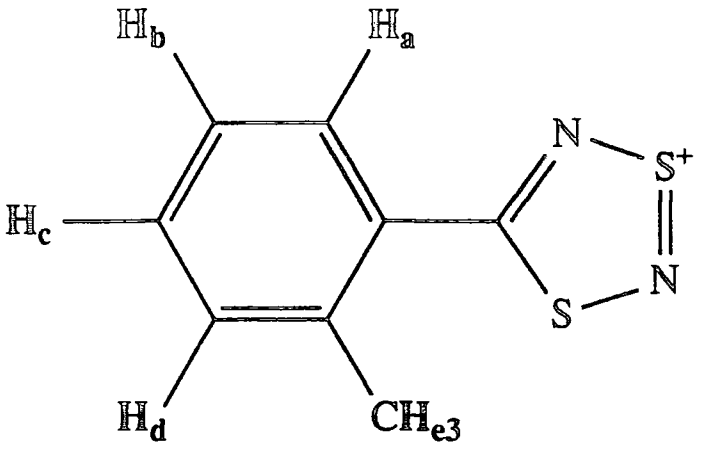


g) *o*-(CH_3)-C_6H_4CN



h) [*o*-(CH_3)-C_6H_4-CNSNS][AsF_6] 11





11

H_a : doublet 8.2 ppm

H_b : doublet of doublets 7.8 ppm

H_c : doublet of doublets 7.6 ppm

H_d : doublet approx. 7.7 ppm

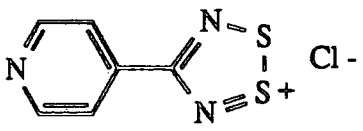
H_e : Singlet 2.8 ppm

Fig. 3.2.8

Tentative assignments for the ^1H NMR spectrum of **11**

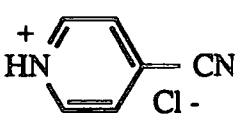
3.2.7 Reaction of NH_4Cl / SCl_2 with 4-Cyanopyridine

Reaction of 4-cyanopyridine with SCl_2 and NH_4Cl under an atmosphere of Cl_2 under reflux for 48 hr did not give the target molecule 4-(4-azaphenyl)-1,2,3,5-dithiadiazolium chloride **12**, but a mixture of unreacted starting materials and a colurless product. After filtration of the reaction mixture and removal of SCl_2 with dry diethyl ether, unreacted 4-cyanopyridine was removed by sublimation *in vacuo*, leaving a mixture of NH_4Cl and another product.



12

A possible explanation for the failure of this reaction to yield **12** is the low nucleophilicity of the nitrile group, due to the presence of the electron-withdrawing pyridyl group. The formation of 1,2,3,5-dithiadiazolium salts from nitriles and NH_4Cl/SCl_2 is driven by nucleophilic attack by the nitrile group on (NSCl), formed *in situ* from NH_4Cl and SCl_2[6]. Electron-withdrawing substituents will decrease electron density on the nitrile group and hence diminish reactivity. In addition, the presence of the basic pyridyl nitrogen in 4-cyanopyridine makes possible a side reaction, *viz* the trapping of HCl (produced in the reaction of NH_4Cl and SCl_2 to form (NSCl)) to form 4-cyanopyridine hydrochloride **13**.



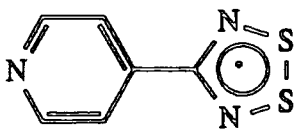
13

The resulting positive charge on the pyridyl group would draw further electron density from the nitrile group and thus diminish its nucleophilicity to the extent that formation of **12** would be extremely slow, if not altogether prevented.

A repeat experiment was attempted, but a leak in the Cl_2 scrubber was found, and the reaction mixture was sealed under Cl_2, and left unattended for six months in a corner of the fume cupboard. After this time, in the process of clearing up unwanted chemicals, the reaction vessel was opened up and worked up in the same way as for 1,2,3,5-dithiadiazolium salt preparations[6]. An orange solid, insoluble in diethyl ether, was obtained, and extracted into SO_2, in which it was found to be highly soluble.

Reaction of this material with excess Ph_3Sb in liquid SO_2 in an ESR tube gave a dark green solution, and an ESR spectrum was obtained. This is shown in Fig. 3.2.9. The spectrum consists of 5 lines, in 1:2:3:2:1 ratio, consistent with one unpaired spin coupling equally to two I=1 nuclei ie 2 x ^{14}N. The hyperfine splitting constant a_N is approx. 0.49 mT, which is a value consistent with the material being a 1,2,3,5-dithiadiazolyl[2].

It was thus concluded that the spectrum was likely to be that of 4-(4-azaphenyl)-1,2,3,5-dithiadiazolyl **14**.



14

Bulk reduction of the precursor material with Ph_3Sb in CH_2Cl_2 gave a dark violet solid from which Ph_3Sb and Ph_3SbCl_2 were removed by extraction with n-hexane. Sublimation (130°C, 10^{-3} mmHg) gave a blue-red dichroic solid. Elemental analyses indicated that this material had an empirical formula consistent with that of **14**. Yield was very low (40 mg sublimed from 750 mg of crude product). The solid state ESR spectrum of the sublimed material is shown in Fig. 3.2.10., and its IR spectrum in Fig. 3.2.11.

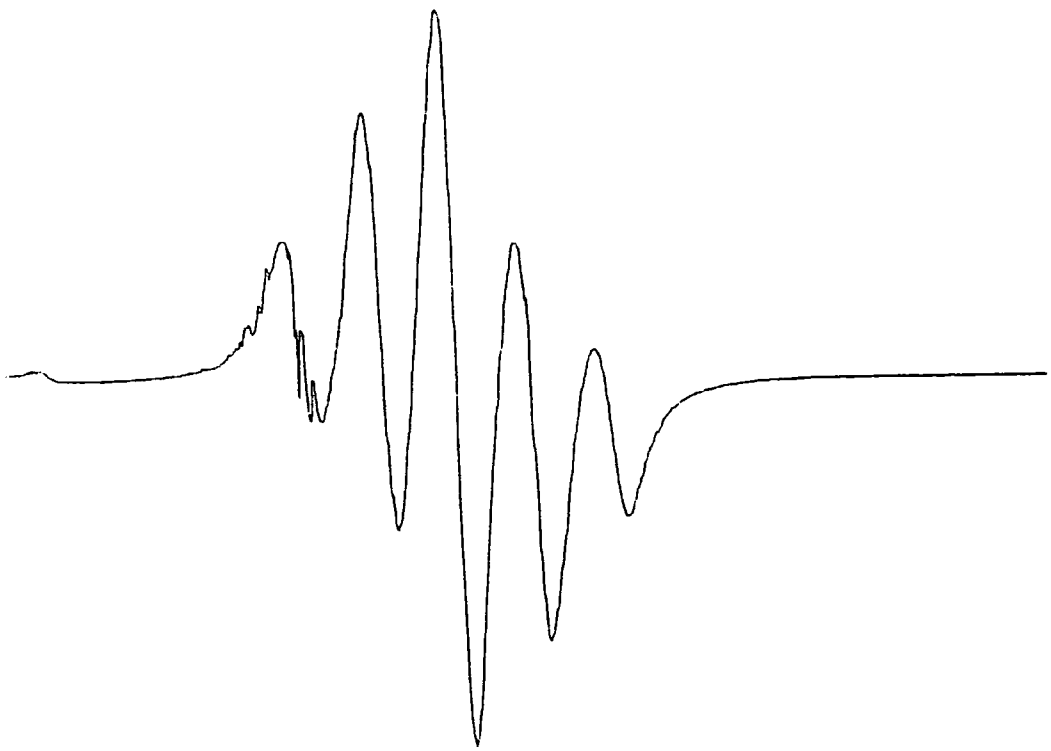


Fig. 3.2.9

Room-temperature ESR spectrum (in SO_2) of 14 generated *in situ*

a_N = 0.49 mT

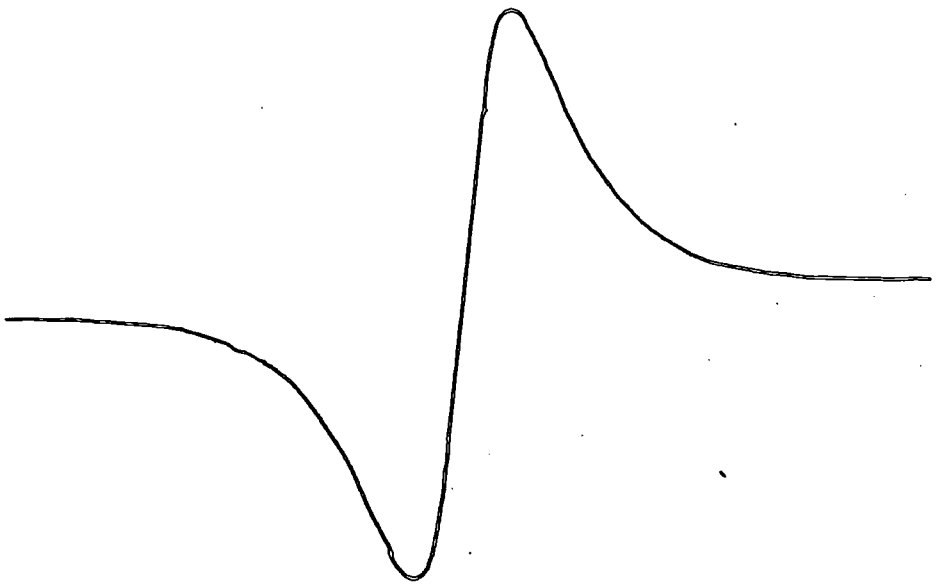


Fig. 3.2.10

Room temperature solid-state ESR spectrum of sublimed 14

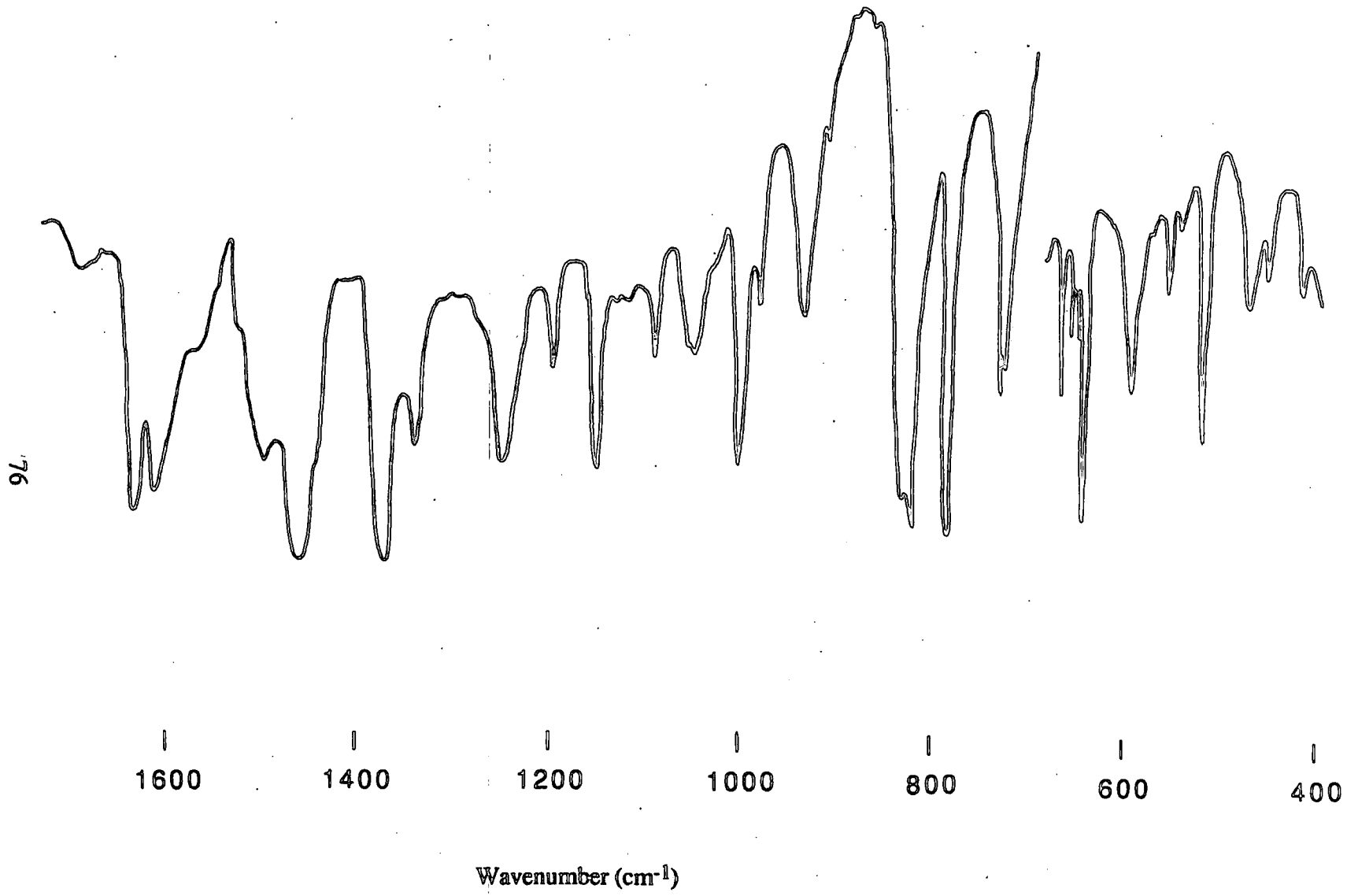
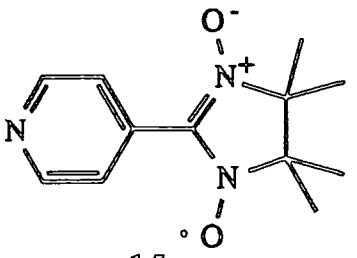


Fig. 3.2.11

IR spectrum (Nujol mull) of sublimed 14

The synthesis of dithiadiazolyl radicals containing substituents with ligating potential may provide an efficient route to metal-radical complexes. Much work has already been done on the nitroxyls. The nitroxyl species NITPy (15) has been incorporated into copper complexes by direct combination of 15 and a precursor complex[7] as shown in Eq. 3.2.1.

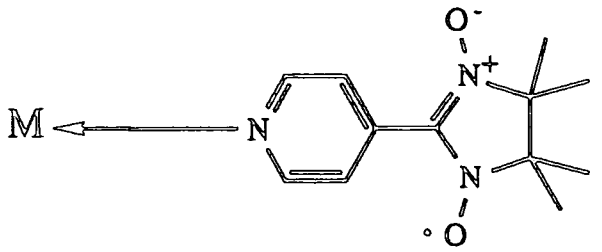


15

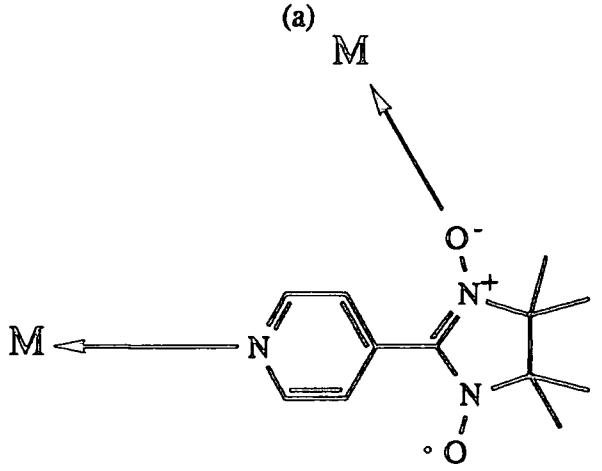
Eq. 3.2.1 $3Cu(hfac)_2 + 2NITPy\ (15) = [Cu(hfac)_2]_3(NITPy)_2\ (16)$

(hfac = hexafluoroacetylacetonato- ligand)

Complex 16 is a chain compound, with ferromagnetic coupling within chains, and antiferromagnetic coupling between chains. In this complex, 15 is coordinated to the metal centre via the pyridyl nitrogen as shown in Fig. 3.2.12a. Other metal-NITPy systems have been prepared with metal-pyridyl coordination[8,9], and also with coordination via the pyridyl ring to one metal centre and one of the oxygens in the nitroxyl ring to an adjacent metal[10,11], as shown in Fig. 3.2.12b. This is clearly a subject meriting further attention.



(a)



(b)

Fig.3.2.12

Modes of coordination of 15 to metals in complexes

a : *via* pyridyl nitrogen only

b : *via* pyridyl nitrogen and nitroxyl oxygen

3.2.8 Reaction of [SNS][AsF_6] with 4-Cyanopyridine

Attempts were made to prepare a salt of the 5-(4-azaphenyl)-1,3,2,4-dithiadiazolium cation π by reaction of 4-cyanopyridine with [SNS][AsF_6] in liquid SO_2, but the clean, high yield reaction hoped for did not occur. A mixture of many different products was obtained, many of which were highly air- and moisture-sensitive. IR spectra of the crude reaction mixture following removal of SO_2 showed bands in all sections of the IR window, including strong N-H stretching bands.

The reasons for the failure of this reaction are no doubt manifold. It is known that [SNS]+ attacks C-H bonds in benzene[2]. It is likely that the C-H bonds adjacent to the pyridyl nitrogen in 4-cyanopyridine, being more polar than the C-H bonds in benzene, will react readily with [SNS]+. In addition, the pyridyl nitrogen may attack [SNS]+ in a Michael-type reaction as shown in Fig. 3.2.13, perhaps leading to an highly reactive intermediate species 17 which then undergoes further transformation. It is clear that the introduction of functionality into a nitrile can transform the reaction with [SNS]+ from a clean, orderly, high yield reaction into a complex, non-trivial system.

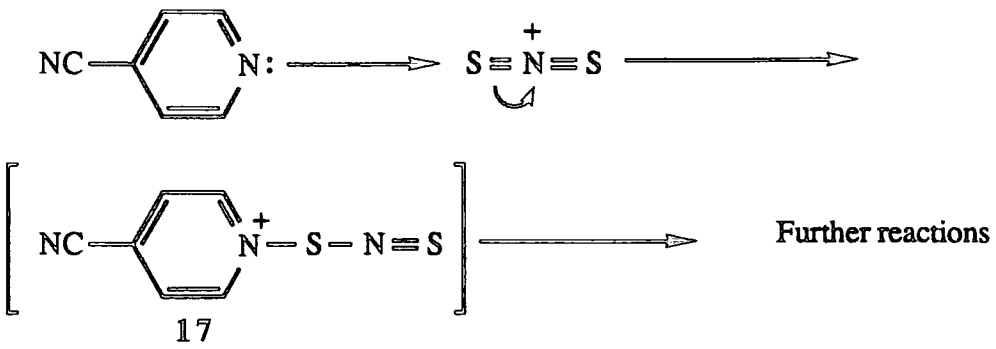


Fig. 3.2.13

Possible attack of pyridyl nitrogen on $[SNS]^+$ leading to reactive species

Experimental

Preparation of [2-F-C_6H_4CNSNS][AsF_6] :

[SNS][AsF_6] (267 mg, 1.0 mmol) was placed in the rear leg of a "dog". 2-Fluorobenzonitrile (0.5 ml, excess) was syringed into the front leg and degassed in a single freeze-thaw cycle. SO_2 was introduced into both legs sufficient to dissolve both reagents. The two solutions were then mixed and stirred for 24 hrs at room temperature. Following removal of solvent the crude product was washed repeatedly with CH_2Cl_2 to remove coloured impurities and residual 2-fluorobenzonitrile. The purified product was dried *in vacuo*.

Appearance : Pale yellow solid, highly moisture-sensitive.

Yield : 368 mg, 0.95 mmol, 95%.

IR (Nujol Mull) : ν_{max} 3315w br, 3100w, 3080w, 1617s, 1595sh, 1570m, 1560sh, 1490s, 1400s, 1310w, 1290sh, 1285m, 1267w, 1237m, 1220w, 1205m, 1165w, 1112m, 1085w br, 1030w, 990s, 980sh, 960w, 915m, 900m, 860w, 815m, 790s, 770s, 700vs br, 635w, 630m, 590w, 580w, 540w, 520w, 455w, 435m, 400s cm^{-1}.

Analysis : Found (required) C : 21.63 (21.66), H : 0.96 (1.04), N : 7.09 (7.22) %.

Preparation of [4-F-C_6H_4CNSNS][AsF_6] :

4-Fluorobenzonitrile (363 mg, 3.0 mmol) and [SNS][AsF_6] (801 mg, 3.0 mmol) were placed together in the rear leg of a "dog". SO_2 was introduced sufficient to dissolve both reagents and the mixture was stirred for 24 hrs at room temperature. Following removal of solvent the crude product was washed repeatedly with CH_2Cl_2 to remove coloured impurities and residual 4-fluorobenzonitrile. The purified product was dried *in vacuo*.

Appearance : Pale yellow solid, highly moisture-sensitive.

Yield : 1.117 g, 2.88 mmol, 96%.

IR (Nujol Mull) : ν_{max} 3120w, 3080w, 1670w, 1607s, 1600sh, 1595sh, 1565sh, 1525sh, 1510m, 1430s, 1410s, 1315m, 1305w, 1255s, 1215w, 1170s, 1110w, 980s, 950w, 913m, 896m, 885w, 845s, 820w, 810sh, 793s, 770w, 700vs br, 630m, 620w, 600w, 570m, 515m, 445m, 435w, 400s cm^{-1}.

Analysis : Found (required) C : 21.30 (21.66), H : 0.95 (1.04), N : 7.14 (7.22) %

^1H NMR (CD_3CN, TMS) : δ 7.54 (dd) 2H, δ 8.41 (dd) 2H

Preparation of [4-F-C_6H_4CNSNS][Cl] :

[4-F-C_6H_4CNSNS][AsF_6] (388 mg, 1.0 mmol) and Bu_4NCl (278 mg, 1.0 mmol) were placed together in the rear leg of a "dog". CH_3CN (5 ml) was introduced into the front leg and degassed in a single freeze-thaw cycle. Upon introduction of the solvent onto the reagent mixture an orange precipitate formed immediately. The mixture was stirred overnight at room temperature, during which time the product had become bright yellow. The supernatant was filtered off and the crude product was washed twice with back-distilled solvent. CH_3CN was pumped off and replaced with CH_2Cl_2 and the product was washed repeatedly. Following removal of CH_2Cl_2 the product was transferred to a closed extractor and extracted into SO_2. It was noticed that a significant amount of insoluble material was left at the frit during extraction. The purified product was dried *in vacuo*.

Appearance : Yellow microcrystalline solid, highly moisture - sensitive.

Yield : 136 mg, 0.58 mmol, 58%.

IR (Nujol Mull) : ν_{max} 3100w, 3060w, 1905w br, 1695w br, 1600sh, 1595s, 1510w, 1430s, 1410s, 1350w br, 1310s, 1240m, 1235sh, 1225w, 1218w, 1165m, 1107w, 1005w, 990m, 857s, 830w, 790s, 770w, 670w, 665sh, 615w, 565w, 515w, 455w br, 435w, 420m, 400w cm^{-1}.

Analysis : Found (required) C : 35.72 (35.82), H : 1.82 (1.72), N : 11.57 (11.94) %

Preparation of [4-Cl-C_6H_4CNSNS][AsF_6] :

4-Chlorobenzonitrile (137 mg, 1.0 mmol) and [SNS][AsF_6] (267 mg, 1.0 mmol) were placed together in the rear leg of a "dog". SO_2 was introduced sufficient to dissolve both reagents and the mixture was stirred for 24 hrs at room temperature. Following removal of solvent the crude product was washed repeatedly with CH_2Cl_2 to remove coloured impurities. The purified product was dried *in vacuo*.

Appearance : Yellow powder.

Yield : 384 mg, 0.95 mmol, 95%.

IR (Nujol Mull) : ν_{max} 3095w, 1595s, 1565w br, 1440sh, 1425s, 1400s, 1320w, 1290w, 1215w, 1190sh, 1185w, 1125w, 1100s, 1072w, 1020w, 990m, 915m, 890w, 840s, 820m, 800s, 720s, 690s br, 630m, 620w, 595w, 580w, 495w, 445m, 400s cm^{-1}.

Analysis : Found (required) C : 20.43 (20.78), H : 1.02 (1.00), 6.95 (6.93) %.

^1H NMR (CD_3CN, TMS) : δ 7.67 (dd) 2H, δ 8.17 (dd) 2H

Preparation of [4-Br-C_6H_4CNSNS][AsF_6] :

4-Bromobenzonitrile (760 mg, 4.18 mmol) and [SNS][AsF_6] (1120 mg, 4.19 mmol) were placed together in the rear leg of a "dog". SO_2 was introduced sufficient to dissolve both reagents and the mixture was stirred for 18 hrs at room temperature. Following removal of solvent the crude product was washed repeatedly with CH_2Cl_2 to remove coloured impurities. The purified product was dried *in vacuo*.

Appearance : Yellow powder.

Yield : 1510 mg, 3.36 mmol, 80%.

IR (Nujol Mull) : ν_{max} 3110w, 1590s, 1420s, 1400s, 1320w, 1310w, 1285w, 1210w, 1190m, 1130w, 1075m, 1020w, 990m, 920m, 890w, 845m, 840m, 820m, 800s, 720s, 690s br, 670m, 630m, 585w, 570w, 480w, 435m, 390s cm^{-1}.

Analysis : Found (required) C : 18.89 (18.72), H : 0.90 (0.89), N : 6.29 (6.23) %

^1H NMR (CD_3CN, TMS) : δ 7.83 (dd) 2H, δ 8.10 (dd) 2H

Preparation of (p-Br-C_6H_4-CN_2S_2)2 :

[4-Br-C_6H_4CNSNS][AsF_6] (1.50g, 3.35 mmol) and Bu_4NCl (1.11g, 4.01 mmol) were placed together in the rear leg of a "dog". CH_3CN was introduced sufficient to cover fully the reaction mixture, and a bright orange precipitate of the chloride [4-Br-C_6H_4CNSNS]Cl formed immediately. the rear leg was sealed off, and Ph_3Sb (593 mg, 1.68 mmol) was introduced into the front leg. CH_3CN was removed *in vacuo* and replaced by CH_2Cl_2 sufficient to dissolve all the Ph_3Sb and cover the mixture of [4-Br-C_6H_4CNSNS]Cl and Bu_4NAsF_6. Upon introduction of the Ph_3Sb solution into the rear leg the mixture was stirred vigorously, and after 5 min. the mixture began to darken rapidly. After 24 hr the rear leg contained a purple-black solution and a large amount of black precipitate. Following removal of solvent *in vacuo* the crude product was loaded into the glove box and transferred to a vacuum sublimer. Purification was achieved by sublimation at 105°C / 10^{-3} mmHg, and three crops of the product were taken.

Appearance: black-red dichroic polycrystalline solid.

Yield: 553 mg, 2.16 mmol, 63% based on *p*-bromobenzonitrile

IR (Nujol Mull) : ν_{max} 1558m, 1495sh, 1400m, 1375vs, 1370sh, 1240wbr, 1177m, 1140sh, 1130m, 1100w, 1068m, 1010m, 928w, 903w, 830sh, 828s, 810m, 778s, 730w, 712m, 698w, 647m, 593w, 550w, 540w, 510m, 480w, 460w, 418w cm^{-1}

Analysis : Found (required) C : 32.35 (32.30), H : 1.54 (1.54), N : 10.82 (9.77) %

Preparation of [2-CH_3-C_6H_4CNSNS][AsF_6] :

[SNS][AsF_6] (534 mg, 2.0 mmol) was placed in the rear leg of a "dog" and sealed off via the vacuum tap. 2-Methylbenzonitrile (*o*-tolunitrile) (0.5 ml) was introduced into the front leg and degassed during three freeze-thaw cycles. SO_2 was intoduced into both legs sufficient to fully dissolve both reagents. The solution of *o*-tolunitrile was then filtered over onto the solution of [SNS][AsF_6], and the resulting solution was stirred overnight at room temperature. Solvent was removed from the crude product and replaced by hexane, with

which the product was washed to remove *o*-tolunitrile. Hexane was removed and replaced with CH_2Cl_2 for a final wash to remove coloured impurities. It was found that the product was significantly more soluble in CH_2Cl_2 than other 1,3,2,4-dithiadiazolium salts, and hence this stage of the preparation was carried out with the reaction vessel immersed in an ice bath. The purified product was dried *in vacuo* following removal of solvent.

Appearance: Bright yellow powder

Yield: 718 mg, 1.87 mmol, 94%

IR (Nujol Mull) : ν_{max} 3070w, 2720w, 2580w, 1607m, 1575sh, 1570w, 1490sh, 1480sh, 1440sh, 1408s, 1375s, 1365sh, 1305sh, 1300m, 1218m, 1200sh, 1175w, 1132w, 1120w, 1060w, 1035wbr, 990sh, 980s, 960w, 920sh, 915m, 910m, 895w, 880w, 870w, 805s, 795w, 785s, 770s, 760s, 750w, 700vsbr, 645w, 635m, 595m, 580sh, 490w, 450m, 430w, 400vs cm^{-1}

Analysis : Found (required) C : 25.06 (25.00), H : 1.81 (1.84), N : 7.28 (7.29) %

^1H NMR (CD_3CN, TMS) : δ 2.77 (s) 3H, δ 7.63 (multiplet) 2H, δ 7.82 (t) 1H, δ 8.20 (d) 1H

Attempted preparation of 4-(4-azaphenyl)-1,2,3,5-dithiadiazolium chloride : Preparation of 4-(4-azaphenyl)-1,2,3,5-dithiadiazolyl :

4-Cyanopyridine (5g, 48 mmol) and NH_4Cl (g, mmol) and SCl_2 (50 ml) were placed together in a three-necked round-bottomed flask with a stirrer bar. The flask was connected to a cylinder of Cl_2 and a Cl_2 vent. Stirring was commenced and the Cl_2 was introduced. A leak was found in the Cl_2 delivery system and the reaction flask was sealed off and left in the back of a fume cupboard and promptly forgotten. After six months it was noticed that the flask was full of a bright orange solid. Excess SCl_2 was filtered off and the orange filter cake was washed repeatedly with cold diethyl ether. Following drying in vacuo the cake was transferred to the glove box and loaded into a closed extractor. The bright orange product was separated from unreacted NH4Cl by extraction into SO_2, inwhich it was

highly soluble. Microanalysis did not confirm that this material was 4-(4-azaphenyl)-1,2,3,5-dithiadiazolium chloride. A sample of this dried material (750 mg) was loaded into a "dog" with an equivalent weight of Ph_3Sb. Upon introduction of solvent (CH_3CN) the mixture began to change colour : from orange to olive green to black over 24 hours. Following removal of solvent *in vacuo* the mixture was loaded into a vacuum sublimer and heated to 130°C at 10^{-3} mmHg. Sublimate was produced as a black-red dichroic solid. Microanalyses were consistent with the formation of 4-(4-azaphenyl)-1,2,3,5-dithiadiazolyl **14** .

Repeating the reaction in an ESR tube with SO_2 as solvent gave an olive-green solution which gave an ESR spectrum in the form of a 1:2:3:2:1 pentet, $a_N = 0.49$ mT.

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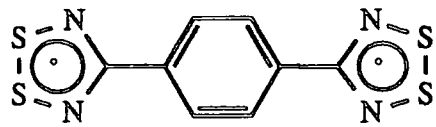
CHAPTER 4

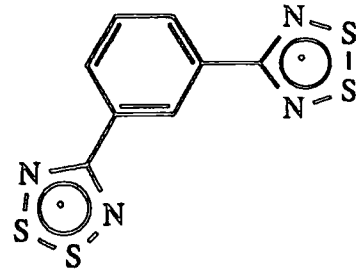
REACTION OF [SNS][AsF_6] WITH DINITRILES : PREPARATION OF BIS-(DITHIADIAZOLIUM) SALTS

4.1 Introduction

Attempts to prepare *bis*-(1,2,3,5-dithiadiazolium) salts by established routes to *mono*-functional salts were unsuccessful[1] until recently, when Oakley and coworkers prepared *meta*- and *para-bis*-(1,2,3,5-dithiadiazolium) chlorides from the reaction of silylated amidines derived from *meta*- and *para*- dicyanobenzene with sulphur dichloride[2-4] and reduced these compounds to give the *bis*-(1,2,3,5-dithiadiazolyl) radicals 1 and 2.



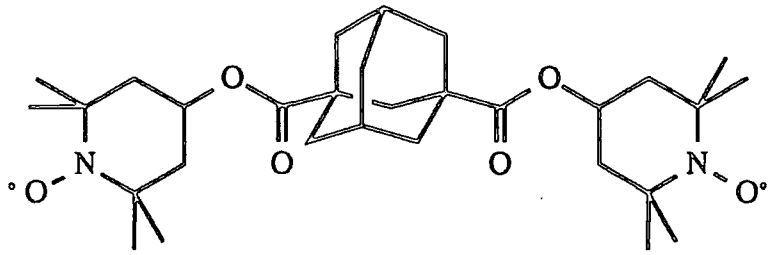
1



2

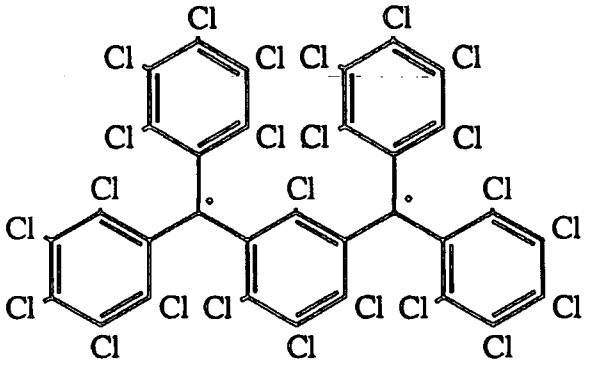
However, a more convenient route to *bis*-(dithiadiazolium) salts was discovered, using the cycloaddition of the dithianitronium cation $[SNS]^+$ to give *bis*-(1,3,2,4-dithiadiazolium) salts in high yield[5]. Following the success of the study of stable *mono*-(dithiadiazolyl) free radicals it was anticipated that the reduction of *bis*-(dithiadiazolium) salts to diradicals would yield some interesting results, and this chapter describes the synthesis of a variety of *bis*-(1,3,2,4-dithiadiazolium) salts, their reduction to radicals and the study of these radicals by ESR spectroscopy, and the reoxidation of a diradical to give a novel *bis*-(tribromide) salt.

The search for high yield syntheses of stable polyradicals with high spin-multiplicity ground states is currently an area of much interest. The nitroxyl radicals are well-known, with many different organic substituents. For example, the stable adamantanoid biradical 3 has been the subject of an X-Ray crystal structure determination[6].



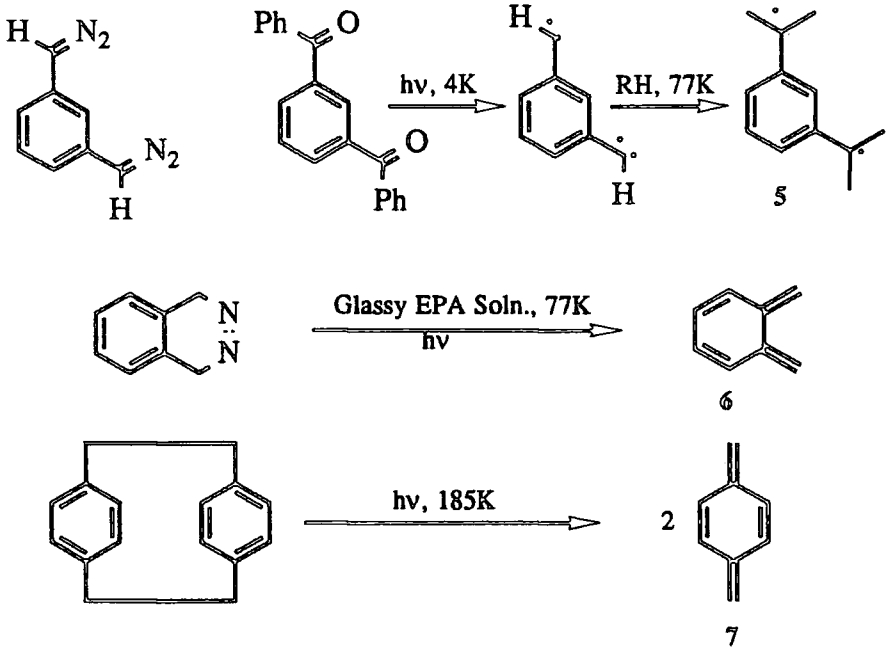
3

A synthetic strategy which has met with some success involves producing radical centres in an highly conjugated system with highly electronegative substituents to promote delocalization of unpaired spins. The pentacyclic perchlorinated system 4 is stable under ambient conditions[7] and exists in three forms due to restricted rotation of the aryl groups. Under ambient conditions the molecule exists as 60% meso form, with the other 40% as an enantiomeric pair.



4

4 is an example of a substituted *m*-xylylene biradical. The xylylenes are a group of biradicals, the simplest of the quinodimethanes. The isomers *m*-xylylene 5[9], *o*-xylylene 6[8] and *p*-xylylene 7[10], shown in Scheme 4.1.1. are unstable compounds under ambient conditions, and are consequently generated by photolysis of a precursor in a host matrix at low temperatures.



Scheme 4.1.1

Synthetic methods for the preparation of xylylenes

These short-lived molecules, and biradicals in general are known to be important reaction intermediates[8-10] (both in thermal reactions such as cycloadditions and isomerizations, and in photochemical reactions), and are the subject of much study. As shown in Fig. 4.1.1, *o*- and *p*-xylylene may be represented by both biradical and quinonoid structures, whereas *m*-xylylene cannot be represented as a Kekulé structure with out resorting to highly strained geometries such as 8. Thus it was predicted that *o*- and *p*-xylylene would be ground state

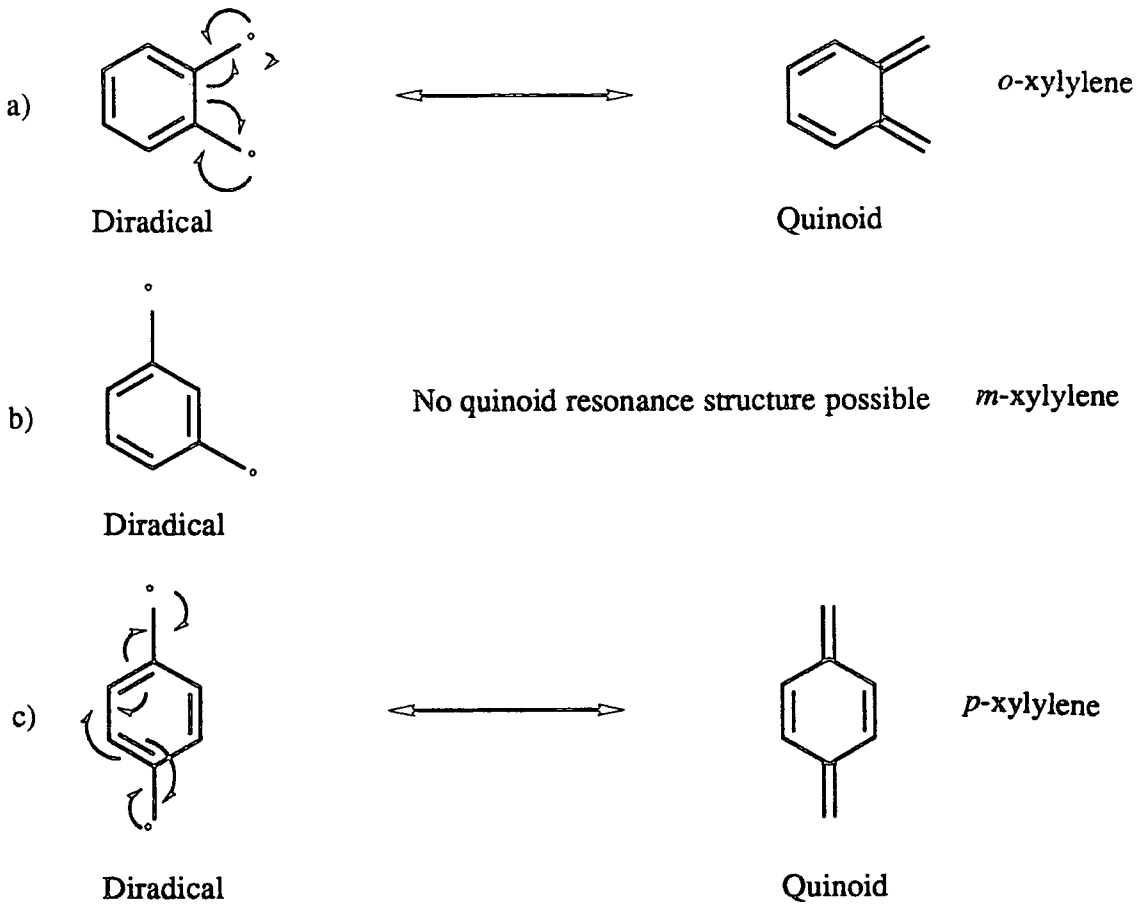
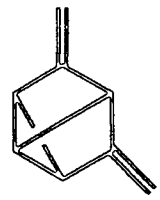


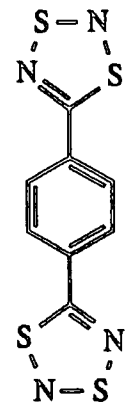
Fig. 4.1.1
Diradical and quinoid resonance structures for o- and p-xylylene : m-xylylene has diradical structure only.

singlets, while *m*-xylylene would have a triplet ground state. This was borne out by experiment, with *o*- and p-xylylenes ESR-silent[8,10] and *m*-xylylene ESR-active[9].



8

For all their interesting properties, the xylylenes and quinodimethanes are unstable under ambient conditions, while the *para-bis*-(1,3,2,4-dithiadiazolyl) ($SNSNCC_6H_4CNSNS$) 9 is stable above room temperature[5].



9

It was hoped that isomers of 9 might be of similar stability. This chapter describes the preparation of a variety of *bis*-(1,3,2,4-dithiadiazolium) salts and their reduction to new *bis*-(dithiadiazolyl) radicals under ambient conditions.

4.2 Results and Discussion

4.2.1 Reaction of [SNS][AsF_6] with 1,2-Dicyanobenzene

Reaction of 1,2-dicyanobenzene with two equivalents of [SNS][AsF_6] gave the corresponding *ortho-bis*-(1,3,2,4-dithiadiazolium) salt [C_6H_4-1,2-$(CNSNS)_2$][AsF_6]$_2$ in 90% yield, a higher yield than previously reported[5]. The preparation reported here was one of several carried out in the course of this work, and it was found that the yield of product could be improved cosiderably by thorough drying of glassware and reagents before use. It was found that the *ortho-bis* (dithiadiazolium) cation was very sensitive to moisture and degradation occurred over a period of minutes in the open atmosphere, and over a longer period in the glove box. The hydrolysis was accompanied by a yellowing of the material, which is colourless when pure. The IR spectrum of [C_6H_4-1,2-$(CNSNS)_2$][AsF_6]$_2$ is shown in Fig. 4.2.1a. Anion metathesis was used to prepare the chloride and bromide from the hexafluoroarsenate, and these were obtained in yields of 68% and 42% respectively, with the relatively low yields attributable to the solubility of the compounds in acetonitrile and dichloromethane, with the bromide more soluble than the chloride.

4.2.2 Reaction of [SNS][AsF_6] with 1,3-Dicyanobenzene

The reaction of two equivalents of [SNS][AsF_6] with 1,3-dicyanobenzene over 2 days gave the *meta-bis*-(1,3,2,4-dithiadiazolium) salt [C_6H_4-1,3-$(CNSNS)_2$][AsF_6]$_2$ in 91% yield, again a higher yield than previously reported[5], and also attributable to care taken with drying of glassware before use. The IR spectrum of the product is shown in Fig. 4.2.1b. ^{1}H NMR spectra of [C_6H_4-1,3-$(CNSNS)_2$][AsF_6]$_2$ and 1,3-dicyanobenzene are shown in Fig. 4.2.2, and the same pattern of signals is seen in both materials, but the signals in the product are shifted downfield relative to the corresponding signals in the starting material, with the largest shift increment observed for the aromatic hydrogen *ortho-* with respect to both cationic rings ($\Delta\delta$ = 1.0 ppm). This is as expected for the introduction of two strongly

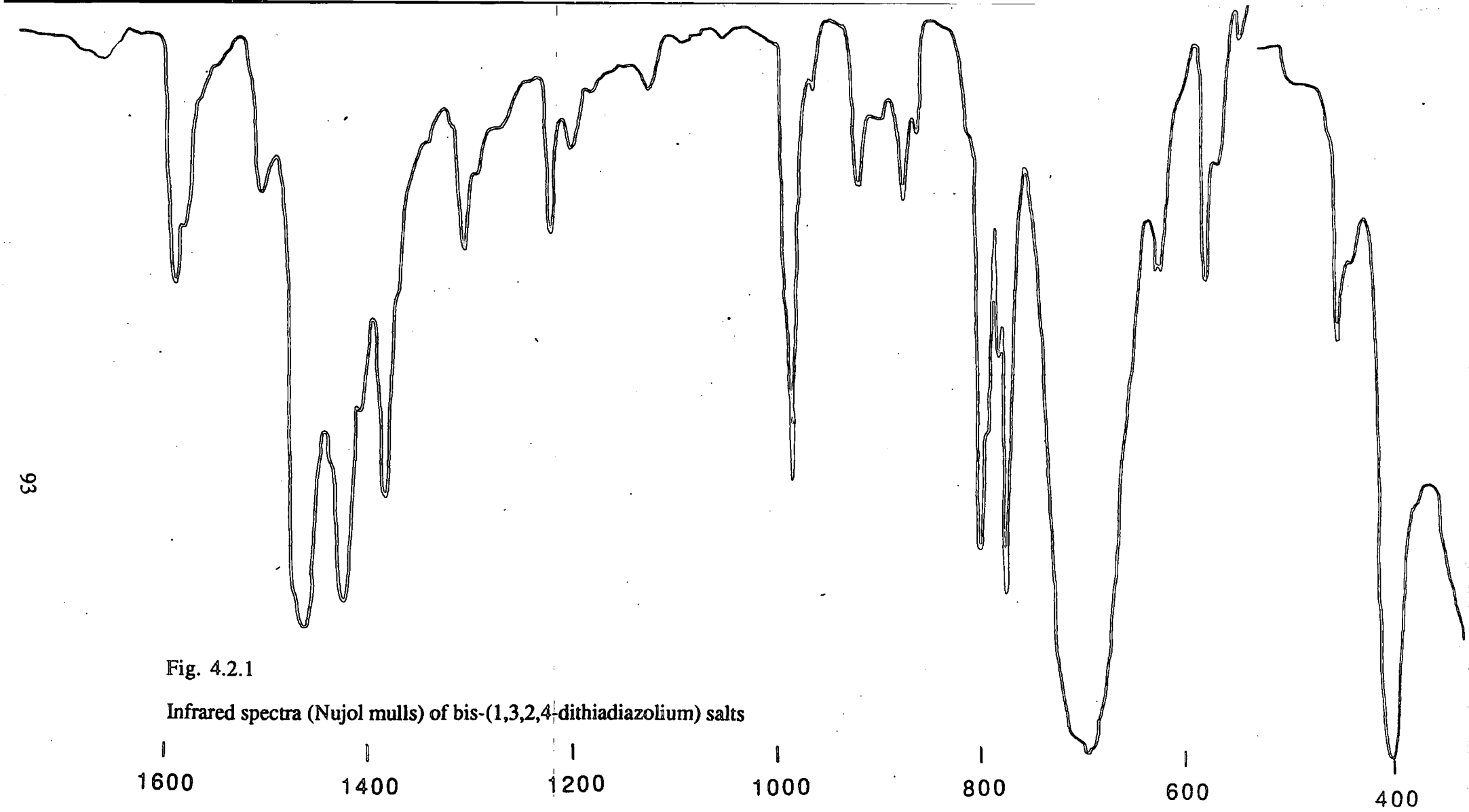
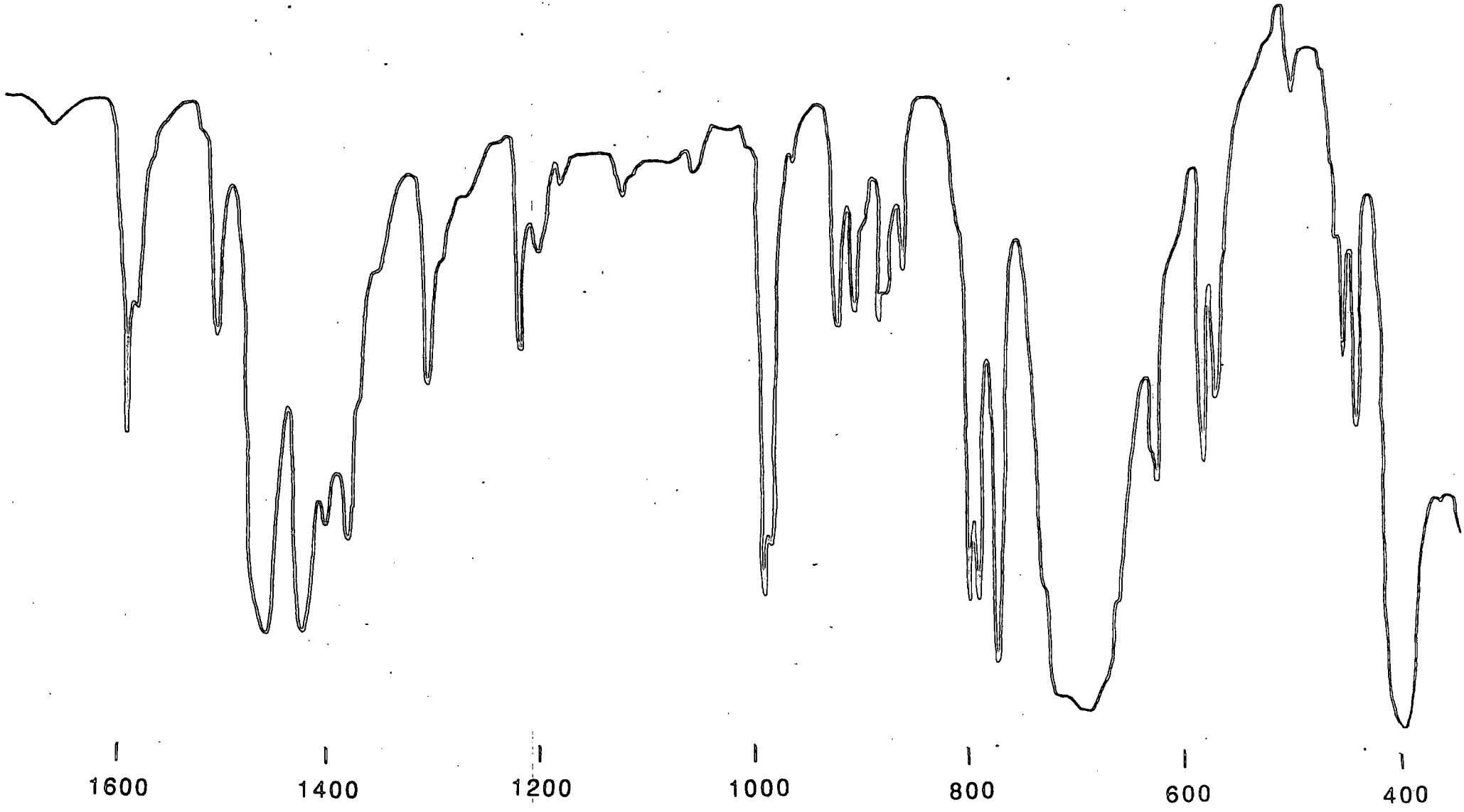


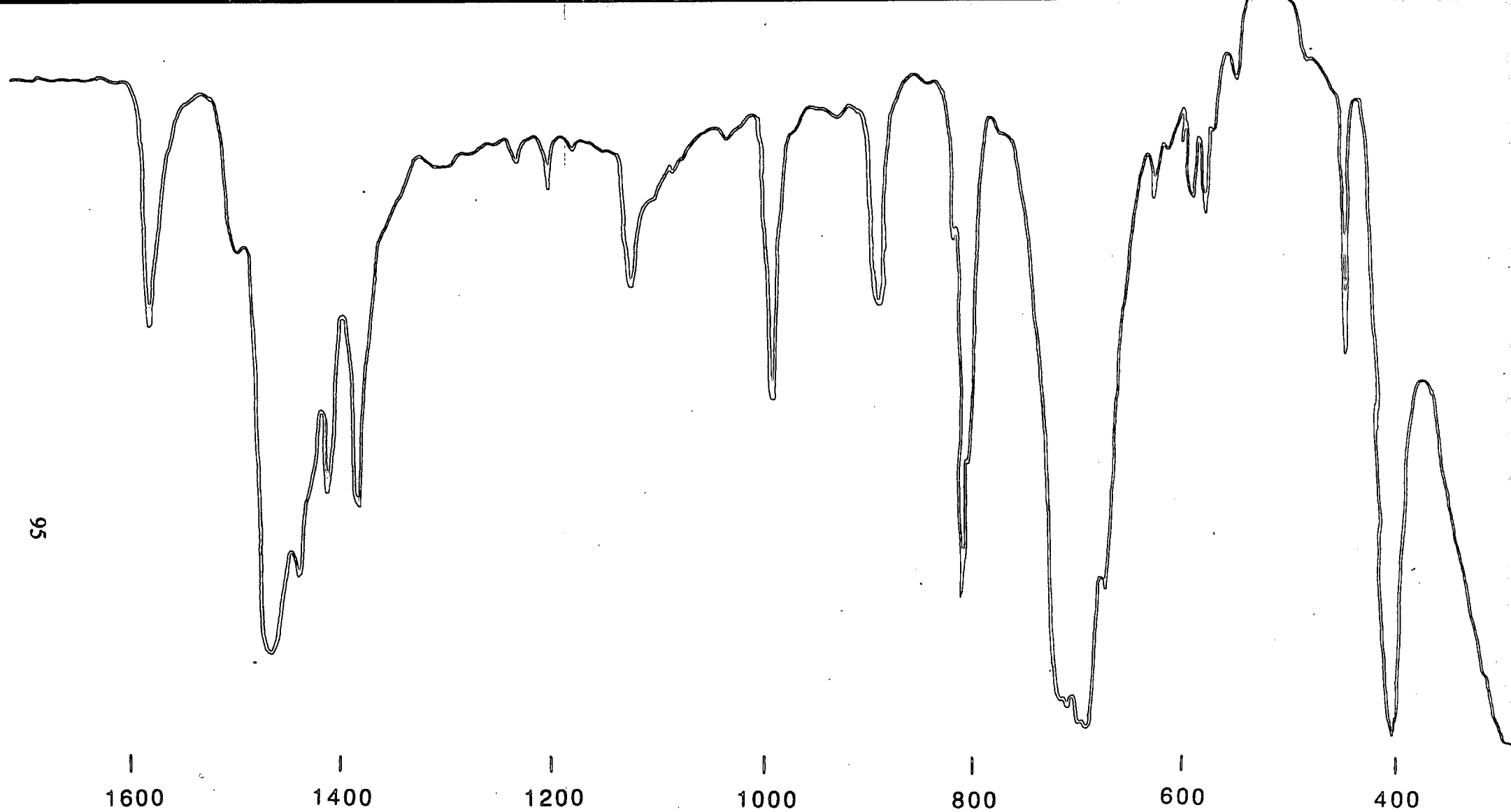
Fig. 4.2.1

Infrared spectra (Nujol mulls) of bis-(1,3,2,4-dithiadiazolium) salts

a) $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2][AsF_6]_2$



b) $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$



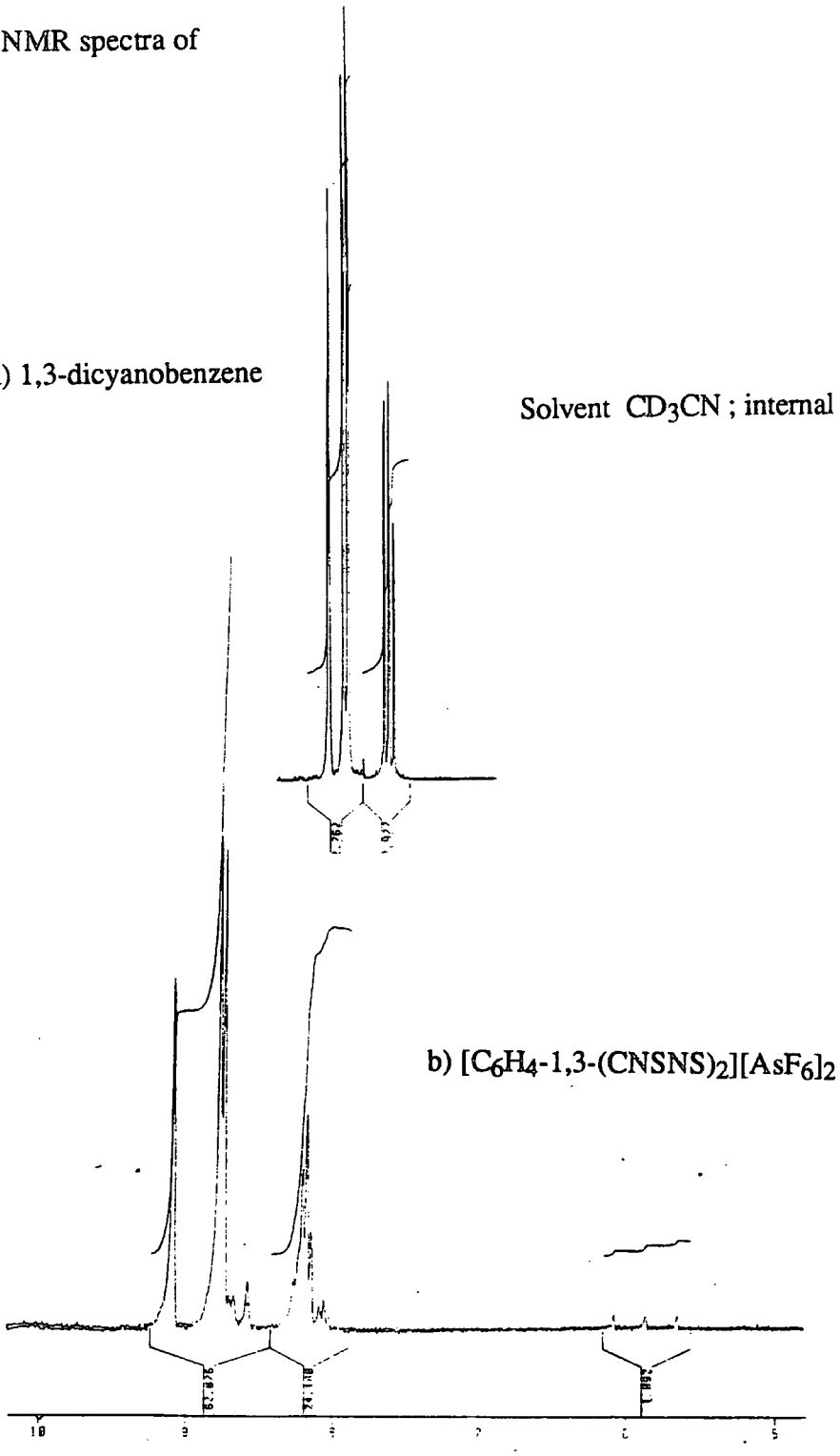
c) $[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$

Fig. 4.2.2

^1H NMR spectra of

a) 1,3-dicyanobenzene

Solvent CD_3CN ; internal reference TMS



b) $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$

electron-withdrawing groups into the molecule, with consequent deshielding of the aromatic hydrogens.

4.2.3 Reaction of [SNS][AsF_6] with 2,6-Dicyanotoluene

Reaction of two equivalents of [SNS][AsF_6] with 2,6-dicyanotoluene over 2 days gave the corresponding *bis*-(1,3,2,4-dithiadiazolium) salt [C_6H_3-2-(CH_3)-1,3-($CNSNS)_2$][$AsF_6]_2$ in 95% yield. The IR spectrum of the product, an off-white powder, is shown in Fig. 4.2.1c. As for other compounds of this type the ^1H NMR spectrum of the product (Fig. 4.2.3) shows the same pattern of signals and splittings but with all signals shifted downfield to an extent dependent on the positions of the various hydrogens relative to the dithiadiazolium cation rings. Resonances due to the three hydrogens of the methyl substituent in the product appear at 2.82 ppm compared with 2.69 ppm in 2,6-dicyanotoluene (a much smaller shift increment than that seen for the meta-dication discussed in Section 4.2.2., where a downfield shift of 1.0 ppm in the product relative to 1,3-dicyanobenzene occurred for the hydrogen between the two cation rings). Larger shift increments are seen for the aromatic hydrogens. The two hydrogens *ortho-* with respect to the dithiadiazolium rings resonate at 8.35 ppm compared with 7.92 ppm in the starting material, and resonance due to the single hydrogen *meta-* with respect to the cation rings appears at 7.95 ppm compared with 7.49 ppm in the starting material.

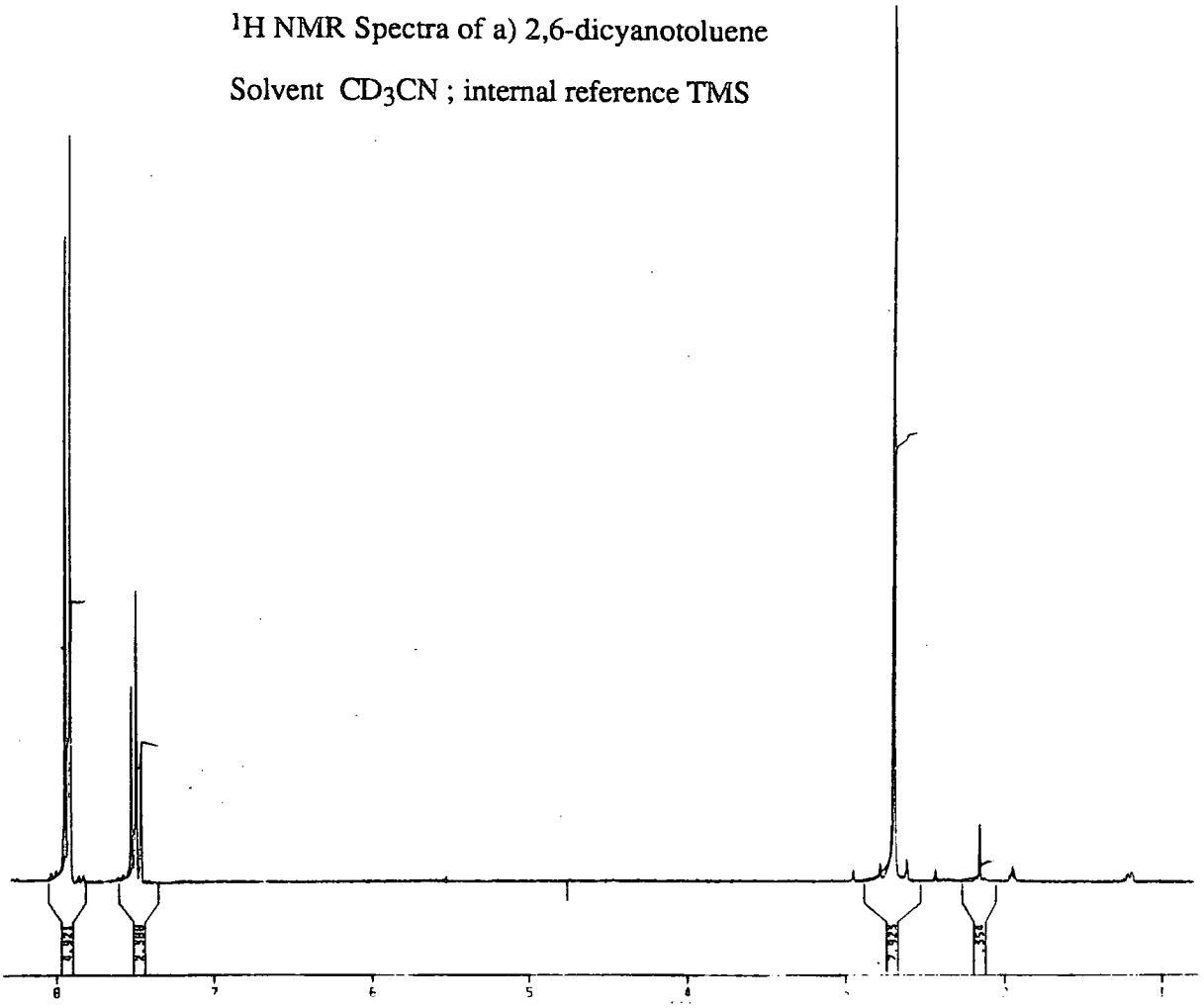
4.2.4 Reaction of [SNS][AsF_6] with 3,4,5,6-Tetrafluoro-1,2-dicyanobenzene

Reaction of two equivalents of [SNS][AsF_6] with one equivalent of tetrafluoro-*o*-dicyanobenzene in SO_2 over 3 days gave an highly soluble product which formed large feathery polycrystalline masses upon removal of solvent. Infrared study showed that the CN stretching band had disappeared, as expected for the formation of a dithiadiazolium salt. This material was also found to be extremely sensitive to moisture, hydrolysing

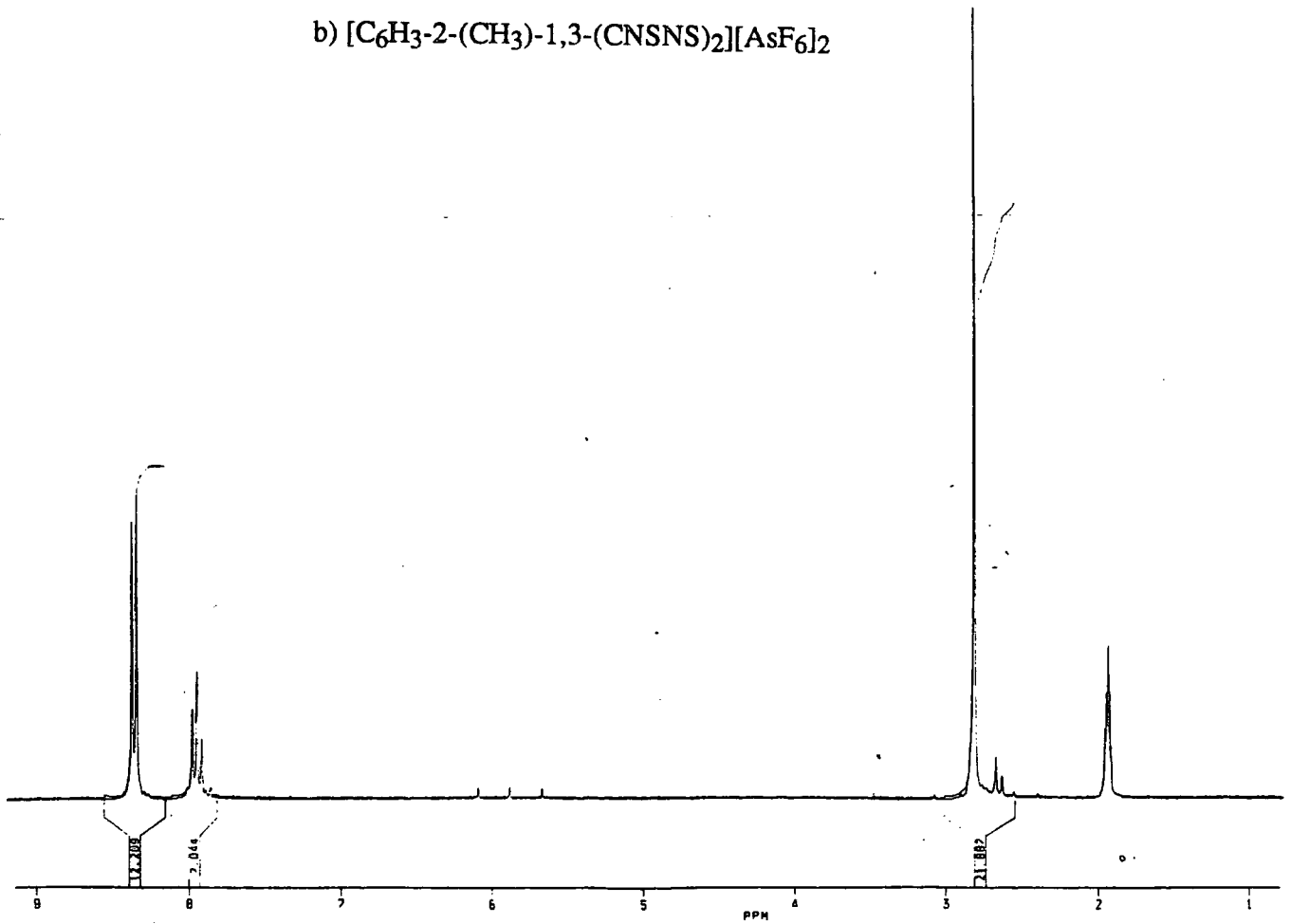
Fig. 4.2.3

^{1}H NMR Spectra of a) 2,6-dicyanotoluene

Solvent CD_3CN ; internal reference TMS



b) $[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$



rapidly in the atmosphere, with decomposition virtually complete in a matter of minutes. Furthermore, this material was found to decompose in the glove box over a period of days, with the initially colorless material turning brown, and thus no further synthetic work was done. The high sensitivity to moisture observed is consistent with the formation of a *bis*-(dithiadiazolium) salt, where the two cationic rings are attached to an aromatic group made highly electron-deficient by the fluoro-substituents. This would result in the dithiadiazolium rings becoming electron-deficient to a greater degree and thus more susceptible to nucleophilic attack. The material was assumed to be $[C_6F_4\text{-}1,2\text{-}(CNSNS)_2][AsF_6]_2$.

4.2.5 Reaction of $[SNS][AsF_6]$ with 2,4,5,6-Tetrafluoro-1,3-dicyanobenzene

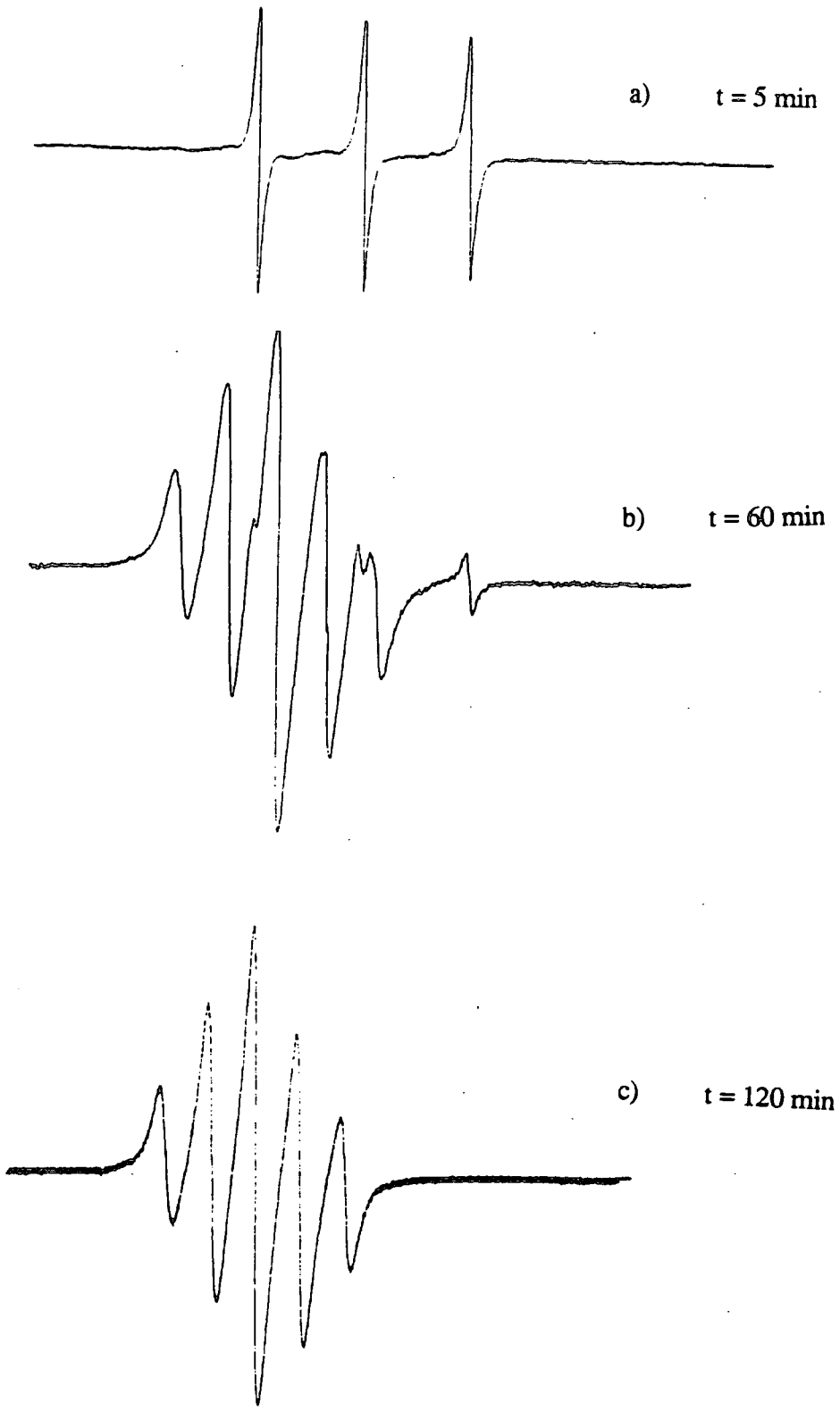
This reaction proceeded as for the ortho-analogue described in 4.2.4., and the product obtained was found to have similar solubility and sensitivity to moisture. The material was assumed to be $[C_6F_4\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$.

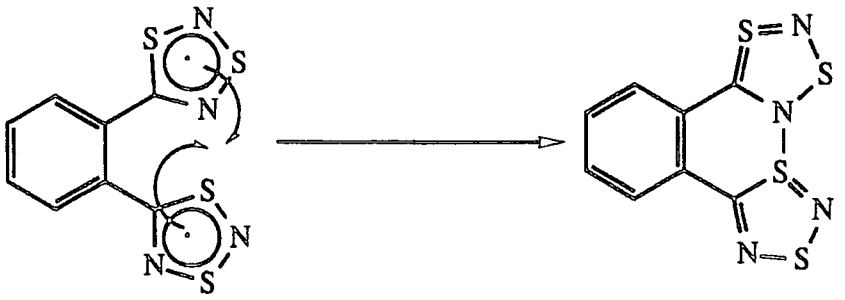
4.2.6 Reduction of bis-(Dithiadiazolium) Salts to Dithiadiazolyl Radicals

Reduction of the chloride salt of the *ortho*-dication $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{2+}$ on a preparative scale gave a mixture of products. Reduction in an ESR tube gave the typical dithiadiazolyl spectra shown in Fig. 4.2.4, with 100% rearrangement to the bis-1,2,3,5-isomer after 2 hours. A marked diminution of signal intensity was observed. This was probably due to degradation of the radical by encroaching moisture, but the possibility of intramolecular reactions such as bond formation between the dithiadiazolyl rings to produce an electron-paired structure as shown in Scheme 4.2.1 can also be visualised.

Fig. 4.2.4

Room temperature ESR spectra (in toluene) of $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot-}$



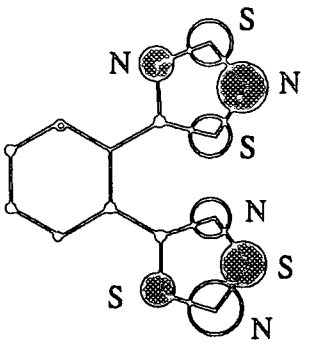


Scheme 4.2.1

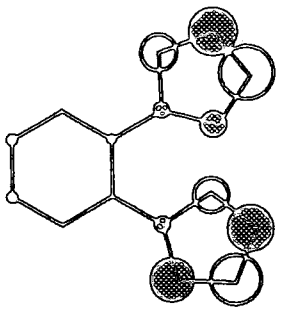
Suggested ring closure reaction of $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot}$ to give a tetracyclic electron-paired structure

Simple Hückel MO calculations for the *ortho*-bis-(1,3,2,4-dithiadiazolyl) are shown in Fig.4.2.5, and the highest unoccupied orbitals consist of a pair of almost degenerate orbitals with the major coefficients on the dithiadiazolyl rings, and negligible delocalization across the 1,2-phenylene ring. It can be seen that the lower-energy orbital of the pair has a sulphur of one dithiadiazolyl ring adjacent to a nitrogen on the other with the coefficients of the molecular orbital of the correct sign to overlap with the formation of a sulphur-nitrogen bond to give a tetracyclic system as shown in Scheme 4.2.1.

A model of the *ortho*-bis-(1,3,2,4-dithiadiazolyl), as shown in Fig.4.2.6, using bond lengths from the X-Ray crystal structure of the *para*-bis-(1,3,2,4-dithiadiazolyl) $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]$[5] and assuming planarity, predicts that these two atoms from adjacent rings are within bonding distance of one another, a distance of around 1.63Å (typical S-N distance 1.63 - 1.65Å). Such intramolecular ring closure was suggested by Rawson[11], but he suggested the formation of a sulphur-sulphur bond following ring rotation. This is not permitted by molecular orbital asymmetry using the MO scheme as shown in Fig. 4.2.5. In addition, intramolecular electron-pairing without additional bond formation to produce an *ortho*-quinoid structure as shown in Fig. 4.2.7 may occur. Analysis of the crystal structure of $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]$[5] suggests that a *para*-quinoid structure is a canonical form of the compound.

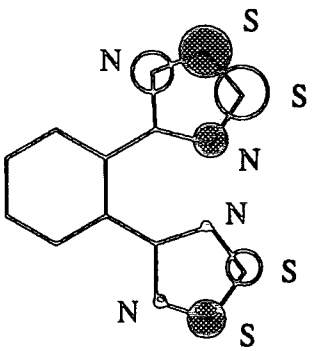


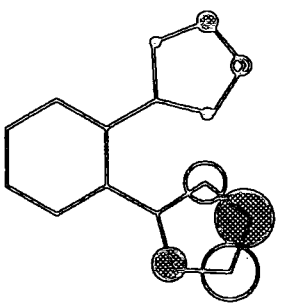
Higher energy



Lower energy

Simple Hückel frontier molecular orbitals for $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot\cdot}$



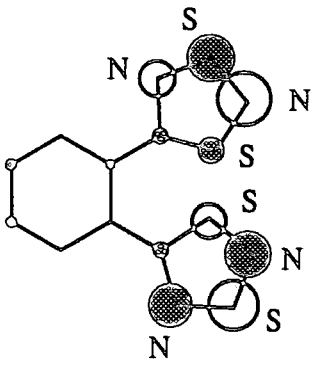


Degenerate pair

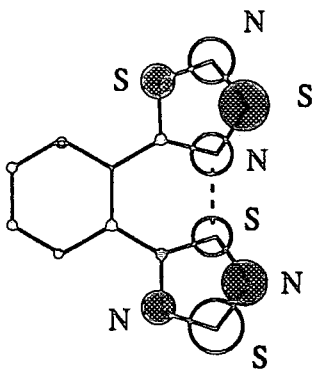
Simple Hückel frontier molecular orbitals for $[C_6H_4\text{-}1,2\text{-}(CNSSN)_2]^{\cdot\cdot}$

Fig. 4.2.5

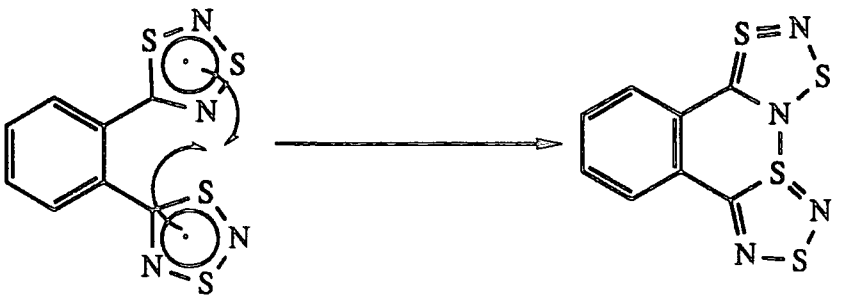
Frontier Hückel molecular orbitals for $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot\cdot}$ and $[C_6H_4\text{-}1,2\text{-}(CNSSN)_2]^{\cdot\cdot}$



S-S interaction forbidden on the grounds of orbital symmetry

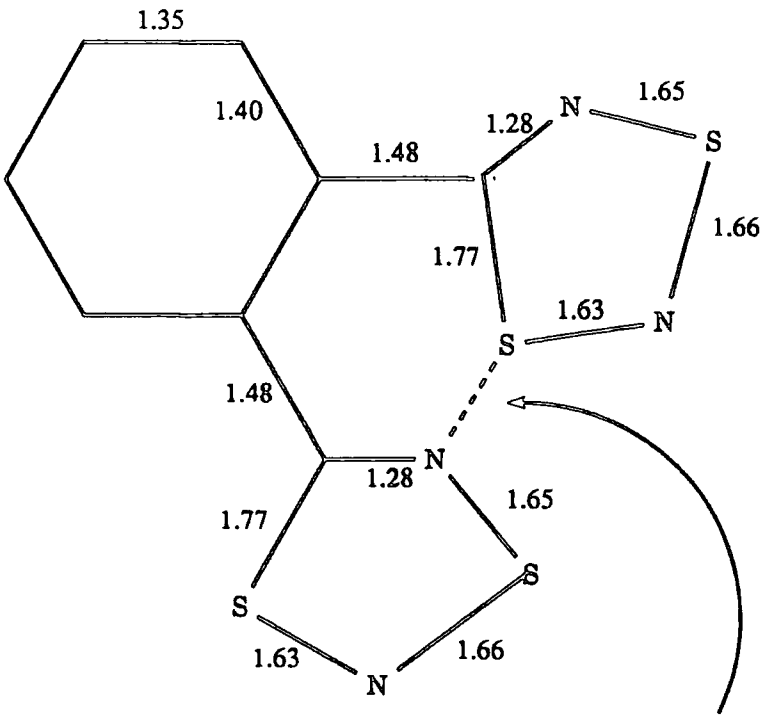


Adjacent S and N, however, have correct symmetry to overlap and form S-N bond



Scheme 4.2.2

Suggested molecular orbital scheme for ring closure reaction of $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot\cdot}$ to give a tetracyclic electron-paired structure (see Scheme 4.2.1)



Distance approx. 1.63 Å, within SN Bonding Distance

Fig. 4.2.6

Model of $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\bullet\bullet}$ using bond lengths

from the X-ray crystal structure of $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]$

(taken from ref. 5)

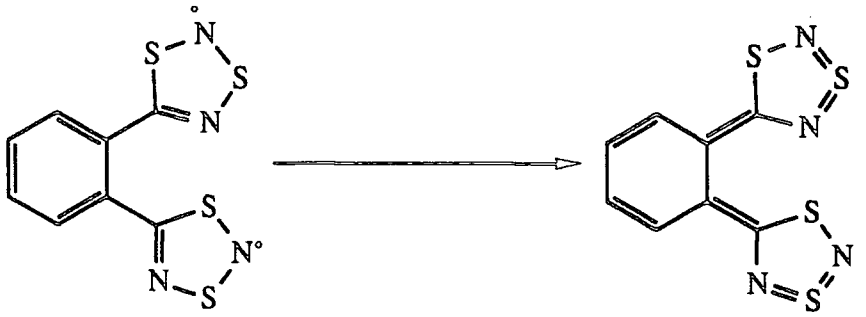


Fig. 4.2.7

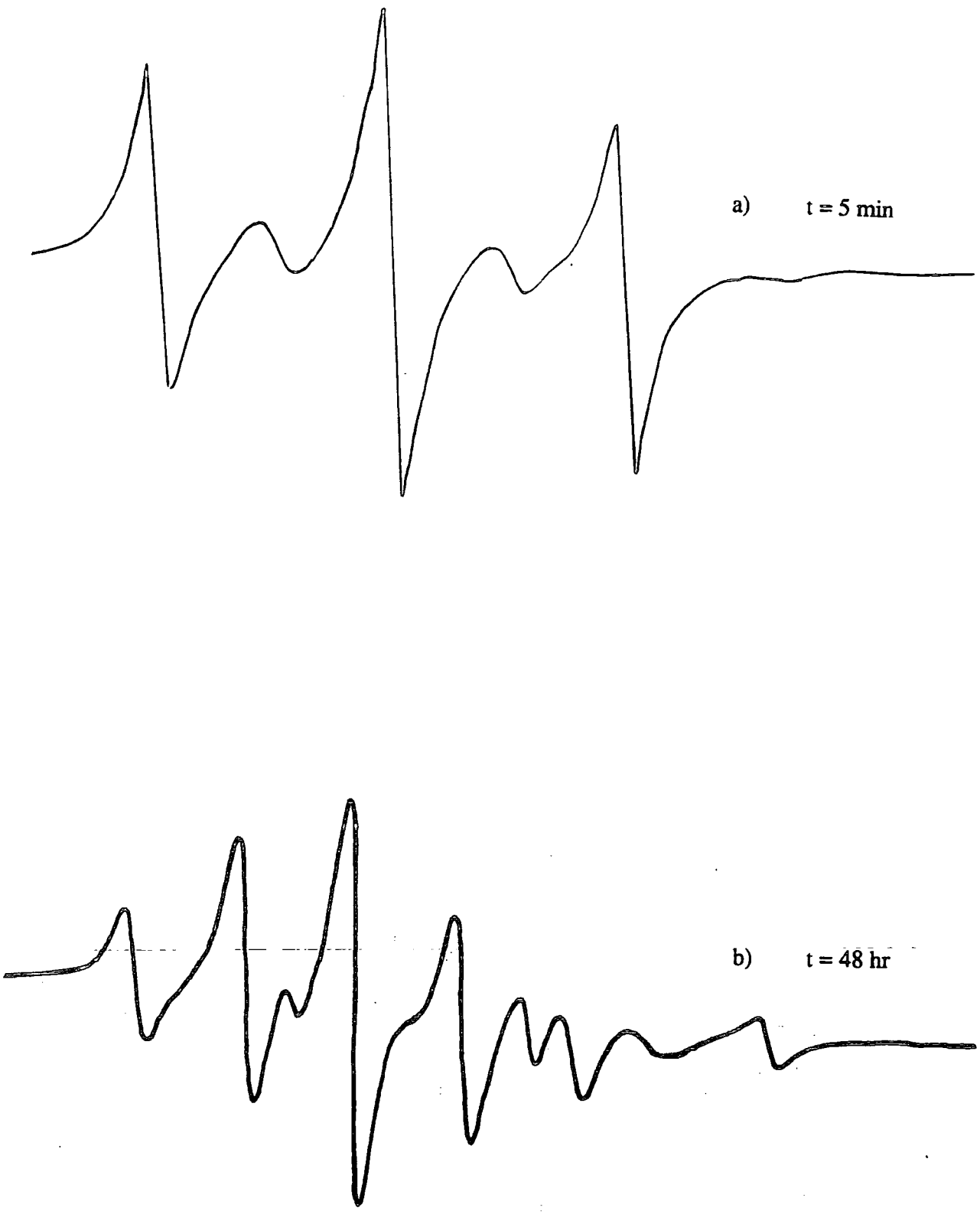
Intramolecular electron-pairing in $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot\cdot}$ to give *ortho*-quinoid structure

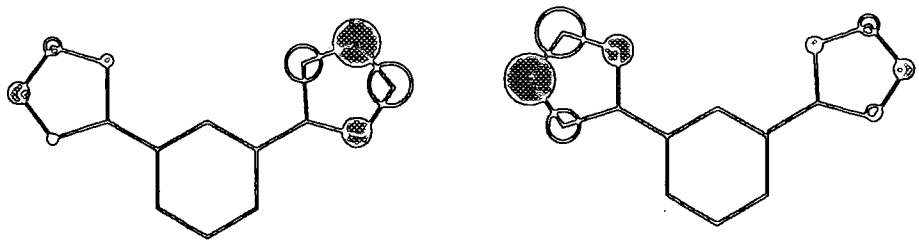
Reduction of the chloride salt of the *meta*-dication $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2]^{2+}$ gave the *bis*-(1,3,2,4-dithiadiazolyl) radical as a sparingly soluble black-brown powder. ESR spectroscopy of toluene solutions of this radical, obtained at room temperature, are shown in Fig. 4.2.8. As for *mono*-(1,3,2,4-dithiadiazolyl)s the spectra consist of a 1:1:1 triplet which over time collapses with the simultaneous emergence of a 1:2:3:2:1 pentet. Hückel molecular orbital calculations for the *meta*-diradical as the bis-(1,3,2,4-dithiadiazolyl) and as the rearrangement product, the bis-(1,2,3,5-dithiadiazolyl) are shown in Fig. 4.2.9.
The electron impact mass spectrum (EI+) of the *m-bis*-(dithiadiazolyl) is summarized in Table 4.2.1, with a breakdown pattern shown in Scheme 4.2.3. The peak at m/e = 78, corresponding to $[S_2N]^+$ appears as the base peak. This is presumably due to the stability of the $[S_2N]^+$ cation, and its formation with the loss of a stable molecule (1,3-dicyanobenzene).

DSC of the *m*-diradical showed a sharp exotherm at 110°C, as shown in Fig. 4.2.10. This behaviour was also observed for $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]$, with a sharp exotherm appearing at 145°C, irrespective of heating rate[5]. X-Ray powder diffraction of the thermolysed material was found to be identical to that of the *bis*-(1,2,3,5-dithiadiazolyl) $[C_6H_4\text{-}1,4\text{-}(CNSSN)_2]$. Furthermore, reheating material which had been heated to 170°C and allowed

Fig. 4.2.8

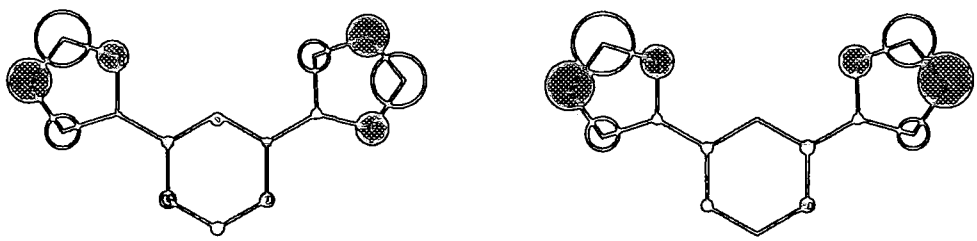
Room temperature ESR spectra (in toluene) of $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2]^{\cdot-}$





Degenerate pair

Simple Hückel frontier molecular orbitals for $[C_6H_4\text{-}1,3\text{-}(CNSSN)_2]^{\cdot\cdot}$



Lower energy Higher energy

Simple Hückel frontier molecular orbitals for $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2]^{\cdot\cdot}$

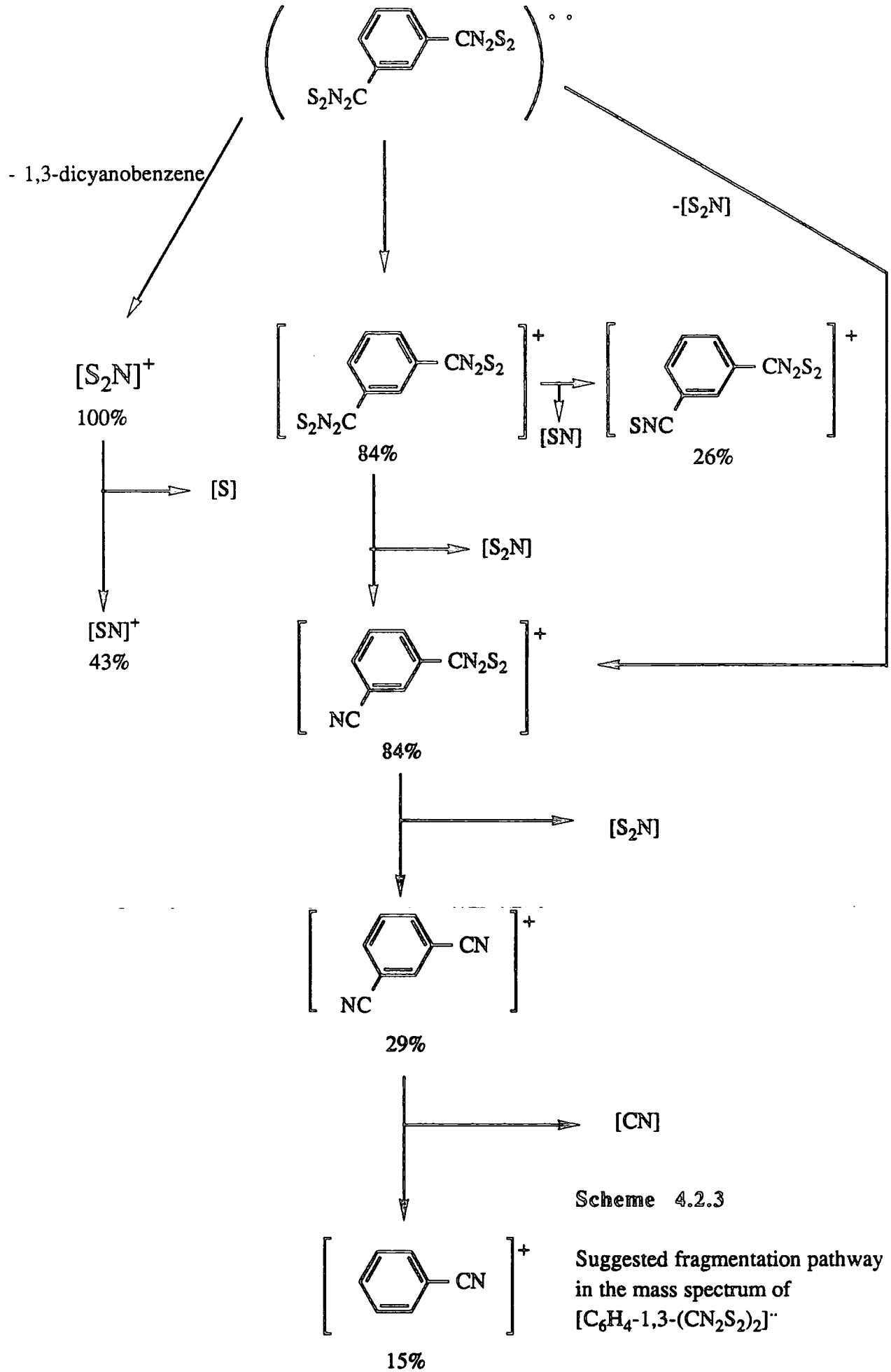
Fig. 4.2.9

Frontier Hückel molecular orbitals for $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2]^{\cdot\cdot}$ and $[C_6H_4\text{-}1,3\text{-}(CNSSN)_2]^{\cdot\cdot}$

TABLE 4.2.1

THE MASS SPECTRUM (EI$^+$) OF (C_6H_4-1,3-$(CN_2S_2)_2$)$^{\cdot\cdot}$

m / e	Relative Intensity (%)	Assignment
46	43	$[SN]^+$
64	25	$[S_2]^+$
78	100	$[S_2N]^+$
102	15	$[C_6H_4CN]^+$
128	29	$[M - 2S_2N]^+$
160	28	$[M - (S_2N + SN)]^+$
206	84	$[M - S_2N]^+$
238	26	$[M - SN]^+$
284	84	M^+



Scheme 4.2.3

Suggested fragmentation pathway in the mass spectrum of $[C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2]^{\cdot\cdot}$

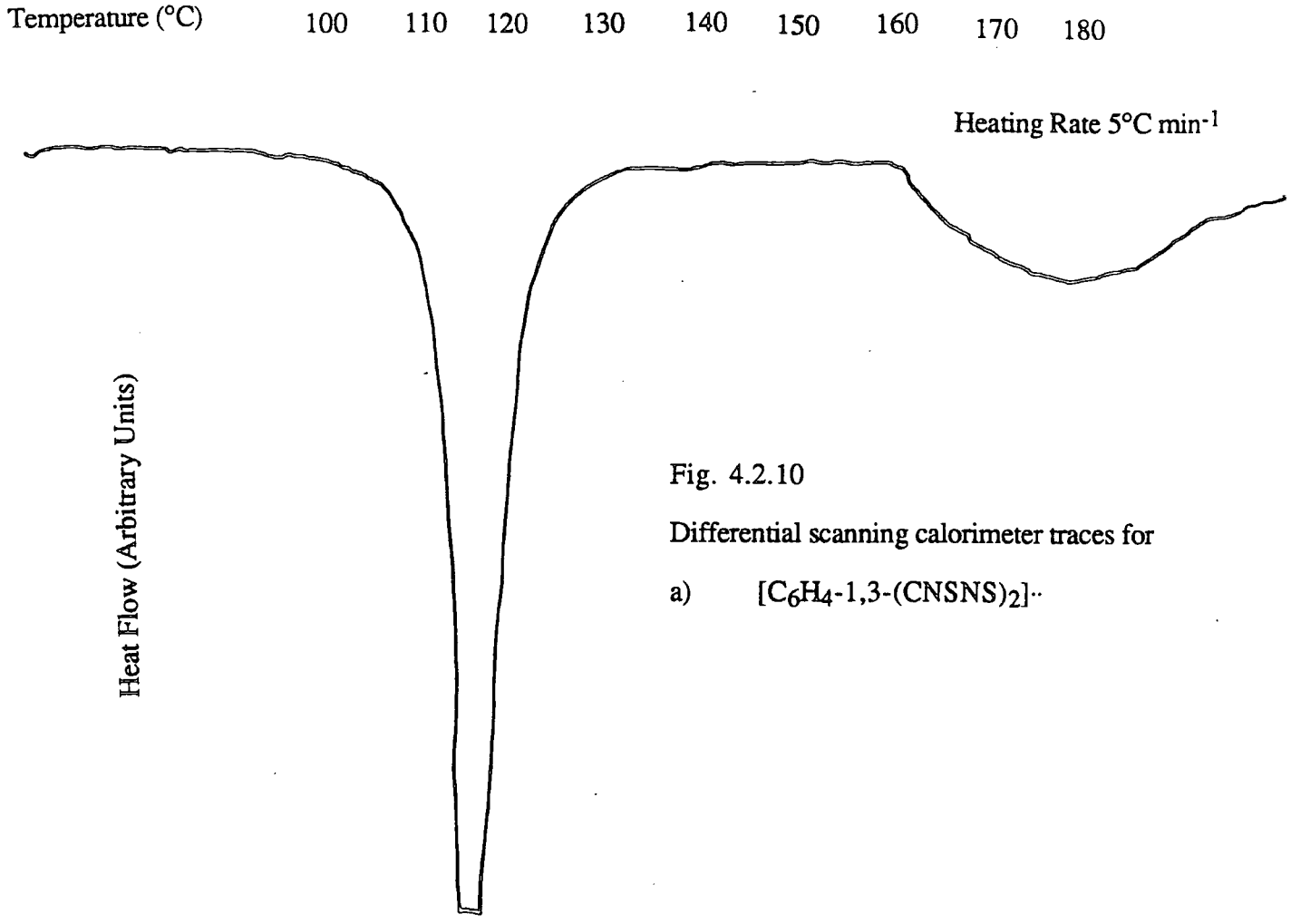
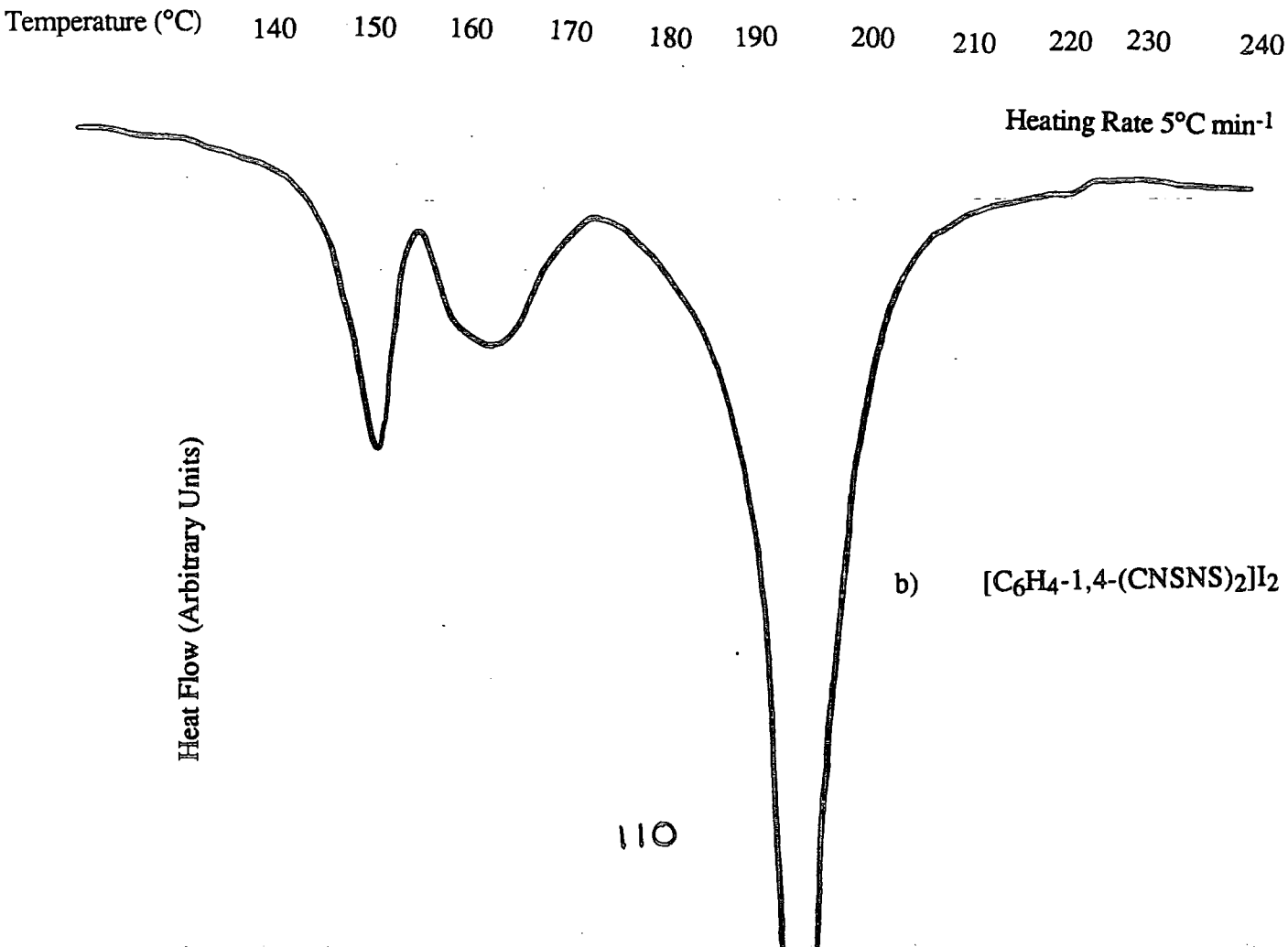


Fig. 4.2.10

Differential scanning calorimeter traces for

a) $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2]$··



b) $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]I_2$

to cool did not show the exotherm at 145°C. In other words this sharp exotherm appears to be associated with the rearrangement of the 1,3,2,4-dithiadiazolyl ring to the 1,2,3,5-dithiadiazolyl isomer in the solid state. Previously this rearrangement had only been reported for monoradicals in solution[12]. The X-Ray crystal structure of $[C_6H_4$-1,4-$(CNSNS)_2]$[5] shows that the molecules are packed such that a dithiadiazolyl ring on one molecule lies above a ring on another molecule as shown in Fig. 4.2.11. This is the correct geometry for the bimolecular rearrangement to occur according to Passmore *et al.*[12]. Heating the 1,3,2,4-dithiadiazolyl gives the required thermal activation for rearrangement, and the exotherm appears as the dithiadiazolyl rings isomerise to the more stable 1,2,3,5-form with the excess energy given out as heat.

ESR spectra of the radicals obtained on reduction of the $[AsF_6]$- salts of the fluoro-dications $[C_6F_4$-1,2-$(CNSNS)_2]^{2+}$ and $[C_6F_4$-1,3-$(CNSNS)_2]^{2+}$ with a molar excess of triphenylantimony in the presence of Bu_4NCl are shown in Figs. 4.2.12 and 4.2.13. The spectra appear as triplets with additional splitting due to coupling to fluorines. Simulations of the spectra are shown alongside. The spectrum of the *ortho*-tetrafluoro-diradical shows coupling to F with a_F = 0.13 mT, and the *meta*-tetrafluoro-diradical exhibits coupling to two equivalent fluorines with a_F = 0.18 mT, in accordance with reported values for other systems e.g. $(F_3CCNSNS)\cdot$[12]. In the latter case the linewidths and couplings were derived from the simulation. The simulations were carried out assuming zero spin-spin exchange between radical centres. In the spectrum of $(C_6F_4$-1,3-$(CNSNS)_2)$.. additional lines are observed at aN/2, and these are similar to the lines seen in the spectra of nitroxyl diradicals indicating weak intramolecular spin exchange[13,14].

As far as the nature of the ground states of these radicals is concerned, there is still work to be done. During this work no half-field splittings were observed, which are typical of higher spin ground state radicals, but predictions based on Radhakrishnan's rule[15,16]

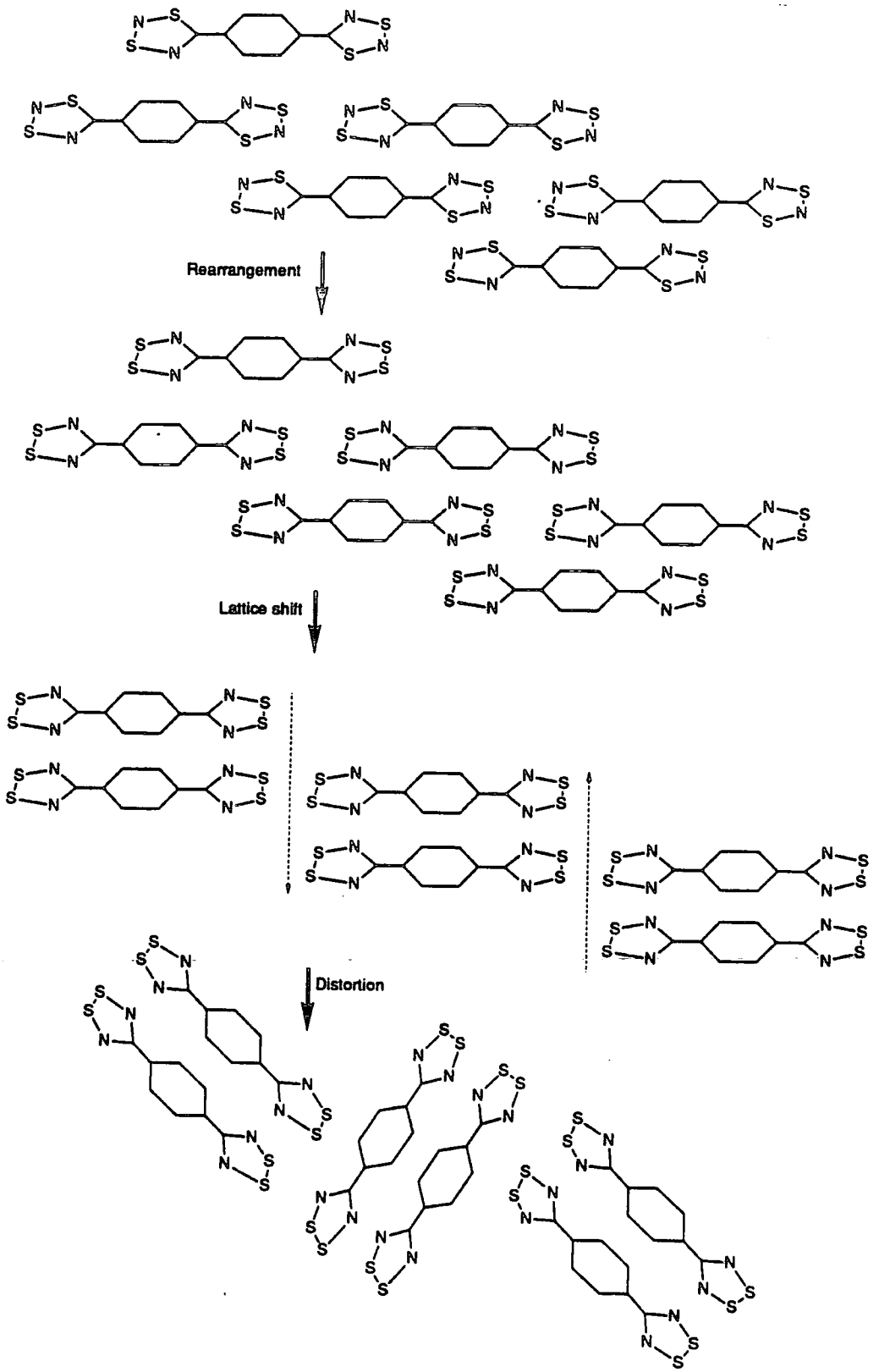


Fig. 4.2.11

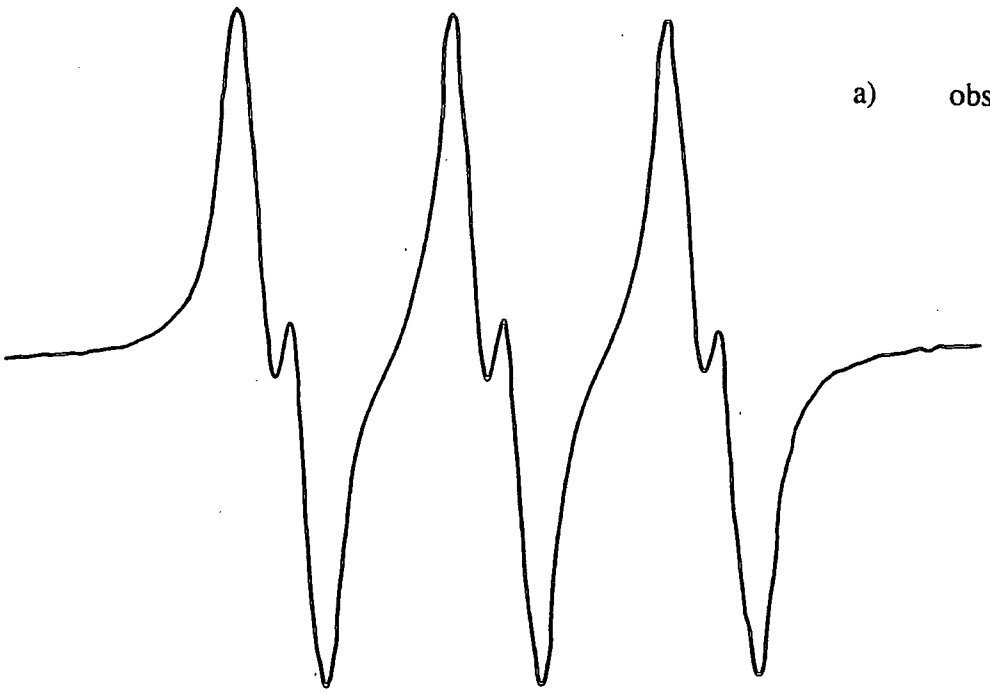
Suggested mechanism for the solid-state thermal rearrangement of $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]$ to $[C_6H_4\text{-}1,4\text{-}(CNSSN)_2]$

$g = 2.0053$
$a_N = 11.45$ G
$a_F = 1.8$ G

Fig. 4.2.12

Room temperature ESR spectrum (in toluene) of $[C_6F_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot-}$

a) observed spectrum



b) simulated spectrum

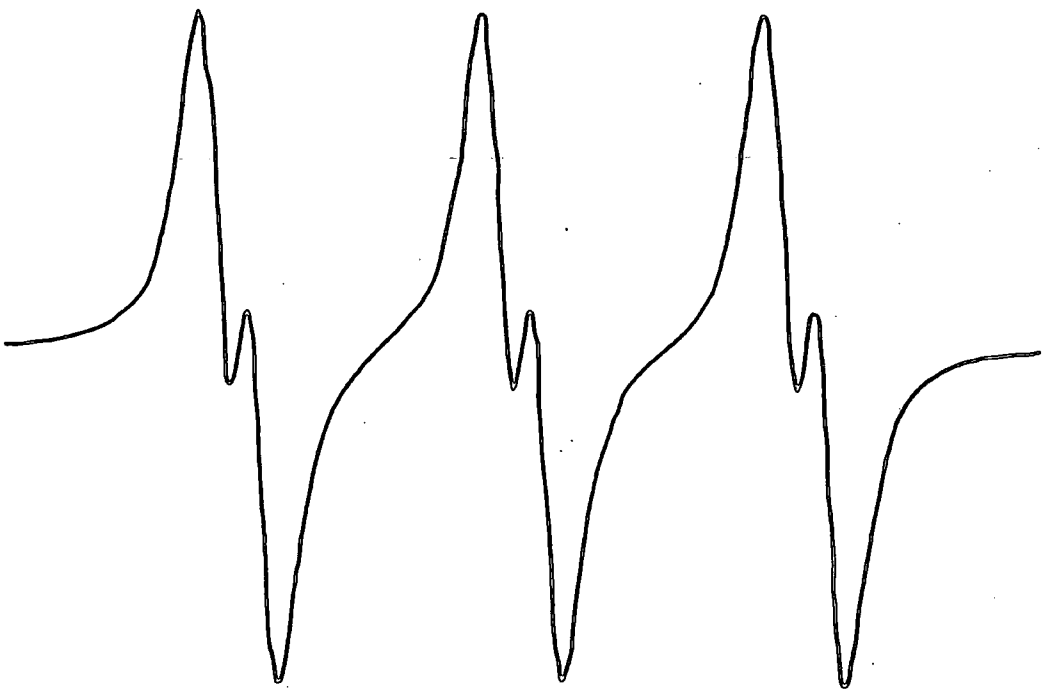


Fig. 4.2.13

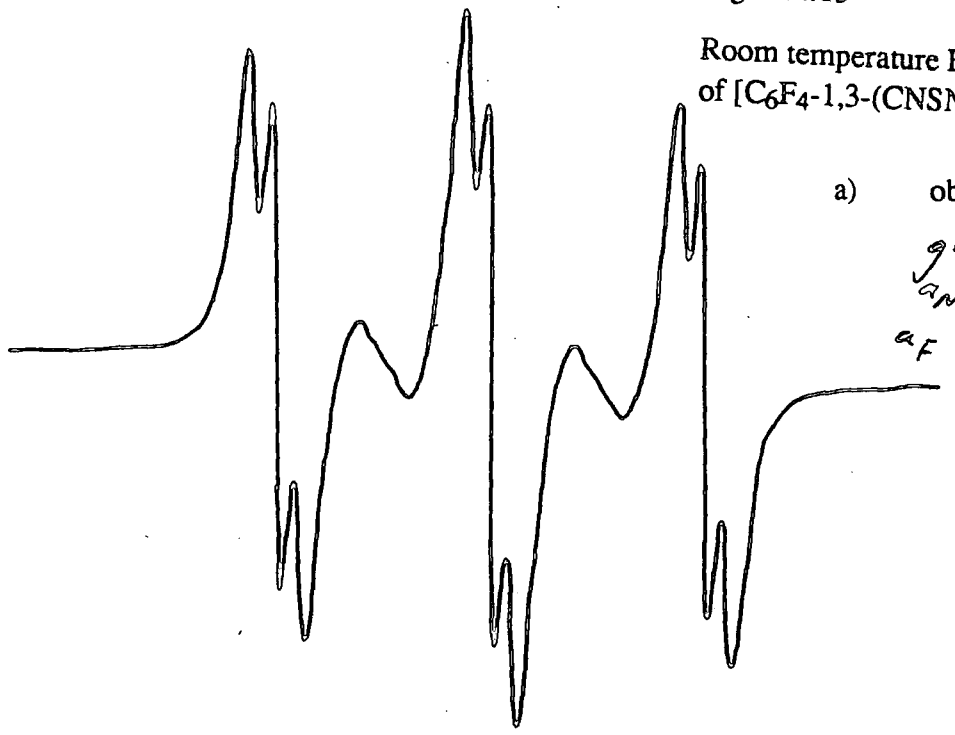
Room temperature ESR spectrum (in toluene) of $[C_6F_4\text{-}1,3\text{-}(CNSNS)_2]^{\cdot-}$

a) observed spectrum

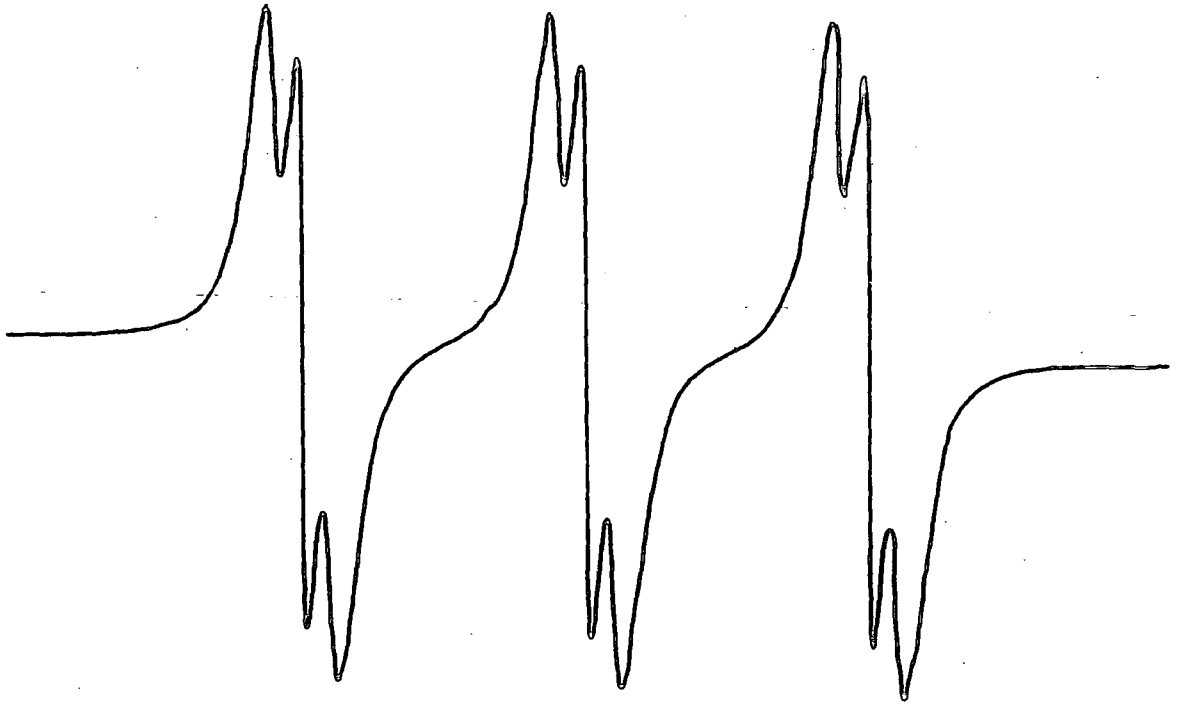
$g = 2.0053$

$a_N = 11.456$

$a_F = 1.36$ 2 F atoms



b) simulated spectrum



suggest that the *ortho-bis*-(dithiadiazolyl) radicals would be singlets and the meta-analogues triplets. Applied to a biradical, the rule states that if the double bonds are distributed such that the number of π-electrons N separating the two radical centres is the lowest possible, the ground state spin S of the molecule will be 0 (singlet) or 1 (triplet) depending on whether N is even or odd.

Application of this rule to *bis*-(dithiadiazolyl)s assuming that each carbon and nitrogen in the molecule contributes a single π-electron to ring bonding and that each sulphur contributes a pair of π-electrons, then N for *ortho-bis*-(dithiadiazolyl)s = 8, and hence S = 0 (singlet) ; for *meta-bis*-(dithiadiazolyl)s N = 9 and hence S = 1 (triplet) ; for *para-bis*-(dithiadiazolyl)s N = 10 and hence S = 0 (singlet). This is shown in Fig. 4.2.14.

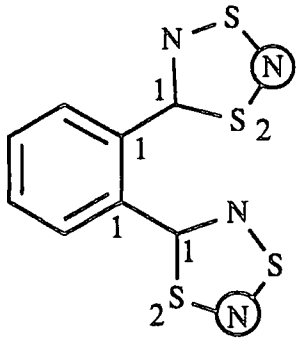
Application of this rule to the xylylenes (Fig. 4.2.15) produces a similar result, which has been borne out by experimental evidence. *ortho*-xylylene[8] and *para*-xylylene[10] have singlet ground states (N = 2 and 4 respectively by Radhakrishnan's rule) whilst meta-xylylene[9] is a triplet (N = 3).

4.2.7. Concentration - dependence of ESR Spectra of *bis*-Dithiadiazolyls

From preparative studies as part of this work it was found that, in general, bis-(1,3,2,4-dithiadiazolyl) radicals could be conveniently prepared and purified in high yield (by reduction of bis-(1,3,2,4-dithiadiazolium) salts) due to the low solubility of the radicals and high solubility of other reaction products in a variety of solvents.

2,6-bis-(Dithiadiazolyl)yl toluene [2-CH_3-C_6H_4-1,3-$(CN_2S_2)_2$] **10** was, however, found to be significantly more soluble, especially in acetonitrile, than related diradicals, a property due, perhaps, to the presence of the methyl substituent. This enhanced solubility was seen to have two main effects, one problematical, and the other distinctly more advantageous; in the first case, **10** was found to be soluble in those solvents used to remove the side products from reduction of the precursor salt, and was consequently obtained in relatively

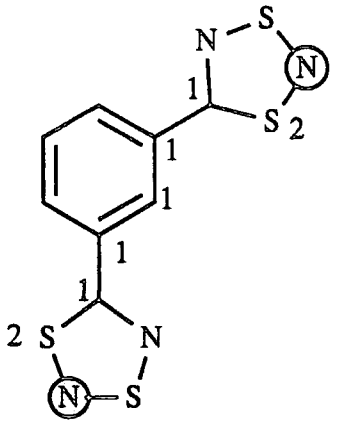
Application of Radhakrishnan's rule to *bis*-(1,3,2,4-dithiadiazolyl)s



$[C_6H_4\text{-}1,2\text{-}(CNSNS)_2]^{\cdot\cdot}$

$\mathbb{S} = 2+1+1+1+1+2 = 8$

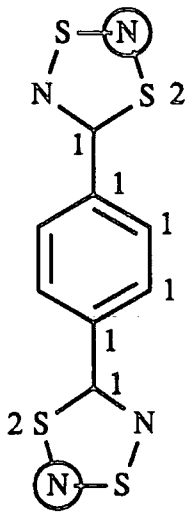
$S = 0$: Singlet



$[C_6H_4\text{-}1,3\text{-}(CNSNS)_2]^{\cdot\cdot}$

$\mathbb{S} = 2+1+1+1+1+1+2 = 9$

$S = 1$: Triplet



$[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]^{\cdot\cdot}$

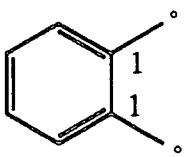
$\mathbb{S} = 2+1+1+1+1+1+1+2 = 10$

$S = 0$: Singlet

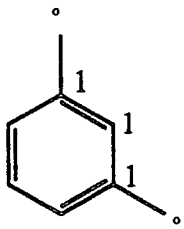
Assuming that the nitrogens shown ringed act as the radical centres, the number of π - electrons separating the two radical centres are added together to give a sum $\mathbb{S}$. If $\mathbb{S}$ is even, then the ground state of the diradical is predicted to be a singlet ($S = 0$ where S is the spin multiplicity). If $\mathbb{S}$ is odd then the ground state is predicted to be a triplet ($S = 1$).
The fact that ESR spectra are observed for all three of the above bis-(1,3,2,4-dithiadiazolyl)s, when this method predicts that the *ortho*- and *para*-isomers should be ESR-silent indicates that the quinoid resonance form is not appreciably more stable than the diradical form, unlike in the xylylenes.

Fig. 4.2.15

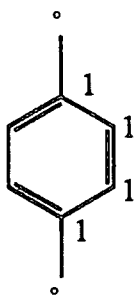
Application of Radhakrishnan's rule to xylylenes



o-xylylene : $\mathbb{S} = 1+1 = 2$
S = 0 : Singlet

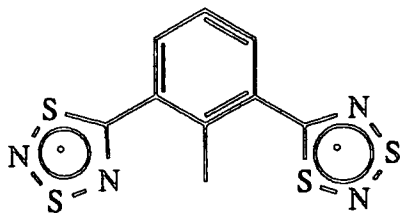


m-xylylene : $\mathbb{S} = 1+1+1 = 3$
S = 1 : Triplet



p-xylylene : $\mathbb{S} = 1+1+1+1 = 4$
S = 0 : Singlet

low yield. In the second case, the high solubility of **10** meant that relatively concentrated solutions could be readily prepared for ESR study of possible concentration effects.



10

The first ESR spectra of **10** were somewhat puzzling. As shown in Fig. 4.2.16a for a toluene solution of **10** generated *in situ* at room temperature, a five-line spectrum with relative intensities approximately 1:1:2:1:1 was obtained. The expected three-line spectrum with relative intensities 1:1:1, shown in Fig. 4.2.16b, was observed after a period of 1 hour. Spectra taken after adding solvent to "ready-mixed" reaction mixtures which had been sealed in tubes for three days gave only the three-line 1:1:1 spectrum. It was thought that the spectrum shown in Fig. 4.2.16b was due to a short-lived impurity.

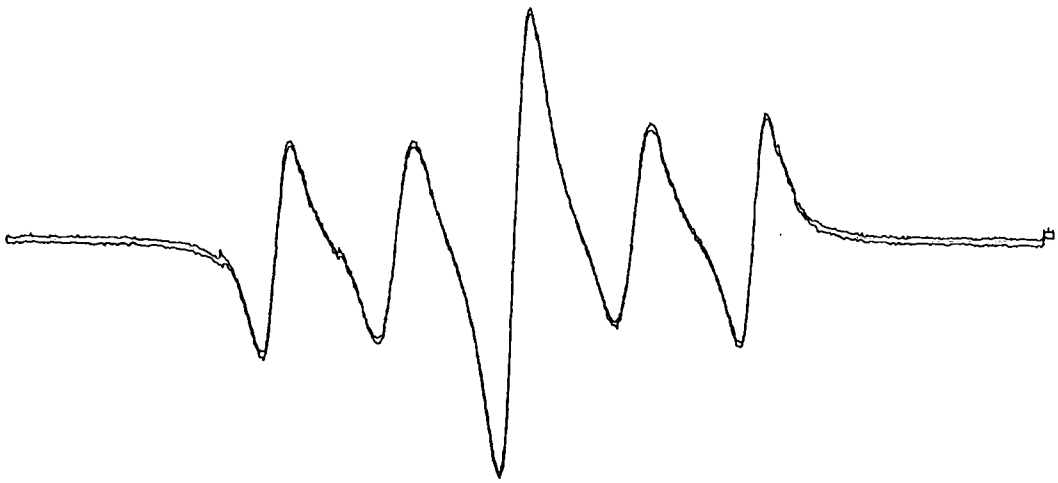
These observations were rationalized in a series of experiments a saturated solution of pure **10**. It was found that the form of the spectrum was dependent on the concentration of the radical in solution. Results are shown in Fig. 4.2.17.

Fig. 4.2.17a shows the spectrum of a saturated benzene solution of **10**, and it can be seen that it cosists of five lines with relative intensities approximately 1:1:2:1:1, the same pattern as shown in Fig. 4.2.16a for a freshly reduced solution of the precursor salt. Dilution of this solution to half saturation concentration (S/2, where S denotes saturation concentration) gave the spectrum shown in Fig. 4.2.17b: the outer most lines have increased in intensity relative to the central line, with concommitent diminution of the two lines immediately adjacent to the central line, giving approximate relative intensities of

Fig. 4.2.16

Room temperature ESR spectra (in toluene) of $[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2]^{\cdot}$ **10** generated in situ

a) t = 5 min

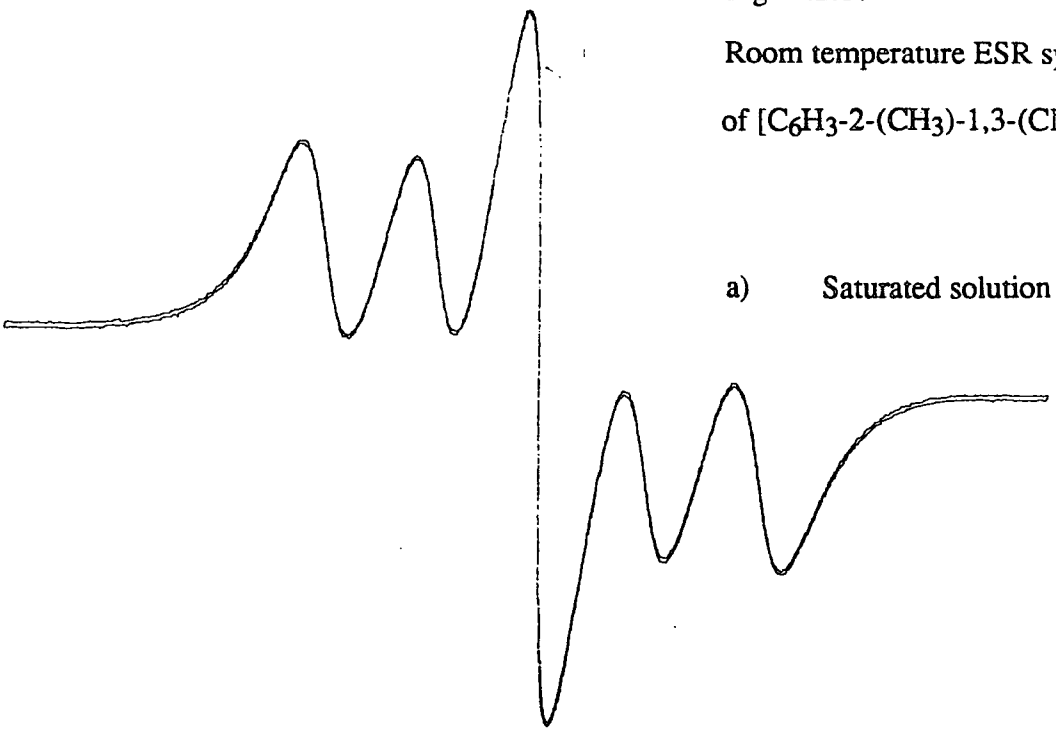


b) t = 60 min

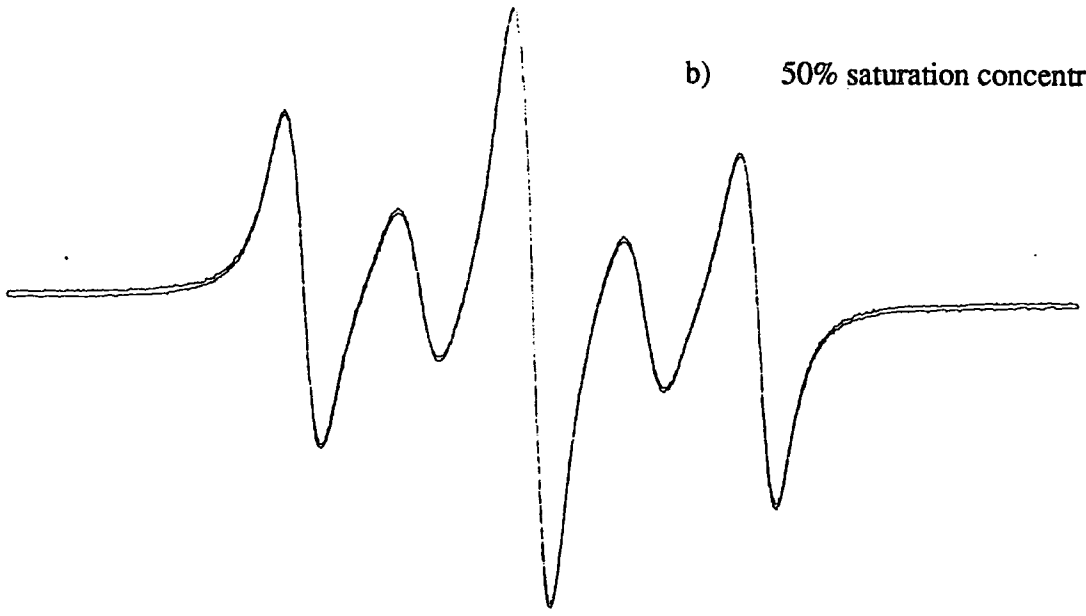
Fig. 4.2.17

Room temperature ESR spectra (in benzene) of $[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2]^{\cdot}$ 10

a) Saturated solution (S)



b) 50% saturation concentration (S/2)



c) 25% saturation concentration (S/4)

2:1:3:2:1. Dilution of this soution to S/4 gave the familiar three-line 1:1:1 spectrum shown in Fig. 4.2.17c.

The observed concentration-dependent ESR behaviour of **10** implies that an intermolecular spin-spin exchange mechanism exists in strong solutions. Intermolecular interactions in dithiadiazolyl solutions are known to facilitate the rearrangement of 1,3,2,4-radicals to the more stable 1,2,3,5-isomer[12]. The nature of the species arising from such interaction in solutions of **10** is still unclear, but given the fact that saturated solutions of **10** are still relatively dilute compared with saturated solutions of *mono*-dithiadiazolyls, it is reasonable to assume that oligomers any higher than dimers will be present only in negligible concentrations.

4.2.8. Temperature - dependence of ESR Spectra of *bis*-Dithiadiazolyls

As described in 4.2.7 above, ESR spectra of bis-(1,3,2,4-dithiadiazolyl)s show concentration-dependence, evidence of intermolecular spin-spin exchange interaction.

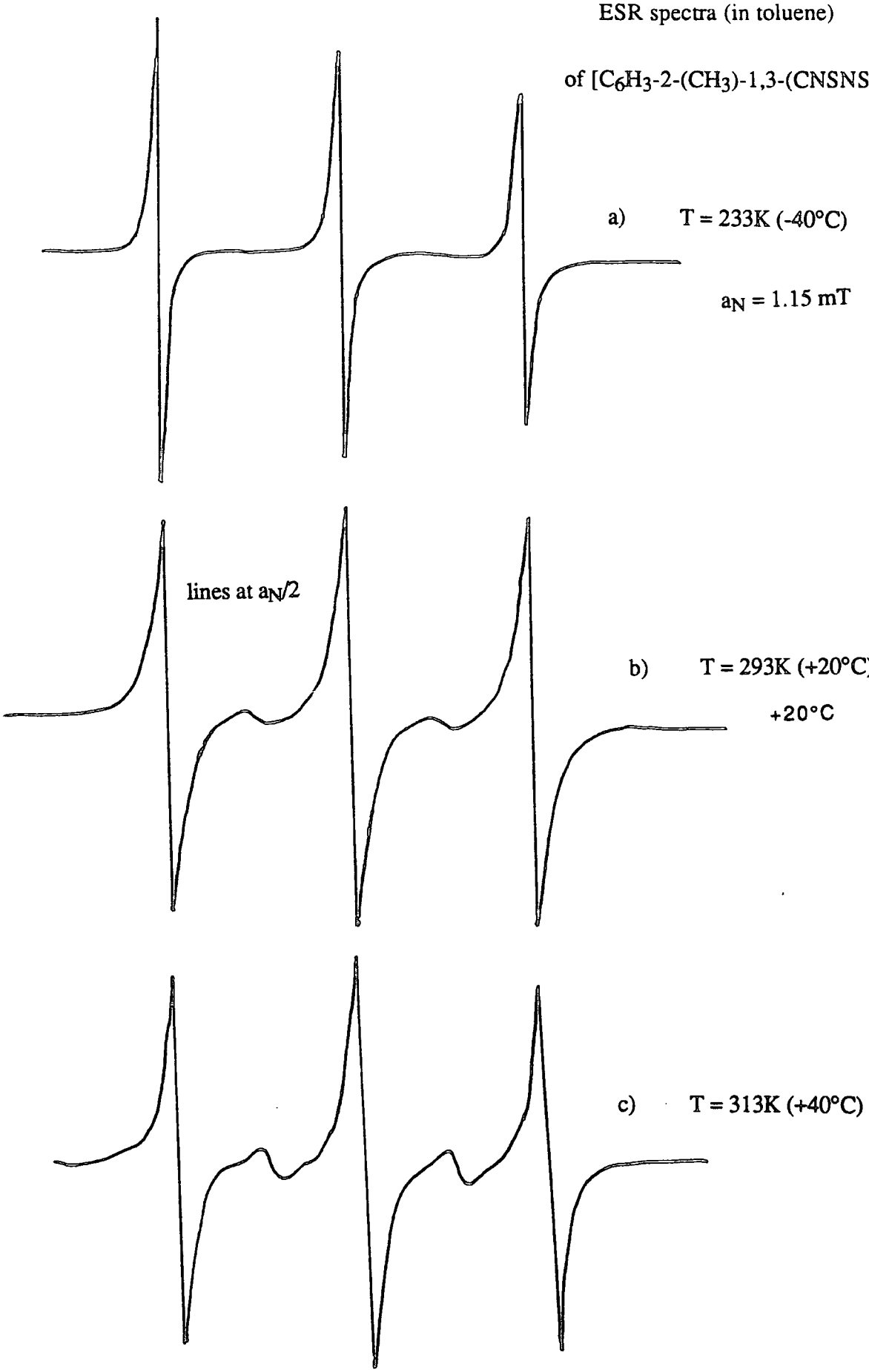
Many examples of *temperature*-dependence of spectra of nitroxyl multiradicals have been reported as evidence for intramolecular interaction[13,14].

ESR spectra of a dilute toluene solution of 2,6-bis-(1,3,2,4-dithiadiazolyl)yl toluene **10** were taken at three different temperatures, and the results are shown in Fig. 4.2.18. All three spectra consist primarily of three lines in approximate ratio 1:1:1 with aN = 1.15 mT, but it was found that broad lines at aN/2 appeared with increasing temperature. At -40°C, as shown in Fig. 4.2.18a, no lines at aN/2 are observed. At +20°C, as shown in Fig. 4.2.18b, these intermediate lines become visible as noticeable humps between the main lines, and at +40°C , as shown in Fig. 4.2.18c they are clearly discernible as individual lines.

Fig. 4.2.18

ESR spectra (in toluene)

of $[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2]^{\cdot}$ 10



Similar behaviour has been observed for nitroxyl multiradicals, and also for solutions of bis-(1,2,3,5-dithiadiazolyl)s, as reported by Oakley and coworkers[17].

4.2.9. Reaction of $(C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2)^{\cdot\cdot}$ with Bromine

Oxidation of the m-diradical with bromine in liquid SO_2 gave a bright red, highly insoluble compound, which was found by microanalysis to contain six bromines to one *bis*-(dithiadiazolium) cation. This product was formed in 82% yield, and from its empirical formula it was deduced that a *bis*-(tribromide) salt $[C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2][Br_3]_2$ had been obtained, the formation of this salt undoubtedly due to the large cation stabilising the tribromide anions. *bis*-(tribromide) salts have been previously reported[18,19], and all feature large transition metal-containing cations. The compound was found to be insoluble in CH_3CN, and decomposed over a period of about 1 hour, presumably to give the bis-monobromide $[C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2]Br_2$ and elemental bromine as shown in Eq. 4.1.

Eq. 4.1 $$[C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2][Br_3]_2 = [C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2]Br_2 + 2Br_2$$

Owing to the highly insoluble and unstable nature of the compound with respect to decomposition, attempts to grow crystals of the *bis*-(tribromide) were unsuccessful.

4.2.10. Reaction of $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2][AsF_6]_2$ with Bu_4NI

Following earlier work by Hey[1], in which $(PhCN_2S_2)_2$ was isolated from the metathesis reaction of a dithiadiazolium salt with Bu_4NI, the preparation of 5,5-(1,4-phenylene)-*bis*-(1,3,2,4-dithiadiazolyl) by the anion metathesis reaction of the *para*-dication $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2][AsF_6]_2$ with Bu_4NI was attempted. Attempts to prepare dithiadiazolium iodides by this route[1] had produced a mixture of dithiadiazolyl dimers and elemental iodine, with the dithiadiazolium iodide undergoing reduction by iodide ion.

Reaction of the dication with two equivalents of Bu_4NI in CH_3CN produced a black microcrystalline solid in 59% yield, and the infrared spectrum of this product was checked against that of a genuine sample of the bis-(dithiadiazolyl) [C_6H_4-1,4-$(CNSNS)_2$]. See Fig. 4.2.19. It is apparent that the two spectra are different, and thus the product compound was analysed. Table 4.2.2 shows the analyses obtained for the product material against calculated values for a number of possible products. The analysis for the reaction product correlates with the calculated values for the diiodide salt [C_6H_4-1,4-$(CNSNS)_2$]I_2.

The mass spectrum of this material (EI+) is summarized in Table 4.2.3 with a suggested breakdown pattern shown in Scheme 4.2.4.

A peak of 35% relative intensity is observedat *m/e* = 284, corresponding to a monocationic species [C_6H_4-1,4-$(CNSNS)_2$]$^+$, and in addition there are peaks assignable to the diiodine monocation $[I_2]^+$ at *m/e* = 254 (relative intensity 75%) and to the monoiodine cation $[I]^+$ at *m/e* = 127 (relative intensity 53%). The relative intensity of the peak at *m/e* = 284 is much greater for this compound than that of the corresponding peaks in the mass spectra of *bis*-(dithiadiazolium) salts of other anions; This may be explained by an electron transfer from iodide anion to dithiadiazolium cation. This electron-transfer may occur in the probe of the mass spectrometer, where the high temperatures and low pressures may favour the process. The presence of peaks corresponding to $[I]^+$ and $[I_2]^+$ in the mass spectrum supports this. They appear strongly in the mass spectrum as aconsequence of their high polarizability / low ionization potential, a condition which is needed for efficient charge-transfer. This process may also occur in the solid state at ambient temperatures, presumably at a much slower rate.

DSC of the iodide gave a sharp exotherm at 195°C with a smaller initial exotherm at 145°C as shown in Fig. 4.2.10. This first exotherm is consistent with the presence of small amounts of the bis-dithiadiazolyl [C_6H_4-1,4-$(CNSSN)_2$] (See Section 4.2.6) arising from

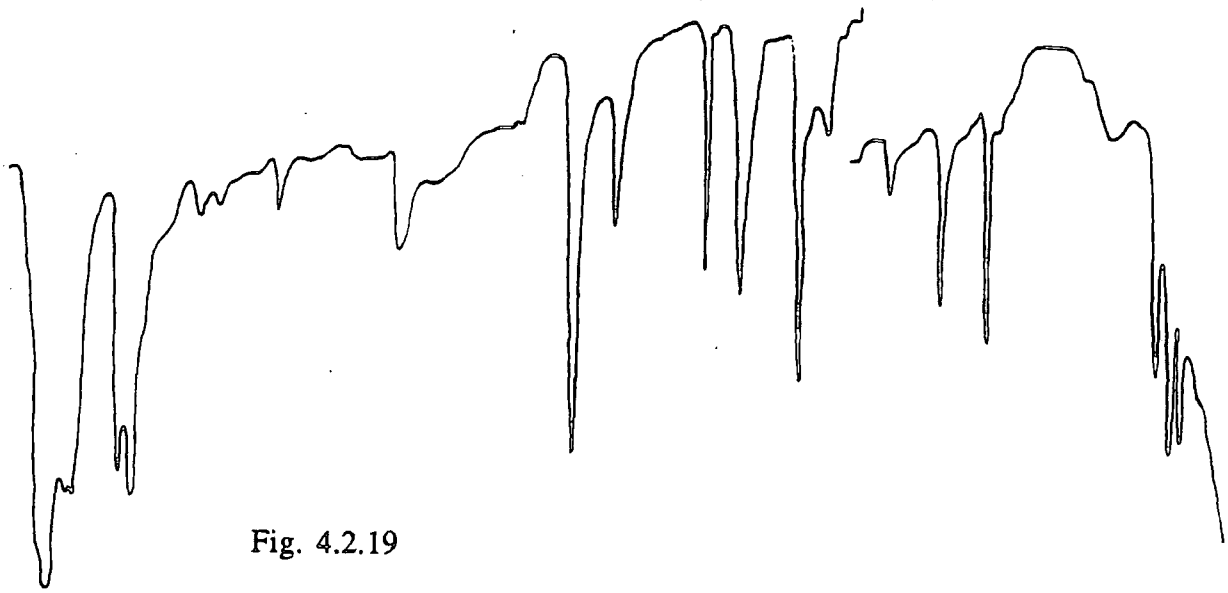
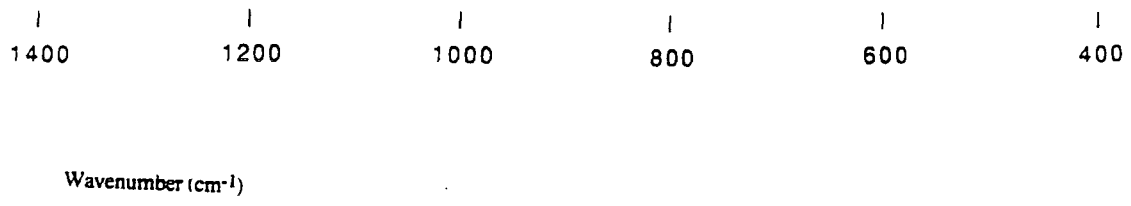


Fig. 4.2.19

Infrared spectra (Nujol mulls) of

a) Product of $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2][AsF_6]_2 + 2\ Bu_4NI$



b) $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]$ (sample prepared by author : spectrum checked against ref. 5)

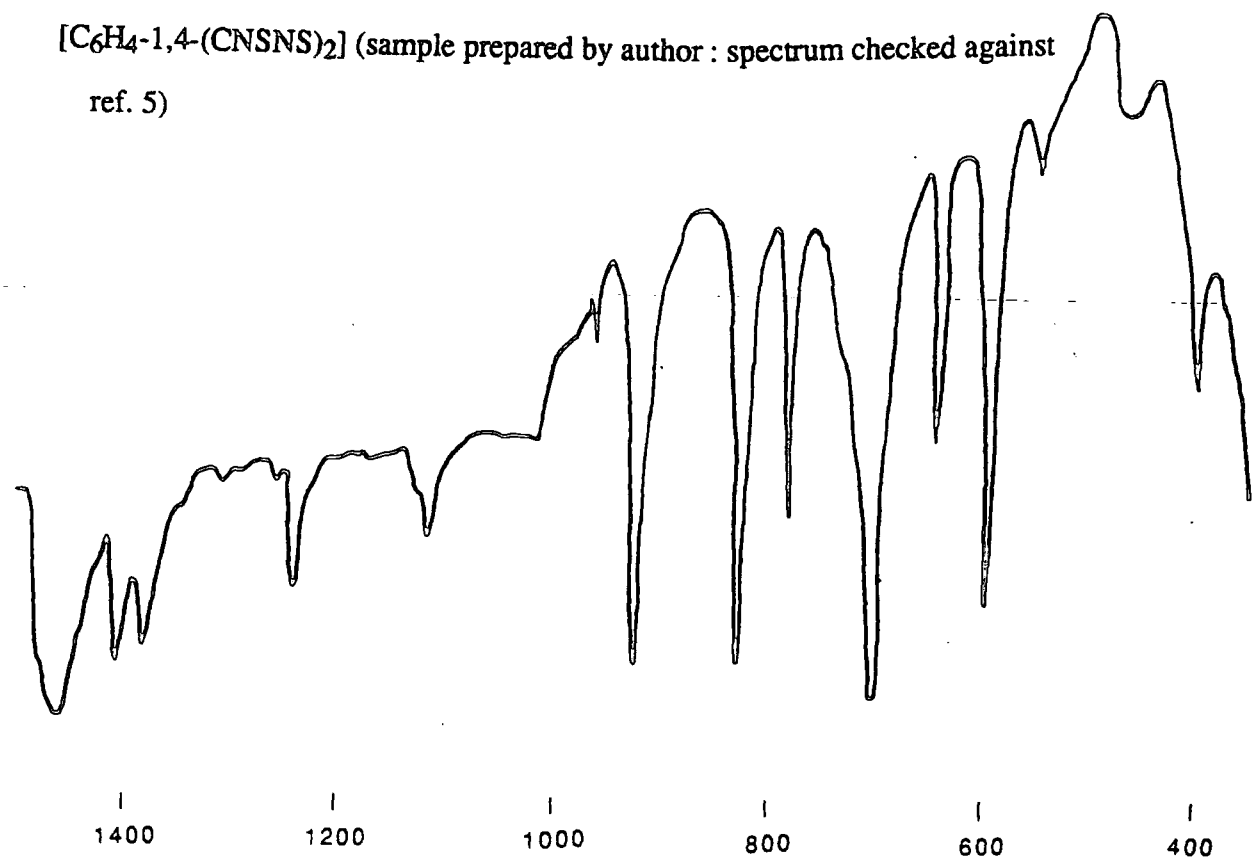


TABLE 4.2.2

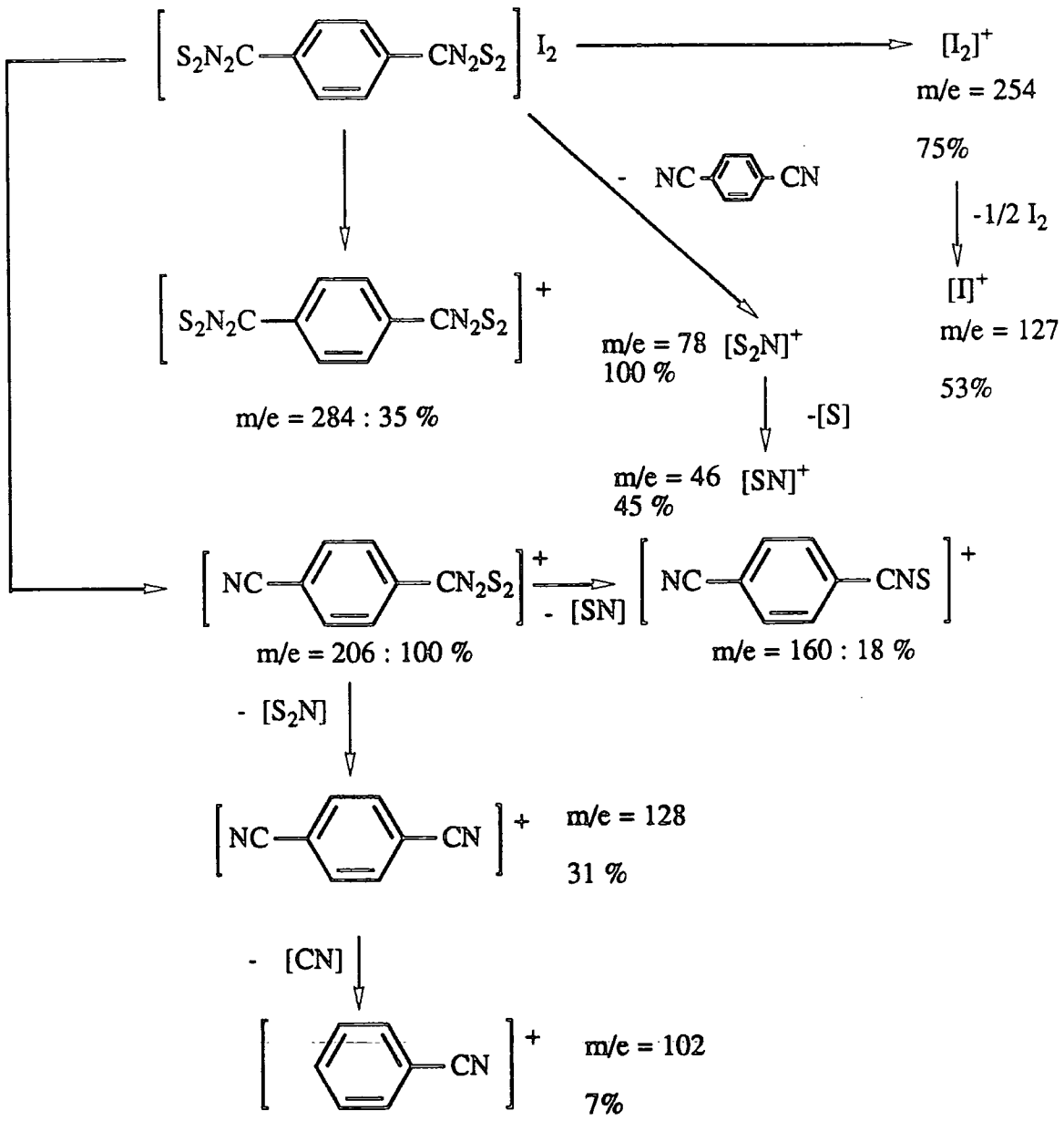
Elemental analyses for the product of the metathesis reaction $2Bu_4NI + [C_6H_4\text{-}1,4\text{-}(CNSNS)_2][AsF_6]_2$ ([p-D'D'][AsF_6]$_2$), compared with calculated values for several possible products

		Calculated Analyses		
Formula	*Mol.Wt*	*%C*	*%H*	*%N*
[*p*-D'D']	284.4	33.76	1.41	19.69
[*p*-D'D'][I]$_2$	538.2	17.83	0.74	10.41
[*p*-D'D'][I_3]$_2$	1045.8	9.18	0.38	5.35
[*p*-D'D']$^+$·[I]$^-$	411.3	23.34	0.97	13.62
[*p*-D'D']$^+$·[I_3]$^-$	665.1	14.43	0.60	8.42
		Observed Analyses		
Reaction Product		17.25	0.65	10.15

TABLE 4.2.3

THE MASS SPECTRUM (EI+) OF $[C_6H_4\text{-}1,4\text{-}(CN_2S_2)_2][I]_2$

m / e	Relative Intensity (%)	Assignment
46	45	$[SN]^+$
64	28	$[S_2]^+$
78	100	$[S_2N]^+$
102	7	$[C_6H_4CN]^+$
127	53	$[I]^+$
128	31	$[NCC_6H_4CN]^+$
160	18	$[NCC_6H_4CNS]^+$
206	100	$[NCC_6H_4CN_2S_2]^+$
254	75	$[I_2]^+$
284	35	$[S_2N_2CC_6H_4CN_2S_2]^+$



Scheme 4.2.4

Suggested fragmentation pathway in the electron impact mass spectrum of $[C_6H_4\text{-}1,4\text{-}(CN_2S_2)_2]I_2$

loss of iodine (It was found that over a long period of time the caps of storage vials in which samples of this material were kept in the glove - box became coloured dark brown, typical of elemental iodine). The large exotherm at 195°C is typical of dithiadiazolyl radical rearrangements in the solid state[20], and yet the material has the empirical formula of a dithiadiazolium salt. This provides further evidence for the dithiadiazolium iodides existing as charge-transfer salts, with radical character but the composition of a salt. In Chapter 5 the preparation of the iodide salt of the trication $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3]^{3+}$ is described, a compound with an empirical formula of three iodines per cation, but which was found to be ESR - active in solution, and which showed thermal properties more typical of a dithiadiazolyl radical. An explanation for this is provided.

Experimental.

Preparation of $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2][AsF_6]_2$ *:*

1,2-Dicyanobenzene (128 mg, 1.0 mmol) and $[SNS][AsF_6]$ (534 mg, 2.0 mmol) were placed together in the rear leg of a "dog". Sulphur dioxide was condensed in sufficient to fully dissolve both reagents, and the mixture was stirred at room temperarure for 48 hrs. Following removal of SO_2, coloured impurities were removed from the crude product by repeated washing with CH_2Cl_2. The purified product was dried *in vacuo*.

Appearance : Off - white microcrystalline solid.

Yield : 596 mg, 0.90 mmol, 90%

IR (NUJOL Mull) : ν_{max} 3080w, 1590m, 1580sh, 1505w, 1420s, 1405sh, 1307w, 1295sh, 1220w, 1200w, 1130w, 985m, 970w, 925w, 900w br, 880w, 865w, 800m, 790sh, 785w, 775s, 700vs br, 630w, 585m, 570w br, 455w, 400vs cm^{-1}

Analysis : Found (required) C : 14.22 (14.49), H : 0.80 (0.60), N : 8.88 (8.45) %

Solubility : SO_2, CH_3CN - Soluble. CH_2Cl_2 - Sparingly soluble

Preparation of $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2][Cl]_2$ *:*

$[C_6H_4\text{-}1,2\text{-}(CNSNS)_2][AsF_6]_2$ (145 mg, 0.22 mmol) and Bu_4NCl (125 mg, 0.45 mmol) were placed in the rear leg of a "dog". CH_3CN was introduced into the front leg and degassed in a single freeze - thaw cycle. Introduction of solvent onto the reaction mixture caused instant reaction with the production of a yellow-orange precipitate. Stirring was continued for 20 mins to ensure complete reaction, and then the supernatant was filtered off. The crude product was washed repeatedly with back - distilled solvent and dried *in vacuo*.

Appearance : Yellow - brown powder, highly moisture - sensitive.

Yield : 52 mg, 0.15 mmol, 68%

IR (NUJOL Mull) : ν_{max} 1590w, 1570sh, 1500w, 1455m, 1420s, 1400s, 1310sh, 1300w, 1290sh, 1260w, 1205sh, 1197m, 1163w, 1120w, 980s, 970m, 935m, 855m, 840s, 792s, 780s, 765s, 730w, 720w, 680w, 670w, 655m, 645w, 625w, 580m, 575m, 505w, 445s, 435m, 400m, 370w cm^{-1}

Analysis : Found (required) C : 27.81 (27.04), H : 1.41 (1.14), N : 15.63 (15.77) %.

Solubility : CH_3CN - sparingly soluble

Preparation of $[C_6H_4\text{-}1,2\text{-}(CNSNS)_2][Br]_2$ *:*

$[C_6H_4\text{-}1,2\text{-}(CNSNS)_2][AsF_6]_2$ (110 mg, 0.17 mmol) and Bu_4NBr (109 mg, 0.34 mmol) were placed in the rear leg of a "dog". CH_3CN was introduced into the front leg and degassed in a single freeze - thaw cycle. Introduction of solvent onto the reaction mixture caused instant reaction with the production of a red - orange precipitate. Stirring was continued for 24 hrs to ensure complete reaction. Following removal of the supernatant by filtration the crude product was washed repeatedly with back - distilled CH_3CN and dried *in vacuo*.

Appearance : Brick-red powder

Yield : 32 mg, 0.07 mmol, 42%

IR (NUJOL Mull) : ν_{max} 1590w br, 1570w, 1495w, 1420m, 1400w, 1307w, 1290w, 1200w, 1192w, 1160w, 973m, 968m, 930w, 847w, 830m, 783m, 770m, 760m, 653m, 630w, 617w, 578m, 570w, 439s, 430w, 390m, 367w cm^{-1}

Analysis : Found (required) C : 21.37 (21.61), H : 0.82 (0.90), 12.57 (12.61) %

Solubility : CH_3CN - sparingly soluble. CH_2Cl2 - insoluble. SO_2 - very soluble

Preparation of $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$ *:*

1,3-Dicyanobenzene (128 mg, 1.0 mmol) and $[SNS][AsF_6]$ (534 mg, 2.0 mmol) were placed together in the rear leg of a "dog". Sulphur dioxide was condensed in sufficient to fully dissolve both reagents, and the mixture was stirred at room temperarure for 48 hrs. Following removal of SO_2, coloured impurities were removed from the crude product by repeated washing with CH_2Cl_2. The purified product was dried *in vacuo*.

Appearance : white microcrystalline solid

Yield : 602 mg, 0.91 mmol, 91%

IR (NUJOL Mull) : ν_{max} 3060w, 1587m, 1577m, 1500m, 1420s, 1400m, 1305m, 1220m, 1203w, 1180w, 1122w, 1060w, 990s, 985s, 977w, 925m, 910m, 900sh, 887m, 880sh, 865w, 800s, 790s, 772s, 700vs br, 628m, 583m, 572m, 505w, 462sh, 455m, 443m, 400vs cm^{-1}

Analysis : Found (required) C : 14.60 (14.49), H : 0.55 (0.60), N : 8.24 (8.45) %

^1H NMR (CD_3CN) : δ 8.18 ppm (t), 1H ; δ 8.76 ppm (d), 2H ; δ 9.10 ppm (d), 1H

Solubility : SO_2, CH_3CN - soluble. CH_2Cl_2 - sparingly soluble . Toluene - insoluble.

Preparation of $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][Cl]_2$ *:*

$[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$ (330 mg, 0.5 mmol) and Bu_4NCl (280 mg, 1.01 mmol) were placed in the rear leg of a "dog". CH_3CN was introduced into the front leg and degassed in a single freeze - thaw cycle. Introduction of solvent onto the reaction mixture

caused instant reaction with the production of a bright yellow precipitate. Stirring was continued for 20 mins to ensure complete reaction, and then the supernatant was filtered off. The crude product was washed repeatedly with back - distilled solvent and dried *in vacuo*.

Appearance : Bright yellow powder.

Yield : 141 mg, 0.40 mmol, 80%.

IR (NUJOL Mull) : ν_{max} 1600w, 1420m, 1400s, 1330w, 1295w, 1250w br, 1190w, 1180sh, 1095w br, 1030w, 990w, 980w, 940w, 915w, 875m, 830w, 825w, 785m, 775m, 690w, 680sh, 670w, 660w, 650w, 605w, 580w, 570m, 460w br, 435w, 415s, 400w cm^{-1}.

Analysis : Found (required) C : 28.81 (27.04), H : 1.61 (1.14), N : 15.83 (15.77) %.

Solubility : SO_2 - sparingly soluble. CH_3CN, CH_2Cl_2 - insoluble.

Preparation of $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][Br]_2$ *:*

$[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$ (147 mg, 0.22 mmol) and Bu_4NBr (142 mg, 0.44 mmol) were placed in the rear leg of a "dog". CH_3CN was introduced into the front leg and degassed in a single freeze - thaw cycle. Introduction of solvent onto the reaction mixture caused instant reaction with the production of a red - orange precipitate. Stirring was continued for 24 hrs to ensure complete reaction. Following removal of the supernatant by filtration the crude product was washed repeatedly with back - distilled CH_3CN, followed by CH_2Cl_2, and dried *in vacuo*.

Appearance : Orange - red powder

Yield : 59 mg, 0.13 mmol, 60%

IR (NUJOL Mull) : ν_{max} 1590w br, 1415m, 1397s, 1195sh, 1170w br, 1030w, 975w, 945m, 927w, 867m, 840w, 812m, 782m, 772m, 720w, 680w, 662w, 650w, 582w, 573m, 440w, 410s, 400sh, 350sh cm^{-1}

Analysis : Found (required) C : 21.57 (21.61), H : 0.89 (0.90), N : 12.51 (12.61) %

Reduction of $[C_6H_4$-1,3-$(CNSNS)_2][Cl]_2$:

$[C_6H_4$-1,3-$(CNSNS)_2][Cl]_2$ (118 mg, 0.33 mmol) and Ph_3Sb (molar excess) were placed in the rear leg of a "dog". CH_3CN was introduced into the front leg and degassed in a single freeze - thaw cycle. Introduction of solvent onto the reaction mixture caused instant darkening of the reaction mixture, first turning dark green, and over time dark brown - black. Stirring was continued for 4 hrs to ensure complete reaction, after which the supernatant was filtered off the black precipitate of product. Residual Ph_3Sb and Ph_3SbCl_2 were removed by repeated washing with back - distilled solvent, and the product was dried *in vacuo*.

Appearance : Dark brown - black powder

Yield : 55 mg, 0.19 mmol, 59%

IR (NUJOL Mull) : ν_{max} 1600w br, 1500sh, 1425sh, 1400s, 1190sh, 1180w, 1100w, 1018w, 1010sh, 920w, 885sh, 880w, 832w, 790m, 780s, 770w, 720m, 705s, 670m, 650w, 640sh, 580w, 540w br, 460w br cm^{-1}.

Analysis : Found C : 31.82, H : 1.48, N : 18.44 %

(C_6H_4-1,3-$(CN_2S_2)_2$) requires C : 33.78, H : 1.42, N : 19.70 %

Mass Spectrum (EI+) : *m/e*, Relative Intensity, Assignment ;

284, 84%, M^+ ; *238*, 26%, $[M - SN]^+$; *206*, 84%, $[M - S_2N]^+$; *160*, 28%, $[M - (S_2N + SN)]^+$; *128*, 29%, $[M - 2S_2N]^+$; *102*, 15%, $[C_6H_4CN]^+$; *78*, 100%, $[S_2N]^+$; *64*, 25%, $[S_2]^+$; *46*, 43%, $[SN]^+$.

DSC : Large, sharp exotherm at 110°C.

Reaction of (C_6H_4-1,3-$(CN_2S_2)_2$) with Bromine :

(C_6H_4-1,3-$(CN_2S_2)_2$) (15 mg, 0.05 mmol) was placed in the rear leg of a "dog" which was then evacuated. SO_2 was introduced and the mixture sonicated briefly to give a fine suspension. Excess bromine was then introduced, and reaction occurred instantaneously to

give a red - orange precipitate. Stirring was continued for 3 hr to ensure complete reaction, and then the supernatant was filtered off. Volatiles were removed in vacuo, and fresh SO_2 was then introduced to wash the product. After repeated washing the product was dried in vacuo.

Appearance : Red - orange powder, highly moisture - sensitive.

Yield : 30 mg, 0.041 mmol, 82%

Analysis : Found C : 11.48, H : 0.55, N : 6.55, Br : 63.20 %

$[C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2][Br]_2$ requires C : 21.63, H : 0.91, N : 12.62, Br : 35.97 %

$[C_6H_4\text{-}1,3\text{-}(CN_2S_2)_2][Br_3]_2$ requires C : 12.58, H : 0.53, N : 7.34, Br : 62.77 %

Preparation of $[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$ *:*

2,6-Dicyanotoluene (142 mg, 1.0 mmol) and $[SNS][AsF_6]$ (534 mg, 2.0 mmol) were placed together in the rear leg of a "dog". Sulphur dioxide was condensed in sufficient to fully dissolve both reagents, and the mixture was stirred at room temperarure for 48 hrs., during which time the product formed as a yellowish precipitate under a brown solution. Following removal of SO_2, coloured impurities were removed from the crude product by repeated washing with CH_2Cl_2. The purified product was dried *in vacuo*.

Appearance : Yellow - white powder

Yield : 642 mg, 1.90 mmol, 95 %

IR (NUJOL Mull) : n_{max} 1580m, 1500w, 1435s, 1410m, 1230w, 1200w, 1180w, 1120w, 990m, 890w, 818sh, 805s, 800sh, 700vs br, 628w, 570w, 580w, 550w, 447m, 400vs cm^{-1}

Analysis : Found (required) C : 15.92 (15.98), H : 0.89 (0.90), N : 8.26 (8.28) %

^1H NMR (CD_3CN) : δ 2.82 ppm (s), 3H ; δ 7.95 ppm (t),1H ; δ 8.35 ppm (d), 2H.

Solubility : SO_2 - sparingly soluble. CH_3CN - very soluble. CH_2Cl_2 - insoluble.

Preparation of $[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2][Cl]_2$:

$[C_6H_3\text{-}2\text{-}(CH_3)\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$ (mg, mmol) and Bu4NCl (mg, mmol) were placed in the rear leg of a "dog". CH_3CN was introduced into the front leg and degassed in a single freeze - thaw cycle. Introduction of solvent onto the reaction mixture caused instant reaction with the formation of a bright yellow precipitate. Stirring was continued for mins to ensure complete reaction, and then the supernatant was filtered off. The crude product was washed repeatedly with back - distilled solvent and dried *in vacuo*.

Appearance : Bright yellow powder.

Yield : 169 mg, 0.46 mmol, 92 %

IR (NUJOL Mull) : ν_{max} 1577m, 1560sh, 1450sh, 1433s, 1410s, 1203w, 1173w, 1120w, 1035w, 988m, 870m, 845w, 817m, 790s, 770w, 720m, 680m, 595w, 585m, 475w, 427s cm^{-1}

Analysis : Found (required) C : 28.36 (29.27), H : 1.60 (1.64), N : 14.65 (15.17) %

Reaction of $[SNS][AsF_6]$ with 3,4,5,6-Tetrafluoro-1,2-dicyanobenzene :

$[SNS][AsF_6]$ (534 mg, 2.0 mmol) and 3,4,5,6-tetrafluoro-1,2-dicyanobenzene (162 mg, 1.0 mmol) were placed together in the rear leg of a "dog". Sulphur dioxide was introduced sufficient to dissolve both reagents and the mixture was stirred at room temperature for three days. Solvent was removed to give a yellow-brown featherlike polycrystalline mass, which was washed free of coloured impurities by repeated washing with dichloromethane. Yield 540 mg.

Reaction of $[SNS][AsF_6]$ with 2,4,5,6-Tetrafluoro-1,3-dicyanobenzene :

$[SNS][AsF_6]$ (534 mg, 2.0 mmol) and 2,4,5,6-tetrafluoro-1,3-dicyanobenzene (162 mg, 1.0 mmol) were placed together in the rear leg of a "dog". The reaction was carried out as for 3,4,5,6-tetrafluoro-1,2-dicyanobenzene above. Yield 586 mg.

Preparation of $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2][I]_2$:

$[C_6H_4\text{-}1,4\text{-}(CNSNS)_2][AsF_6]_2$ (217 mg, 0.33 mmol) and Bu_4NI (247 mg, 0.67 mmol) were placed together in the rear leg of a "dog". CH_3CN (5 ml) was introduced into the other leg and degassed in a single freeze-thaw cycle. Introduction of solvent onto the reaction mixture produced a black precipitate immediately. The reaction mixture was stirred for 24 hrs at room temperature, and then the supernatant was filtered off. CH_3CN was pumped off and replaced with CH_2Cl_2, with which the crude product was washed repeatedly. Following removal of CH_2Cl_2, SO_2 was introduced and the product was washed several times. Finally the product was washed continuously for 3 days in a closed extractor by cycling CH_2Cl_2 under vacuum. The washed product was dried *in vacuo*.

Appearance : Black microcrystalline solid.

Yield : 105 mg, 0.20 mmol, 59%

IR (NUJOL Mull) : ν_{max} 1510w, 1440sh, 1433sh, 1392sh, 1315w, 1295w, 1240w, 1125w, 962s, 920m, 835m, 800m, 745s, 720w, 662w, 613m, 570m, 455w br, 410m, 400m, 390w cm^{-1}.

Mass Spectrum (EI+) : *m/e*, Relative Intensity, Assignment ;

284, 35%, $[S_2N_2CC_6H_4CN_2S_2]^+$; *254*, 75%, $[I_2]^+$; *206*, 100%, $[S_2N_2CC_6H_4CN]^+$; *160*, 18%, $[SNCC_6H_4CN]^+$; *128*, 28%, $[NCC_6H_4CN]^+$; *127*, 53%, $[I]^+$; *102*, 7%, $[C_6H_4CN]^+$; *78*, 100%, $[S_2N]^+$; *64*, 28%, $[S_2]^+$; *46*, 45%, $[SN]^+$.

DSC : Small exotherm at 145°C, Large, sharp exotherm at 195°C.

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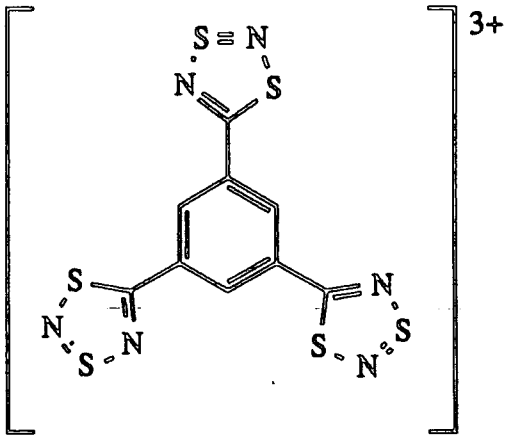
CHAPTER 5

REACTION OF [SNS][ASF_6] WITH 1,3,5-TRICYANOBENZENE : PREPARATION OF TRIS-(DITHIADIAZOLIUM) SALTS

5.1 Introduction

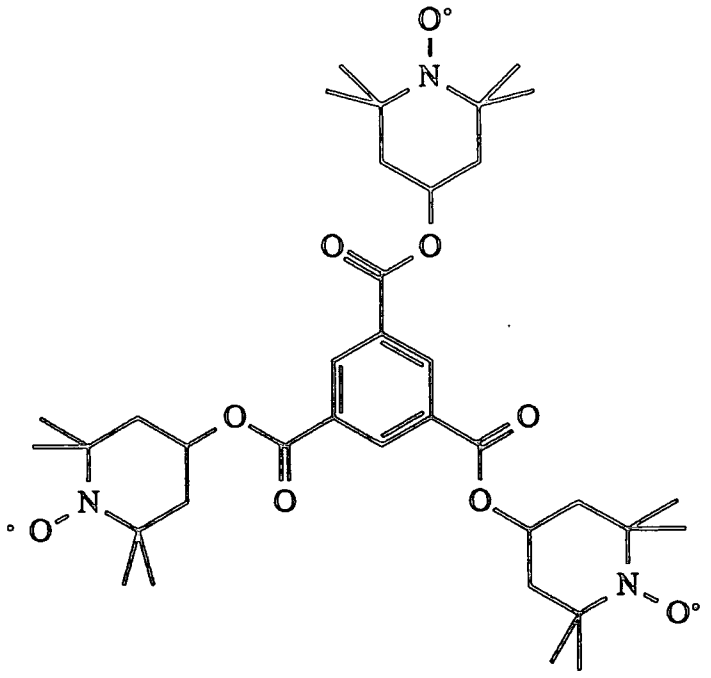
The cycloaddition of [SNS][AsF_6] to nitriles has thus far shown itself to be a general route to *mono-* and *bis-*(1,3,2,4-dithiadiazolium) salts. Preliminary work by Rawson[1] in this laboratory showed that the reaction could be easily used to prepare a *tris-*(dithiadiazolium) salt in high yield from 1,3,5-tricyanobenzene, and in this chapter the syntheses of a variety of salts of the trication [C_6H_3-1,3,5-$(CNSNS)_3]^{3+}$ (1) and the reduction of the trication to a stable triradical are described. The preparation of stable high spin multiplicity radicals has recently been the subject of a great deal of research, since such materials may be useful as precursors to molecular magnets.



1

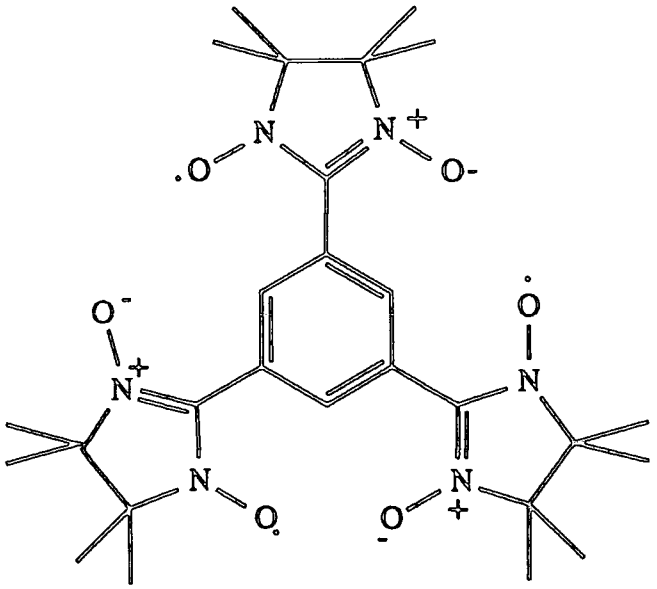
Much early work on stable triradicals involved the well-known nitroxyls, available commercially as spin probes. Biradicals and then triradicals with a variety of different substituents were synthesized and studied. This family of radicals are characteristically insoluble in many solvents, and are stable at elevated temperatures.

Triradical 2, reported in 1965[2], was the subject of a thorough study of the ESR lineshapes in solution[3].



2

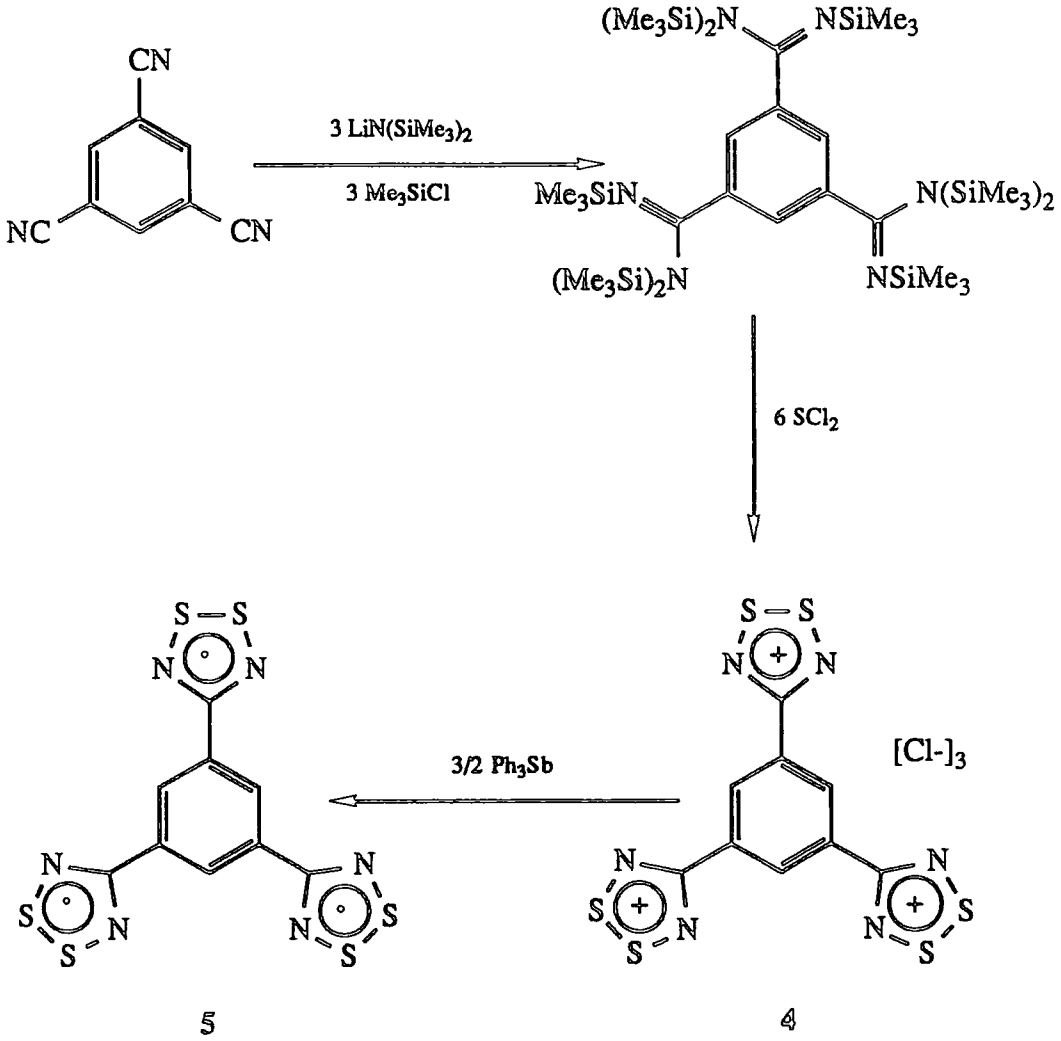
Recently the unusual "nitroxyl nitroxide triradical 3 was reported[4], with solution ESR spectra and a magnetic study indicating magnetic behaviour typical of neither a ferromagnet nor a typical paramagnet.



3

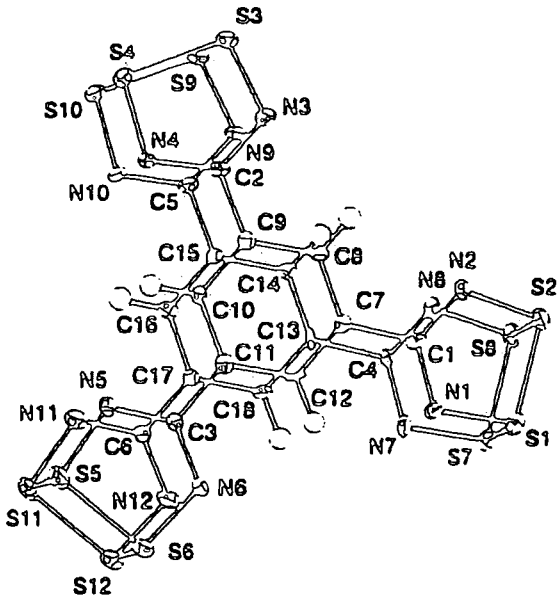
Problems of low solubility in all solvents except chloroform meant that a crystal structure could not be obtained, and it was from the world of sulphur-nitrogen chemistry that a crystal structure of a stable triradical finally appeared.

Oakley and coworkers have met with much success in the field of the 1,2,3,5-dithiadiazolyls, using the reaction of sulphur dichloride with silylated amidines derived from nitriles (see Chapter 1, Section 1.2.1c, p.3). Using the amidine derivative of 1,3,5-tricyanobenzene, the *tris*-(1,2,3,5-dithiadiazolium) salt 4 was prepared[5] and reduced to the *tris*-(1,2,3,5-dithiadiazolyl) 5 as shown in Scheme 5.1.1. Sublimation at high-temperature under high vacuum gave crystals of 5 suitable for X-Ray analysis, and the crystal structure[5] of 5 is shown in Fig. 5.1.1.



Scheme 5.1.1

Preparation of *tris*-(1,2,3,5-dithiadiazolium) salt 4 and its reduction to *tris*-(1,2,3,5-dithiadiazolyl) 5



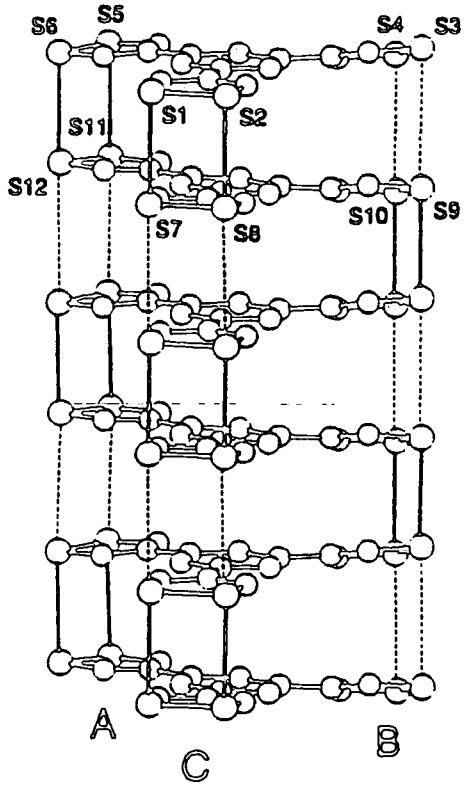


Fig. 5.1.1

X-Ray crystal structure of 5

(Reproduced from Ref. 5)

5.2 Results and Discussion

5.2.1 Reaction of [SNS][AsF_6] with 1,3,5-Tricyanobenzene

The reaction of 1,3,5-tricyanobenzene with [SNS][AsF_6] in 1:3 ratio gave the tris-(1,3,2,4-dithiadiazolium) hexafluoroarsenate (1[AsF_6]$_3$) in 70% yield, a lower yield than in the case of mononitriles, where quantitative yields are the norm. This may be due to the occurrence of side reactions wherein C-H bonds on the aromatic ring are attacked by [SNS]+. The reaction of [SNS][AsF_6] with benzene was found to give a mixture of products[6], whereas no reaction was observed with perfluorobenzene[6]. No evidence of other products in the isolated tris-(dithiadiazolium) salt was found from ^{1}H NMR, the only signal being a singlet at δ = 9.46 ppm relative to TMS.

^{13}C NMR in CD_3CN, shown in Fig. 5.2.1, consists of three signals at 128.8 ppm, 137.8 ppm and 200.3 ppm, the latter signal assignable to the carbons in the dithiadiazolium rings[6]. If other products were formed in the reaction it is likely that they were removed during washing of the crude product. Indeed, the reaction produced a considerable amount of a dark brown tarry residue, which was not analysed. The IR spectra of [C_6H_3-1,3,5-(CNSNS)$_3$][AsF_6]$_3$ and some salts of other anions are shown in Fig. 5.2.2.

Salts of other anions were easily prepared from the hexafluoroarsenate by anion metathesis in acetonitrile. Using tetrabutylammonium halides the chloride and iodide were prepared in yields of 75% and 79% respectively. These salts formed as precipitates from acetonitrile, the chloride (1Cl_3) as a bright yellow amorphous powder and the iodide (1I_3) as black microcrystals. As expected for salts of a trication and monoanions the compounds were insoluble in liquid sulphur dioxide[7] and common organic solvents.

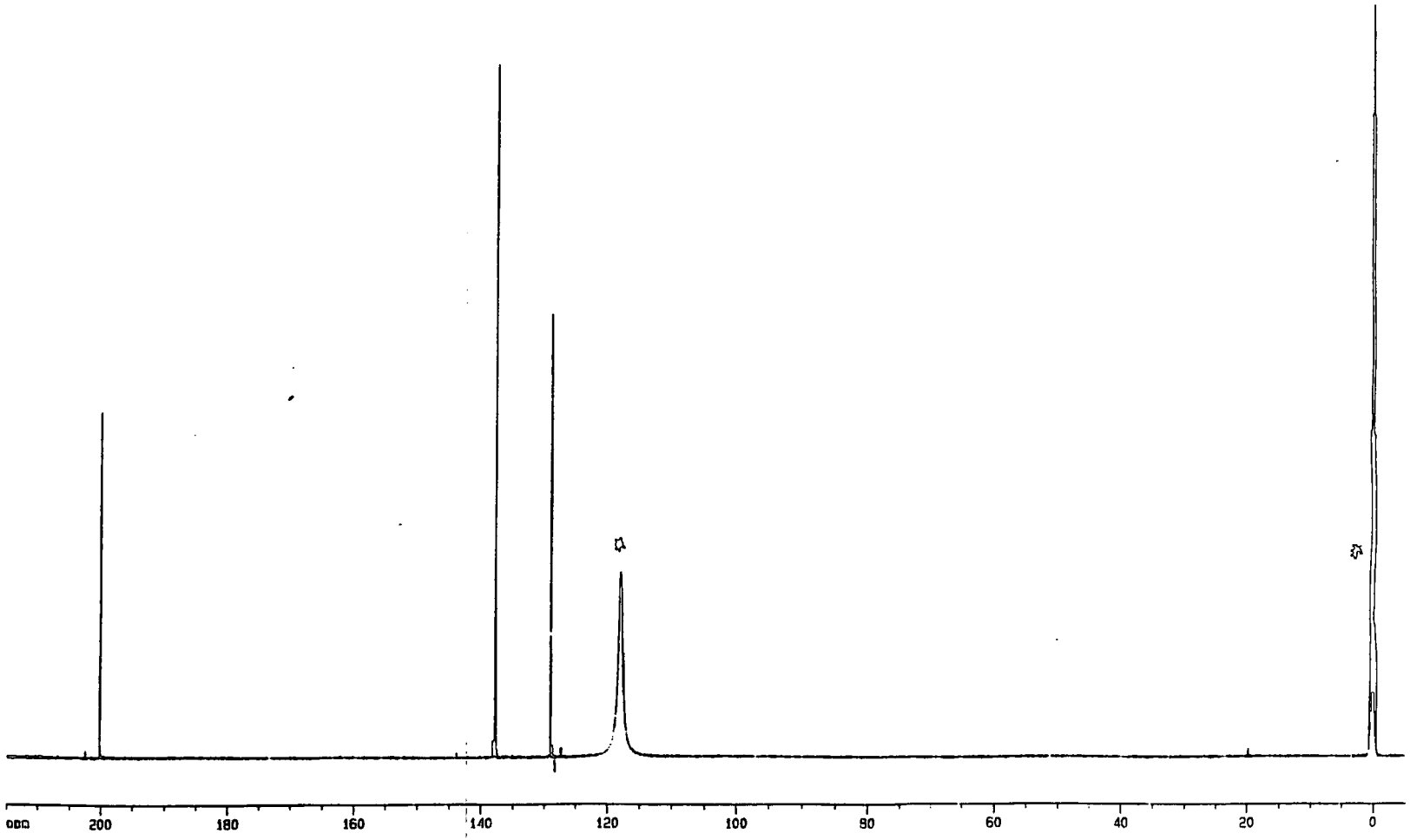


Fig. 5.2.1

^{13}C NMR (in CD_3CN) of $\mathbb{1}[AsF_6]_3$

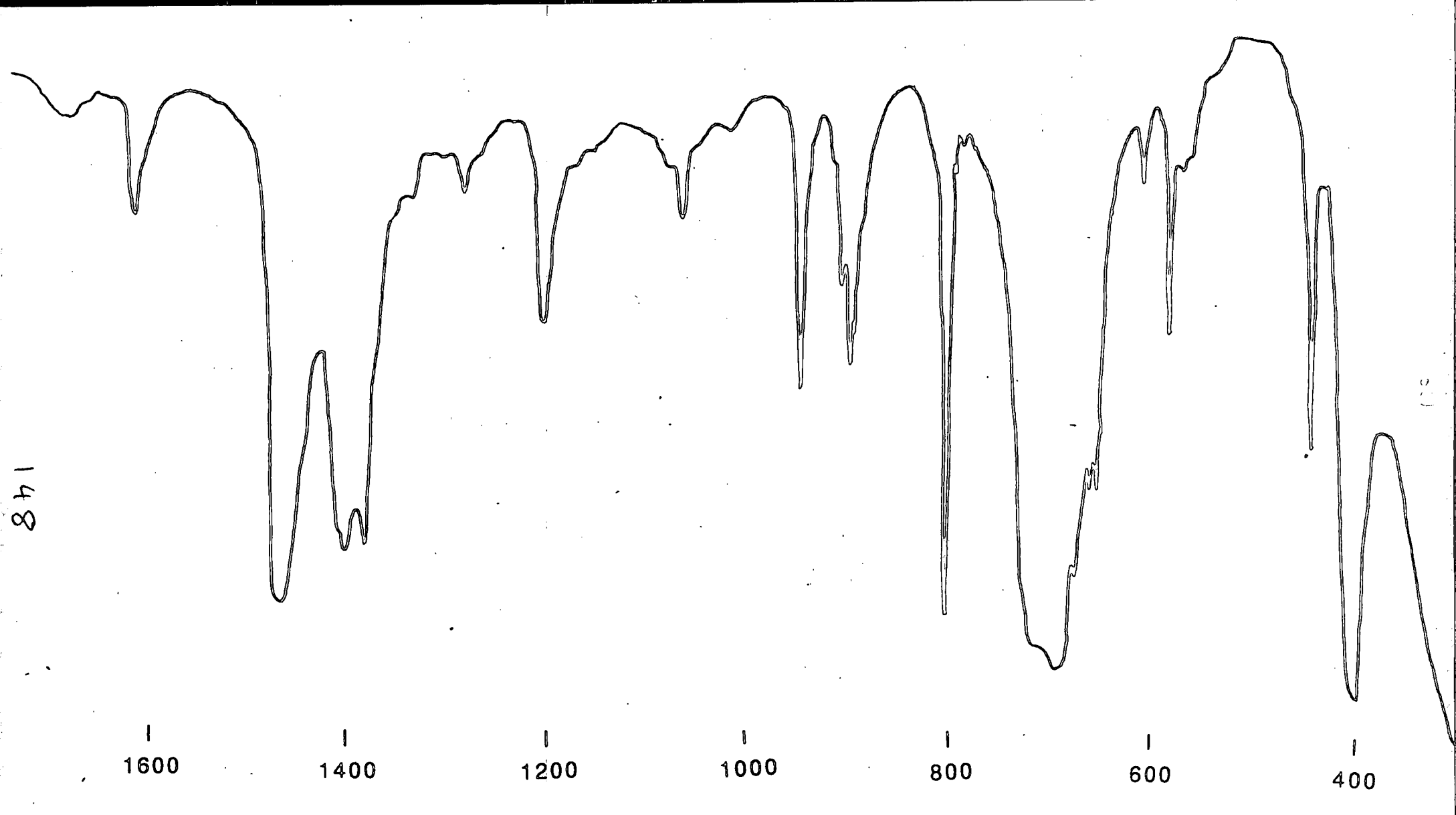
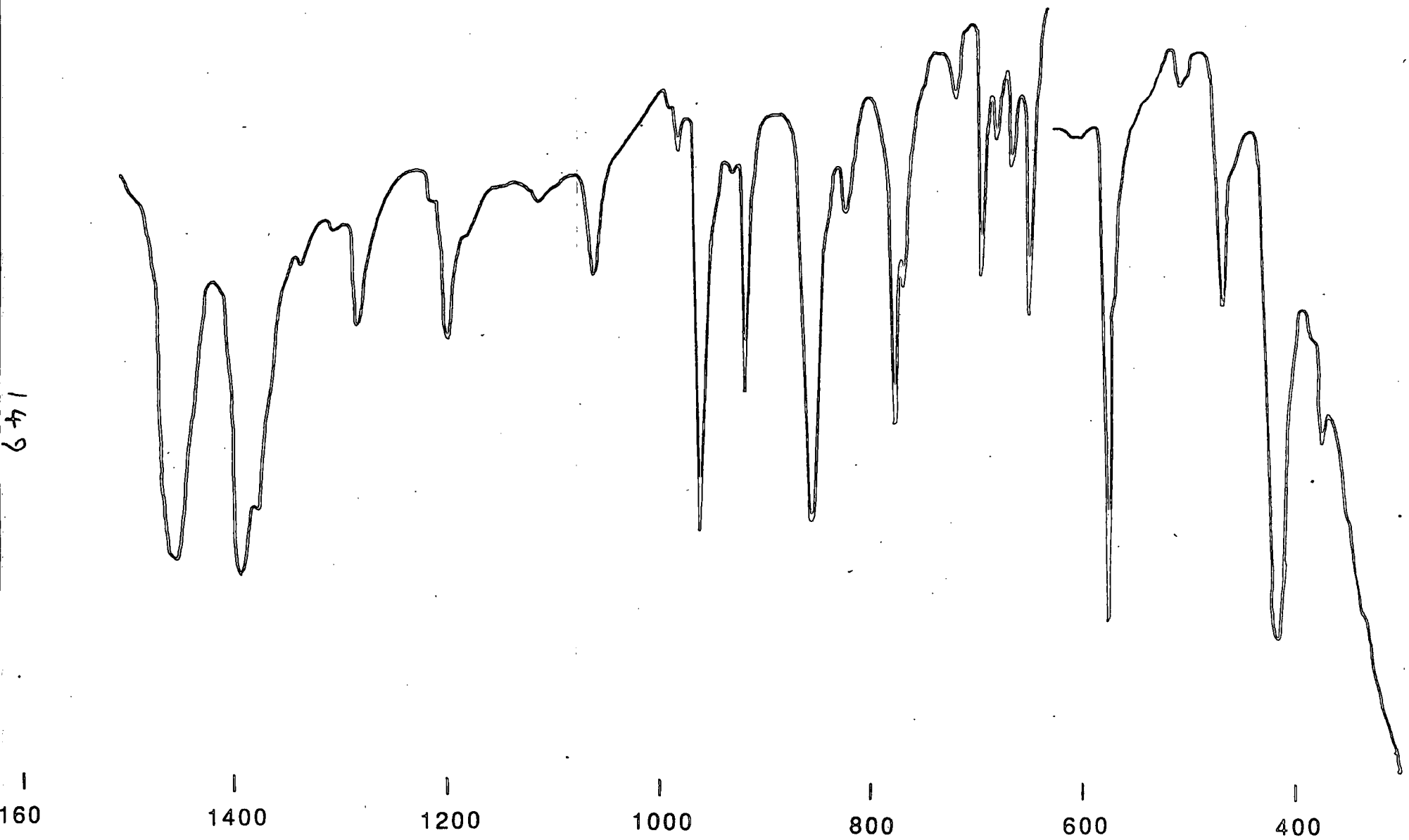


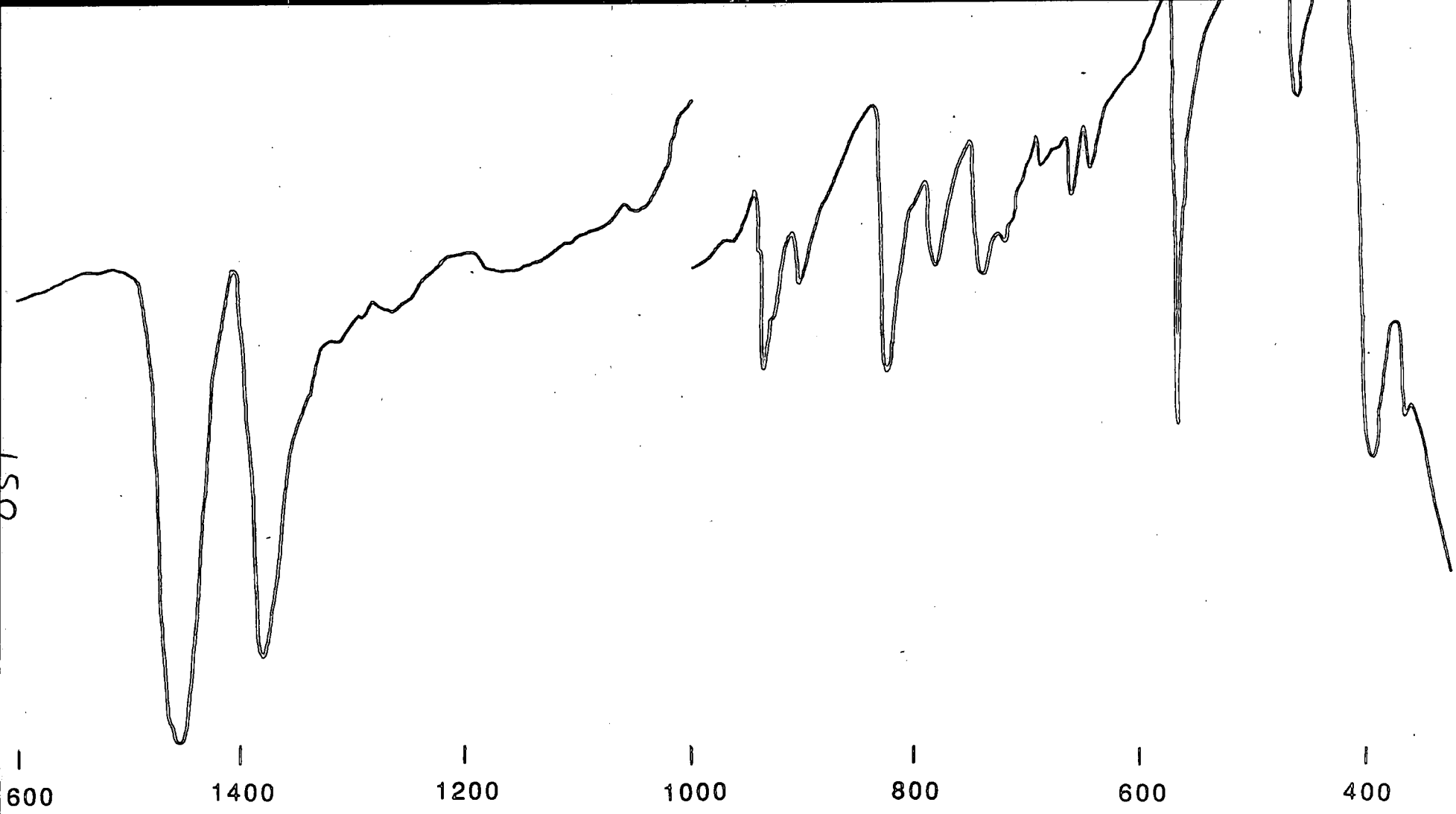
Fig. 5.2.2

IR spectra (Nujol mulls) of some salts of I

a) $I[AsF_6]_3$



b ICl_3



c) II_3

The electron impact mass spectrum (EI+) of the chloride ($\mathbb{1}Cl_3$) is summarized in Table 5.2.1, with a suggested fragmentation pattern in Scheme 5.2.1.

Table 5.2.1

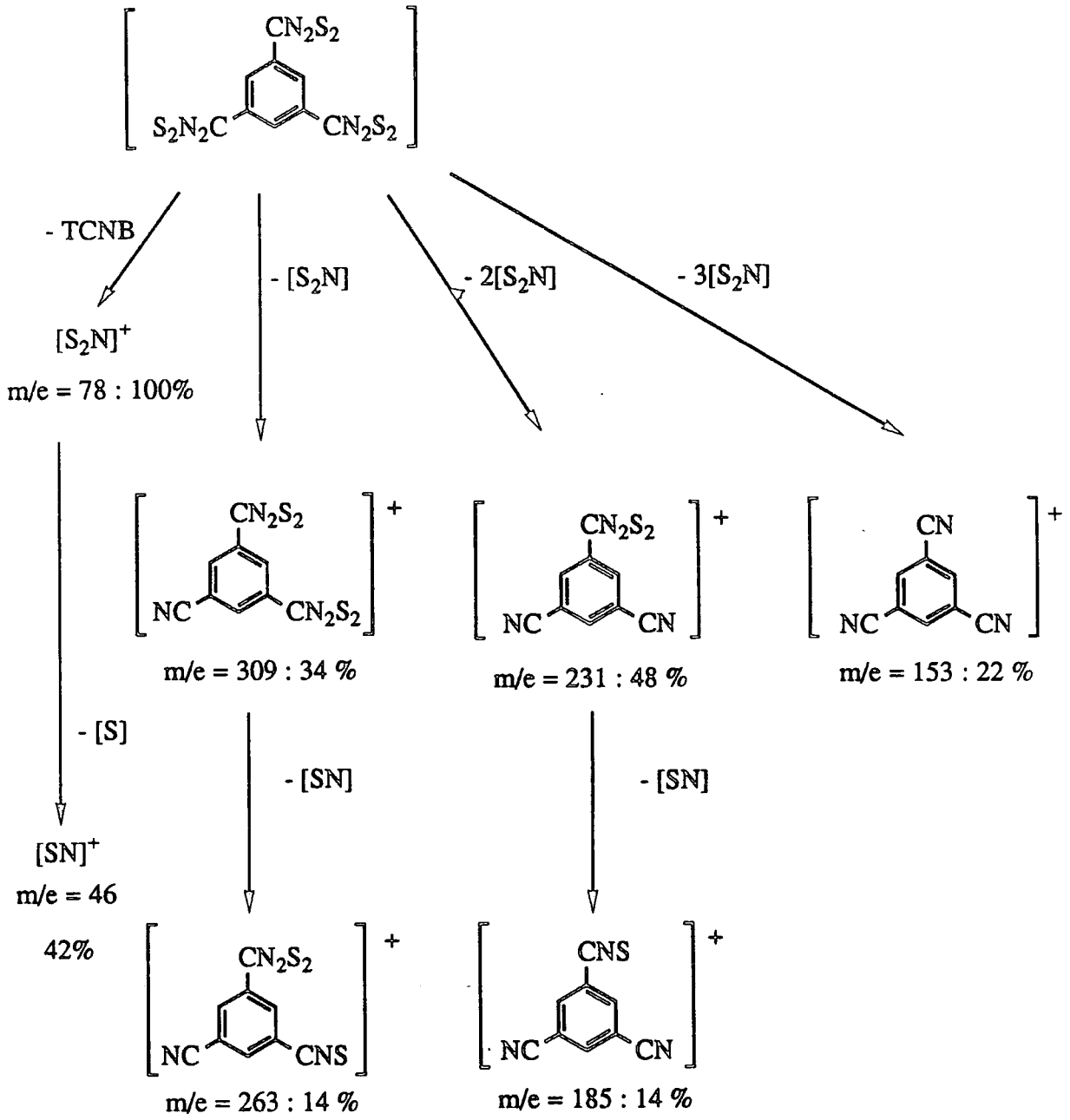
MASS SPECTRUM (EI+) OF $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3][Cl]_3$ ($\mathbb{1}Cl_3$)

m / e	Relative Intensity (%)	Assignment
46	48	$[SN]^+$
64	53	$[S_2]^+$
78	100	$[S_2N]^+$
153	22	$[M - 3S_2N]^+$
185	14	$[M - (2S_2N + SN)]^+$
231	48	$[M - 2S_2N]^+$
263	14	$[M - (S_2N + SN)]^+$
309	34	$[M - S_2N]^+$

(M denotes the species $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]$)

5.2.2 Reduction of $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][Cl]_3$

Reduction of the trication with a molar excess of triphenylantimony in CH_3CN produced a sparingly soluble brown-black powder. As shown in Table 5.2.2, elemental analysis of this material indicated that the triradical $(C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3)^{\cdots}$ was the product of the reaction, produced in 72% yield.



Scheme 5.2.1

Suggested fragmentation pattern in the mass spectrum of $\mathbb{1}Cl_3$

Table 5.2.2

Observed and calculated chemical composition for the product of the reduction of $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][Cl]_3$ ($\mathbb{1}Cl_3$) with excess Ph_3Sb.

	Analysis (% w/w)		
	C	H	N
Observed	27.73	0.82	21.60
Calculated for $(C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3)\cdots$	27.89	0.78	21.69

The material was identified by ESR spectroscopy as a 1,3,2,4-dithiadiazolyl radical. The room temperature ESR spectrum in toluene of this radical generated *in situ* from the chloride is shown in Fig. 5.2.3.

As with other radicals of this type there is a rearrangement to the 1,2,3,5-dithiadiazolyl isomer. Elemental analysis indicated that full reduction to the triradical $(C_6H_3\text{-}1,3,5\text{-}(CN_2S_2))\cdots$ 6 had taken place. Material produced from preparative scale experiments gave a similar ESR spectrum to that from the *in situ* experiments, as shown in Fig. 5.2.4. In this spectrumthe 1:2:3:2:1 pentet typical of the 1,2,3,5-dithiadiazolyl ring is clearly visible although the triplet still dominates.

The compound gave an infrared spectrum as shown in Fig. 5.2.5.

Fig. 5.2.3

ESR spectrum (in toluene) of reduction product of $\mathbb{1}Cl_3$

(generated *in situ*)

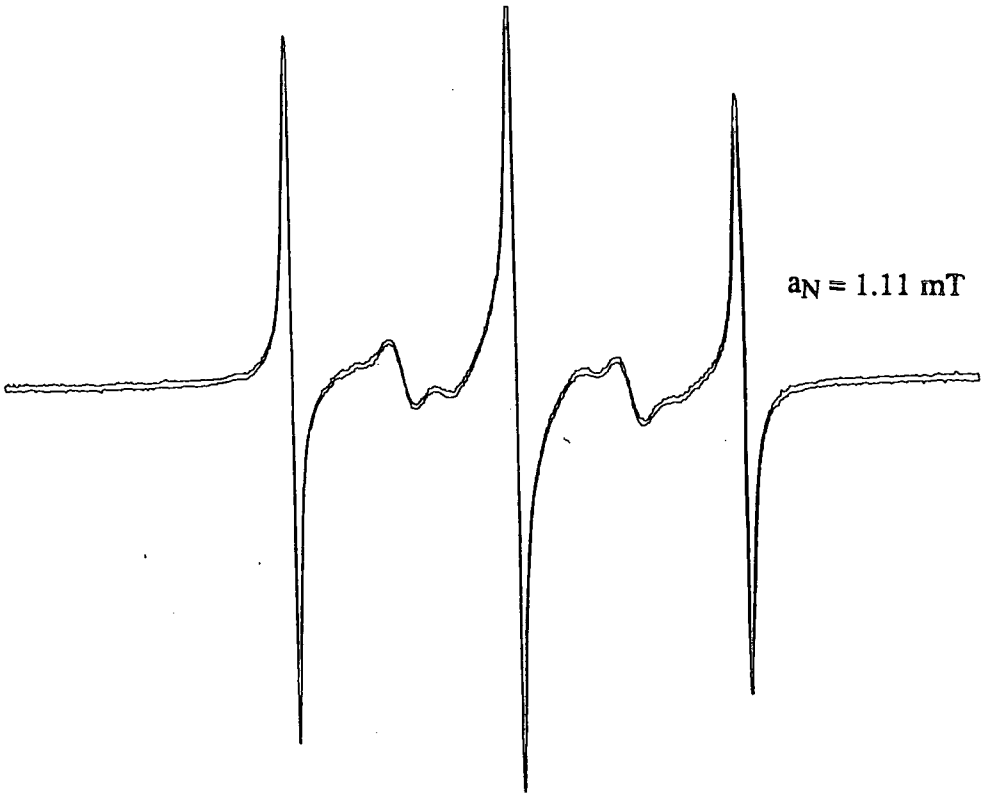
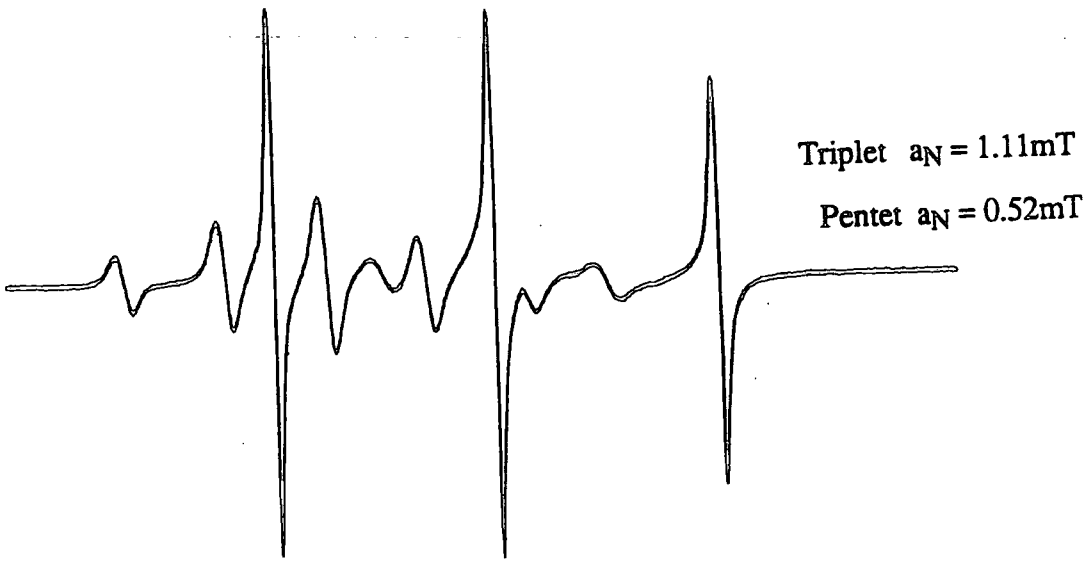


Fig. 5.2.4

ESR spectrum (in toluene) of reduction product of $\mathbb{1}Cl_3$

(preparative experiment)



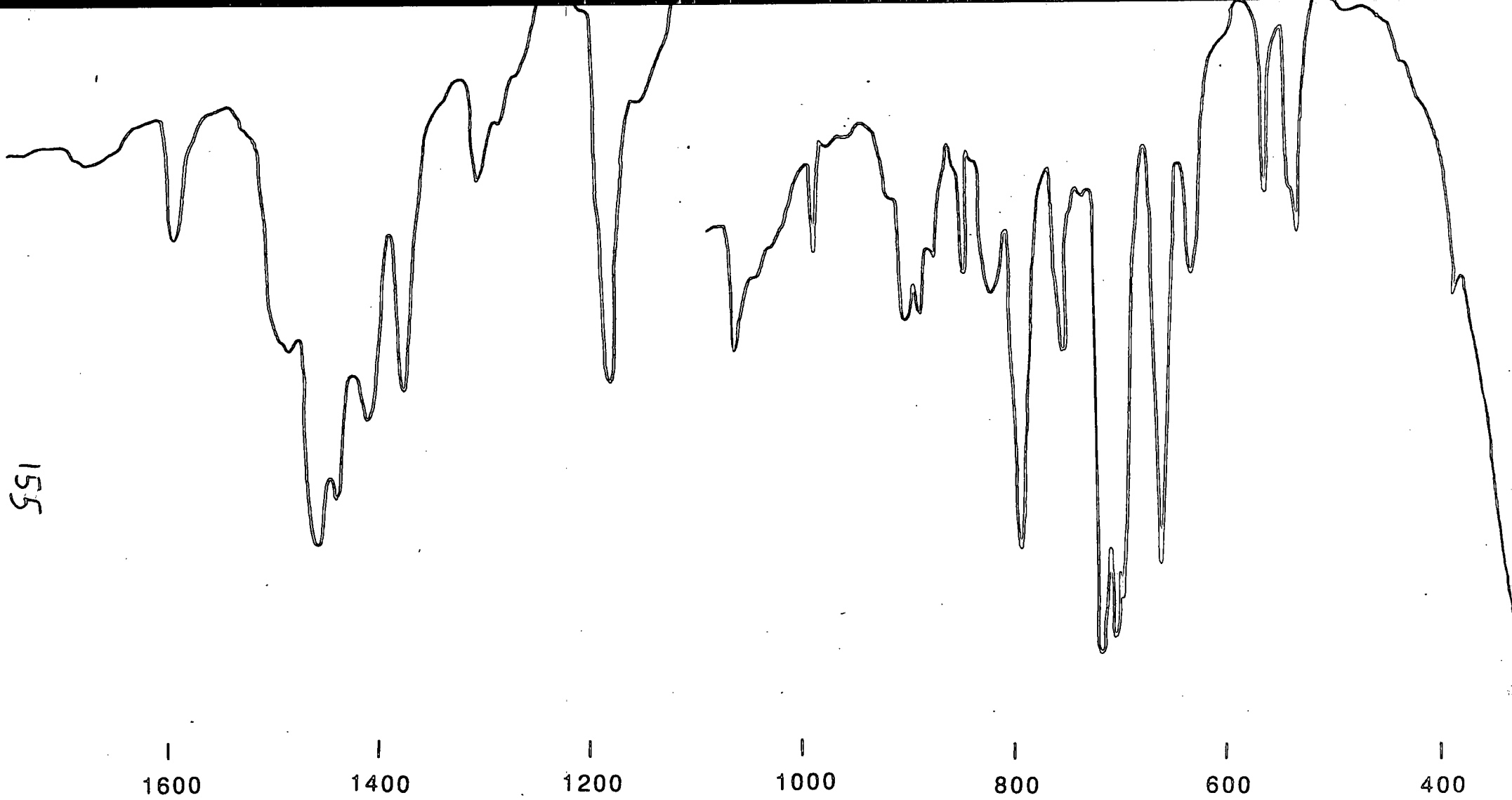


Fig. 5.2.5

IR spectrum (Nujol mull) of reduction product of ICl_3 (preparative experiment)

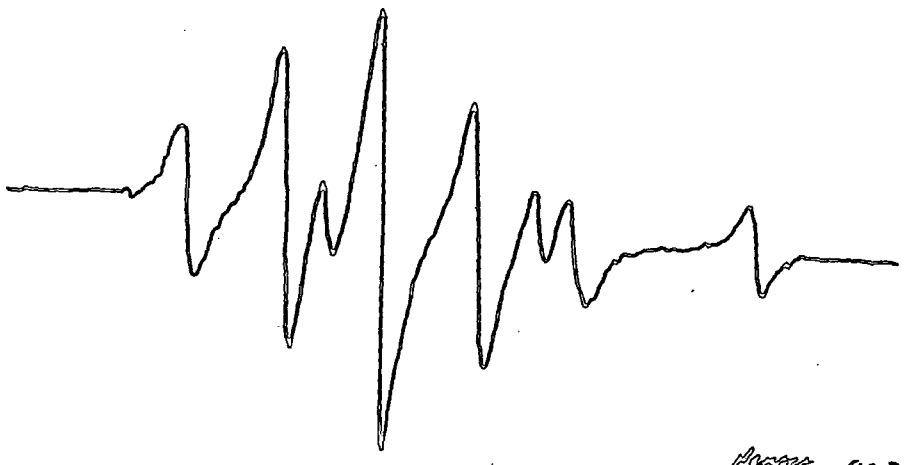
In the course of further study it was found that the reduction of $\mathbb{1}Cl_3$ to **6** with subsequent rearrangement occurred even in the solid state. An ESR tube was packed under nitrogen with a mixture of $\mathbb{1}Cl_3$ and Ph_3Sb, sealed without addition of solvent and taken from Durham to Cambridge for ESR study. When the tube was unpacked it was found that the mixture had changed from yellow-white to black. When toluene was added and the ESR spectrum recorded (t = 2 min), the spectrum shown in Fig. 5.2.6a was obtained. The predominant pattern is a 1:2:3:2:1 pentet, a_N = 0.52 mT, corresponding to the 1,2,3,5-dithiadiazolyl ring. Also clearly visible is the 1:1:1 triplet, a_N = 1.14 mT, corresponding to the 1,3,2,4-dithiadiazolyl ring. As was shown in Fig. 5.2.3, generation of **6** *in situ* gives the 1:1:1 triplet alone. The rearrangement observed in these experiments must have occurred in the solid state during the time between loading the ESR tube with the $\mathbb{1}Cl_3/Ph_3Sb$ mixture and recording the spectra, a period of about three days.

After 48 hours the spectrum was recorded again, and is shown in Fig. 5.2.6b. The spectrum consists almost entirely of the pentet, indicating approx. 100% rearrangement of **6** to Oakley's *tris*-(1,2,3,5-dithiadiazolyl) **5**. A signal corresponding to the 1,3,2,4-dithiadiazolyl ring was only detectable if the signal was amplified 100 times, and this is also shown in Fig. 5.2.6b.

Rearrangement of **6** to **5** in solution is slow due to the very low solubility of **6** in all organic solvents. It is thus likely that rearrangement occurs in a stepwise fashion, 'one ring per molecule at a time' as shown in Scheme 5.2.3, with the formation of head-to-tail dimers **7** leading to mixed dithiadiazolyl species **8** and **9** before full rearrangement to **5**.

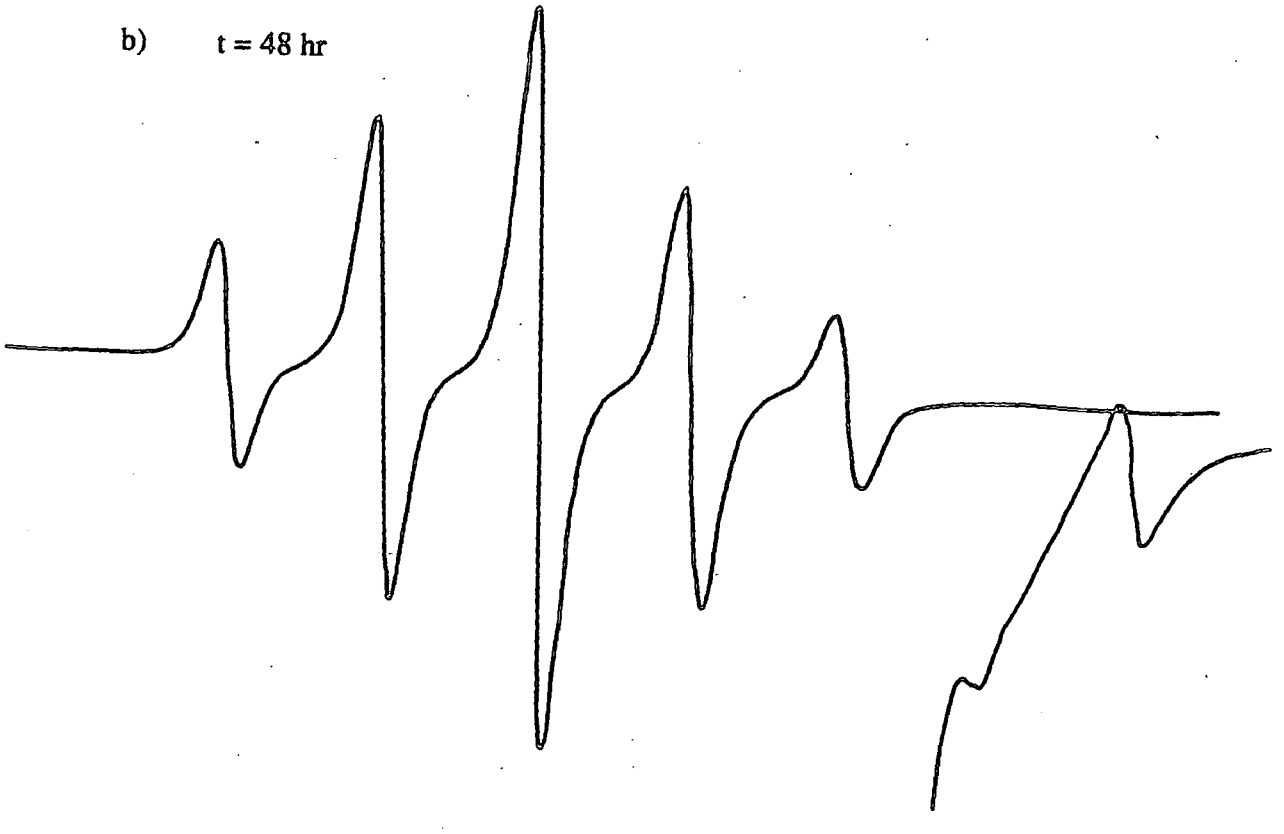
It was found that **6** sublimed slowly at 180°C under high vacuum (10^{-7} mmHg) to give very small crystalline masses, unsuitable for X-Ray analysis. In addition, the traps on the vacuum line contained small amounts of a white solid (probably sulphur), a blue film

a) t = 2min



Nitroxide $g = 2.0104$
Triplet $g = 2.0053$
$a_N^D = 5.25G$
$a_N^T = 11.4G$

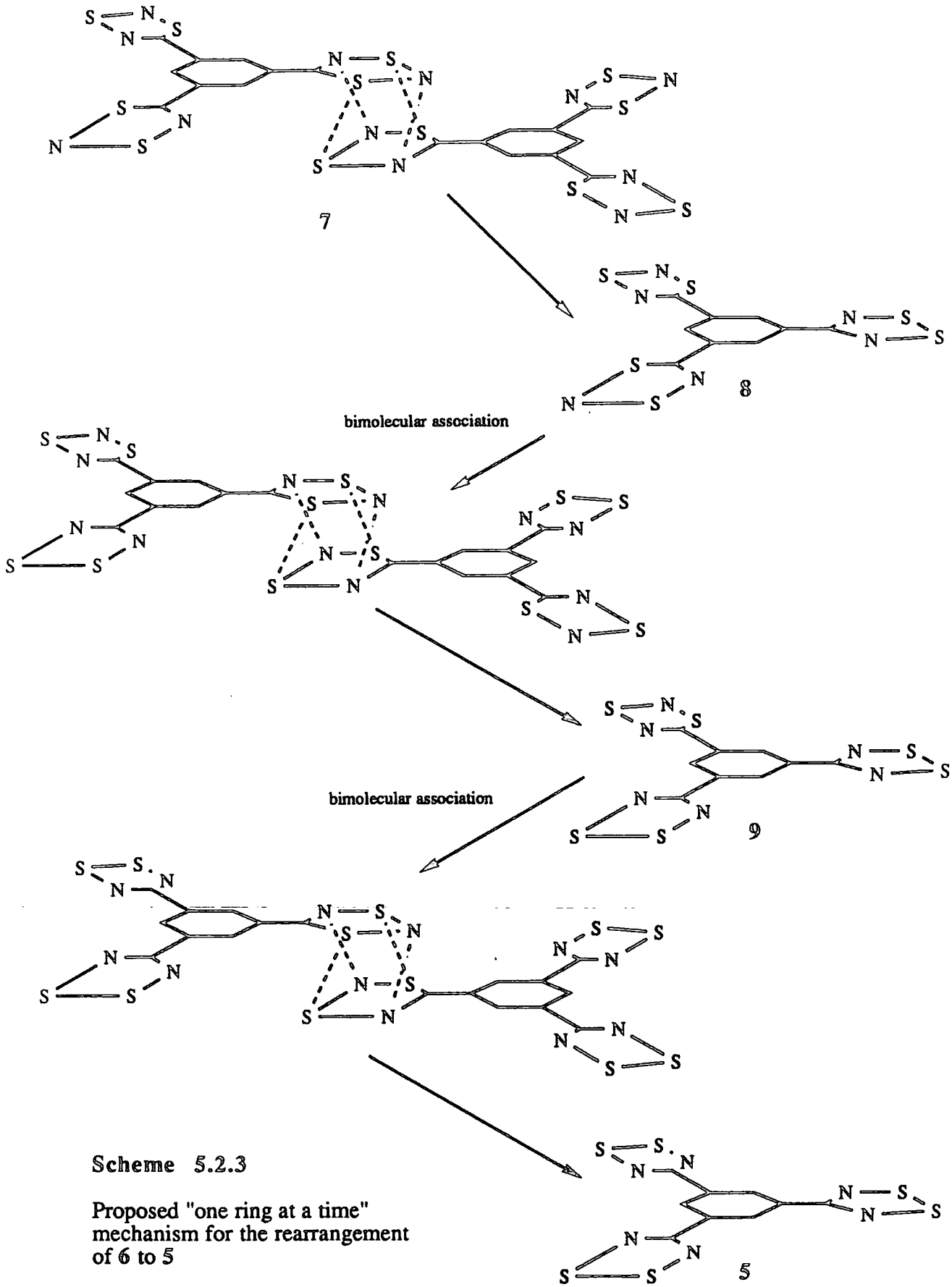
b) t = 48 hr



Remains of triplet x100

Fig. 5.2.6

ESR spectra of **6** (in toluene) with addition of solvent onto a solid mixture of $1Cl_3$ and Ph_3Sb



Scheme 5.2.3

Proposed "one ring at a time" mechanism for the rearrangement of 6 to 5

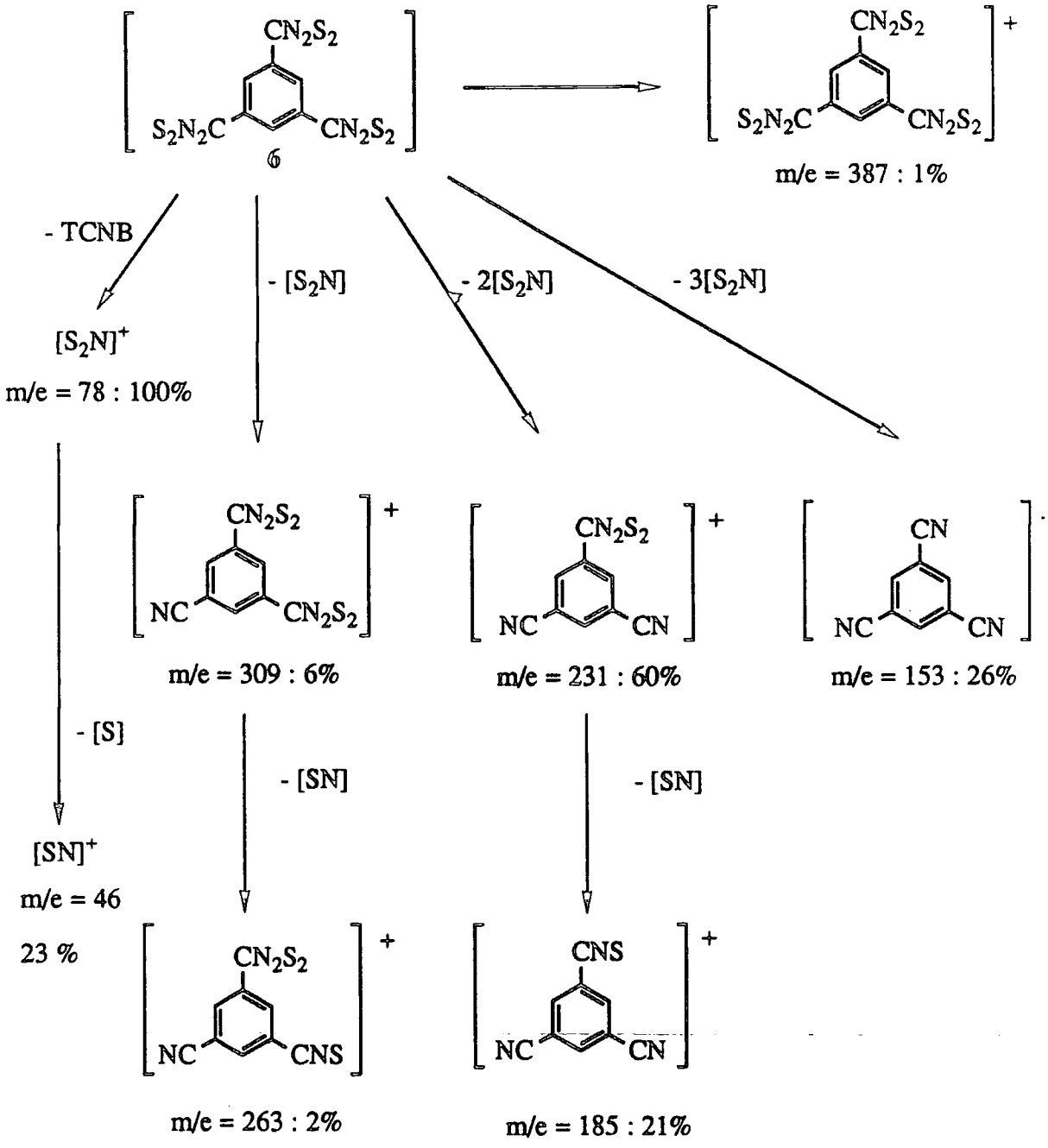
(possibly a small amount of sublimed poly(sulphur nitride) $(SN)_x$ from decomposition of the sublimate / residue at high temperature) and a brown solid of unknown composition). Electron impact mass spectrometry data for the crystalline sublimate are summarized in Table 5.2.3, with a suggested fragmentation pattern shown in Scheme 5.2.4.

Table 5.2.3

THE MASS SPECTRUM (EI^+) OF SUBLIMED [C_6H_3-1,3,5-$(CN_2S_2)_3$] (6)

m / e	Relative Intensity (%)	Assignment
46	23	$[SN]^+$
64	21	$[S_2]^+$
78	100	$[S_2N]^+$
153	26	$[M - 3S_2N]^+$
185	21	$[M - (2S_2N + SN)]^+$
231	60	$[M - 2S_2N]^+$
263	2	$[M - (S_2N + SN)]^+$
309	6	$[M - S_2N]^+$
387	1	M+

DSC of the freshly-precipitated triradical showed that the material was stable up to 290°C, and that above this temperature a large, sharp exotherm occurred, which was not observed when reheating material which had been allowed to cool. As outlined in Chapter 4, these large exotherms have been observed for a number of *bis*-(1,3,2,4-dithiadiazolyl)s, and



Scheme 5.2.4

Suggested fragmentation pattern in the mass spectrum of sublimed **6**

appear to be attributable to the solid-state rearrangement of 1,3,2,4-dithiadiazolyls to 1,2,3,5-dithiadiazolyls, a process which was first observed for *mono*-(1,3,2,4-dithiadiazolyl)s in solution[8]. A DSC trace for the triradical is shown in Fig. 5.2.7.

As for other 1,3,2,4-dithiadiazolyls (from a model study[9] on the *para-bis*-(1,3,2,4-dithiadiazolyl) [C_6H_4-1,4-$(CNSNS)_2$] the occurrence of a large, sharp, irreversible exotherm on heating the triradical may be explained by rearrangement of the 1,3,2,4-dithiadiazolyl ring to the more stable 1,2,3,5-dithiadiazolyl isomer. For the triradical this occurs at a much higher temperature than for the *bis*-(1,3,2,4-dithiadiazolyl)s, which rearrange generally below 150°C. The high rearrangement temperature for the triradical is consistent with a high thermal activation energy to drive the rearrangement process with the subsequent rearrangement of the whole solid-state structure, which in this case involves three radical rings per molecule as opposed to two.

Simple Hückel molecular orbital calculations for the *tris*-(1,3,2,4-dithiadiazolyl) radical 6 (shown in Fig. 5.2.8) indicate that the frontier orbitals where the extra electrons from reduction reside are not a triply degenerate set, but a single orbital at slightly lower energy to a doubly degenerate set. This would mean that the triradical would have a singlet ground state. Further calculations for the fully rearranged triradical 5, shown in Fig. 5.2.9., give the frontier orbitals as a triply degenerate set, and thus a quadruplet ground state would be predicted using Hünd's Rule.

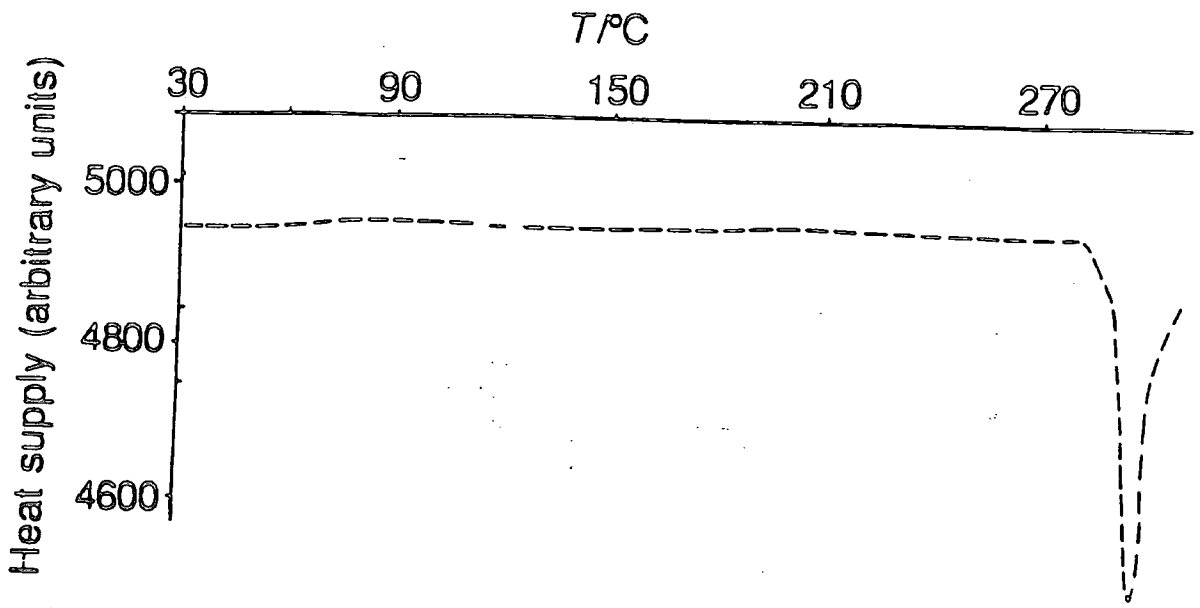
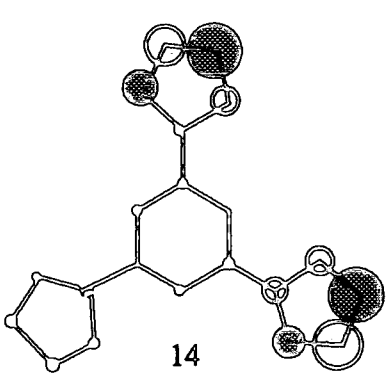


Fig. 5.2.7

DSC trace for 6

Relative Energies (β)



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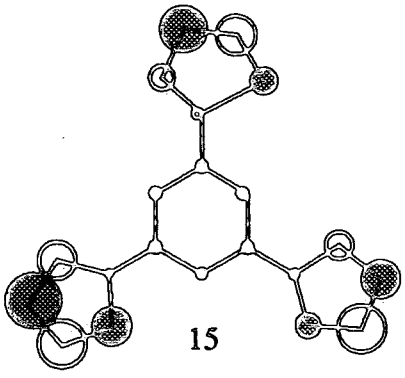
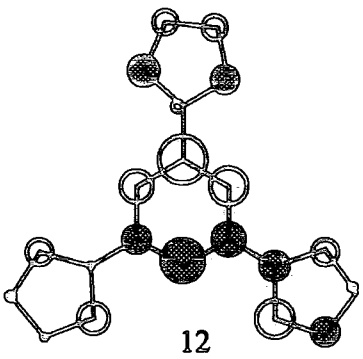


15

L.U.M.O. Trication. H.O.M.O. Triradical

13 14 15



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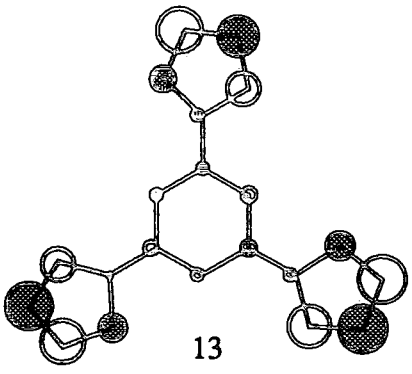

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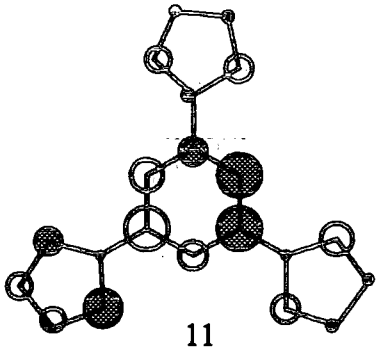
H.O.M.O. Trication

11 12



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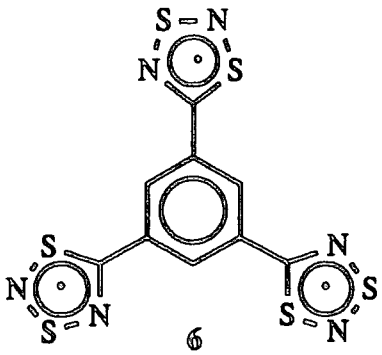
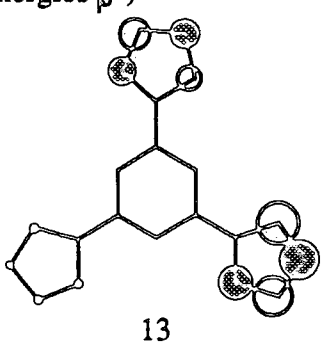


6

Fig. 5.2.8

Simple Hückel frontier orbitals for 6

Relative Energies β)



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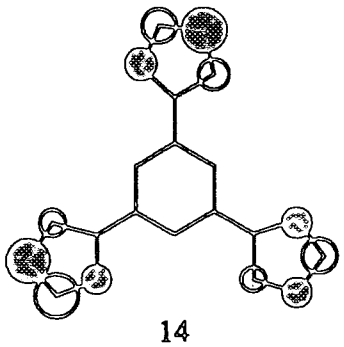

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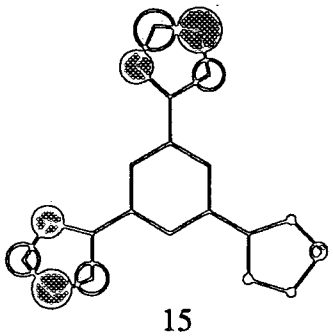

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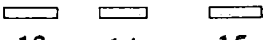
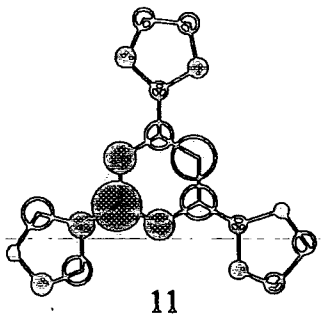


13 14 15 L.U.M.O. Trication, H.O.M.O. Triradical

11 12 H.O.M.O. Trication



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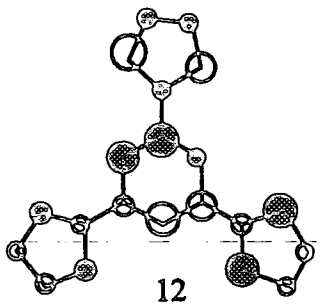

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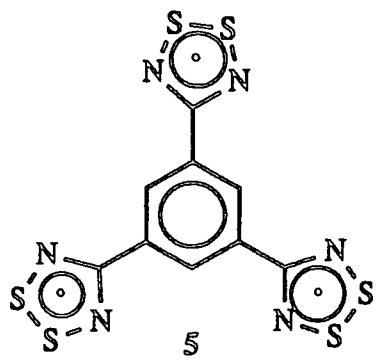


5

Fig. 5.2.9

Simple Hückel frontier orbitals for 5

5.2.3 Reaction of $(C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3)^{\cdots}$ with Bromine

As discussed previously, reduction of the chloride salt of the trication gave a sparingly soluble brown-black powder which gave a typical 1,3,2,4-dithiadiazolyl ESR spectrum in toluene, showing rearrangement over a period of approximately 3 - 5 days to the 1,2,3,5-dithiadiazolyl isomer. As shown in Table 5.2.2, elemental analysis of this material indicated that the triradical $(C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3)^{\cdots}$ **6** was the product of the reaction, and a reoxidation experiment was carried out to verify the composition of the radical.

Reaction of the triradical with elemental bromine produced a brick-red insoluble powder with elemental analysis indicating a ratio of nine bromines per cation, *ie* a *tris*-(tribromide) salt $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3][Br_3]_3$ (**1**$[Br_3]_3$).

This result is analogous to that obtained from the reaction of the *meta*-diradical $(C_6H_4\text{-}1,3\text{-}(CN_2S_2)^{\cdot}$ (described in Chapter 4) where a *bis*-(tribromide) with six bromines per cation was obtained. The stability of these salts is very probably due to the large cations, which stabilise the tribromide anions. *bis*-(Tribromide) salts have been reported, with large metal-containing cations such as the square antiprismatic complex $[(12\text{-Crown-4})_2Mn][Br_3]_2$[10], and the oxometallic species $[L_2M_2O_5][Br_3]_2$ (M = Mo, W ; L = 1,4,7-triazacyclononane)[11,12]. To date no other *tris*-(tribromides) have been reported.

1$[Br_3]_3$ was insoluble in liquid sulphur dioxide and decomposed in acetonitrile, and crystals could not be obtained. It is reasonable to suggest that the tribromide ions will reside between the dithiadiazolium rings of the cation as shown in Fig. 5.2.10

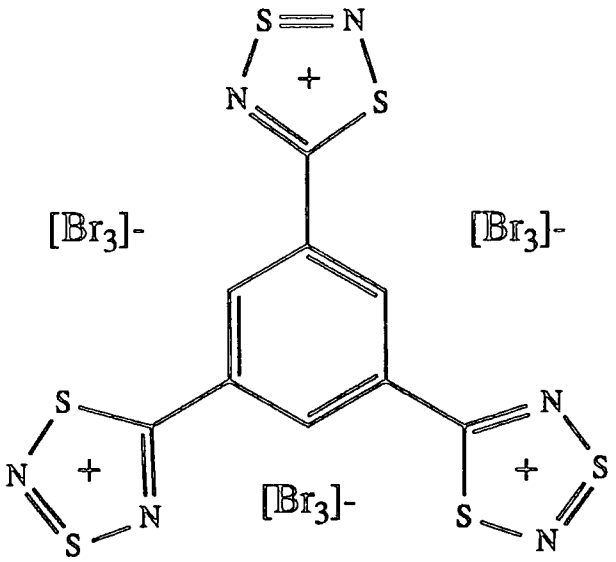


Fig. 5.2.10

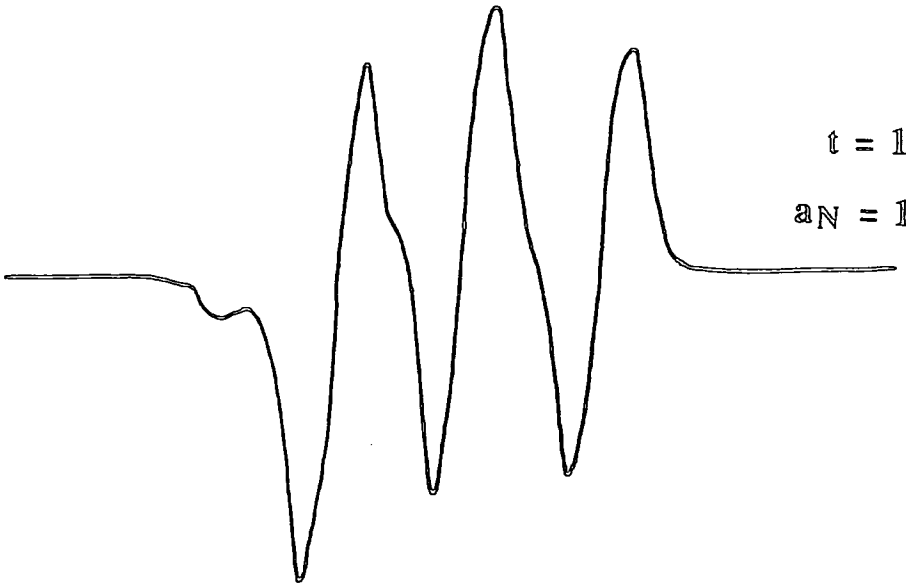
Suggested arrangement of the tribromide anions around the trication in $\mathbb{1}[Br_3]_3$

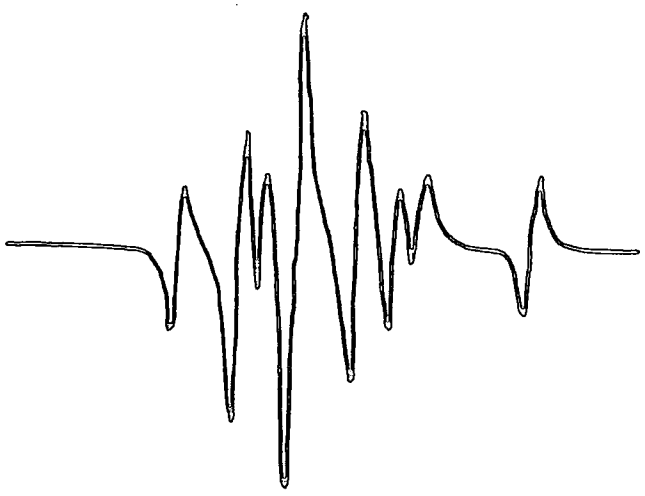
$\mathbb{1}[Br_3]_3$ was found to decompose on heating with the loss of bromine, to give presumably the *tris*-(monobromide) $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3][Br]_3$ as the product. The high bromine content of this material make it a reasonably stable solid source of elemental bromine, and it is likely that other large trications will form similar compounds and find applications as small-scale brominating agents.

5.2.4 Reaction of $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$ with Bu_4NI

It was found that the reaction of the trication hexafluoroarsenate with tetrabutlyammonium iodide in an ESR tube produced a signal typical of dithiadiazolyl radicals. The spectra are shown in Fig. 5.2.11.

As in the case of reduction of dithiadiazolium salts the spectrum appeared as a 1:1:1 triplet, aN = 1.09 mT which over time collapsed with the simultaneous emergence of a 1:2:3:2:1





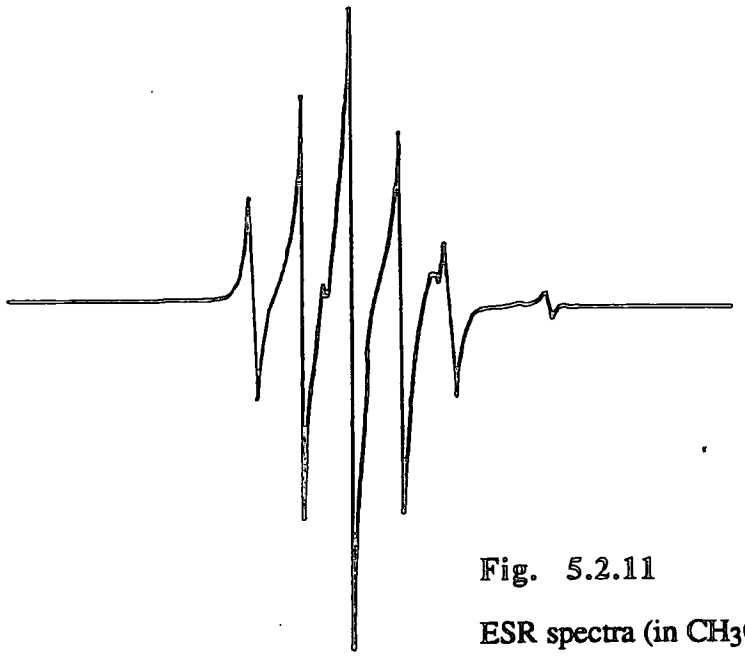


Fig. 5.2.11

ESR spectra (in CH_3CN) of the product of the reaction $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3 + 3Bu_4NI$

pentet, aN = 0.52 mT. The same reaction on the preparative scale gave the product with elemental analysis confirming an empirical formula of three iodines per cation.

The ESR activity observed in this system may be explained by an equilibrium or equilibria being set up between the diamagnetic *tris*-(*mono*-iodide) $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]^{3+}[I^-]_3$ ($\mathbb{1}I_3$) and a *diradical-monocation triiodide* salt $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]^{+\cdot}[I_3^-]$ by a process of anion-cation electron transfer : two iodide anions reduce one dithiadiazolium ring each and become I_2, which then associates with the remaining iodide anion to become $[I_3]^-$.

There is evidence for this from DSC studies of this compound, where a sharp exotherm typical of dithiadiazolyl multiradicals is seen at around 125°C, as shown in Fig.5.2.12. This exotherm is associated with the solid state rearrangement to 1,2,3,5-dithiadiazolyls[9], and was seen in Chapter 4 for the *meta*-diradical $(C_6H_4\text{-}1,3\text{-}(CNSNS)_2)^{\cdot\cdot}$ and the iodide salt $[C_6H_4\text{-}1,4\text{-}(CNSNS)_2]I_2$. In Chapter 4 a possible mechanism of this rearrangement was discussed.

Further evidence is provided by comparison of the mass spectra of the chloride and iodide. Table 5.2.4 shows the electron impact (EI+) mass spectrum of the iodide, with a fragmentation pattern shown in Scheme 5.2.5. The spectrum of the chloride ($\mathbb{1}Cl_3$) is shown in Table 5.2.1.

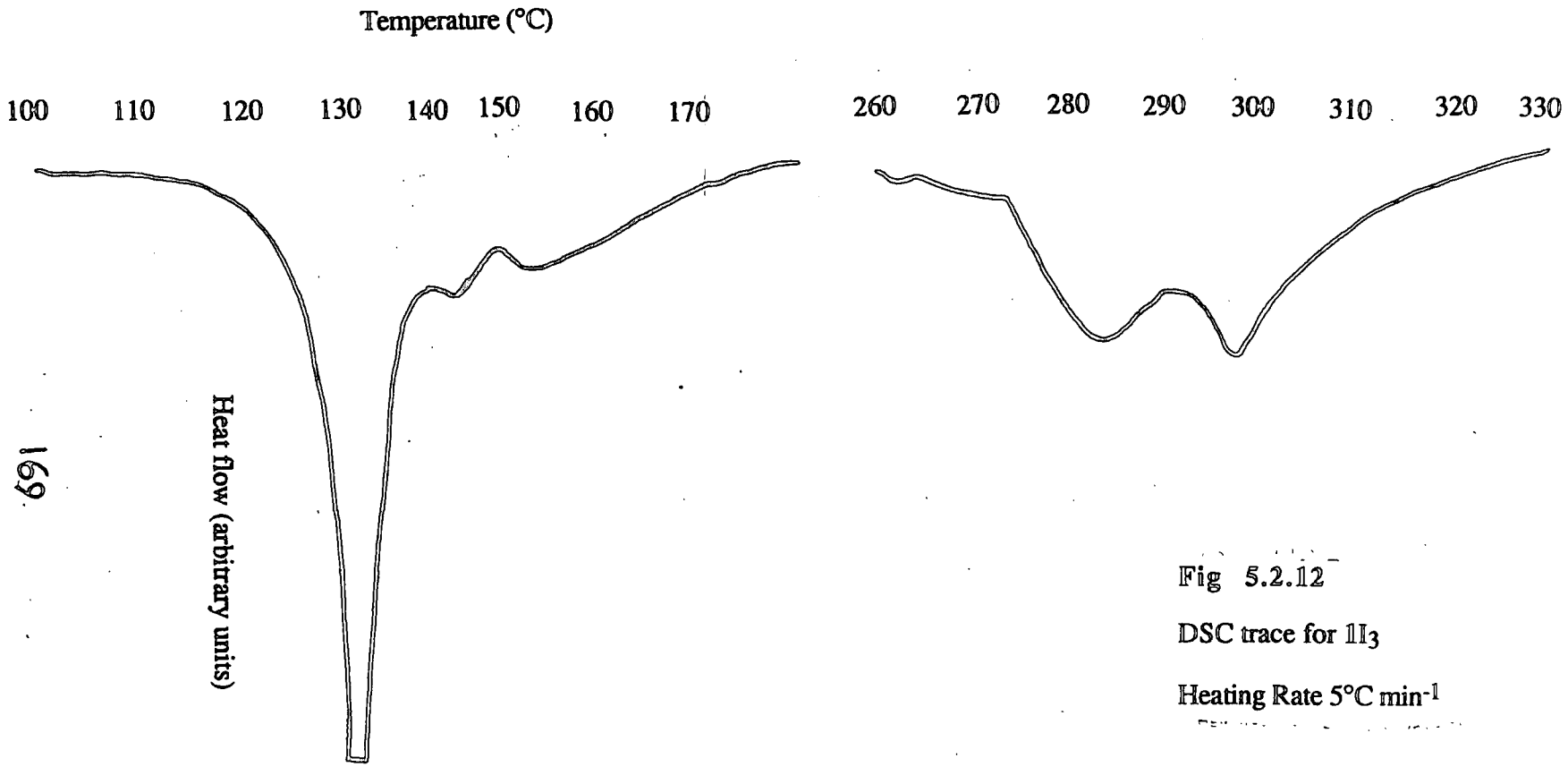


Fig 5.2.12

DSC trace for $1I_3$

Heating Rate 5°C min^{-1}

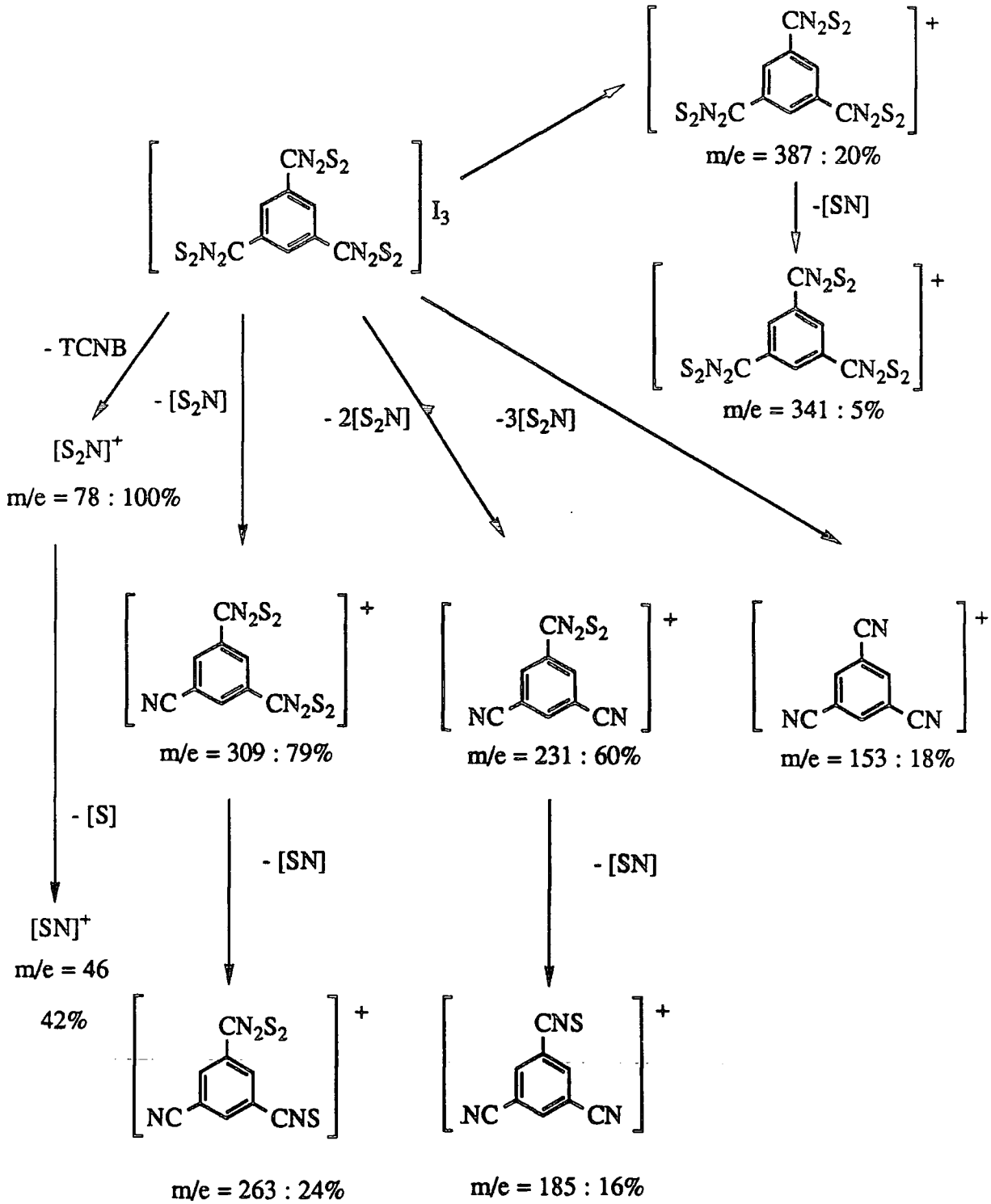
Table 5.2.4

THE MASS SPECTRUM (EI+) OF $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]\ I_3$

m / e	Relative Intensity (%)	Assignment
46	42	$[SN]^+$
64	38	$[S_2]^+$
78	100	$[S_2N]^+$
153	18	$[M - 3S_2N]^+$
185	16	$[M - (2S_2N + SN)]^+$
231	60	$[M - 2S_2N]^+$
263	24	$[M - (S_2N + SN)]^+$
309	79	$[M - S_2N]^+$
341	5	$[M - SN]^+$
387	20	M+

(M denotes the species $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]$)

As can be seen, the iodide gives a peak at m/e = 387, relative abundance 20%, assignable to the species $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]^+$ whereas the chloride ($1Cl_3$) gives no peak at this mass, the highest peak being at 309, consistent with the loss of $[S_2N]^+$ from the cation (see Table 5.2.1. The appearance of a reasonably strong peak with the same mass as the trication in the mass spectrum of the iodide salt thus suggests that the compound does not consist of a trication and three anions, but rather a diradical monocation with a triiodide counterion. Given that reaction of the triradical $(C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3)\cdots$ with bromine as



Scheme 5.2.5

Suggested fragmentation pattern in the mass spectrum of $\mathbf{1}I_3$

described in 5.2.3 produces a stable compound containing three tribromide anions per cation, it is reasonble to suggest that a compound containing one triiodide anion per cation would be stable also.

The iodide salt of the trication $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]^{3+}$ ($1I_3$) was obtained as a black microcrystalline precipitate from acetonitrile, and attempts to grow single crystals suitable for X-Ray analysis were unsuccessful. The interesting ESR, mass spectral and DSC properties observed for this material suggest that the solid-state structure will be a fascinating subject for further study. The slow disproportionation to radical and iodine imply that the structure of the compound in the solid state is far from static, but rather is in a constant state of flux with charge transfer from iodide ion to 1,3,2,4-dithiadiazolium cation to give 1,3,2,4-dithiadiazolyl species which subsequently undergo rearrangement to the more stable 1,2,3,5-dithiadiazolyl form, with an associated rearrangement of solid state structure, as has been observed for the two isomers of the *para-bis*-(dithiadiazolyl) (C_6H_4-1,4-$(CN_2S_2)_2$)[9].

5.2.5 Conclusions and Suggestions for Further Work

It is clear from this work that the chemistry of the 1,3,2,4-dithiadiazolium salts and their related radicals is full of surprises. from the same trication a stable triradical, ESR-active iodide and tris-(tribromide) have been prepared and isolated. It is also apparent that these compounds are anything but static products. The triradical and the iodide undergo rearrangement to 1,2,3,5-dithiadiazolyl species, with the iodide undergoing this rearrangement at a much lower temperature than the triradical.

It is clearly of importance to understand the structural nature of such interesting compounds.

5.3 Experimental

Preparation of $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$

1,3,5-Tricyanobenzene (153 mg, 1.0 mmol) and $[SNS][AsF_6]$ (801 mg, 3.0 mmol) were placed in separate legs of a "dog". Sulphur dioxide was introduced sufficient to fully dissolve both reagents. After mixing, the solution was stirred at room temperature for 5 days, during which time the product formed as a colourless crystalline precipitate. Following removal of solvent the product was washed clean of coloured impurities with a small amount of SO_2, and then by exhaustive washing with CH_2Cl_2. The product was dried *in vacuo*.

Appearance : Colourless microcrystalline solid

Yield : 668 mg, 0.70 mmol, 70%

IR (Nujol mull) : ν_{max} 3040w, 1608m, 1397s, 1330w, 1280w, 1200m, 1150w, 1080sh, 1065m, 945m, 910sh, 895m, 800s, 720vs br, 610w, 582m, 572sh, 440ms, 390vs cm^{-1}

Analysis : Found (required) C : 11.20 (11.32), H : 0.34 (0.31), N : 8.62 (8.80), As : %

^1H NMR (CD_3CN) : δ 9.46 ppm (s)

^{13}C NMR (CD_3CN) : δ 128.8 ppm, δ 137.8 ppm (Aryl C), δ 200.3 ppm (CNSNS)

Solubility : CH_3CN - very soluble. SO_2 - sparingly soluble. CH_2Cl_2 - insoluble

Preparation of $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][Cl]_3$

$[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$ (318 mg, 0.33 mmol) and Bu_4NCl (278 mg, 1.0 mmol) were placed in the rear leg of a "dog". CH_3CN (5 ml) was syringed against a nitrogen flow into the front leg and degassed by a single freeze-thaw cycle. Upon distillation of the solvent onto the reaction mixture a bright yellow precipitate formed immediately. After stirring for 1 hr the colourless supernatant (containing Bu_4NAsF_6) was filtered off and the product washed repeatedly with back-distilled solvent, followed by drying *in vacuo*.

Appearance : Bright yellow powder

Yield : 123 mg, 0.25 mmol, 75 %

IR : (Nujol mull) : ν_{max} 1395s, 1340w, 1310w br, 1278w, 1217sh, 1200w, 1182sh, 1117w br, 1065w, 990sh, 985w, 963s, 932w, 920m, 855s, 823w, 775s, 770m, 697m, 680w, 668w, 652m, 580s, 510w br, 475m, 413s, 375w cm^{-1}

Analysis : Found (required) C : 21.55 (21.87), H : 0.69 (0.61), N : 16.86 (17.01) %

Solubility : CH_3CN, CH_2Cl_2, hexane, toluene, SO_2 - insoluble

Mass Spectrum (EI+) : *m/e*, Relative Intensity, Assignment ;

309, 34%, $[M - S_2N]^+$; *263*, 14%, $[M - (S_2N + SN)]^+$; *231*, 48%, $[M - 2S_2N]^+$; *185*, 14%, $[M - (2S_2N + SN)]^+$; *153*, 22%, $[M - 3S_2N]^+$; *78*, 100% , $[S_2N]^+$; *64*, 52%, $[S_2]^+$; *46*, 47%, $[SN]^+$.

(M denotes the species C_6H_3-1,3,5-$(CN_2S_2)_3$)

Preparation of $[C_6H_3$-*1,3,5-(CNSNS)*$_3][I]_3$

$[C_6H_3$-1,3,5-$(CNSNS)_3][AsF_6]_3$ (318 mg, 0.33 mmol) and Bu4NI (369 mg, 1.0 mmol) were placed in the rear leg of a "dog". CH_3CN (5 ml) was introduced into the front leg and degassed. Upon introduction of solvent onto the reaction mixture a black precipitate formed immediately. The mixture was stirred for 24 hr to ensure complete reaction, after which time the supernatant was filtered off. Crude product was then transferred to a closed extractor and washed for a further 24 hr with cycling CH_2Cl_2. The purified product was dried *in vacuo*.

Appearance : Black microcrystalline solid

Yield : 200 mg, 0.26 mmol, 79 %

IR (Nujol mull) : ν_{max} 1390sh, 933w, 925sh, 905w, 825m, 785w, 740w, 660w, 640w, 567s, 510w, 460w, 395s, 365w cm^{-1}

Analysis : Found (required) C : 13.87 (14.07), H : 0.40 (0.39), N : 10.88 (10.94) %

Solubility : CH_3CN - sparingly soluble. CH_2Cl_2, SO_2 - insoluble

Mass Spectrum (EI+) : *m/e*, Relative Intensity, Assignment ;

387, 20%, M^+ ; *341*, 5%, $[M - SN]^+$; *309*, 79%, $[M - S_2N]^+$; *263*, 24%, $[M - (S_2N + SN)]^+$; *231*, 60%, $[M - 2S_2N]^+$; *185*, 16%, $[M - (2S_2N + SN)]^+$; *153*, 18%, $[M - 3S_2N]^+$; *78*, 100%, $[S_2N]^+$; *64*, 38%, $[S_2]^+$; *46*, 42%, $[SN]^+$.

(M denotes the species C_6H_3-1,3,5-$(CN_2S_2)_3$)

DSC : Sharp exotherm onset at 125°C

Preparation of $[C_6H_3$-1,3,5-$(CNSNS)_3][I]_3$: ESR tube Reaction

$[C_6H_3$-1,3,5-$(CNSNS)_3][AsF_6]_3$ (8 mg, 8.4 μmol) and Bu_4NI (11mg, 30 μmol) were ground together to produce an intimate mixture, and a small amount of this mixture was placed in a flame-dried quartz ESR tube. CH_3CN was syringed in and an immediate black colouration was produced. ESR spectra were taken at room temperature after 15 minutes, 16 hrs and 14 days.

t = 15 mins : broad 1:1:1 triplet, g = approx. 2.005, aN = 1.09 - 1.10 mT.

t = 16 hrs : 1:1:1 triplet, g = approx. 2.005, aN = 1.10 mT ;

1:2:3:2:1 pentet, g = approx. 2.01, aN = 0.52 mT.

t = 14 days : main signal 1:2:3:2:1 pentet, g = approx. 2.01, aN = 0.52 mT ;

very small 1:1:1 triplet, g = approx. 2.005, aN = 1.10 mT.

Reduction of $[C_6H_3$-1,3,5-$(CNSNS)_3][Cl]_3$

$[C_6H_3$-1,3,5-$(CNSNS)_3][Cl]_3$ (200mg, 0.4 mmol) and Ph_3Sb (282mg, 0.8mmol, excess) were placed together in the rear leg of a "dog". CH_3CN (5ml) was introduced into the other leg and degassed . It was noticed that even in the absence of solvent the reaction mixture began to turn black indicating reaction. Upon introduction of solvent onto the reagent mixture a rapid darkening occurred, and a brown-black precipitate formed. The mixture was sonicated for 30 sec. and then stirred for a further 5 min. to ensure complete reaction,

after which time the supernatant was removed by filtration and the product washed repeatedly with back-distilled solvent. The product was dried *in vacuo*.

Appearance : Brown-black powder

Yield : 111mg, 0.29mmol, 72%

IR (Nujol mull) : ν_{max} 3160sh, 3030sh, 1680w br, 1595w, 1490m, 1440s, 1415m, 1310w, 1290w, 1185m, 1068w, 1050sh, 1035sh, 1035sh, 992w, 920sh, 915w, 905sh, 892w, 880w, 853w, 835sh, 830w, 795s, 760w, 740w, 720s, 705s, 695s, 663s, 638w, 570w, 545sh, 540m, 390w cm^{-1}.

Analysis : Found (required) C : 27.73 (27.89), H : 0.82 (0.78), N : 21.60 (21.69) %

ESR Spectrum (Toluene, RT) : 1:1:1 triplet, a_N = 1.11 mT ; smaller, broad lines at $a_N/2$. 1:2:3:2:1 pentet, a_N = 0.52 mT

Reaction of $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]$ *with* Br_2 *; Preparation of* $[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3][Br_3]_3$.

$[C_6H_3\text{-}1,3,5\text{-}(CN_2S_2)_3]$ (50 mg, 0.13 mmol) was placed in the rear leg of a "dog". Sulphur dioxide was introduced and the mixture sonicated briefly to produce a fine suspension. A solution of excess bromine in SO_2 was introduced into the front leg and distilled onto the reagent suspension. A brick - red precipitate formed immediately. The mixture was sonicated for 5 minutes to ensure complete reaction, and the supernatant was filtered off. The Br_2 / SO_2 mixture was removed and replaced by fresh SO_2, with which the product was repeatedly washed before drying *in vacuo*.

Appearance : Brick - red powder

Yield : 126 mg, 0.11 mmol, 88 %

Analysis : Found (required) C : 9.87 (9.77), H : 0.33 (0.27), N : 7.32 (7.60), Br : 64.72 (64.98) %.

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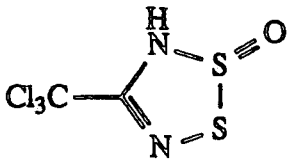
CHAPTER 6

REACTIONS OF 1,3,2,4-DITHIADIAZOLIUM SALTS WITH SOME OXYGEN NUCLEOPHILES

6.1 Introduction

The family of dithiadiazolium salts are, like many other compounds of sulphur and nitrogen, readily decomposed by water, and so inert atmosphere / dry box methods are essential to the study of this class of compounds. Surprisingly, the actual chemistry of the hydrolysis reaction has received very little attention. Previous work in this laboratory[1] on 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride which had been exposed to the atmosphere for a short time quoted Mass Spectral evidence for a product of formula $Cl_3CN(H)S(O)SN$ 1. This suggested structure bears a resemblance[2] to the hydrolysis product 3 of the so-called Hertz compound (1,2,3-benzodithiazolium chloride) 2.



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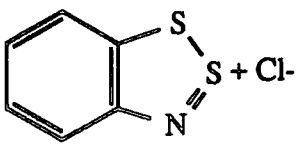

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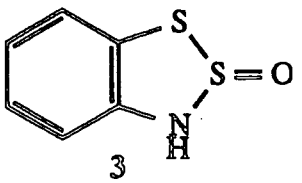


3

From the earliest days of [SNS]+ chemistry, it was noted[3] that atmospheric moisture degraded [SNS]+ salts, with appearance of N-H stretching vibrations in the IR spectra of partially hydrolysed material. A more detailed study of the hydrolysis was not undertaken, which is not surprising considering the precious nature of the [SNS]+ salts : why go to the trouble of

deliberately destroying the valuable product of a potentially hazardous synthesis when the products of its wonderful addition reaction were simply waiting to be prepared?

The hydrolysis of dithiadiazolium salts has a similar history : unloved, unstudied, the reaction took on the mantle of an unwelcome nuisance, rather than a potential source of interesting chemistry, a reaction truly fundamental to this class of compounds. It has been seen as merely the source of endless frustration to the research student, its occurrence simply a sign that it was time to regenerate the drying elements in the glovebox. This neglect of the hydrolysis of sulphur-nitrogen compounds can be seen to stem principally from its rather unattractive nature, accompanied by the precipitation of sticky white elemental sulphur.

With such a bad name, the author felt that there must be something of interest in the reaction, and considering the willingness with which water attacks dithiadiazolium salts, it was decided to take a step into the darker recesses of dithiadiazolium salt chemistry.

Dithiadiazolium salts are also highly reactive toward a variety of nucleophiles such as amines, alcohols, organolithium compounds[4], and as discovered during the course of this work, dithiadiazolium salts will initiate the polymerization of tetrahydrofuran to give high molecular weight poly(THF). The reaction of [PhCNSNS][AsF_6] with water and 2-methyl-2-propanol (t-butanol) were studied, and in the latter case, ^1H NMR of the reaction revealed a complex and highly dynamic mixture of products which changed over a period of time. In this chapter the reactions are described, and some tentative conclusions are drawn concerning reaction mechanisms and reaction products.

6.2 Results and Discussion

6.2.1 Reaction of [PhCNSNS][AsF_6] with Water

The reaction of 5-phenyl-1,3,2,4-dithiadiazolium hexafluoroarsenate with one equivalent of water (1:1 reaction) in acetonitrile was studied by infrared and nuclear magnetic resonance spectroscopies. Elemental sulphur was precipitated, and the soluble fraction was found to consist of a 1:1 mixture of unreacted [PhCNSNS][AsF_6] and a second product. The infrared spectrum of the soluble fraction following removal of solvent is shown in Fig. 6.2.1a.

Reaction of [PhCNSNS][AsF_6] with two equivalents of water (1:2 reaction) also gave elemental sulphur and a colourless soluble fraction, the infrared spectrum of which is shown in Fig. 6.2.1b.

The spectrum of unreacted [PhCNSNS][AsF_6] is shown in Fig. 6.2.1c, and it may be seen that the spectrum of the soluble fraction from the 1:1 reaction (Fig. 6.2.1a) is produced by the addition of the spectrum of the 1:2 product (Fig. 6.2.1b) and that of unreacted [PhCNSNS][AsF_6] (Fig. 6.2.1c). Thus, infrared data indicate that the 1:1 reaction gives a mixture of unreacted [PhCNSNS][AsF_6] and an hydrolysis product, and that the hydrolysis product is formed by the reaction of one equivalent of [PhCNSNS][AsF_6] with two equivalents of water.

The spectrum of the 1:2 hydrolysis product features three strong bands between 3000 and 3500 cm-1 with no other bands at higher wavenumber. These bands are therefore assignable to NH stretching vibrations rather than OH .

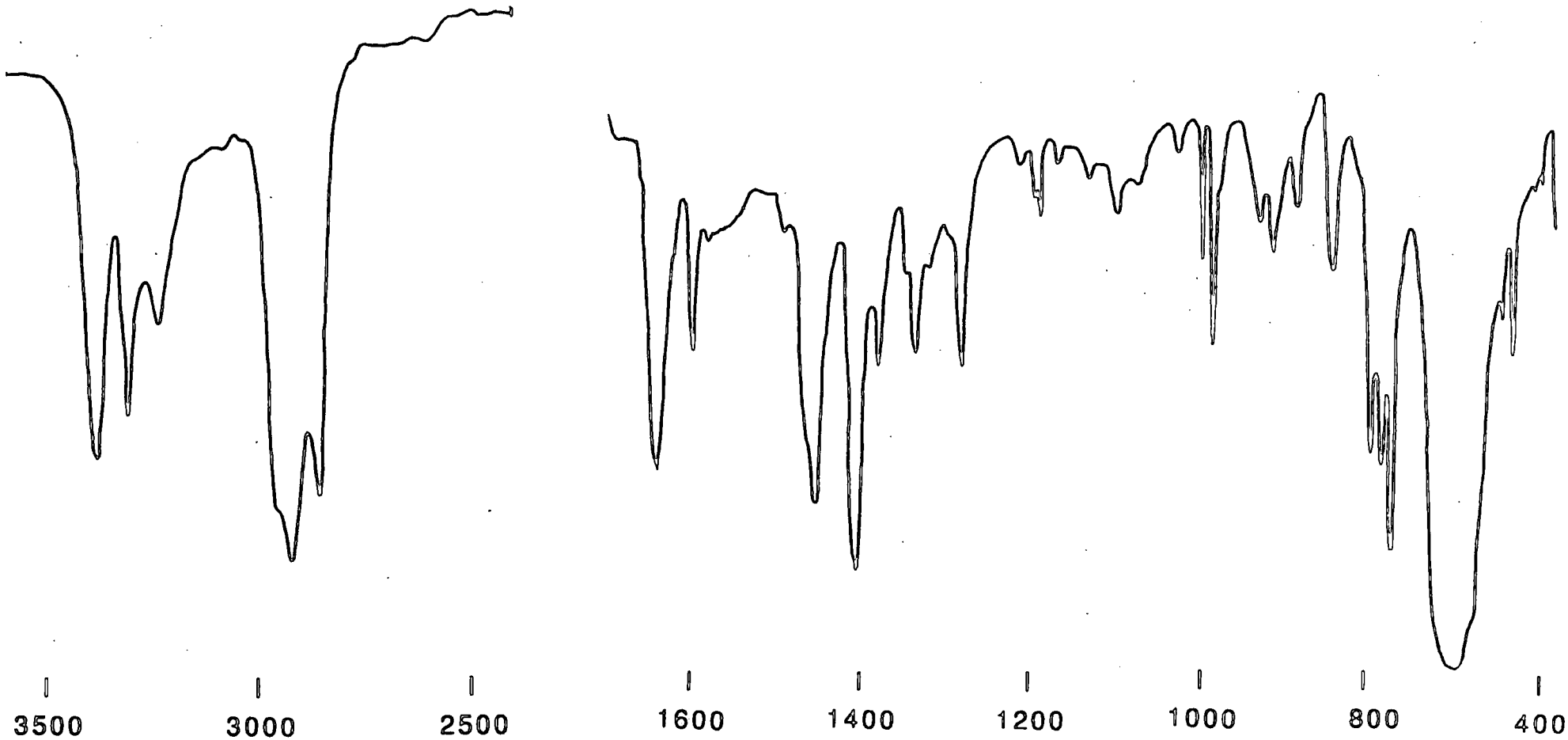


Fig. 6.2.1a

$[PhCNSNS][AsF_6] + H_2O$
SO_2 - Soluble Fraction
Nujol Mull

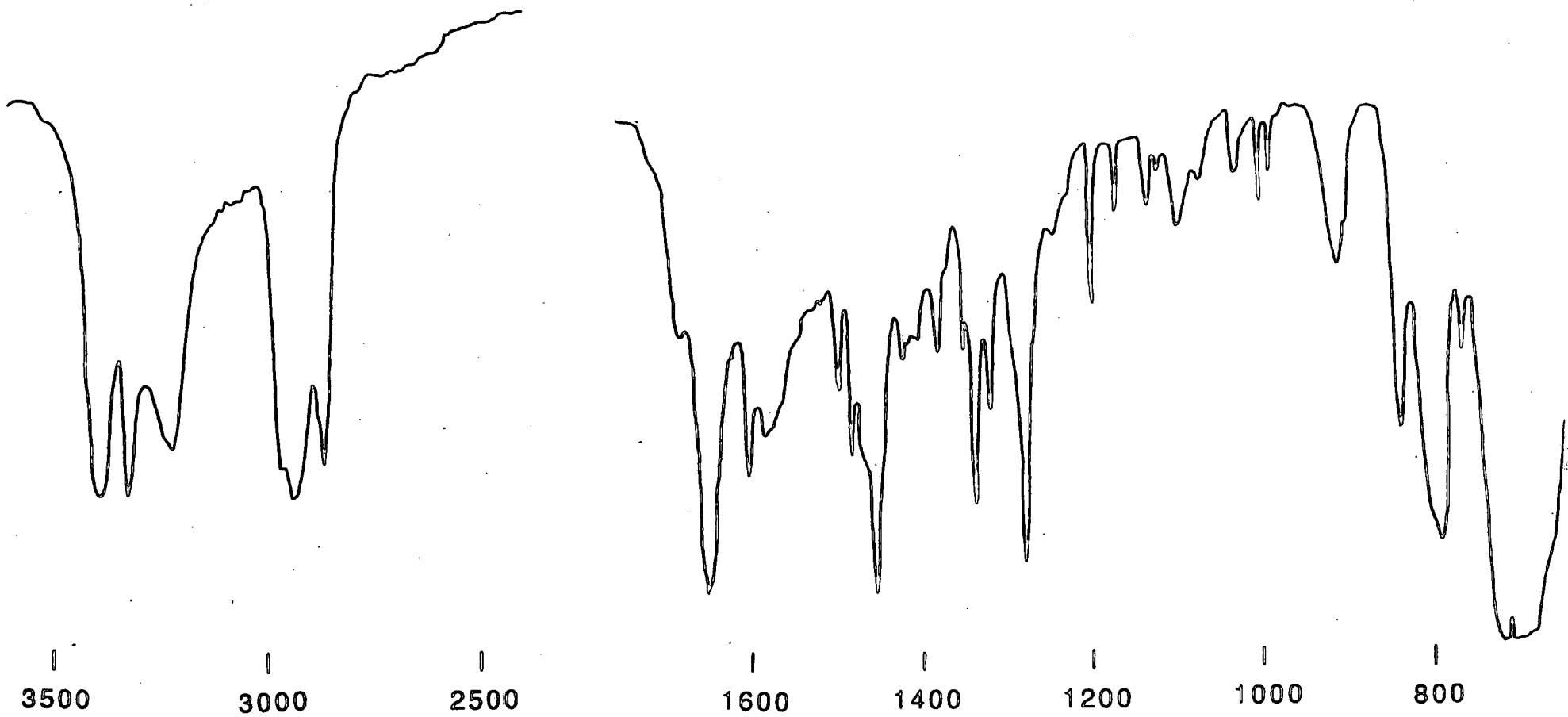


Fig. 6.2.1b

[PhCNSNS][AsF_6] + $2H_2O$
SO_2 - Soluble Product
Nujol Mull

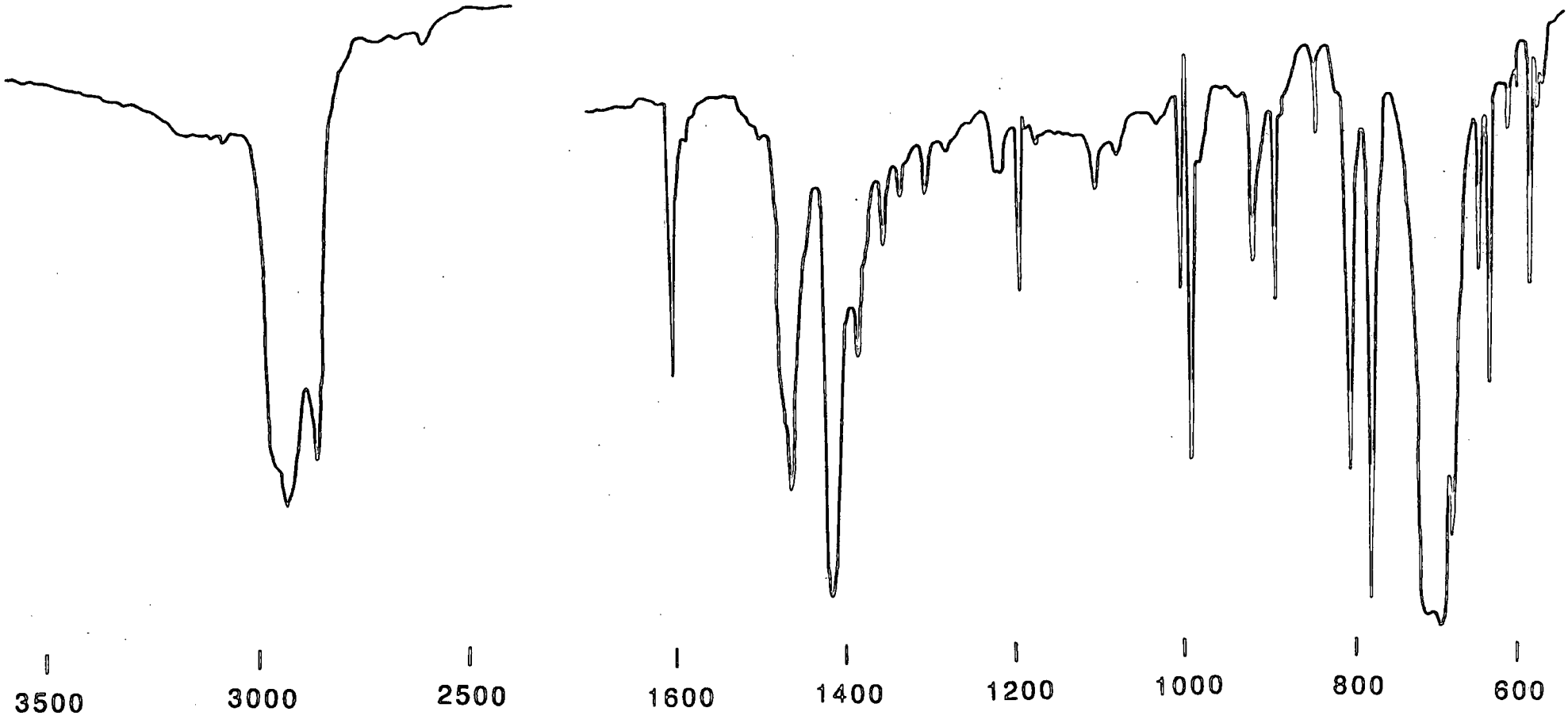


Fig. 6.2.1c

[PhCNSNS][AsF_6]
Nujol Mull

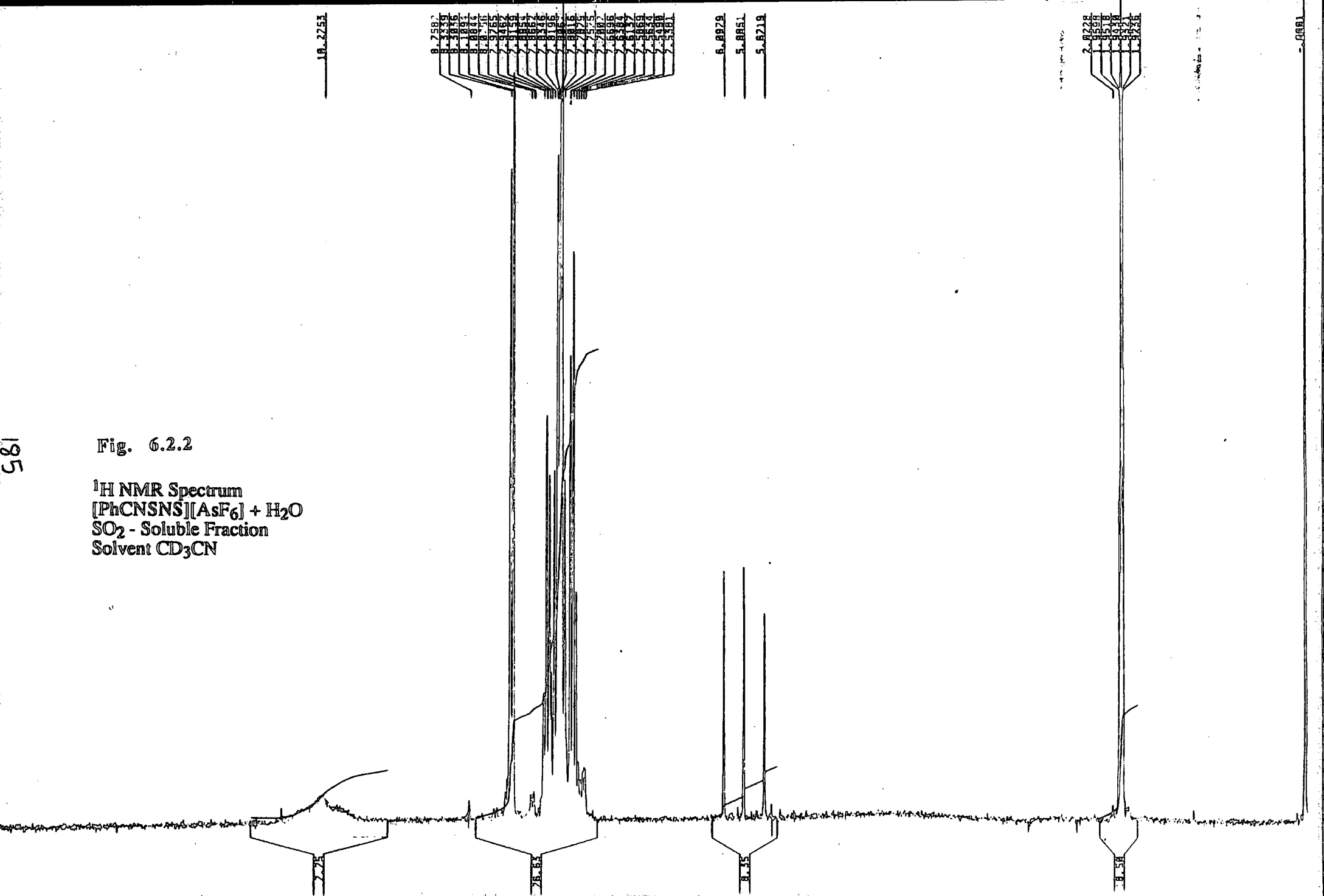


Fig. 6.2.2

^{1}H NMR Spectrum
[PhCNSNS][AsF_6] + H_2O
SO_2 - Soluble Fraction
Solvent CD_3CN

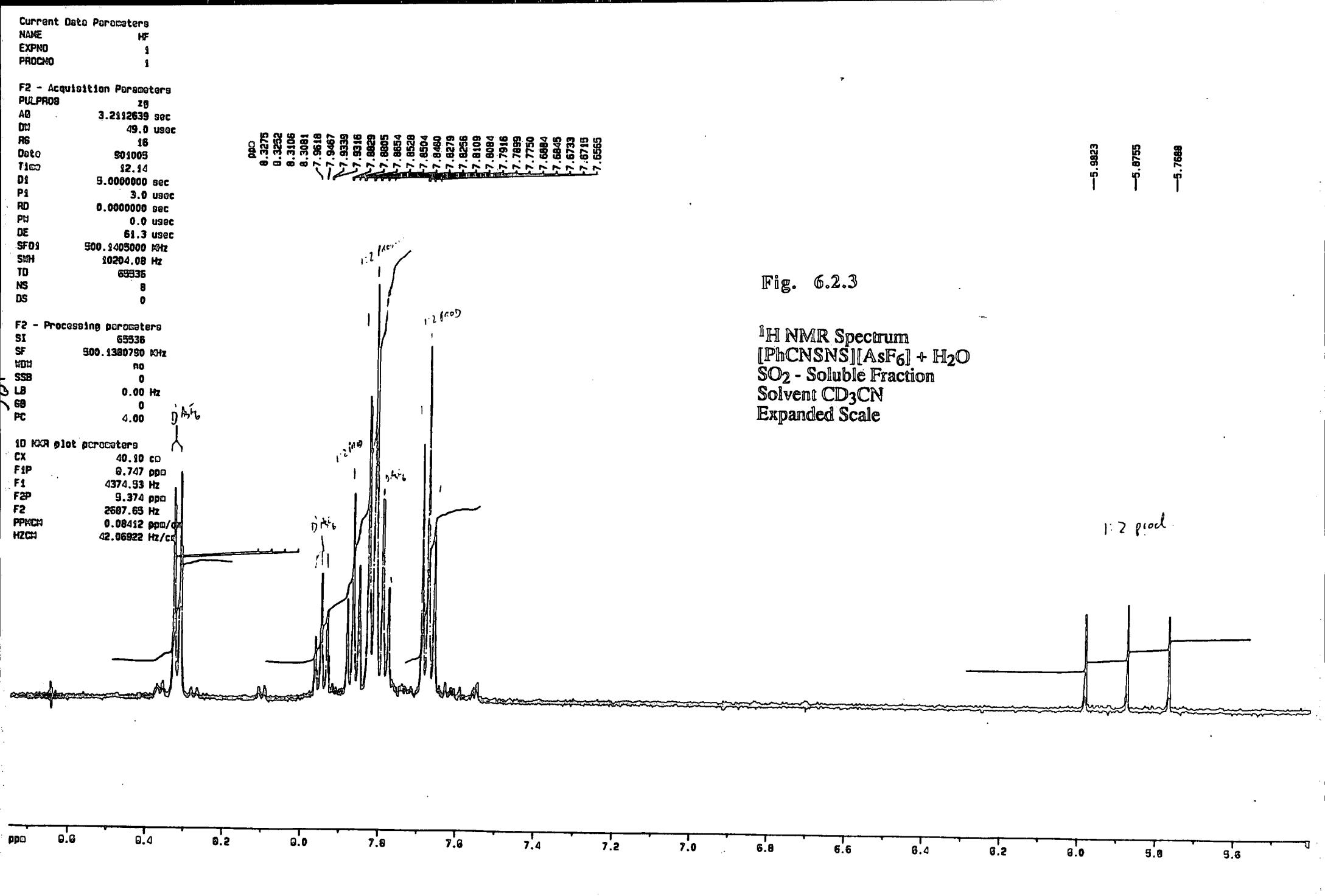
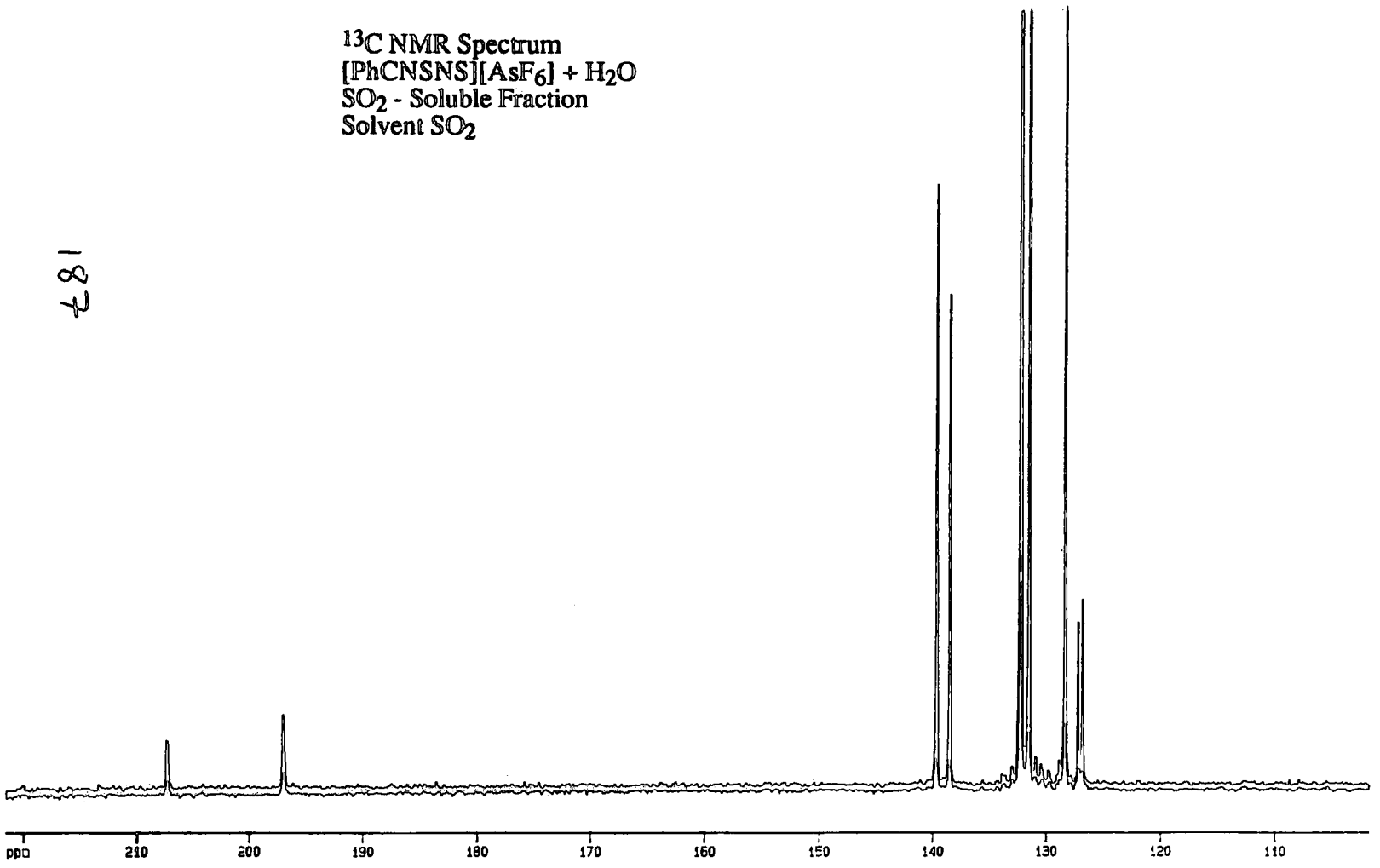


Fig. 6.2.3

^{1}H NMR Spectrum
[PhCNSNS][AsF$_6$] + H$_2$O
SO$_2$ - Soluble Fraction
Solvent CD$_3$CN
Expanded Scale

Fig. 6.2.4

^{13}C NMR Spectrum
$[PhCNSNS][AsF_6] + H_2O$
SO_2 - Soluble Fraction
Solvent SO_2



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PROCNO 1

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FIDRES 0.476837 Hz
DW 16.0 usec
RG 512
HL1 13 dB
D1 1.0000000 sec
D11 0.0300000 sec
P1 12.5 usec
RD 0.0000000 sec
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DE 20.0 usec
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SW 31250.00 Hz
TD 65536
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DS 4

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GB 0
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1D NMR plot parameters
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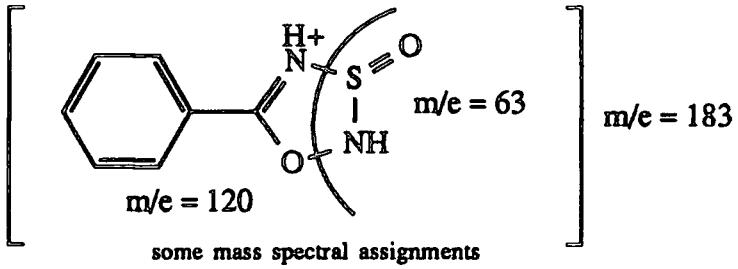
F1 27833.33 Hz
F2P 101.699 ppm
F2 12784.02 Hz
PPMCM 3.99423 ppm/cm
HZCM 502.31152 Hz/cm

^1H NMR of the 1:1 reaction product shows that the mixture contains two main products containing a monosubstituted benzene ring, as shown in Fig. 6.2.2. Fig. 6.2.3 shows the spectrum of the same material on an expanded scale : resonances in the aromatic region assignable to [PhCNSNS][AsF_6] (d 8.31ppm, d 7.94ppm and 7.80 ppm) and another product (d 7.65 ppm and d 7.83 ppm) are present. In addition to the aromatic resonances there are two other signals of approximately equal area at 5.89 ppm (1:1:1 triplet) and 10.29 ppm (broad, unresolved) which can be assigned to NH rather than OH due to the absence of OH bands in the infrared.

^{13}C NMR in liquid SO_2, as shown in Fig. 6.2.4, shows that there are two monosubstituted aromatic compounds present, as evidenced by the two sets of aryl resonances between 120 and 140 ppm and the two signals in the carbonyl region between 190 and 210 ppm. This is consistent with the deduction, based on the infrared data, that the product is formed by reaction of [PhCNSNS][AsF_6] with two equivalents of water.

The mass spectrum of the 1:1 reaction product gave peaks assignable to [PhCNSNS]+ at m/e = 181, relative intensity 6%, and a peak at 183 of relative intensity 1% which is almost certainly due to the 1:2 rection product of [PhCNSNS][AsF_6] with water. This corresponds to a fragment of formula [PhCON(H)S(O)NH]+, shown in Fig. 6.2.5. Peaks corresponding to the expected breakdown of such a species were also observed, at m/e = 120 (20%, [PhCONH]+), 63 (12%, [HNSO]+) and 62 (5%, [NSO]+).

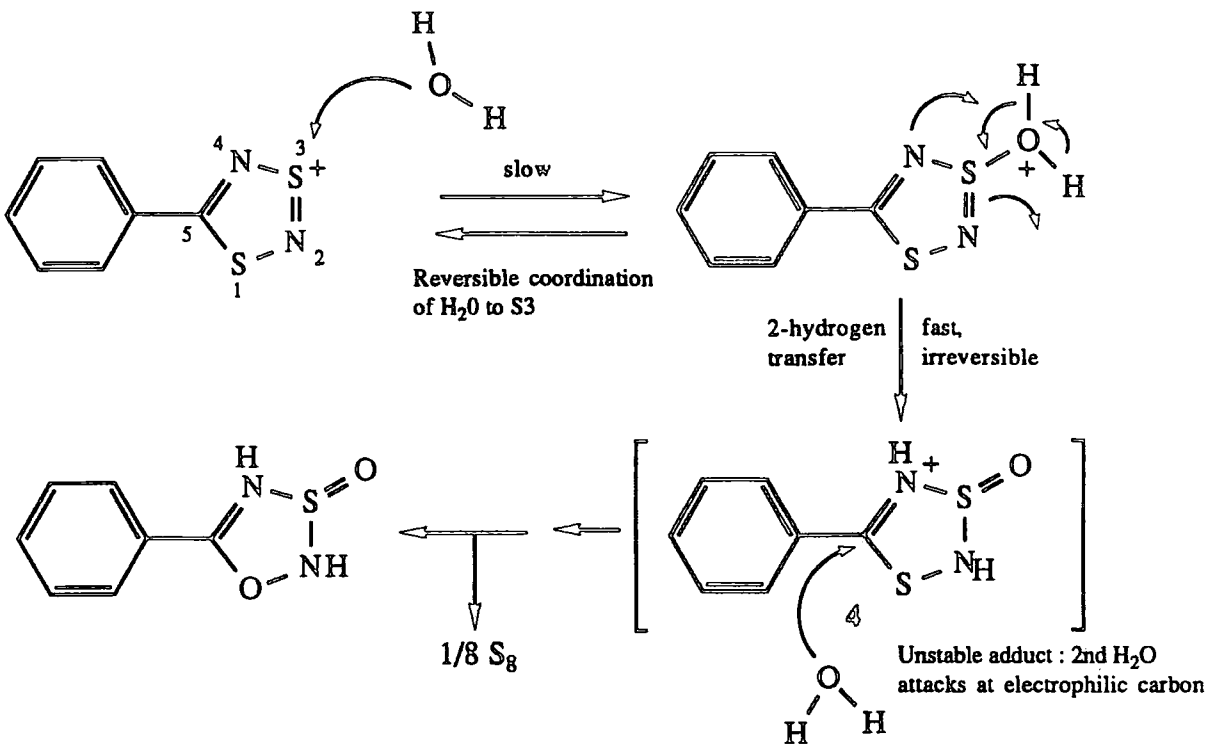


some mass spectral assignments

Fig. 6.2.5

Suggested structure for the cation in the product of the reaction [PhCNSNS][AsF_6] + $2H_2O$

The reaction of 1,3,2,4-dithiadiazolium salts with water thus appears to proceed by the attack of two water molecules per dithiadiazolium ring without producing an isolable 1:1 product. Reaction is likely to be initiated by the coordination of water to sulphur 3 in the ring, the seat of positive charge. This coordination is probably reversible, since precipitation of sulphur signalling breakup of the dithiadiazolium ring did not occur for up to 1 minute after adding the water. A suggested scheme for the reaction is shown in Scheme 6.2.1.



Scheme 6.2.1

Suggested mechanism for the reaction of $[PhCNSNS]^+$

with water

Coordination of water to the positively - charged sulphur is followed by transfer of both hydrogens from water to the nitrogens in the dithiadiazolium ring to give an unstable intermediate 1:1 adduct (4), which then undergoes attack from a second water molecule at the highly electrophilic ring carbon, followed by the elimination of sulphur and formation of the 1:2 reaction product.

The reaction thus described consists of three steps; the first, involving the attack of the first molecule of water, being slow, giving rise to an intermediate which undergoes intramolecular hydrogen transfer to give a second intermediate, highly activated toward further attack by a second molecule of water, which attacks in a fast third step, eliminating elemental sulphur and forming the 1:2 hydrolysis product.

Fig. 6.2.6 shows the ^1H NMR spectrum of the SO_2-soluble fraction from the reaction of [PhCNSNS][AsF_6] with water in 1:2 ratio. The spectrum is much simpler than that of the 1:1 reaction product shown in Figs. 6.2.2 and 6.2.3.

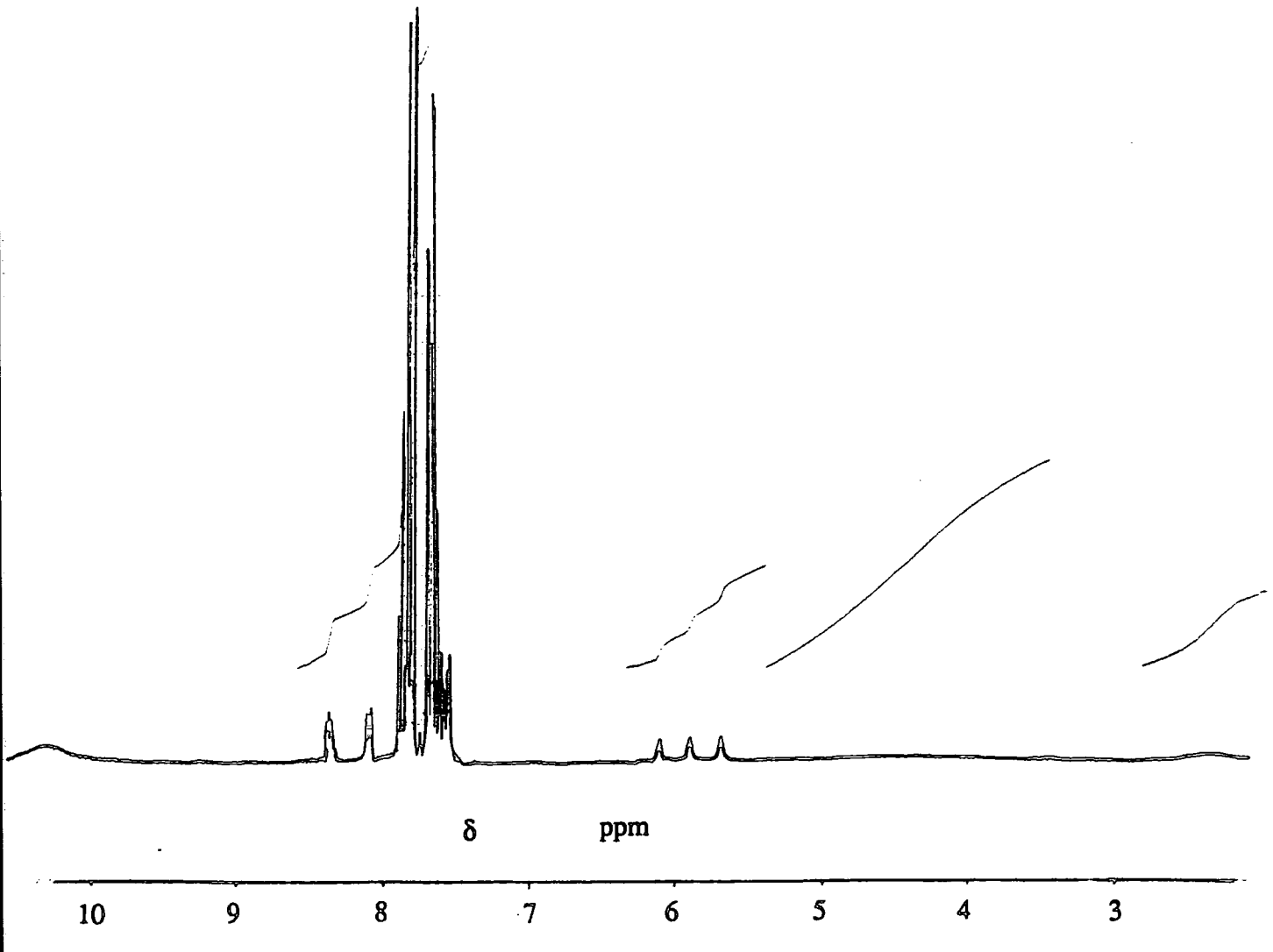
A 1:1:1 triplet at δ 5.8 ppm and a broad peak at δ 10.2 ppm of the same peak area correspond to hydrogens bonded directly to nitrogen : the triplet at 5.8 ppm arising from coupling of the spin of ^1H (I = 1/2) with the quadrupole of ^{14}N (I = 1). This pattern has a familiar ring to it, appearing in the ESR spectra of 1,3,2,4-dithiadiazolyls, and arising from the coupling of unpaired electron spins with ^{14}N. In the aryl region of the spectrum small peaks corresponding to residual [PhCNSNS][AsF_6] are seen at δ 8.3 ppm, 7.9 ppm and 7.7 ppm, but the dominant signals are those at 7.84 ppm and 7.6 ppm, corresponding to the 1:2 reaction product. These signals were observed in the spectrum of the 1:1 reaction product (Fig. 6.2.2), and this NMR evidence complements the IR data (Fig. 6.2.1) in indicating that the stoichiometry of the reaction of [PhCNSNS][AsF_6] with water is 1:2.

The 1:2 reaction product itself was found to be highly sensitive to further hydrolysis, and decomposition with the loss of sulphur occurred on standing even in thoroughly - dried apparatus. Microanalysis on this material were inconclusive, and hence the suggested structure of the product (Fig. 6.2.5) is based on the combined IR, NMR and MS data.

As stated briefly in Section 6.1 previous work[1] on the hydrolysis of the 1,2,3,5-dithiadiazolium salt [$Cl_3CCNSSN$][Cl] by the atmosphere gave a series of peaks in the mass spectrum corresponding to a compound 1. This compound also underwent further hydrolysis, and infrared studies of the hydrolysis of the related compound [PhCNSSN][Cl] showed that one of the products of this "ultimate hydolysis" was PhCN. During the experimental work on the hydrolysis of [PhCNSNS][AsF_6] it was discovered that, follwing the removal of solvent on the vacum line, the cold trap smelled of PhCN and SO_2. It may be that these are also products of ultimate hydrolysis of 1,3,2,4-dithiadiazolium salts, along with sulphur and ammonia as the ammonium salt of the conjugate acid of the anion. Certainly, a balanced equation for this model

Fig. 6.2.6

^1H NMR Spectrum
$[PhCNSNS][AsF_6] + 2H_2O$
SO_2 - Soluble Fraction
Solvent CD_3CN



reaction can be written down, as shown below (Eq. 6.2.1). Note that in this equation two equivalents of water are required, and in effect the equation is the same as that for the hydrolysis of 1,2,3,5-dithiadiazolium salts proposed by Durrant[1] (Eq. 6.2.2).

Eq. 6.2.1 $[PhCNSNS][AsF_6] + 2H_2O = PhCN + SO_2 + 1/8S_8 + NH_4AsF_6$

Eq. 6.2.2 $[RCNSSN]Cl + 2H_2O = RCN + SO_2 + 1/8S_8 + NH_4Cl$

However, it was noticed that the product from the 1:2 reaction of $[PhCNSNS][AsF_6]$ with water underwent further hydrolysis, and furthermore its IR spectrum contained no CN stretch. It can thus be concluded that Eq. 6.2.1 is incorrect. A different model equation describing the hydrolysis of one equivalent of $[PhCNSNS][AsF_6]$ by *three* equivalents of water to give benzamide instead of benzonitrile as a product is shown below as Eq. 6.2.3.

Eq. 6.2.3 $[PhCNSNS][AsF_6] + 3H_2O = PhCONH_2 + SO_2 + 1/8S_8 + NH_4AsF_6$

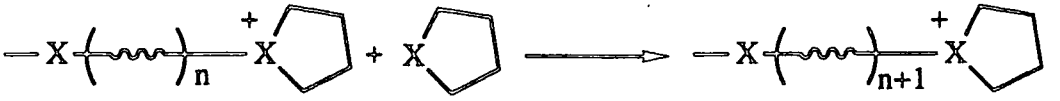
The suggested structure for the product 4 of the 1:2 reaction shown in Fig. 6.2.5 can certainly be visualised as undergoing a decomposition to benzamide rather than dehydrating to benzonitrile, and it may be that benzonitrile is formed as a minor product. The hydrolysis reaction of dithiadiazolium salts is clearly a complex reaction, and much work is still to be done until it is completely understood.

6.2.2 Dithiadiazolium Salts as Initiators of the Cationic Ring - Opening Polymerization of Tetrahydrofuran

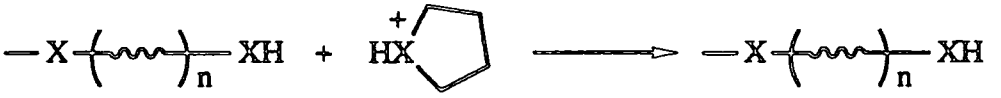
6.2.2a Background

Cationic Ring - Opening Polymerization (C.R.O.P.) is an important industrial route to polymers, in particular poly(formaldehyde), obtained from 1,3,5-trioxane, and poly(tetrahydrofuran), the latter of which finds use as a soft segment for polyurethanes, and at lower molecular weight, as a solvent.

C.R.O.P. may proceed by one of two general mechanisms ; Scheme 6.2.2 shows the activated chain end (A.C.E.) machanism, where propagation proceeds via nucleophilic attack by a monomer molecule on the onium ion at the end of a growing polymer chain. For a long time this was accepted as the only mechanism of C.R.O.P., but recently it has been shown[5,6] that C.R.O.P. may proceed via a charged monomer molecule (e.g. $[THF.H]^+$ from protonation of the oxygen in THF) adding to a neutral polymer chain. This *activated monomer* (A.M.) mechanism is shown in Scheme 6.2.3.



Scheme 6.2.2 Activated Chain-End Mechanism (A.C.E)



Scheme 6.2.3 Activated Monomer Mechanism (A.M.)

In summary, the A.C.E. mechanism the onium ion is part of the growing polymer chain, whereas in the A.M. mechanism the onium ion is a chemically-transformed monomer molecule adding to a neutral polymer chain.

The driving force for C.R.O.P. is relief of ring strain upon ring - opening. Three - and four - membered rings are highly strained and are thus readily polymerizable e.g. oxiranes, aziridines and episulphides. Six - membered rings e.g. tetrahydropyran have much lower ring strain and are thus not always polymerizable. Table 6.2.1 shows a selection of heterocyclic monomers which undergo C.R.O.P.

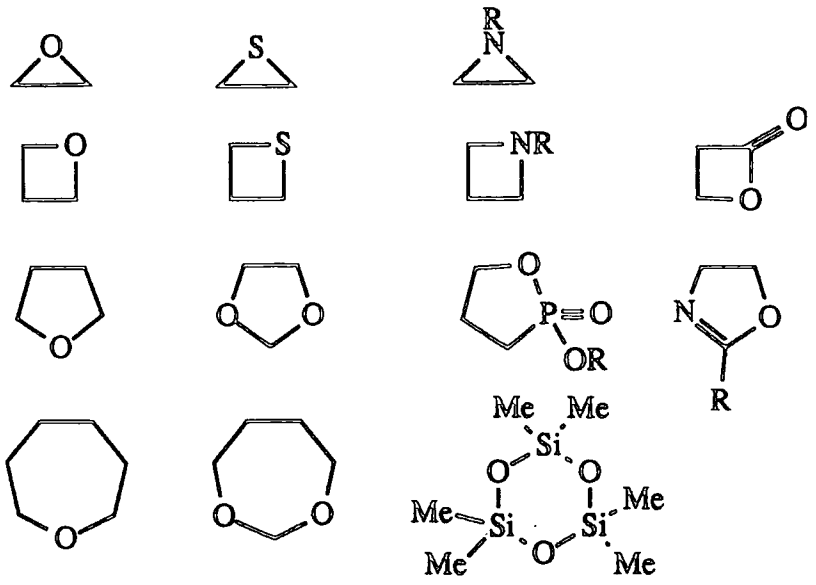
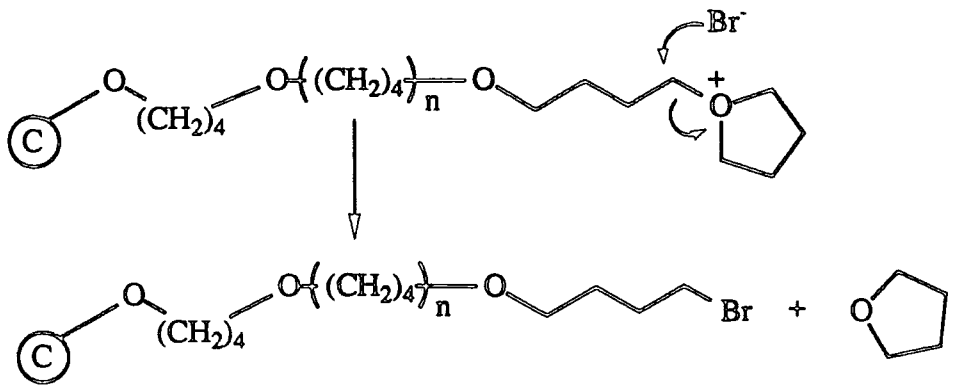


Table 6.2.1 Some monomers polymerizable by C.R.O.P

Initiation of C.R.O.P. involves the interaction of a monomer molecule with an electrophile or cationogen, so as to generate an onium ion, which is the active species in both mechanisms of C.R.O.P. Carbocations and acylium ions form tertiary onium ions by direct alkylation or acylation of the monomer molecule. Strong protic acids form secondary onium ions by protonation.

For propagation to occur the onium ion must be associated with a hard, non-nucleophilic anion e.g. AsF_6^-, SbF_6^-, ClO_4^-, in order to prevent termination by the formation of a covalent bond between the growing polymer chain and the counterion of the cationogen. Nucleophilic counterions e.g. Cl^-, Br^- are used for terminating C.R.O.P. reactions because of this, and experimentally C.R.O.P. reactions may be efficiently terminated by addition of LiBr . Scheme 6.2.4 shows the mechanism of termination of A.C.E. polymerization of THF by addition of bromide ion.



Scheme 6.2.4 Termination of C.R.O.P of THF by bromide ion
(A.C.E. mechanism)
Ⓒ denotes cationic initiator

6.2.2b Initiation of THF Polymerization by 1,3,2,4-Dithiadiazolium Salts

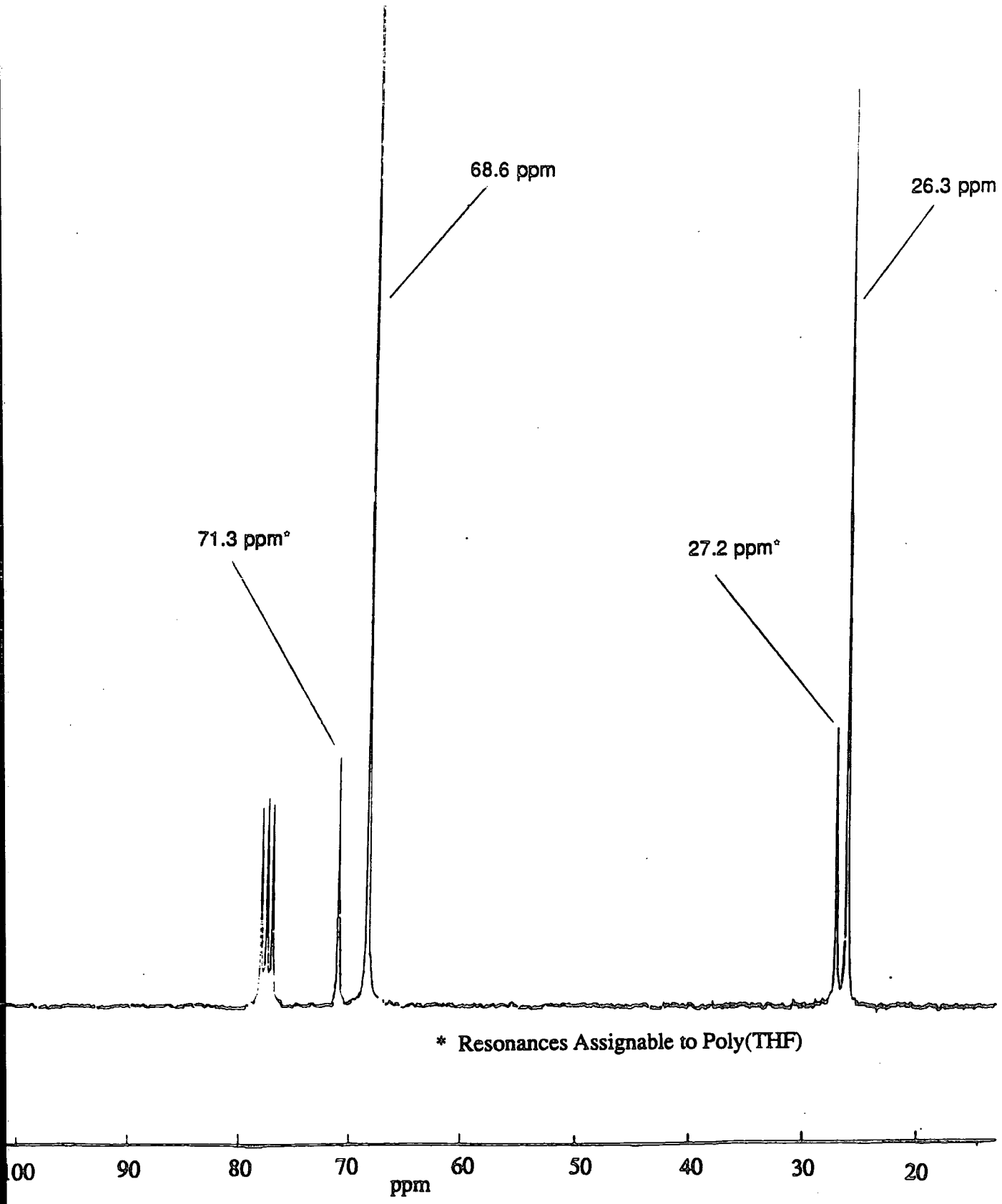
During attempts to grow single crystals of bis- and tris-dithiadiazolium salts for X-Ray structure determination it was noticed that solutions in THF formed gels over a period of time, and thus an initial study of the initiation of C.R.O.P. by dithiadiazolium salts was undertaken. *Mono-*, *bis-* and *tris-*(dithiadiazolium) AsF_6^- salts were found to initiate C.R.O.P. of neat THF to give colourless gels, and the polymers thus formed were isolated by dissolution of the gel in dichloromethane, addition of a small amount of methanol, evaporation of the resulting solution. Removal of the lower boiling fraction (CH_2Cl_2) enriched the mixture with methanol, and the polymer was precipitated. Pure polymer samples were obtained as colourless rubbery solids.

^{13}C NMR of poly(THF) gels in THF show resonances assignable to the free monomer and the polymer. Figs. 6.2.7, 6.2.8 and 6.2.9 show ^{13}C NMR spectra of polymerizing THF using *mono-*, *bis-* and *tris* - (dithiadiazolium) salts as initiators. Major resonances at *c.* 24 and 66 ppm are assignable to THF monomer, while the smaller signals at *c.* 26 and 69 ppm are due to the polymer[7].

Samples of poly(THF) initiated by 5-phenyl-1,3,2,4-dithiadiazolium hexafluoroarsenate [PhCNSNS][AsF_6] and 5,5',5''- phenine-1,3,5-*tris*-(1,3,2,4-dithiadiazolium)

Fig. 6.2.7

^{13}C NMR Spectrum of Polymerizing THF
Initiator [PhCNSNS][AsF_6]
Solvent $CDCl_3$



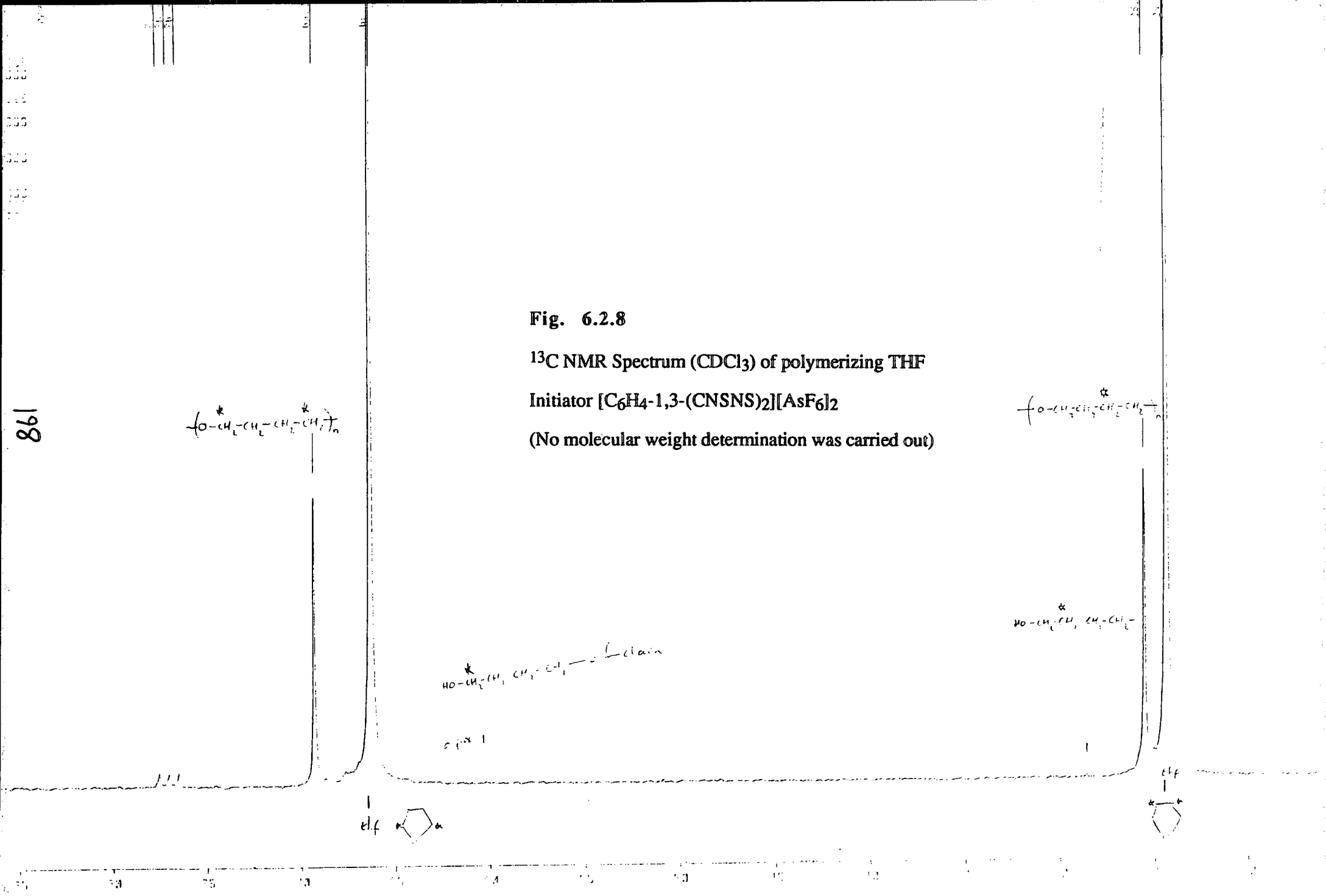


Fig. 6.2.8

^{13}C NMR Spectrum ($CDCl_3$) of polymerizing THF

Initiator $[C_6H_4\text{-}1,3\text{-}(CNSNS)_2][AsF_6]_2$

(No molecular weight determination was carried out)

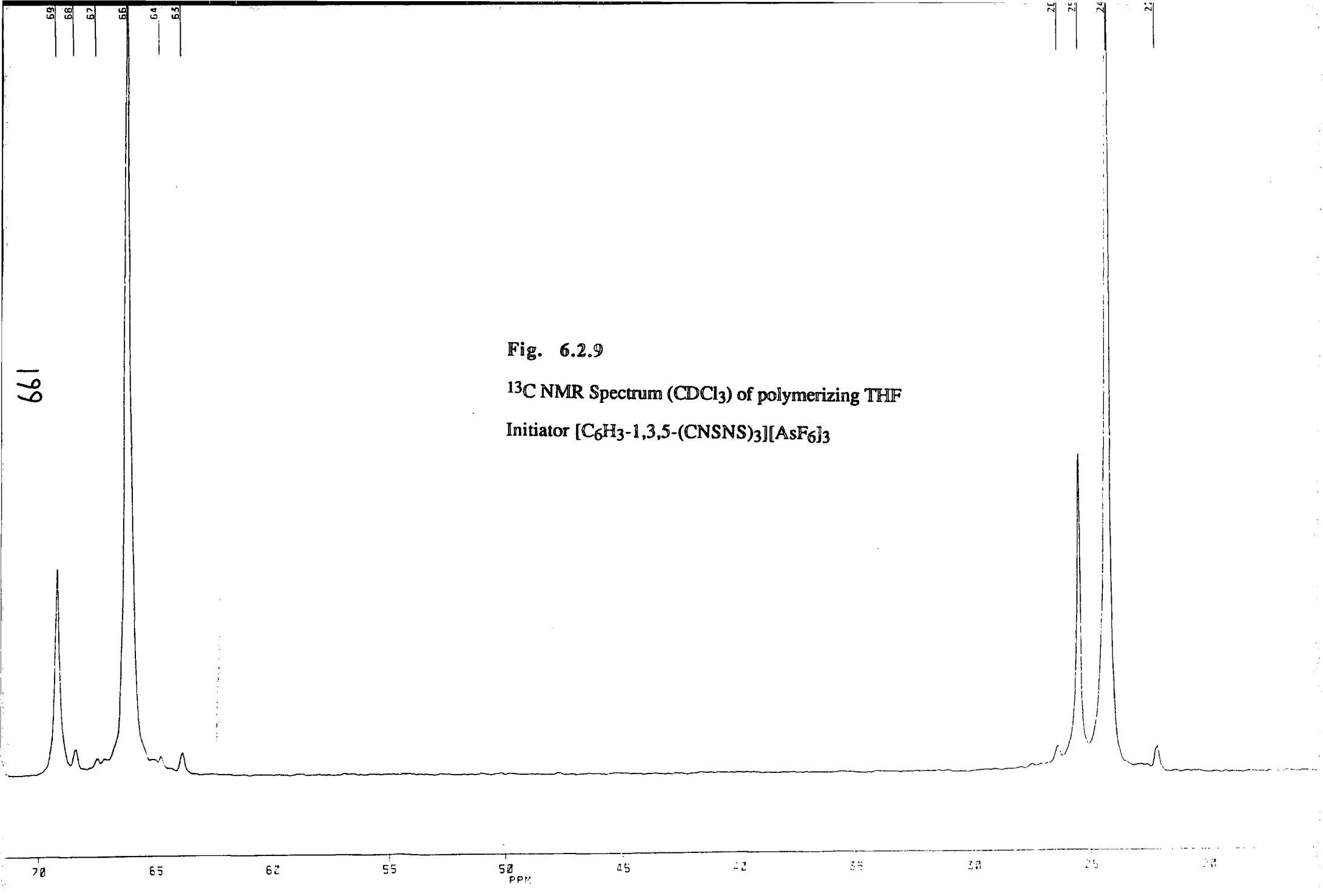


Fig. 6.2.9

^{13}C NMR Spectrum ($CDCl_3$) of polymerizing THF

Initiator $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$

hexafluoroarsenate $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$ were the subject of molecular weight determinations by gel permeation chromatography, and the polymers were found to be of high molecular weight and low polydispersity, indicating little branching during polymerization. Figs. 6.2.10 and 6.2.11 show molecular weight distributions for both polymer samples, and Table 6.2.2 shows a summary of the analysis data.

Table 6.2.2

Molecular weight data for poly (THF) from polymerizations initiated by 1,3,2,4-dithiadiazolium cations

	Initiator	
	[PhCNSNS][AsF_6]	$[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$
M_w ($gmol^{-1}$)	198700	190000
M_n ($gmol^{-1}$)	389700	306300
M_z ($gmol^{-1}$)	671400	434900
Polydispersity $= M_w / M_n$	1.96	1.61

Infrared spectra of the polymers were obtained by casting films from CH_2Cl_2 solution onto KBr plates, and spectra thus obtained are shown in Figs. 6.2.12 and 6.2.13.

DSC of poly(THF) initiated by [PhCNSNS][AsF_6] showed a small endotherm at about 27°C, corresponding to evaporation of trapped solvent (CH_2Cl_2) and precipitating agent (MeOH). The trace, shown in Fig. 6.2.14, shows that the polymer sample was thermally stable up to about 225°C, when decomposition occurred, indicated by the sharp exotherm and subsequent broad decomposition profile.

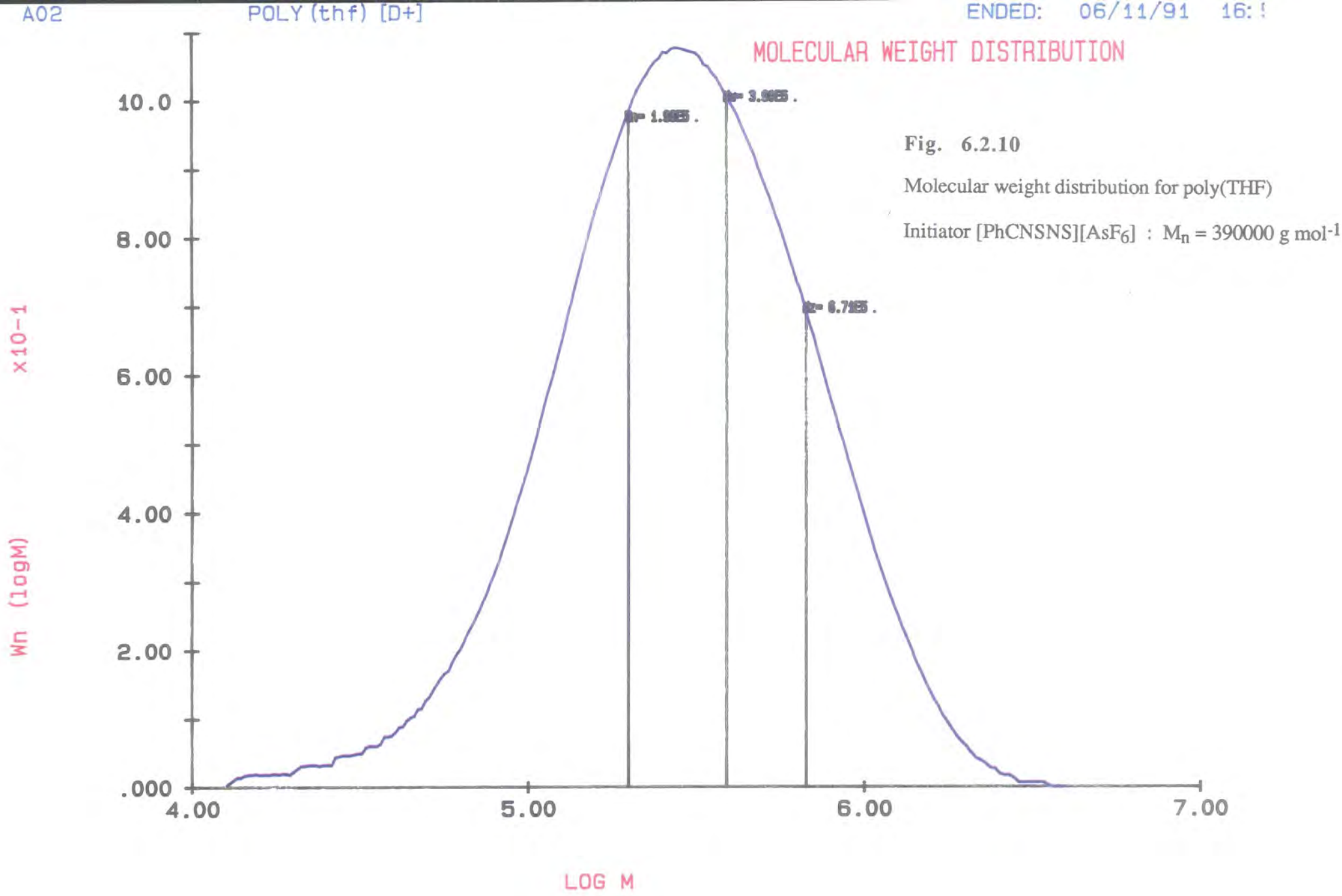


Fig. 6.2.10

Molecular weight distribution for poly(THF)

Initiator [PhCNSNS][AsF_6] : M_n = 390000 g mol^{-1}

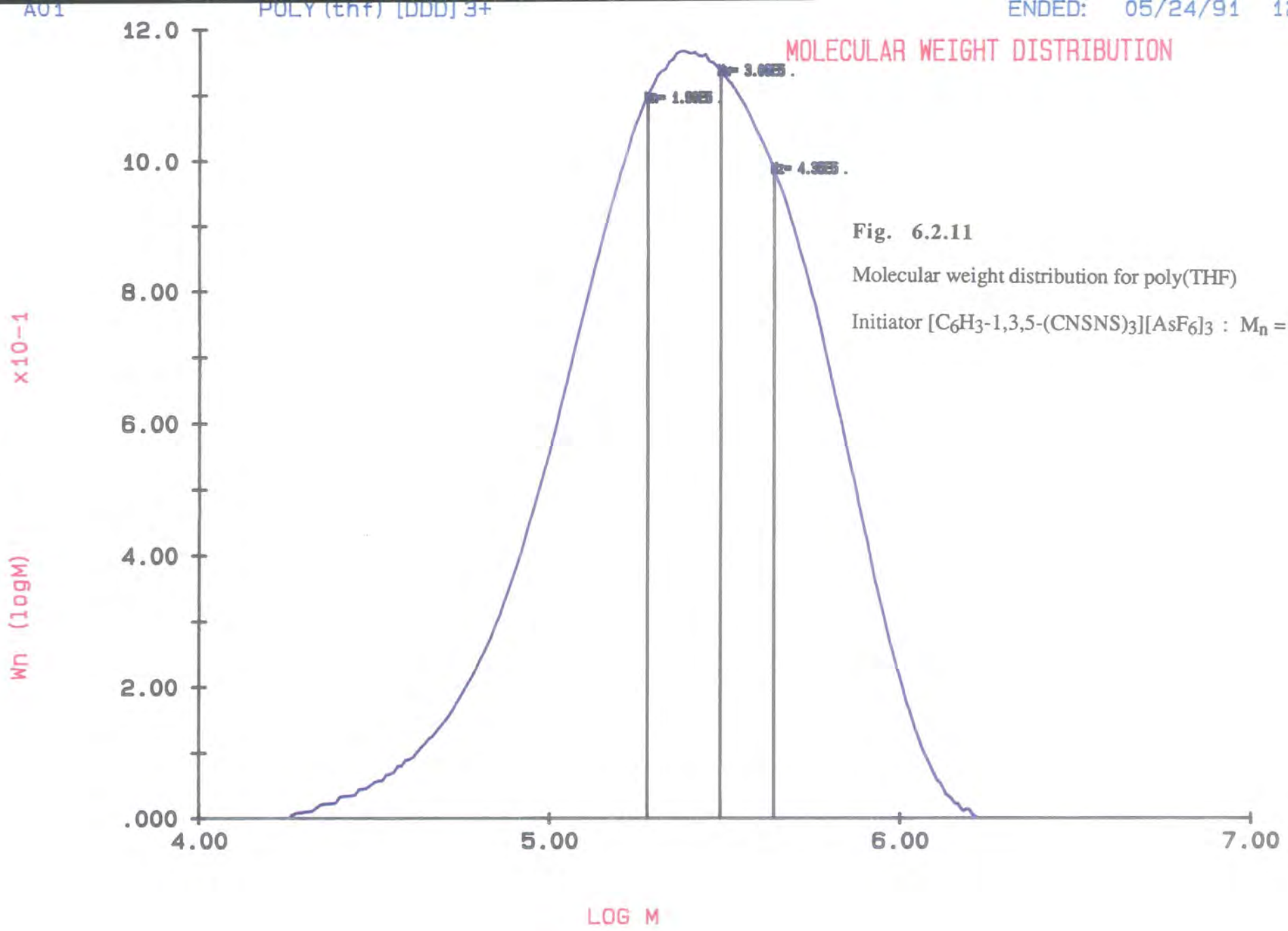


Fig. 6.2.11

Molecular weight distribution for poly(THF)

Initiator $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$: M_n = 306300 g mol

Fig. 6.2.12

Poly (THF) Film IR Spectrum
THF + Initiator [PhCNSNS][AsF_6]
M_w = 390000 $gmol^{-1}$

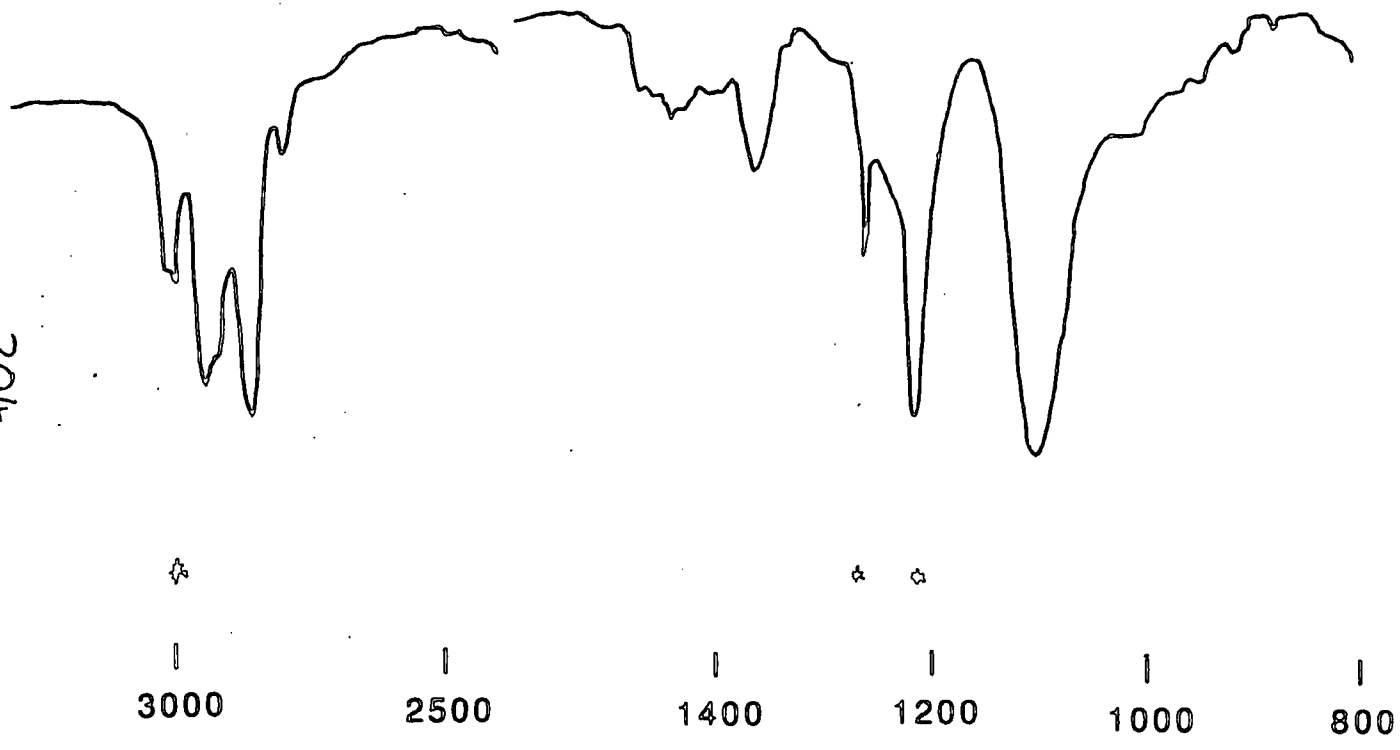


Fig. 6.2.13

Poly (THF) Film IR Spectrum
THF + Initiator $[C_6H_3\text{-}1,3,5\text{-}(CNSNS)_3][AsF_6]_3$
M_w = 306300 $gmol^{-1}$

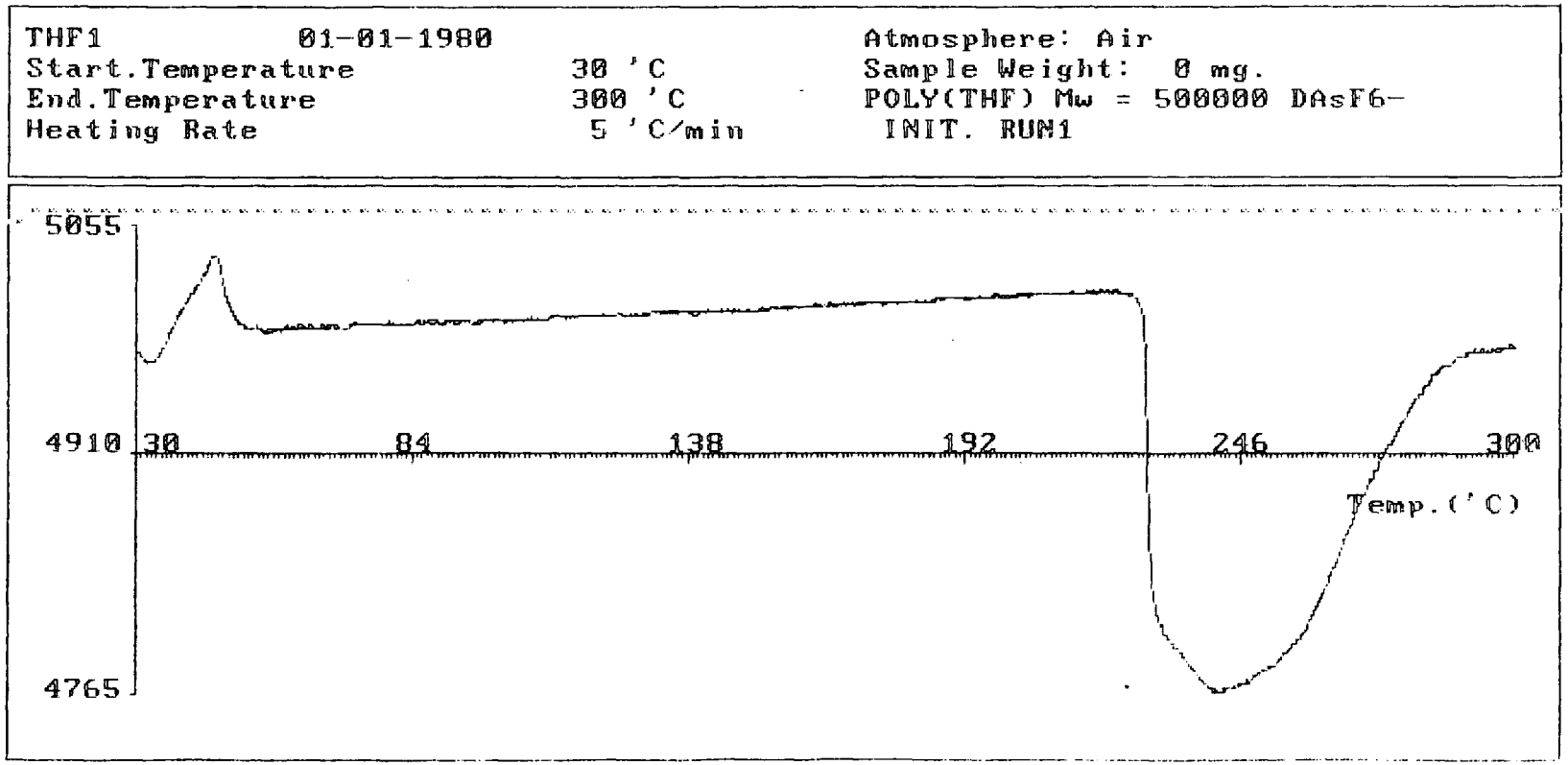


Fig. 6.2.14

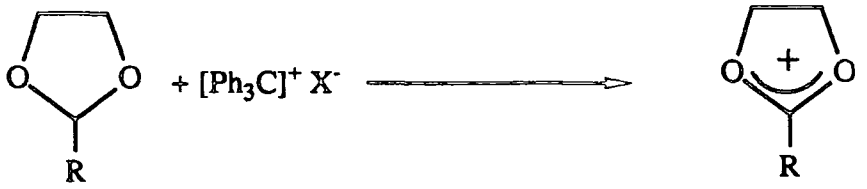
DSC trace for poly(THF)

Initiator [PhCNSNS][AsF_6]

[SNS][AsF_6] has been shown[8] to initiate C.R.O.P. of THF, and it is known that the mechanism of generation of the oxonium ion involves radical intermediates including $[S_3N_2]^{+\cdot}$. These are seen as a dark brown colouration when [SNS][AsF_6] is dissolved in THF. It was also observed that the rate of polymerization was severely reduced by addition of a base, implying that the active species is a secondary oxonium ion ie $[THF.H]^+$.

Dissolution of dithiadiazolium salts in neat THF did not produce a brown colouration, and no esr activity was observed. Thus the mechanism of initiation by dithiadiazolium salts appears to be purely ionic.

The mechanism of C.R.O.P. initiation by a number of compounds has been studied, and a common thread is the formation of a covalent bond between the oxygen of THF and a cationic species. For kinetic studies of the C.R.O.P. of THF 1,3-dioxolenium salts have been extensively studied[9-12] since they give fast, quantitative addition to THF i.e. initiation proceeds at a faster rate than propagation. 1,3-Dioxolenium salts are prepared by abstraction of an acidic hydrogen from 1,3-dioxolene by trityl salts. This is shown in Scheme 6.2.5.



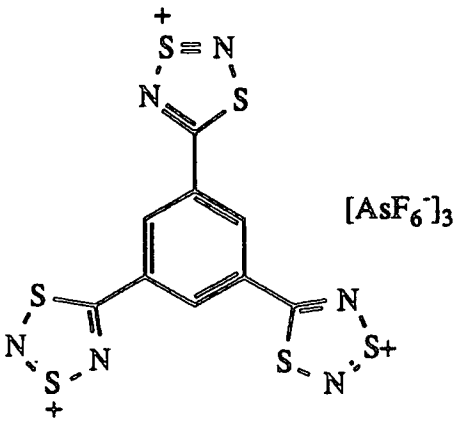
Scheme 6.2.5

Preparation of 1,3-dioxolenium salts

The nature of the initiating species has been elucidated by ^1H NMR, with the rate of appearance of the formate hydrogen acting as a probe for kinetic studies.

Other initiators where the initiation mechanism is understood may be used to prepare high molecular weight poly(THF), but the slower rate of initiation makes them unsuitable for kinetic studies. Superacids and their anhydrides or esters [13-15] (protonation), trialkyloxonium salts [16-18] (alkylation) and oxycarbenium salts[15] (acylation) have all been extensively studied.

Multifunctional oxycarbenium salts were used to initiate C.R.O.P. of THF to prepare starburst polymers. It was shown by kinetic studies[19] that each cationogenic site in the initiator molecule gave rise to a polymer chain, indicating that such initiators could be used to prepare dendritic polymeric materials. It was found during this work that THF polymerization initiated by the *tris*-(dithiadiazolium) salt 4 produced a solid gel after 24 hrs, whereas initiating polymerization with 5-phenyl-1,3,2,4-dithiadiazolium cation $[PhCNSNS]^+$ produced a solid gel after 7 days under similar conditions.



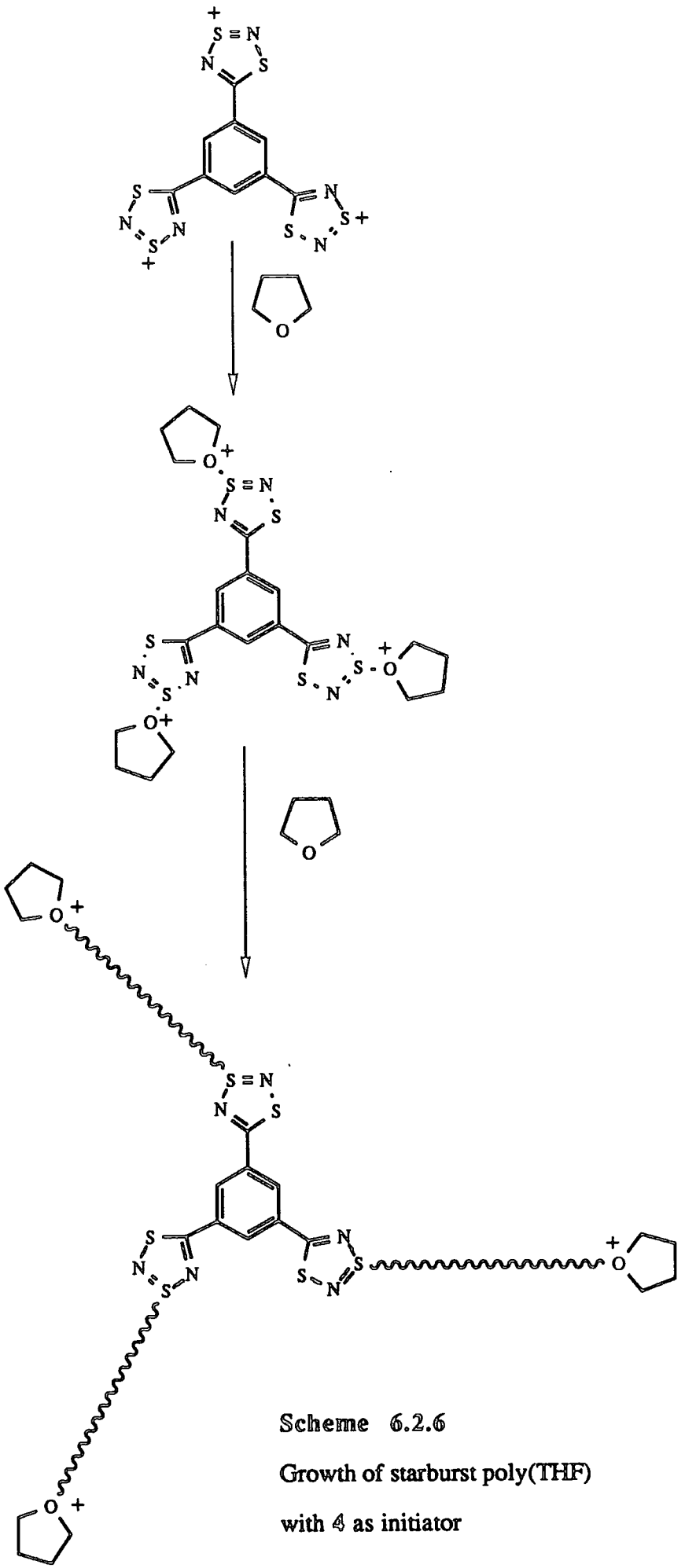
4

Quantitative rate data for dithiadiazolium salts as initiators have yet to be obtained, but it is predicted that multifunctional salts will initiate at a faster rate than monofuctional analogues. Scheme 6.2.6 shows the formation of a dendritic polymer with 4 as the initiator.

Such multifunctional initiators are now the subject of much interest, and new examples are regularly reported[20-25].

A remarkable tetrafunctional initiator reported recently[26] is the tetrabromoperoxo compound BDBP 5, shown in Scheme 6.2.7. Metathesis of 5 with $AgSbF_6$ in the presence of THF abstracts the benzylic bromines to give benzylic cations in association with $[SbF_6]^-$. Reaction with monomeric THF then gives a four-armed polymeric species. This polymer was then used to initiate radical polymerization of styrene via the peroxide group to give a branched styrene-THF block copolymer.

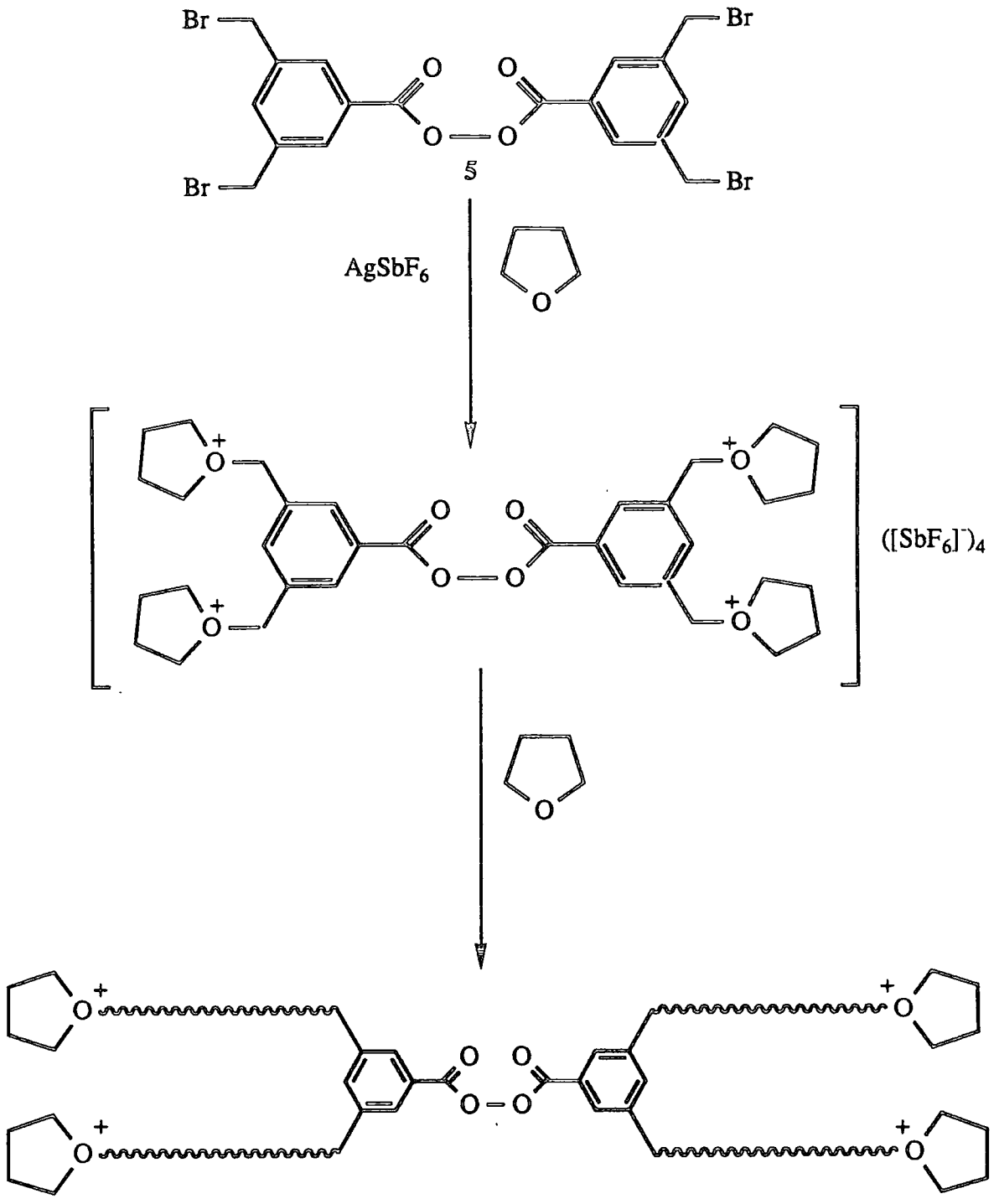
Attempts to elucidate the nature of the active species in C.R.O.P. of THF by dithiadiazolium salts by ^1H NMR proved unsuccessful. Fig. 6.2.15 shows the ^1H NMR spectrum of a 1:1



Scheme 6.2.6

Growth of starburst poly(THF)

with 4 as initiator



Scheme 6.2.7

Polymerization of THF with tetrafunctional initiator 5

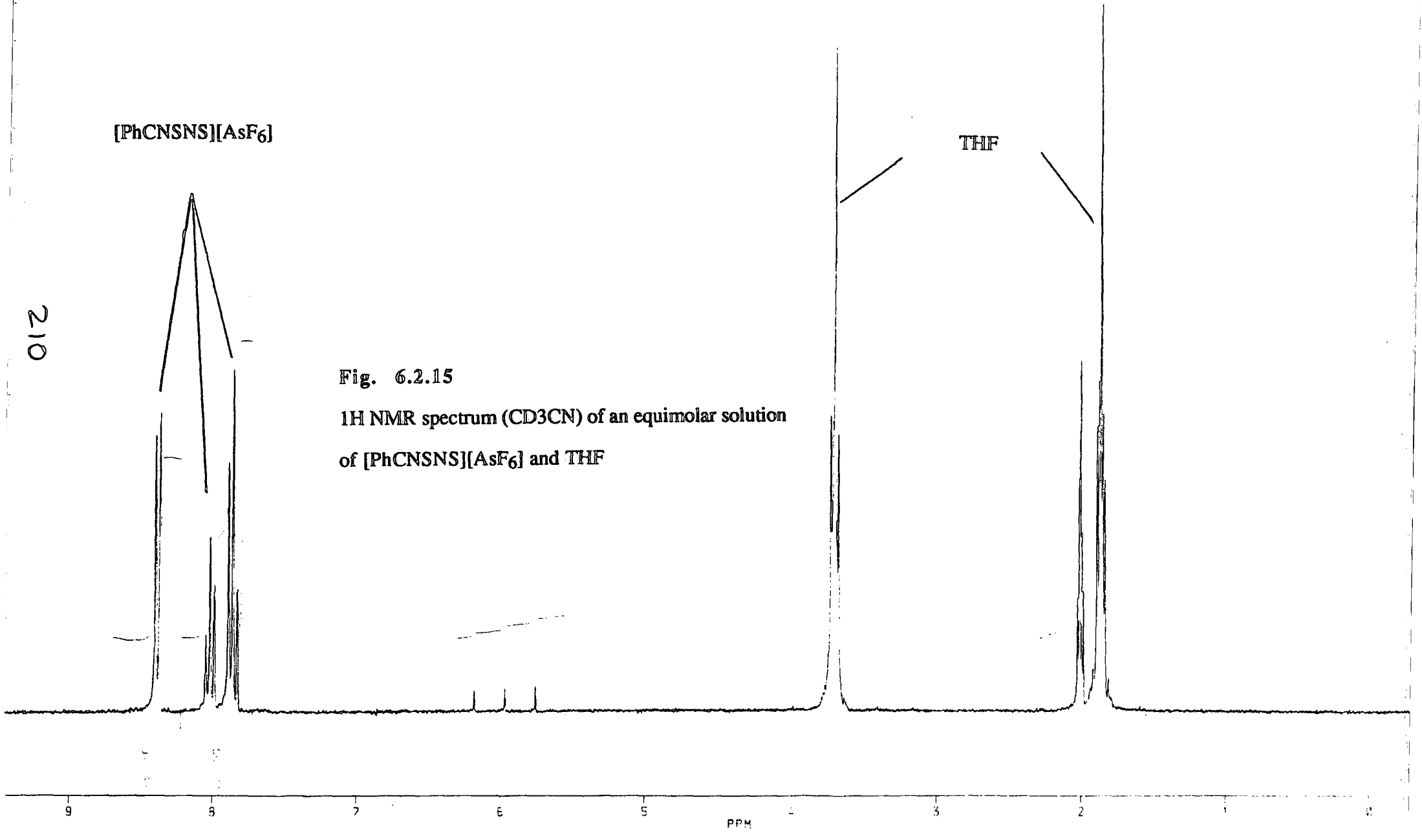
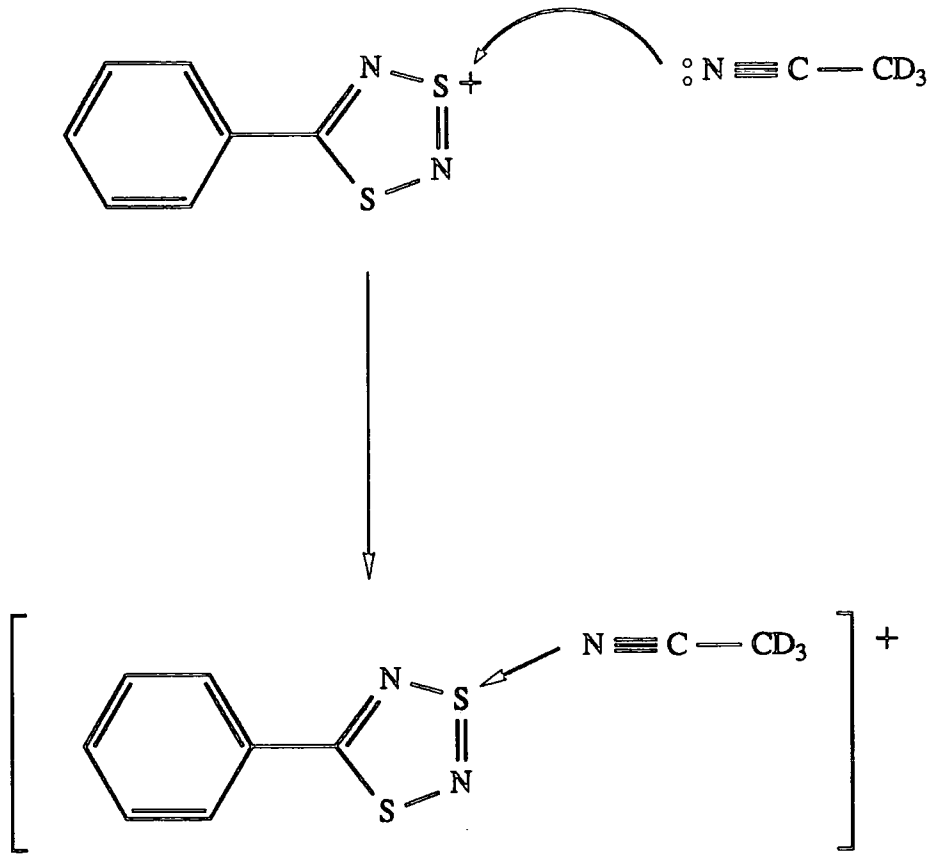


Fig. 6.2.15

1H NMR spectrum (CD3CN) of an equimolar solution of [PhCNSNS][AsF_6] and THF



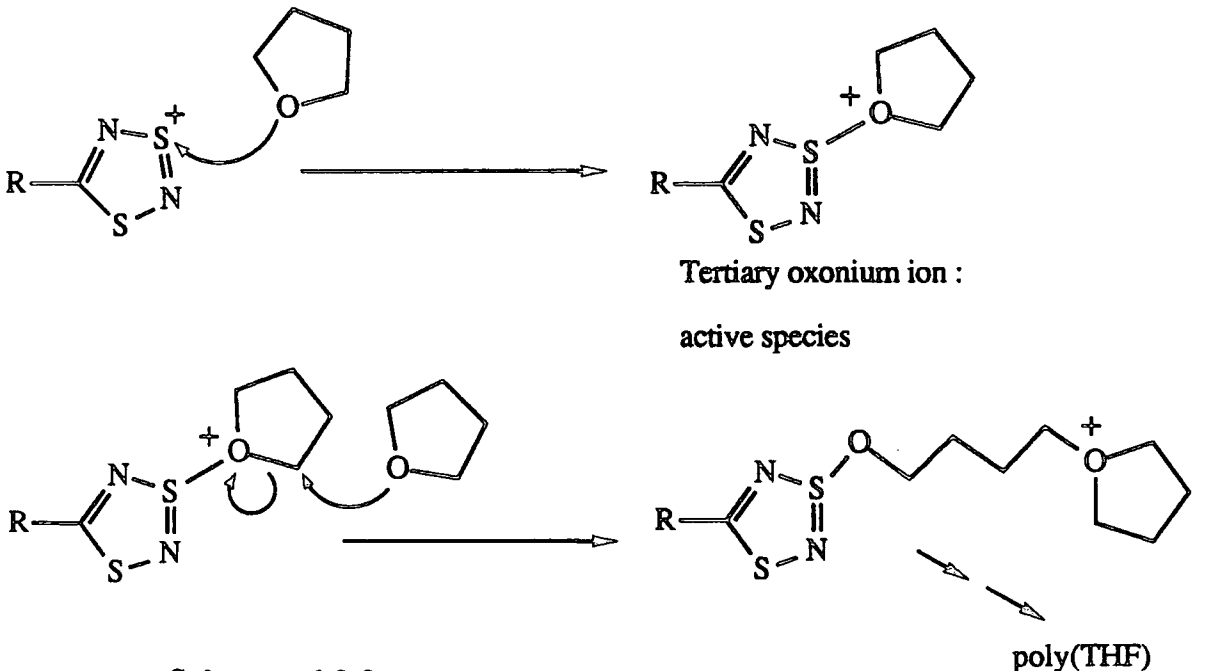
Scheme 6.2.8

Solvation of $[PhCNSNS]^+$ by CD_3CN with coordination of the nitrile nitrogen to the charge-bearing sulphur

mixture of 5-phenyl-1,3,2,4-dithiadiazolium AsF_6^- salt and THF in CD_3CN. Resonances assignable to THF occur at the same position as in the free monomer. It would be expected that coordination of a THF molecule to the positively-charged sulphur atom in the dithiadiazolium ring (thus introducing the positive charge onto the oxygen of THF) would cause a significant downfield shift of the adjacent hydrogens.

A possible explanation for this is that solvent and THF are in competition to coordinate and solvate the cation. Dithiadiazolium salts are highly soluble in both CH_3CN and THF, and the observed spectra may be explained by CD_3CN (which is present in large excess) being solely involved in cation solvation. This is shown in Scheme 6.2.8.

The proposed mechanism, shown in Scheme 6.2.9, is thus a *pseudoacylation*, with a covalent bond being formed between the positively-charged sulphur on the dithiadiazolium ring and the oxygen of THF. The tertiary oxonium ion thus formed will subsequently undergo attack by a second THF molecule, thus effecting propagation.



Scheme 6.2.9

Proposed mechanism for the initiation of THF polymerization by 1,3,2,4-dithiadiazolium cation

6.2.3 Reaction of [PhCNSNS][AsF_6] with 2-methyl-2-propanol

Reaction of [PhCNSNS][AsF_6] with 2-methyl-2-propanol in 1:1 ratio was studied by ^1H NMR spectroscopy over a period of 25 days, and the reaction was found to be very complex. ^1H NMR spectra of the aliphatic region for this reaction are shown in Fig. 6.2.16. At t = 5min (Fig. 6.2.16 a), the spectrum consists of two main signals at 1.17 ppm (CH_3) and 2.53 ppm (OH). After 210 min (Fig. 6.2.16 b) other signals are visible ; singlets at 0.93, 1.09, 1.37, 1.43, 1.72 and 1.76 ppm as well as the main signals at 1.17 and c. 2.5 ppm. In addition, a doublet of doublets typical of an AB spin system appears centred at c. 3.08 ppm. This must arise from the degradation of the t-butyl group of the alcohol, but the nature of the species responsible is not known.

As time progresses these signals increase in intensity as the primary signals decrease. After 24 hr (Fig. 6.2.16 c) singlets at 1.55 and 3.57 ppm have appeared.

After 8 days (Fig. 6.2.16 e) the doublet of doublets at 3.08 ppm has disappeared and the singlet at 3.58 ppm has increased in intensity. An additional signal at 1.25 ppm has appeared and the singlet at 1.72 and 1.76 ppm have disappeared.

After 25 days (Fig. 6.2.16 f) the spectrum has returned to a simple form. The signals due to 2-methyl-2-propanol have disappeared completely, and the spectrum consists of 4 main signals, all singlets, at 1.36, 1.38, 1.55 and 3.57 ppm. The singlet at 3.57 ppm is interesting because it is at too high a shift to be due to a t-butyl group, and is more likely to be due to a methyl group with an electron-withdrawing substituent. During the reaction no precipitation was observed, unlike the hydrolysis reaction described in 6.2.1. This suggests that the CN_2S_2 heterocycle of the dithiadiazolium salt remains intact with alcohols, and that a complex mixture of products is formed.

Reaction is likely to begin, as in the reactions with water and THF, with the coordination of the oxygen of the nucleophile to the positively-charged sulphur in the dithiadiazolium ring. Following this step it is likely that there is hydrogen transfer from the nuceophile oxygen to one of the nitrogens on the ring, as evidenced by the appearance of a 1:1:1 triplet in the ^1H NMR spectrum (Fig. 6.2.16g).

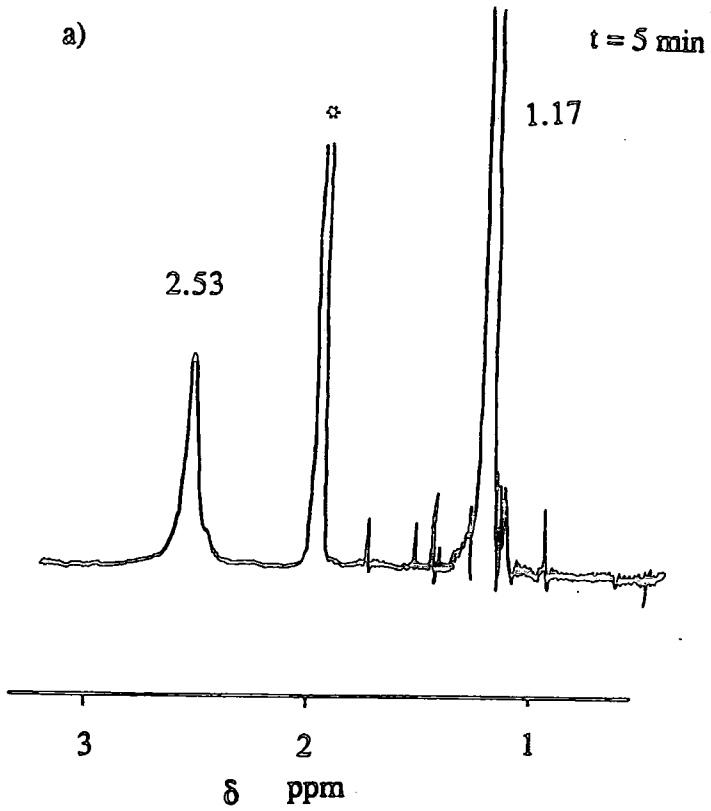
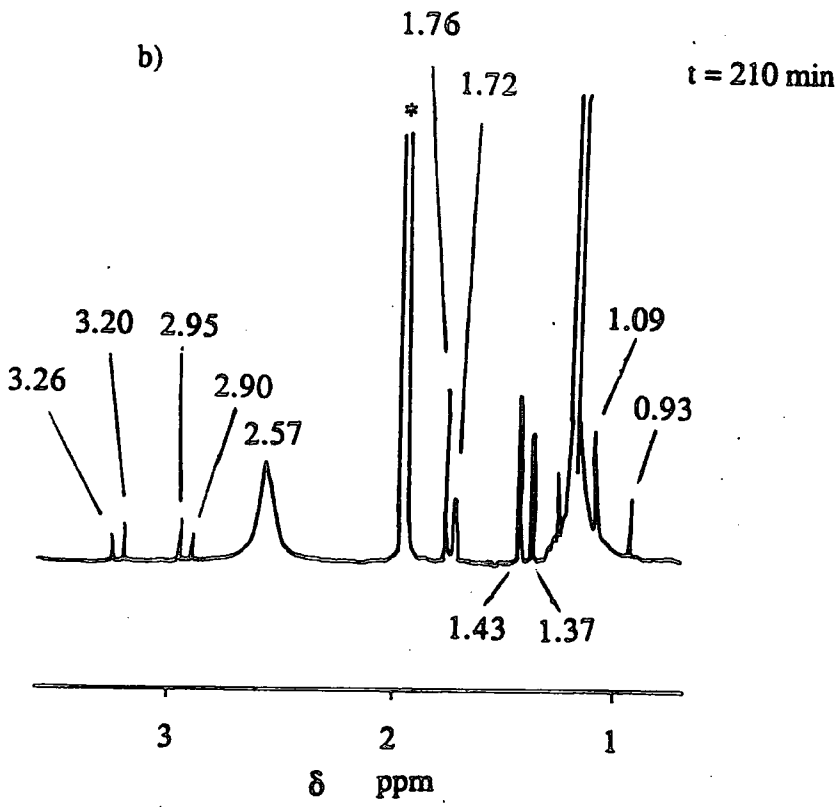


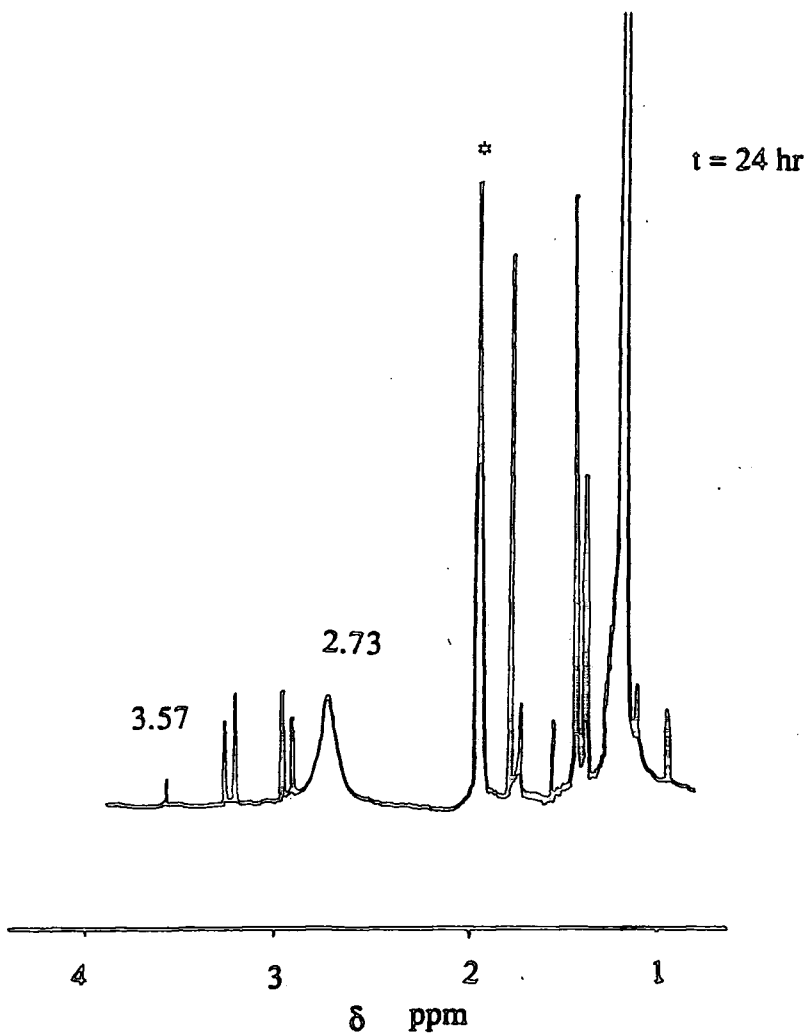
Fig. 6.2.16

^{1}H NMR Spectra
[PhCNSNS][AsF_6] + ^{t}BuOH
Solvent CD_3CN
Reference TMS

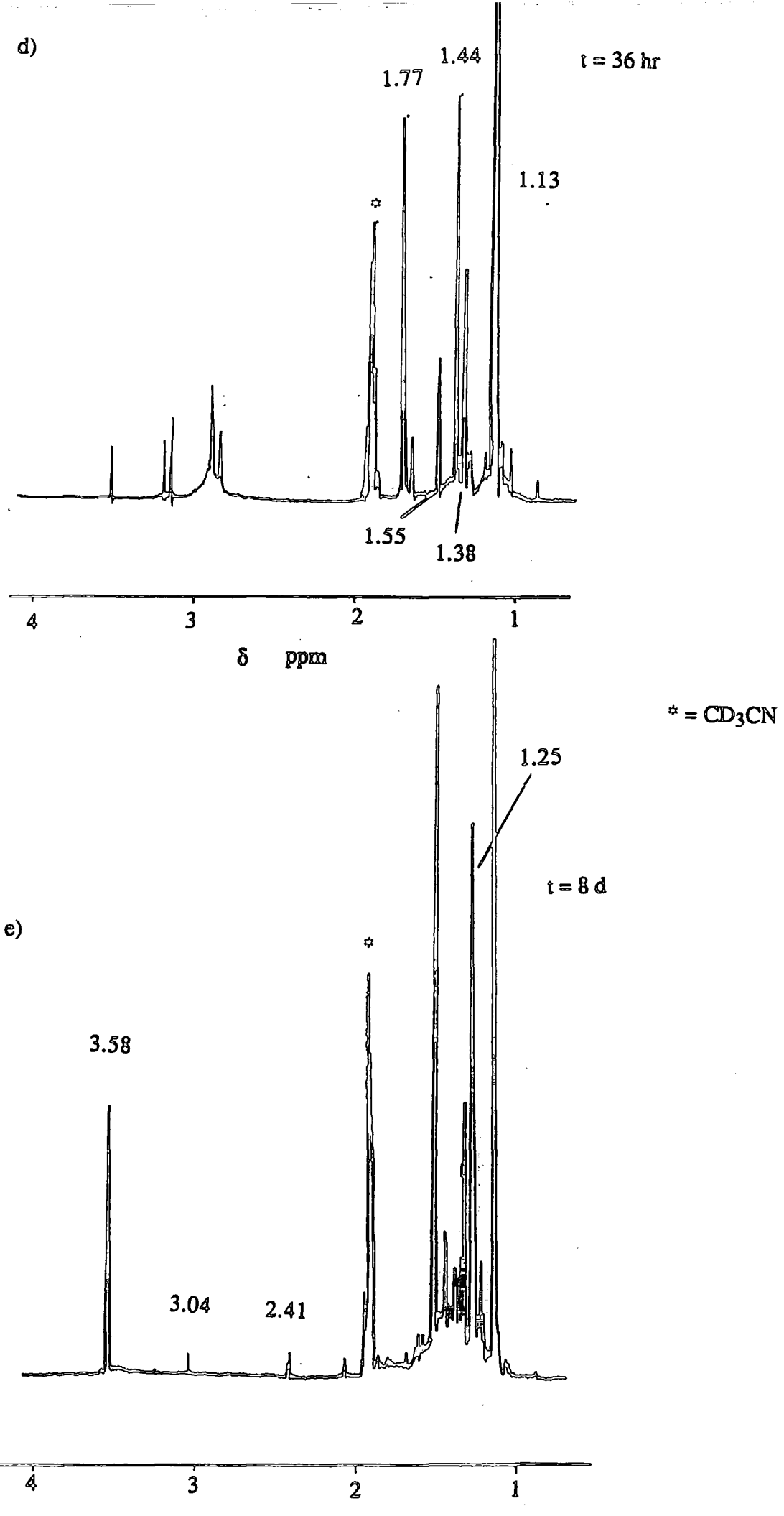


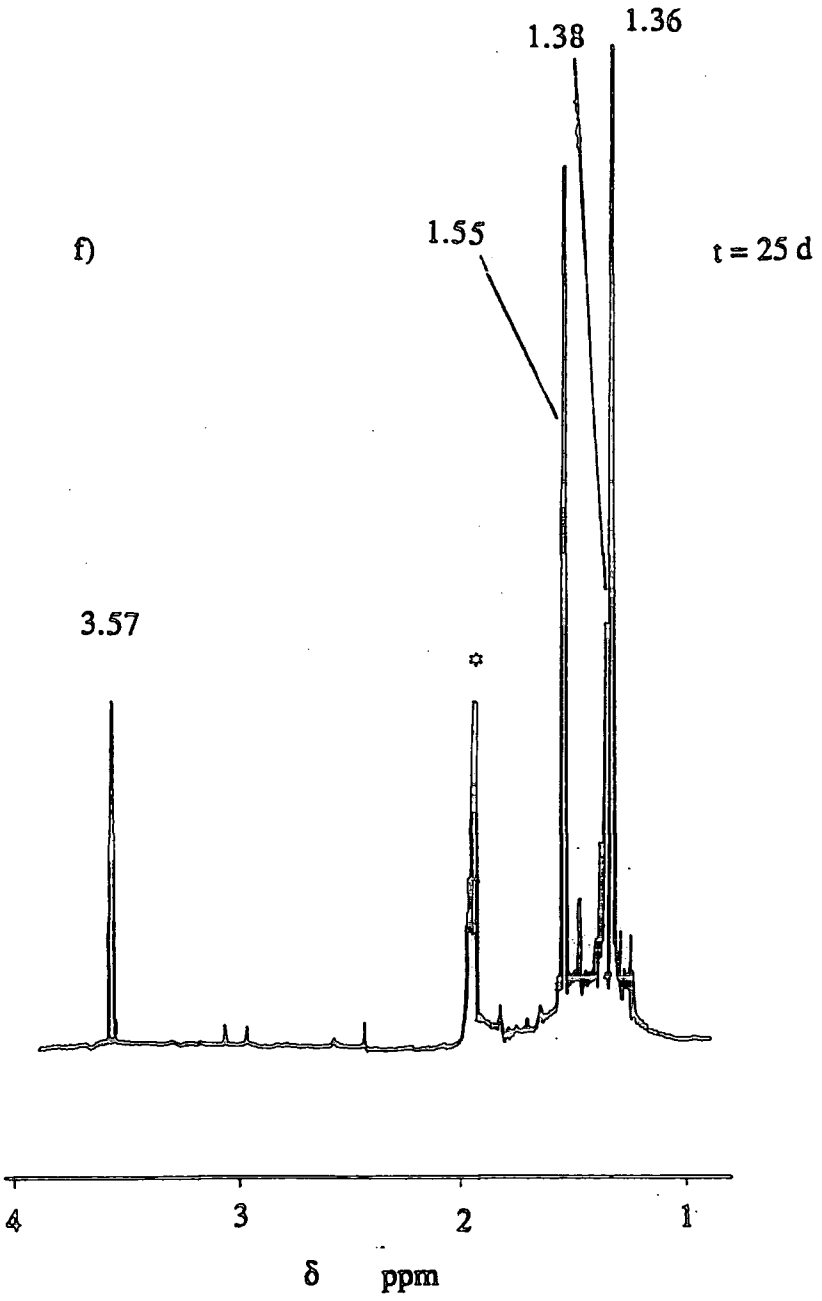
* = CD_3CN

c)



* = CD_3CN


d)
1.44
1.77
t = 36 hr
1.13
1.55
1.38
4
3
2
1
δ ppm
* = CD3CN
1.25
t = 8 d
e)
3.58
3.04
2.41
4
3
2
1
δ ppm



✲ = CD_3CN

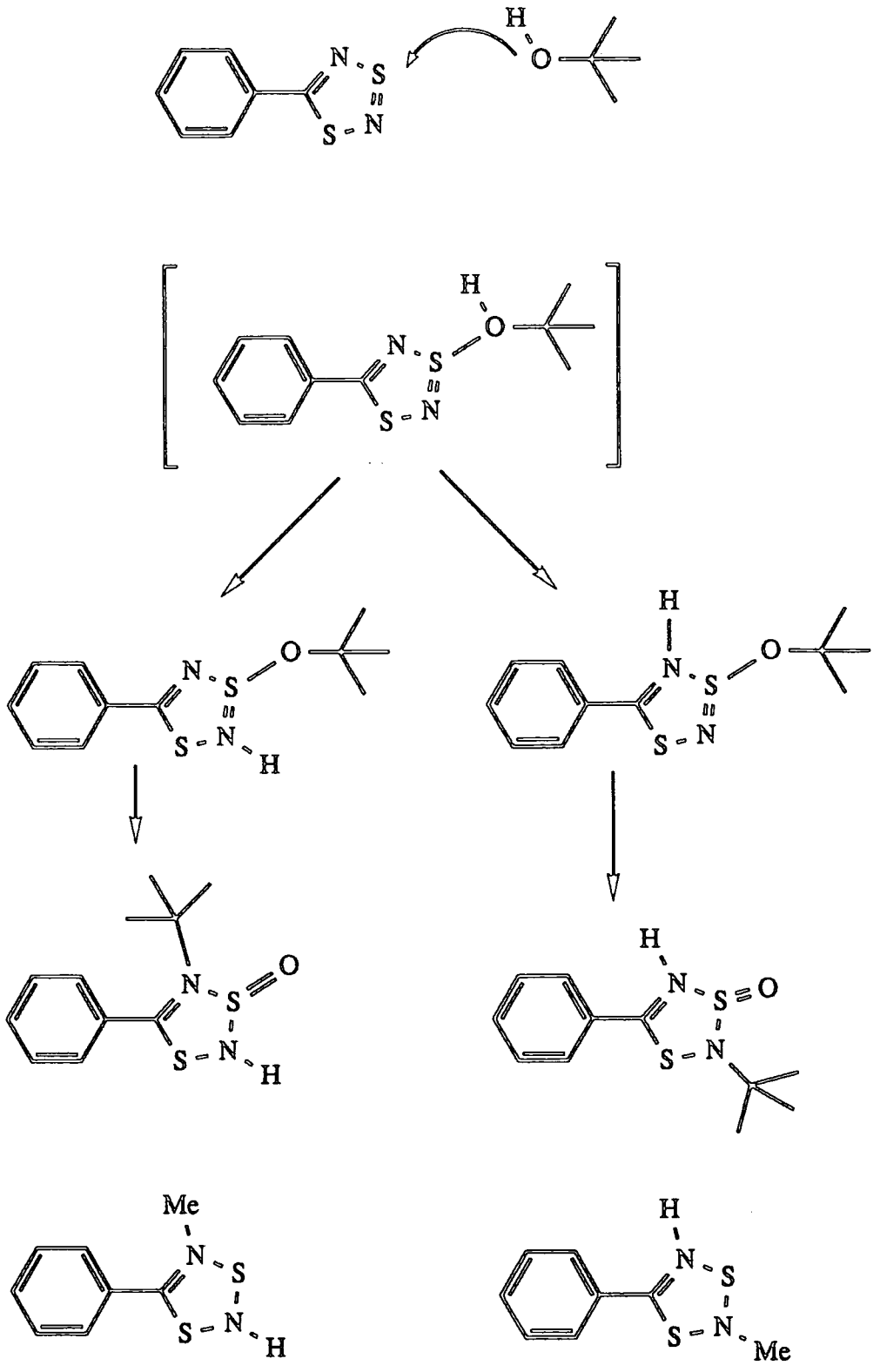
Following this stage it would then appear that a complex series of reactions occurs to give rise to the complex NMR spectra observed. A number of possible reaction products with a scheme for their formation is shown in Scheme 6.2.10.

6.2.4 Conclusions and Suggestions for Further Work

It has been found that 1,3,2,4-dithiadiazolium salts initiate C.R.O.P. of THF, and polymers of high molecular weight and reasonably low polydispersities have been prepared. At present only polymerization in the bulk has been carried out, and since THF polymerization is known to be "living" under suitable conditions, it would be desirable to study the initiation of C.R.O.P. by dithiadiazolium salts under more controlled conditions. Furthermore, a study of a wider range of cationically polymerizable monomers, both cyclic and acyclic, with dithiadiazolium salts is required.

The use of *bis*- and *tris*-(dithiadiazolium) salts as C.R.O.P. initiators has much potential as a route to dendritic and starburst polymers, a group of compounds with great potential as new materials for specialist applications. This would be a very interesting area for further study.

In addition to this, the reaction of dithiadiazolium salts with simple nucleophiles such as water and alcohols has been shown to be surprisingly complex. Much work needs to be done to determine the nature of the complex product mixture formed in the reaction of dithiadiazolium salts with alcohols, and also on the mechanisms of these reactions with nucleophiles. Much interesting synthetic chemistry undoubtedly lies around the corner.



Scheme 6.2.10

Some Suggested Products for The Reaction of

[PhCNSNS][AsF_6] with 2-Methyl-2-Propanol

in 1:1 Ratio

6.3 Experimental

Preparation of [PhCNSNS][AsF_6]

[SNS][AsF_6] (1.43g, 5.35 mmol) was placed in the rear leg of a "dog". Under a counterflow of dry N_2 PhCN (9 ml) was syringed in. The mixture began to give out a considerable amount of heat, and thus the reaction vessel was cooled in a bath of liquid nitrogen and transferred onto the steel vacuum line. Following evacuation of the reaction vessel a small amount of SO_2 was introduced onto the reaction mixture to solubilise [SNS][AsF_6]. The mixture was stirred for 1hr to give a dark blue solution over a dark green crystalline solid. The supernatant was decanted off and the mixture of residual PhCN and SO_2 were removed *in vacuo*. CH_2Cl_2 was introduced and the solid product washed repeatedly to give a yellow, highly crystalline product which was dried *in vacuo*.

Appearance : Bright yellow crystalline solid.

Yield : 1.44g, 3.90 mmol, 73% purified product.

IR (Nujol mull) : vmax 3075w, 2600w, 1600m, 1460s, 1410s, 1350w, 1330w, 1300w, 1280w, 1220w, 1215w, 1190m, 1105w, 1075w, 1000m, 988s, 980sh, 915m, 890m, 840w, 800s, 775s, 710sh, 690vs br, 675s, 650w, 635m, 615w, 587m, 580w, 442m, 400s cm^{-1}

Analysis : Found (required) : C 22.65 (22.71) ; H 1.29 (1.36) ; N 7.60 (7.57) %.

^1H NMR (CD_3CN) : δ 8.32 ppm, d (2H) δ 7.94 ppm dd (1H) δ 7.78 ppm dd (2H)

Reaction of [PhCNSNS][AsF_6] with Water, 1:1 Stoichiometry

[PhCNSNS][AsF_6] (370 mg, 1.0 mmol) was dissolved in dry CH_3CN (5 ml). Under a counterflow of dry N_2 an aliquot of a solution of water in dry CH_3CN (2ml of 0.52 mol dm^{-3} H_2O in CH_3CN, 1.04 mmol H_20 added) was added slowly to the stirred solution of [PhCNSNS][AsF_6]. Stirring was continued for 4 hr, during which time the solution became turbid and paled in colour from yellow to yellow-white, but no precipitation was observed. Removal of solvent gave a pale yellow polycrystalline mass. The material was transferred to a closed extractor and SO_2 was introduced. Cycling of SO_2 gave a pale yellow soluble extract

and an off-white insoluble residue which appeared to be elemental sulphur. The soluble extract was dried *in vacuo*.

Appearance : pale yellow polycrystalline solid.

IR (NUJOL Mull) : ν_{max} 3380s, 3300m, 3220m, 1690w br, 1645sh, 1640s, 1625sh, 1600m, 1580w, 1495w br, 1457s, 1405s, 1350w, 1335m, 1300sh, 1282m, 1215w br, 1200w, 1190w, 1170w, 1135w, 1103w, 1075w br, 1030w, 1000m, 990m, 985sh, 933w, 915w, 890w, 845w, 800s, 785s, 775s, 700vs br, 650w, 635w, 610w, 585w, 575sh, 570w, 565sh, 460w, 400w, 400vs cm^{-1}.

^1H NMR (CD_3CN) : δ10.29 ppm broad unresolved signal : δ8.32 ppm d : δ7.94 ppm dd : δ7.83 ppm multiplet : δ 7.67 ppm dd : δ7.78 ppm dd : δ5.9 ppm 1:1:1 triplet : signals at δ 10.29 ppm and δ 5.9 ppm of approximately equal relative area *viz* approx. 10% of the total area of all the other signals.

^{13}C NMR (decoupled) (SO_2) : 207.3 ppm : 197.0 ppm : 139.7 ppm : 138.5 ppm : 132.4 ppm : 132.3 ppm : 131.6 ppm : 128.4 ppm : 127.2 ppm : 126.8 ppm ($CDCl_3$ external reference).

Mass Spectrum (EI+) : *m/z*, Relative Intensity, Assignment.

183, 1%, $[PhCON(H)S(O)NH]^+$; *181*, 6%, $[PhCNSNS]^+$; *149*, 25%, $[PhCN_2S]^+$; *120*, 20%, $[PhCONH]^+$; *104*, 41%, $[PhCNH]^+$; *103*, 100%, $[PhCN]^+$; *63*, 12%, $[HNSO]^+$; *62*, 5%, $[NSO]^+$.

Reaction of [PhCNSNS][AsF6] with Water, 1:2 Stoichiometry

[PhCNSNS][AsF_6] (370 mg, 1.0 mmol) was dissolved in dry CH_3CN (5 ml). Under a counterflow of dry N_2 an aliquot of a solution of water in dry CH_3CN (4ml of 0.52 mol dm^{-3} H_2O in CH_3CN, 2.08 mmol H_20 added) was added slowly to the stirred solution of [PhCNSNS][AsF_6]. Stirring was continued for 4 hr, during which time the solution became turbid and paled in colour from yellow to white, and precipitation of an off-white solid was observed : this solid appeared to be elemental sulphur. Removal of solvent gave a white non-crystalline mass. The material was transferred to a closed extractor and SO_2 was introduced. Cycling of SO_2 gave a colourless soluble extract and an off-white insoluble residue which appeared to be elemental sulphur. The soluble extract was dried *in vacuo*.

Appearance : white powder.

IR (Nujol mull) : vmax 3380s, 3310s, 3200m, 1685w, 1647s, 1600w, 1580w br, 1495w, 1455s, 1420w, 1405w, 1370w, 1350w, 1335m, 1320w, 1280s, 1245w, 1200w, 1170w, 1135w, 1120w, 1100w br, 1070w, 1030w, 1000w, 985w, 910w br, 835m, 800sh, 790m, 760w, 710-690vs br, 570m, 450sh, 400s cm^{-1}.

^1H NMR (CD_3CN) : δ 10.29 ppm broad unresolved signal : δ 7.83 ppm multiplet : δ 7.65 ppm dd. Small signals also observed at δ 8.35 ppm and δ 7.97 ppm.

Polymerization of Tetrahydrofuran Initiated by 1,3,2,4-Dithiadiazolium Salts

Polymerizations were carried out on neat THF. In a typical experiment a small amount of a dithiadiazolium salt (1-15 mg) was dissolved in THF (2-15 ml) under dry nitrogen and the reaction vessel sealed. Over a period of days, dependent on the nature of the initiator, the solution increased in viscosity, eventually forming a solid gel. To isolate the polymer the reaction vessel was opened up and the gel dissolved in dichloromethane. It was noted that a large amount of solvent (c. 250 ml) was required to dissolve the gel, indicating polymer of high molecular weight. To the polymer solution one fifth part by volume of methanol was added and the solution evaporated to dryness on a rotary evaporator. As dichloromethane was removed the enrichment of the solution in methanol caused precipitation of the polymer as a colourless elastic solid. Samples of poly(thf) initiated by 5-phenyl-1,3,2,4-dithiadiazolium hxafluoroarsenate and 5,5',5''-phenine-1,3,5-tris-(1,3,2,4-dithiadiazolium) hexafluoroarsenate were characterised by GPC, NMR and IR spectroscopy.

Poly(THF) ; [PhCNSNS][AsF_6] as initiator.

M_w (avg) : 389700 g mol^{-1}

M_n (avg) : 198700 g mol^{-1}

Polydispersity Ratio M_w/M_n : 1.962

IR (Polymer film) : ν_{max} 2940s, 2860s, 2800m, 2740w, 1488w, 1470w, 1452m, 1440w, 1417w, 1373m, 1320sh, 1305w br, 1250w, 1215w, 1115vs br, 1030w br, 985w, 965w, 830w br, 750w br, 705w br cm^{-1}

^{13}C NMR : 26.3 ppm, 68.6 ppm (THF) ; 27.2 ppm, 71.3 ppm (poly (THF))

Poly(THF) ; $[C_6H_3$-1,3,5-$(CNSNS)_3][AsF_6]_3$ as initiator.

M_w (avg) : 306300 g mol^{-1}

M_n (avg) : 190000 g mol^{-1}

Polydispersity Ratio M_w/M_n : 1.612

IR (Polymer film) : ν_{max} 3020sh*, 3000m*, 2940s, 2920sh, 2860s, 2800w, 1490w, 1470w, 1450w, 1440w, 1415w br, 1370m br, 1270m*, 1220s*, 1105vs br, 1025w, 960w br, 935w, 890w, 750vs*, 705w, 665m* cm^{-1}

[* : Absorptions assignable to CH_2Cl_2, fromwhich the polymer film was cast]

^{13}C NMR : 24.3 ppm, 66.1 ppm (THF) ; 25.5 ppm, 69.2 ppm (poly (THF))

Reaction of [PhCNSNS][AsF_6] with 2-Methyl-2-propanol, 1:1 Ratio, NMR Tube Reaction

[PhCNSNS][AsF_6] (185 mg, 0.5 mmol) was dissolved in CD_3CN (2 ml) in a "dog" reaction vessel. 2-Methyl-2-propanol (47 ml, 0.5 mmol) was syringed in under a counterflow of dry nitrogen and the mixture was shaken for 5 minutes. A 0.5 ml aliquot of the reaction mixture was then transferred to a ^1H NMR tube, and the spectrum was recorded periodically.

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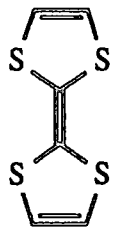
CHAPTER 7

REACTIONS OF $(PhCN_2S_2)_2$ WITH SOME HALOGEN COMPOUNDS

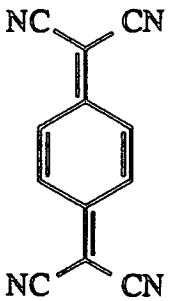
7.1 Introduction

Activated quinones e.g. perhalogenated benzoquinones find widespread use in industry as dehydrogenating agents in the preparation of polycyclic aromatic hydrocarbons. Recently, however, there has been increased interest in the chemistry of these compounds because of their properties as electron acceptors in the preparation of charge - transfer (C.T.) salts.

In 1973 the synthesis of the 1:1 complex of tetrathiafulvalene (TTF) (1) with the ubiquitous acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) (2) was reported[1], and this compound showed a semiconductor - metal transition at 66K.



1

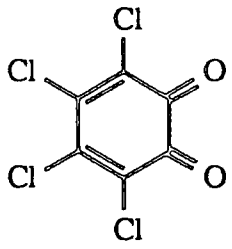


2

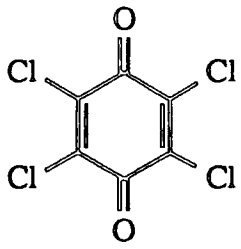
The crystal structure of the complex[2] consisted of homologous stacks of [TTF] radical cations and [TCNQ] radical anions. This compound was the most powerful conductor of any organic compound known up until that time, and as a result, interest in such materials mushroomed.

C.T. complexes of activated quinones such as *o*-chloranil (3) and *p*-chloranil (4) with a range of donors including polycyclic aromatic hydrocarbons[3,4], amines[5], phenols[6] and even dimethyl sulphoxide[7] have been reported and extensively studied. Particularly

interesting are a series of polymeric C.T. complexes, with chloranil associated with a polymeric matrix, for example silylated polyacetylene[8], in which charge transfer occurs between the polymer backbone and chloranil to produce radical centres.



3



4

In the light of the recent interest in such donor-acceptor materials it was felt that the stable dithiadiazolyl free radicals might form interesting charge-transfer compounds with suitable acceptors. Previous work in this laboratory[9] on the reaction between $(PhCN_2S_2)_2$ and TCNQ produced a mixture of products with a range of $(PhCN_2S_2)$ / TCNQ ratios. It was decided to attempt similar reactions with *o*-chloranil as the acceptor in an effort to prepare better - defined products.

Charge-transfer complexes of both *o*- and *p*-chloranil with aromatic hydrocarbons had been prepared[10] by grinding together an equimolar mixture of the quinone and the hydrocarbon, with the charge-transfer salt forming on intimate contact between the donor (hydrocarbon) and the acceptor (*o*/*p*-chloranil). As a preliminary synthetic strategy it was hoped that the same method, using 4-phenyl-1,2,3,5-dithiadiazolyl dimer $(PhCNSSN)_2$ with an activated quinone, might produce similar 1:1 charge-transfer salts $[PhCNSSN^+][Q\cdot^-]$ where Q is the radical anion derived from the activated quinone.

7.2 Results and Discussion

7.2.1 Reaction of $(PhCN_2S_2)_2$ with 3,4,5,6-Tetrachloro-1,2-benzoquinone (*o*-Chloranil)

Grinding together an equimolar mixture of $(PhCN_2S_2)$· and *o*-chloranil in the solid state to give an intimate mixture did not produce a reaction. The infrared spectrum of the mixture is shown in Fig. 7.2.1, with all bands assignable to either *o*-chloranil (*) or $(PhCN_2S_2)_2$ (+). It was found that the reaction of $(PhCN_2S_2)_2$ with *o*-chloranil at room temperature in toluene did not produce a charge-transfer salt, but instead a dechlorination reaction occurred to give $[PhCN_2S_2][Cl]$ as one of the products. The infrared spectrum of this material was found to be identical to that of a pure sample[11] and is shown in Fig. 7.2.2.

The other product, a bright red powder, derived from *o*-chloranil, was found to be of low solubility in a range of solvents and thermally stable to above 300°C. Its infrared spectrum is shown in Fig. 7.2.3.

The mass spectrum of this product showed a series of peaks at *m/e* = 420-424, consistent with a product of symmetrical coupling following halide abstraction. A possible explanation for this is that the reaction proceeds *via* abstraction of halide radical *ortho* with respect to the carbonyl oxygens (due to the combined electron-withdrawing effects of the *ortho* carbonyl group and the adjacent C-Cl bond) to give $[PhCN_2S_2][Cl]$ and a quinone-derived radical (5) which then undergoes dimerization to give a coupled product (6). This scenario is summarized in Scheme 7.2.1.

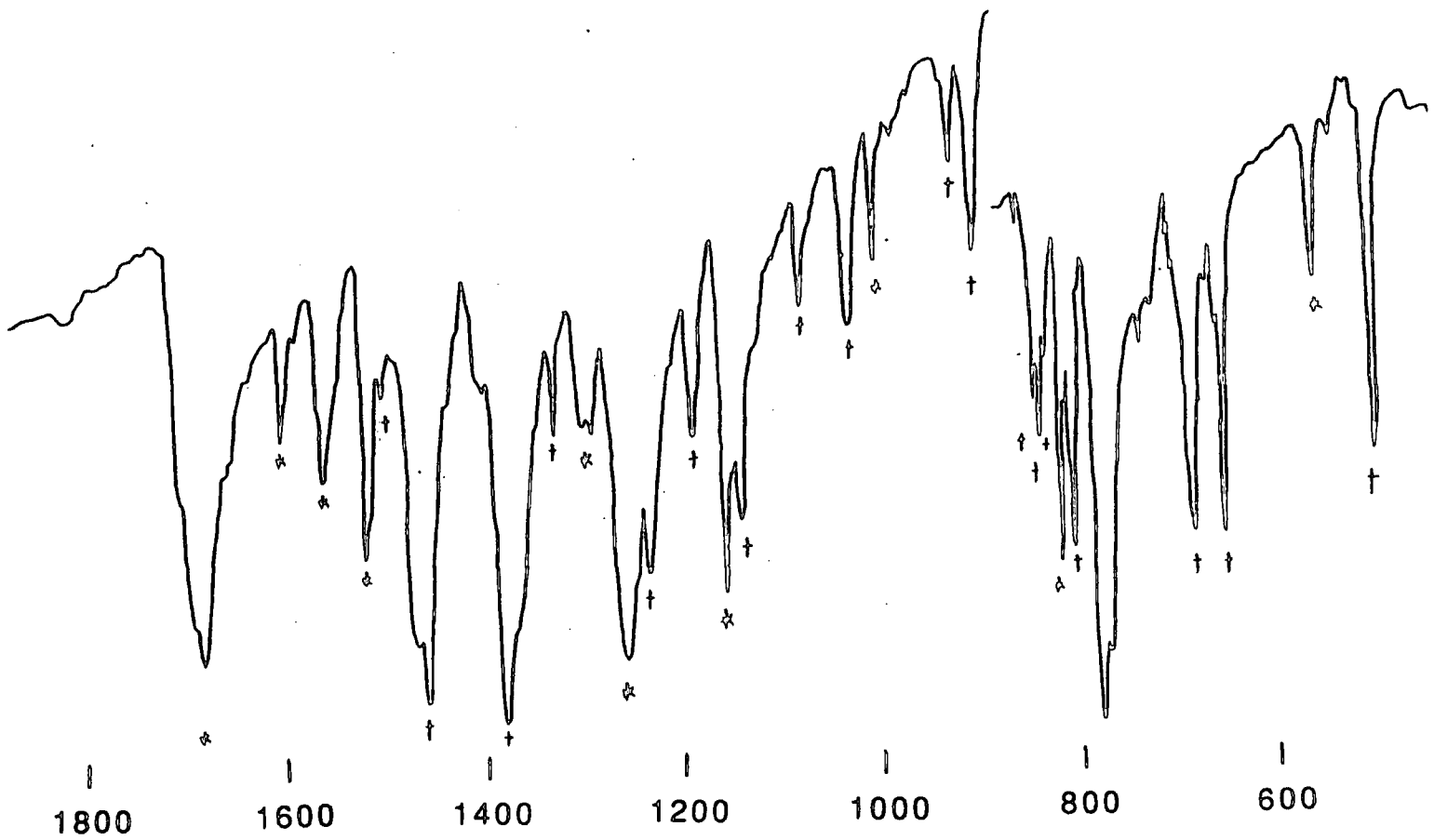


Fig. 7.2.1

IR spectrum (Nujol mull) of the solid-state finely-ground equimolar mixture of (PhCNSSN)· + *o*-chloranil (3)

(*) : bands assignable to 3

(+) : bands assignable to (PhCNSSN)·

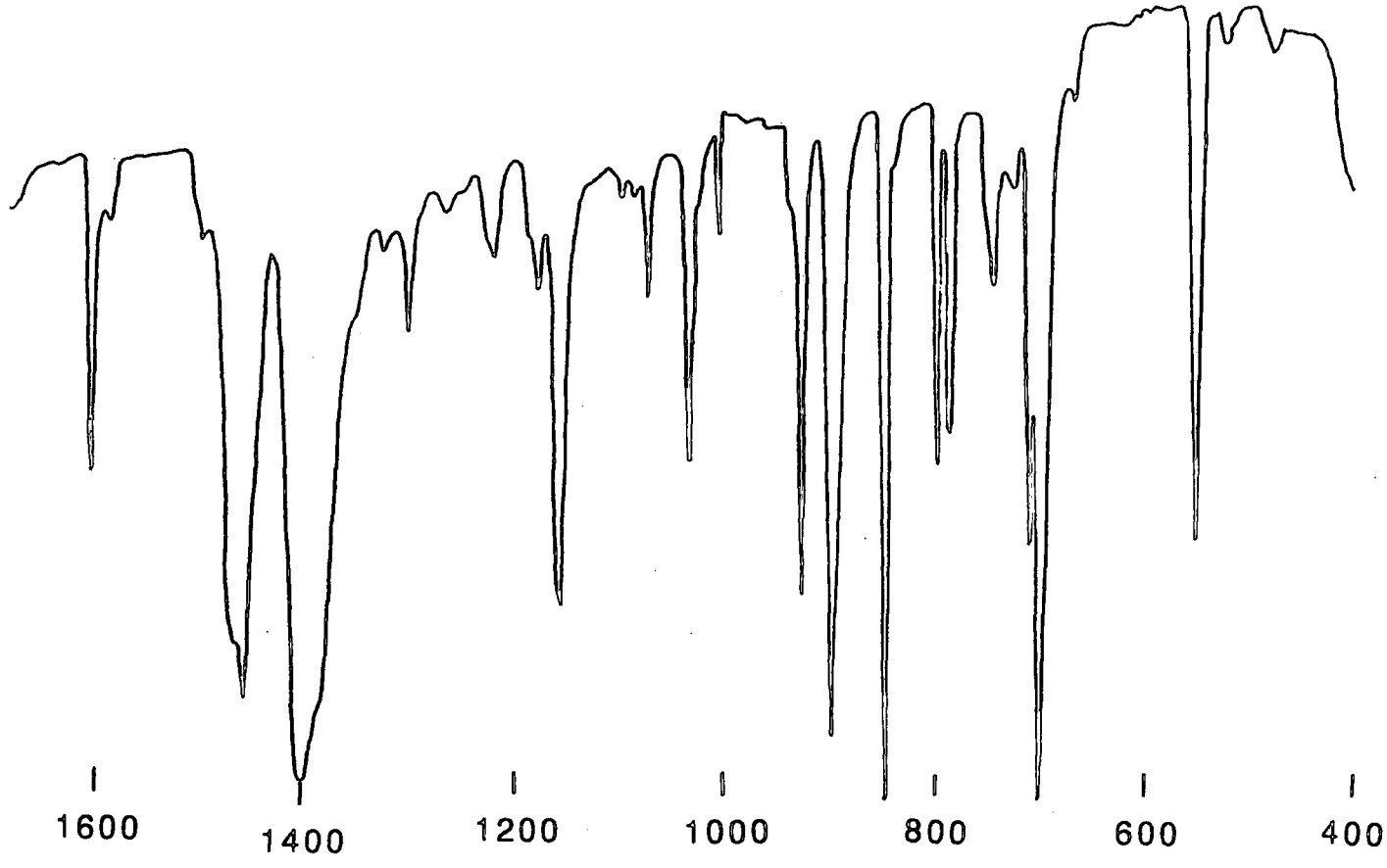


Fig. 7.2.2

IR spectrum (Nujol mull) of [PhCNSSN]Cl

from the reaction (PhCNSSN)· + *o*-chloranil (3)

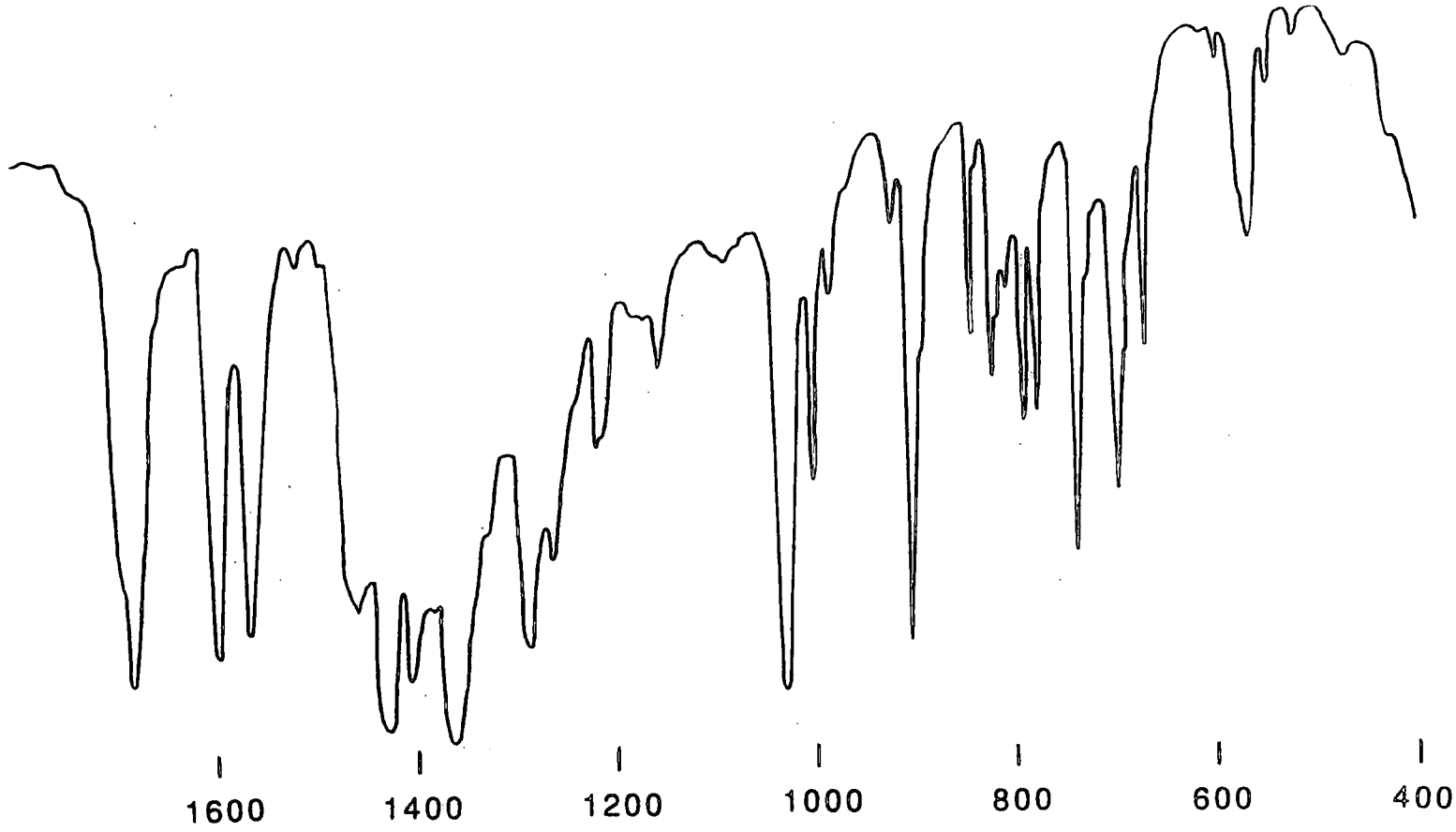
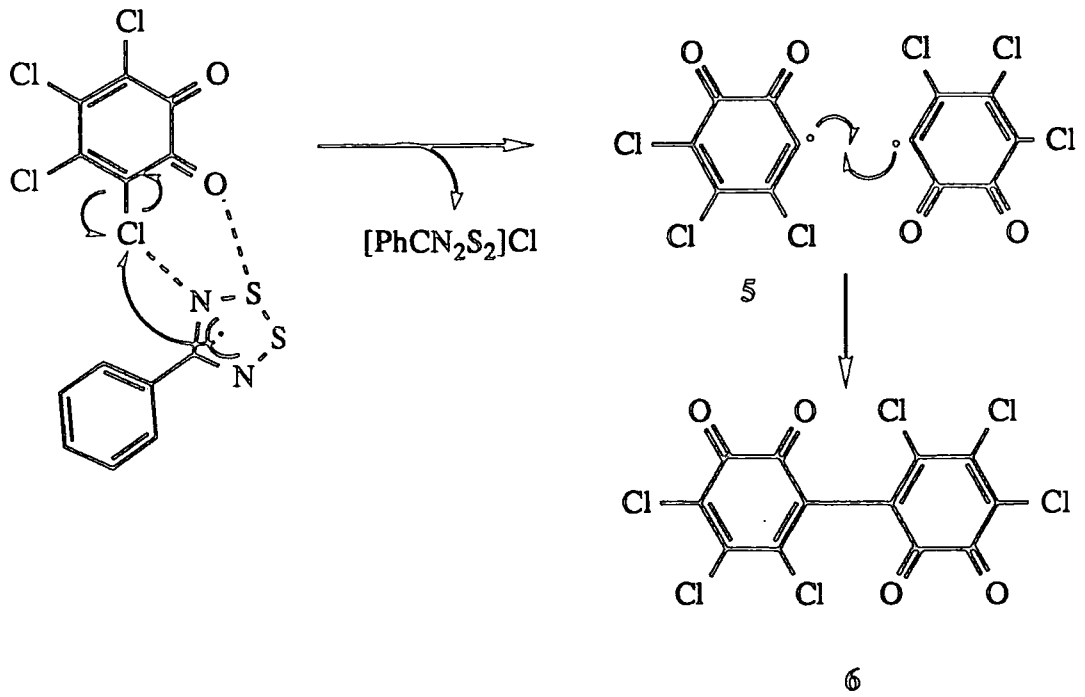


Fig. 7.2.3

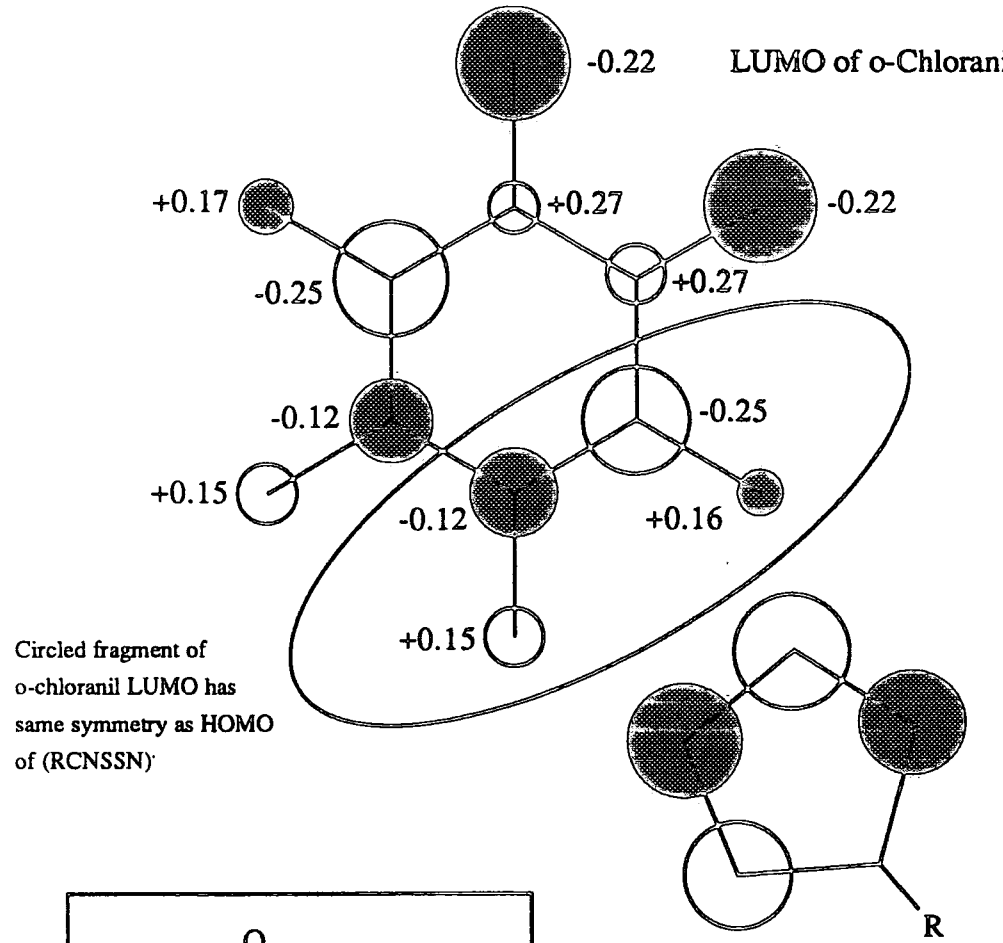
IR spectrum (Nujol mull) of the chloranil-derived product from the reaction (PhCNSSN)· + *o*-chloranil (3)

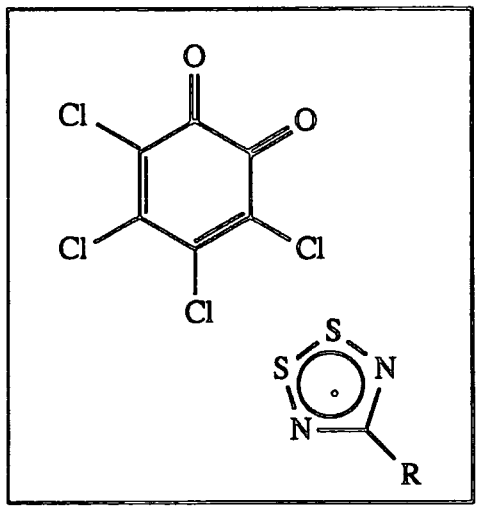


Scheme 7.2.1

Suggested reaction mechanism for the dechlorination and coupling of *o*-chloranil by $(PhCNSSN)_2$

PM3 molecular orbital calculations using X-Ray crystal structure data[12] for *ortho*-chloranil produce a LUMO as shown in Fig. 7.2.4. In the same diagram the SOMO of $(PhCN_2S_2)\cdot$ is shown. It can be seen that the LUMO of *o*-chloranil has a plane of symmetry whilst the SOMO of the radical is asymmetric. Thus head-to-head or head-to tail (*cf.* rearrangement of 1,3,2,4-dithiadiazolyls to 1,2,3,5-dithiadiazolyls) interaction of the two species is forbidden on the grounds of orbital symmetry. However, from Fig. 7.2.4 it can be seen that the fragment of the LUMO comprising the carbons *ortho-* and *meta-* with respect to the carbonyl groups and their chloro-substituents is of the same symmetry as the SOMO of the radical. The two species could therefore interact *via* orbital overlap as shown in Fig. 7.2.5. In this arrangement the chlorines lie above the nitrogens in the radical, and in the dithiadiazolyl radical the nitrogens accommodate the unpaired spin[13]. Electron flow from

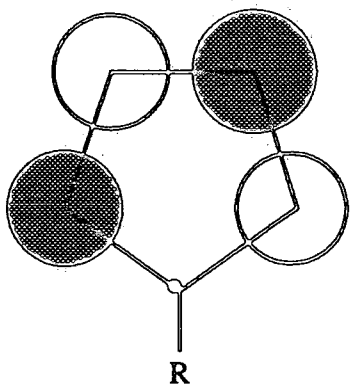


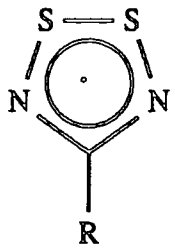


PM3 Calculation of the LUMO of o-chloranil with net atomic charges ; Note that the C-Cl bonds ortho- with respect to the carbonyl groups are more polar than the meta- C-Cl bonds ; The HOMO of the 1,2,3,5 - (dithiadiazolyl) radical is also shown ; the HOMO of the radical and the fragment of the LUMO of o-chloranil circled in the diagram are of the sam symmetry, and may interact to bring about dehalogenation of the quinone.

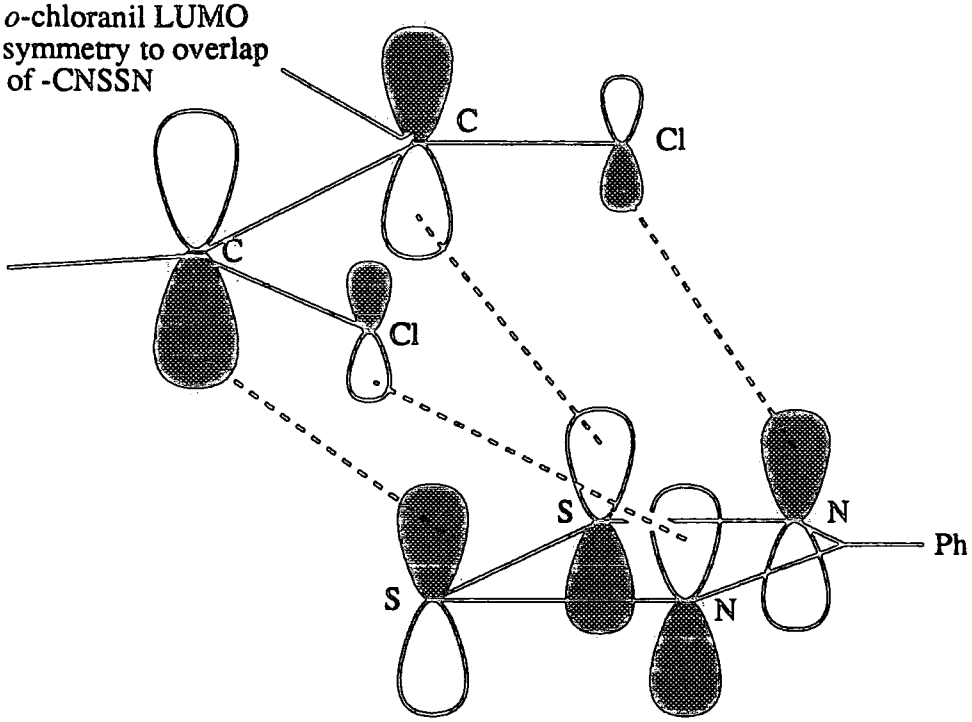
Fig. 7.2.4 PM3 LUMO of *o*-chloranil with net atomic charges

HOMO of -CNSSN





Fragment of *o*-chloranil LUMO with correct symmetry to overlap with HOMO of -CNSSN



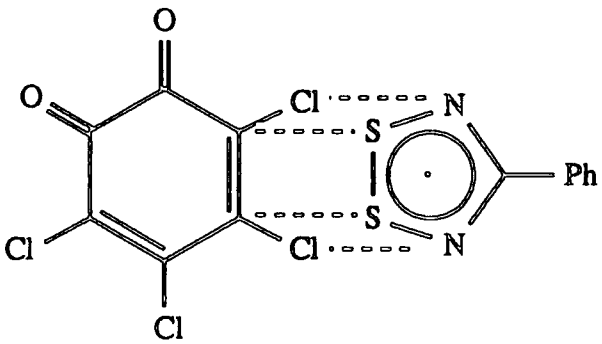


Fig. 7.2.5

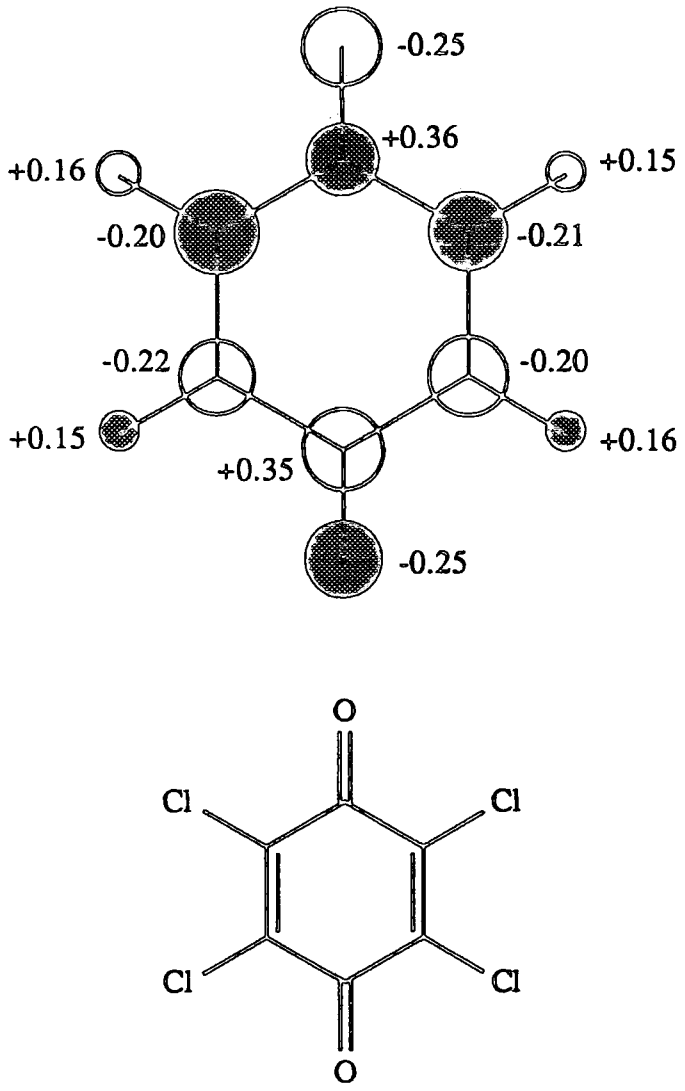
Suggested mecanism for the interaction of o-chloranil and (PhCNSSN)·

the SOMO of the radical occurs, into a fragment of the chloranil LUMO which is antibonding with respect to the C-Cl bond, and thus this bond will lengthen and weaken. This may facilitate the scission of the C-Cl bond by the radical.

It is interesting to note that according to the MO calculations the chlorines in *o*-chloranil carry a net positive charge, with their associated carbons carrying a negative charge. The net atomic charges from PM3 calculations are shown in Fig. 7.2.4. It can be seen that the C-Cl bonds *ortho-* with respect to the carbonyl groups are considerably more polar than the corresponding bonds in the *meta-* position.

It could thus be predicted that the *ortho-* chlorines are preferentially removed by dithiadiazolyl radical. It may be that the initial interaction of *o*-chloranil and dithiadiazolyl radical is due to coulombic attraction : the sulphurs in the radical carry a net positive charge, whilst the nitrogens carry a negative charge, and the dithiadiazolyl ring thus possesses a dipole. PM3 calculations show that (as expected) *o*-chloranil possesses a large dipole with the "end" of the molecule incorporating the carbonyl groups bearing the negative charge and the "end" comprising the C-Cl bonds bearing a net positive charge.

o-Chloranil is well-known as an electron acceptor, both in the preparation of C.T. materials, and also in synthesis of other materials via C.T. intermediates. Diphenyl disulphides form C.T. complexes with chloranil[14] and undergo oxidation to sulphonium cations. These cations then undergo electrophilic substitution reactions at the aromatic groups of Ph_2S_2, and have provided a route to ultrapure poly (*p*-phenylene sulphide)s.



PM3 Calculation of the LUMO of *p*-chloranil with net atomic charges, showing the equivalence of the C-Cl bonds, unlike *o*-chloranil, where the C-Cl bonds ortho- with respect to the carbonyl groups are more polarised than the meta- C-Cl bonds.

Fig. 7.2.6 PM3 LUMO of *p*-chloranil with net atomic charges

7.2.2 Reaction of $(PhCN_2S_2)_2$ with 2,3,5,6-Tetrachloro-1,4-benzoquinone (*p*-Chloranil)

It was found that the same reaction using *p*-chloranil did not work, even in refluxing toluene. Work- up of the reaction mixture gave highly crystalline unreacted *p*-chloranil. The reasons for this are not clear. It is known[10] that *p*-chloranil acts as a dehydrogenation agent at a rate 1500-2000 times slower than *o*-chloranil. PM3 MO calculations using X-Ray crystal structure data for *p*-chloranil[15] produce a LUMO as shown in Fig. 7.2.6. As in the case of *o*-chloranil the chlorine atoms bear a net positive charge, but as a result of the symmetry of the molecule there is no net dipole.

p-Chloranil has 3 orthogonal two-fold axes of rotation ($3C_2$) whereas *o*-chloranil has only one. *p*-Chloranil also possesses two vertical mirror planes and one horizontal plane ; *o*-chloranil has one vertical and one horizontal plane. Finally, the *p*-chloranil molecule is centrosymmetrical, while *o*-chloranil is non-centrosymmetric. As a result of its high symmetry the *p*-chloranil molecule has no net dipole, which is not the case for *o*-chloranil ; its two carbonyl groups are adjacent and the molecule thus possesses a dipole.

Furthermore, all the chlorines in *p*-chloranil are equivalent and hence there is no polarization of one C-Cl bond relative to the others. The chlorines in *o*-chloranil occupy two different environments ie positions 3 / 6 with one neighbouring chlorine and one neighbouring carbonyl group, and positions 4 / 5 , with two neighbouring chlorines. Thus it would be predicted that a C-Cl bond in one of these two environments would be polarized to a different extent relative to a bond in the other. As a result of this one pair of C-Cl bonds must be stronger than the other pair and *vice versa*.

7.2.3 Reaction of $(PhCN_2S_2)_2$ with 2,3,5,6-Tetrafluoro-1,4-benzoquinone

$(PhCN_2S_2)_2$ did not react with 2,3,5,6-tetrafluoro-1,4-benzoquinone, and it would be reasonable to predict that reaction with the *ortho* - analogue would not produce a reaction, owing to the strength of the C-F bond.

It was hoped that in the light of the reaction with *o*-chloranil, this might provide a method to prepare the as yet elusive dithiadiazolium fluorides. In previous work by I.B. Gorrell in this laboratory[9], the reaction between $(PhCN_2S_2)_2$ and AgF_2 in CCl_4 gave a dark green solid with chemical analysis consistent with the formula $[PhCN_2S_2][F]$. However, heating this material under vacuum in a sublimation vessel gave $(PhCN_2S_2)_2$ as sublimate and a yellow-brown residue, which showed IR bands characteristic of both dithiadiazolium and dithiadiazolyl species. Gorrell concluded that mixed valence species e.g. $[PhCN_2S_2]_2[F]$ and $[PhCN_2S_2]_3[F]$, analogous to the chlorides $[PhCN_2S_2]_2[Cl]$ and $[PhCN_2S_2]_3[Cl]$[16].

Mass spectral analysis of the sublimate from the reaction of $(PhCN_2S_2)_2$ with AgF_2 provided evidence for this, with peaks observed at 181 ($[PhCN_2S_2]^+$), 200 ($[PhCN_2S_2F]^+$) and 381 ($[(PhCN_2S_2)_2F]^+$). The presence of the peak at 200 implies that the dithiadiazolium fluoride is more likely to incorporate fluorine covalently bonded to the CN_2S_2 ring, rather than as fluoride ion. A reliable general synthetic route to dithiadiazolium fluorides still remains elusive, however.

Part of the problem is due to insufficient characterization of the products of these reactions. Recent work in this laboratory[17], using specially-dried Me_4NF as a metathesis reagent with $[PhCNSNS][AsF_6]$ gave a dichroic red / green crystalline solid with microanalyses consistent with the formula $[PhCN_2S_2][F]$, but the crystals formed were unsuitable for single crystal structure determination, and so the full character of this compound remains

uncertain. The colour of the compound, similar to that of the dithiadiazolyl radicals, suggests that the fluorine may be present covalently bonded to the CN_2S_2 ring rather than as fluoride ion, and in the mass spectrum the peak of highest mass occurs at m/e = 200, corresponding to ($[PhCN_2S_2F]^+$), consistent with a covalent species. The same reaction using the isomeric 1,2,3,5-dithiadiazolium salt [PhCNSSN][AsF_6] did not yield an isolable product, and the reasons for this are unclear. Repeated attempts at these reactions with full characterization of products should provide much information on these most elusive of dithiadiazolium salts.

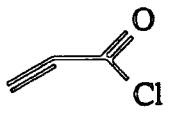
7.2.4 Reactions of $(PhCN_2S_2)_2$ with Other Halogen Compounds

$(PhCN_2S_2)_2$ has already been shown to be a dehalogenating agent, and dithiadiazolium salts are readily prepared from dithiadiazolyl radicals by reaction with elemental halogens[11], and also by halogenated compounds e.g. SO_2Cl_2 and $SOCl_2$ to give dithiadiazolium chlorides[11] and recently by ring contraction[18] reactions with sulphur-nitrogen cationic species to give interesting mixed valence species, *viz* $[(PhCN_2S_2)_2Cl][S_3N_3]$ with $[S_5N_5][Cl]$ and $[PhCN_2S_2][S_3N_2][Cl]$ with $[S_4N_3][Cl]$.

Carbon-halogen bond scission by dithiadiazolyls has already been observed[9], with the formation of butane-2,3-dione and 4-phenyl-1,2,3,5-dithiadiazolium bromide from the reaction of $(PhCN_2S_2)_2$ with ethanoylbromide.

From this work it was found that $[PhCN_2S_2][Cl]$ was obtained by treatment of $(PhCN_2S_2)_2$ with oxalyl chloride in a vigourous reaction involving the liberation of a gas, likely to be CO. Reaction with benzoyl chloride proceeded only very slowly, and no reaction was observed between $(PhCN_2S_2)_2$ and 4-bromobenzonitrile. It is therefore predicted that for the dehalogenation of organic compounds by dithiadiazolyl radicals to occur efficiently the halogen must be in an electron-withdrawing environment so as to weaken the carbon-halogen bond, and also that the reaction will occur faster for bromo-compounds than for chloro-compounds, owing to the weaker C-Br bond.

$(PhCNSSN)_2$ was found to react very slowly with acryloyl chloride (propene caboxylic acid chloride, 7). Addition of 7 to a vigourously-stirred toluene solution of $(PhCNSSN)_2$ initiated a slow reaction, with small deposits of a yellow-orange powder (presumably [PhCNSSN]Cl) appearing over the course of three weeks. It was also noticed that the reaction solution increased in viscosity, possibly due to polymerization of 7 initiated by $(PhCNSSN)_2$.



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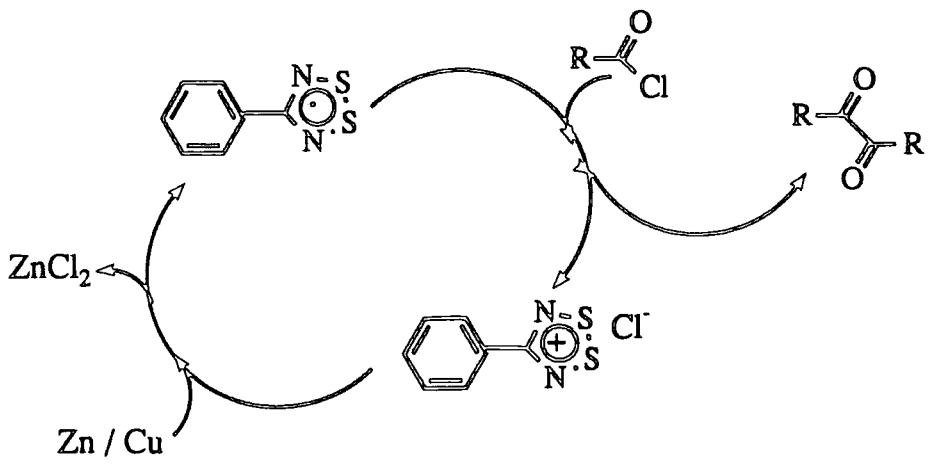
7.2.5 Mechanistic Aspects

The reduction of 1,2,3,5-dithiadiazolium halide salts to 1,2,3,5-dithiadiazolyl radicals is a facile process, and can be effected by many different reducing agents e.g. Zn, Mg etc. This work has shown that the reverse reaction (halide abstraction) with formation of symmetrical coupling products is also facile, and thus dithiadiazolyl radicals have potential as mild dehalogenation catalysts. Scheme 7.2.2 shows a suggested catalytic cycle.



Scheme 7.2.2

Suggested catalytic cycle

involving $(PhCNSSN)_2$ in the

coupling of acyl chlorides to give

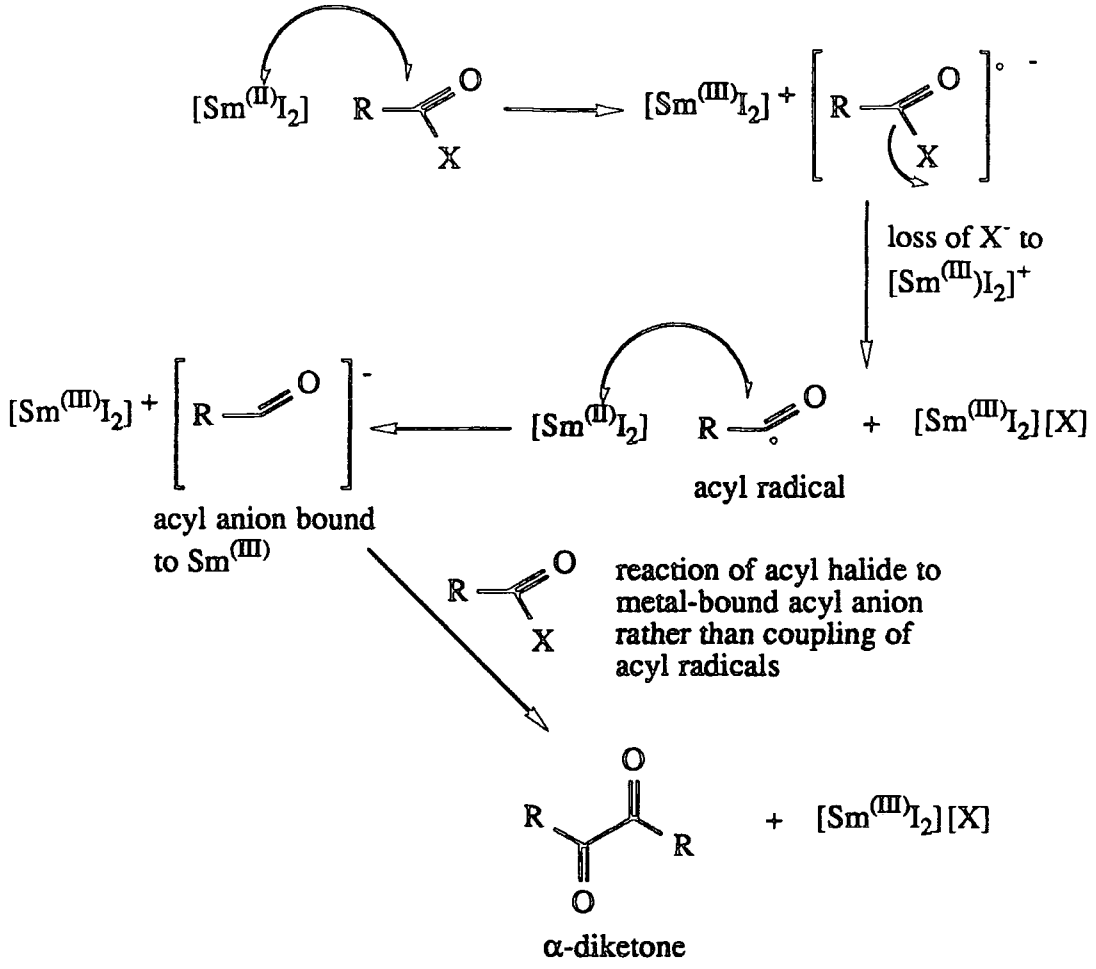
α-diketones

Reaction between the halogenated substrate and the 1,2,3,5-dithiadiazolyl radical (present in *catalytic* amount) may take place to give the 1,2,3,5-dithiadiazolium salt and the coupling product. The dithiadiazolium salt would then be reduced by a reductive dehalogenating agent e.g. a mild reducing metal (present in stoichiometric amount with respect to the substrate) to regenerate the dithiadiazolyl radical, and thus the process would repeat itself until all the substrate was used up. The resulting dithiadiazolium salt would be reduced by the remaining reducing agent, leaving the radical present at the end of reaction.

Various reagents are available for effecting symmetrical coupling reactions by halogen abstraction eg Pd-catalysed systems using electrolysis[19], tin compounds[20], and non-

catalysed systems utilising finely-divided metals[21] but many of these are either highly toxic e.g. pyrophoric lead[22] or expensive (e.g. diiodosamarium[23]). The preparation of α-diketones from acyl halides by diiodosamarium is thought to proceed via a mechanism in which coupling of acyl radicals following halide abstraction is not a key process[23,24]. See Scheme 7.2.3.

In the first step of the reaction electron transfer from SmI_2 to the acyl halide occurs to give a radical anion (RCOX) which rapidly decomposes to give halide anion and the acyl radical $(RCO)\cdot$. In the next stage, rather than coupling of two acyl radicals to give the α-diketone, it is thought that the acyl radical undergoes reduction by SmI_2 to give acyl anion $[RCO]^-$ bound to $[SmI_2]^+$. This acyl anion equivalent species is then attacked by acyl halide to give the α-diketone and SmI_2X. It is debatable that an analogous mechanism occurs in the reaction between $(PhCN_2S_2)_2$ and *o*-chloranil, since the initial electron transfer from $(PhCN_2S_2)\cdot$ to *o*-chloranil would give the dithiadiazolium salt of the chloranilide radical anion, which is a stable species[3,4,7], and would be unlikely to dechlorinate to give chloride ion and the derived radical. In this case the reaction may be a concerted process.



Scheme 7.2.3

Preparation of α-diketones from acyl halides using diiodosamarium (after Ref. 23)

7.3 Experimental

Attempted solid-state reaction of $(PhCN_2S_2)_2$ with 3,4,5,6-Tetrachloro-1,2-benzoquinone (o-Chloranil)

$(PhCN_2S_2)_2$ (362 mg, 1.0 mmol) and 3,4,5,6-tetrachloro-1,2-benzoquinone (492 mg, 2.0 mmol) were placed together in an agate mortar and ground together thoroughly over a period of 15 minutes inside the glove box. A small amount of the mixture was mixed with Nujol to make a mull, and spread out on KBr IR plates. All bands in the resulting spectrum were assignable to either *o*-chloranil or $(PhCN_2S_2)_2$.

Reaction of $(PhCN_2S_2)_2$ with 3,4,5,6-Tetrachloro-1,2-benzoquinone (o-Chloranil)

$(PhCN_2S_2)_2$ (362 mg, 1.0 mmol) and 3,4,5,6-tetrachloro-1,2-benzoquinone (492 mg, 2.0 mmol) were placed together in a Schlenk vessel and dissolved in toluene (10 ml). The reaction mixture was stirred at room temperature for 3 days, during which time a bright yellow precipitate formed under a red solution. The supernatant was removed by filtration and the precipitate was washed with fresh toluene (3 x 5 ml) and dried *in vacuo*. This product was identified as $[PhCN_2S_2][Cl]$ by infared spectroscopy :

IR (Nujol Mull) : ν_{max} 1790w br, 1740w br, 1680w br, 1603m, 1585w, 1500w, 1455s, 1400s, 1320w, 1300w, 1260w, 1250w br, 1215w br, 1185sh, 1175w, 1152m, 1095w, 1082w, 1070w, 1030m, 1025sh, 935sh, 923m, 895s, 845s, 835sh, 795m, 780m, 740w, 705m, 695s, 660w, 550m, 520w, 470w cm^{-1}.

The filtrate was dried *in vacuo* to yield a dark red powder.

IR (Nujol Mull) : ν_{max} 1690sh, 1670s, 1595s, 1565s, 1520w, 1425s br, 1405s, 1360s br, 1335sh, 1285s, 1263m, 1220w, 1215sh, 1157w, 1090w br, 1030s, 1003m, 985w, 922w, 905s, 895sh, 845m, 822m, 820sh, 805w, 790m, 780m, 740m, 697m, 670m, 600w, 580sh, 570m br, 550w, 520w, 470w, 425sh cm^{-1}.

Mass spectrum (EI+) : Peaks at *m/e* = 420-424, corresponding to a fragment of empirical formula $(C_6Cl_3O_2)_2$: Also peaks at *m/e* = 181 ($[PhCNSSN]^+$), 135 ($[PhCNS]^+$) and 103 ($[PhCN]^+$) consistent with residual $(PhCNSSN)_2$.

Reaction of $(PhCN_2S_2)_2$ with 2,3,5,6-Tetrachloro-1,4-benzoquinone (p-Chloranil)

$(PhCN_2S_2)_2$ (362 mg, 1.0 mmol) and 2,3,5,6-tetrachloro-1,4-benzoquinone (492 mg, 2.0 mmol) were refluxed in toluene (10 ml) under an atmosphere of dry nitrogen for 12 hours. Upon cooling the reaction mixture a yellow-green crystalline precipitate formed. The crystals were washed with cold toluene (5 ml) and were identified as unreacted *p*-chloranil from the infrared spectrum :

IR (Nujol Mull) : spectrum identical with spectrum of recrystallized *p*-chloranil.

ν_{max} : 1690sh, 1680vs, 1653s, 1585sh, 1570s, 1550w, 1490m, 1370w, 1260s, 1238m, 1210w, 1110vs br, 180sh, 970w br, 915w, 907m, 845w br, 790sh, 755s, 710vs, 700w, 460w cm^{-1}

Analysis : Found : C 29.29% : *p*-chloranil requires C 29.31%

Reaction of $(PhCN_2S_2)_2$ with 2,3,5,6-Tetrafluoro-1,4-benzoquinone

$(PhCN_2S_2)_2$ (362 mg, 1.0 mmol) and 2,3,5,6-tetrafluoro-1,4-benzoquinone (360 mg, 2.0 mmol) were stirred together at room temperature in toluene (5 ml). No reaction was observed after three weeks.

Reaction of $(PhCN_2S_2)_2$ with Oxalyl Chloride $(COCl)_2$

$(PhCN_2S_2)_2$ (120 mg, 0.67 mmol) was dissolved in toluene (2 ml) and stirred vigourously. Oxalyl chloride (2ml, excess) was syringed in dropwise. Reaction occurred instantly with evolution of gas (probably CO) and formation of a bright yellow precipitate. The solution rapidly became colourless as $(PhCN_2S_2)_2$ was used up in the reaction. The supernatant was filtered off and the precipitate washed with cold toluene, followed by

drying *in vacuo*. The precipitate was identified by infrared spectroscopy as $[PhCN_2S_2][Cl]$ with some additional carbonyl-type absorptions, probably due to residual unreacted oxalyl chloride. Yield 134 mg, 0.62 mmol, 92% (recovered).

Reaction of $(PhCN_2S_2)_2$ with Benzoyl Chloride PhCOCl

$(PhCN_2S_2)_2$ (181 mg, 0.5 mmol) was dissolved in toluene (10 ml). Benzoyl chloride (1ml, excess) was syringed in and the mixture stirred. Reaction occurred very slowly, with precipitation of a small amount of a yellow precipitate over a period of four weeks. The reaction was abandoned.

Reaction of $(PhCN_2S_2)_2$ with Acryloyl Chloride CH_2=CHCOCl

$(PhCN_2S_2)_2$ (482 mg, 1.33 mmol) was dissolved in toluene (2 ml). Acryloyl chloride (0.25 ml, 278 mg, 3.1 mmol) was added dropwise with stirring. Reaction occurred over a period of 3 weeks to give a yellow-orange precipitate of $[PhCN_2S_2][Cl]$, and the mixture also increased in viscosity, suggesting that polymerization of the acryloyl chloride had occurred.

Reaction of $(PhCN_2S_2)_2$ with 4-Bromobenzonitrile

$(PhCN_2S_2)_2$ (181 mg, 0.5 mmol) and 4-bromobenzonitrile (182 mg, 1.0 mmol) were stirred together at room temperature in toluene (2 ml) for two weeks. No precipitation of a product e.g. $[PhCN_2S_2][Br]$ was observed.

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APPENDIX 1

THE X-RAY CRYSTAL STRUCTURE OF 4-(4-CHLOROPHENYL)-1,2,3,5-DITHIADIAZOLIUM HEXAFLUOROARSENATE (V)

A.1.1 Preparation and Crystal Growth

[4-Cl-C_6H_4CNSSN][AsF_6] was prepared by the metathesis of [4-Cl-C_6H_4CNSSN][Cl] with $AgAsF_6$ in liquid SO_2, using a "dog" reaction vessel. The soluble product was separated from insoluble AgCl by filtration. Yield 97%.

Crystals suitable for X-Ray structure determination were grown by slow evaporation of a solution in liquid SO_2. The solution was made up in one leg of a "dog" and tap water was run slowly over the other leg to provide a temperature gradient. The resulting crystals were carefully dried in vacuo to minimize crystal shattering during solvent removal. Suitable crystals were picked in the glove box to prevent decomposition. Crystals were mounted in Lindemann capillaries and checked for quality by precession photography. The structure of a suitable crystal was determined by Dr. David Ando, S.E.R.C. Crystallography Service, Queen Mary College, London.

A.2.2 [4-Cl-C_6H_4-CNSSN][AsF_6] Structural Data

TABLE A1.1 : Crystal Data, Data Collection and Structural Refinement

CRYSTAL DATA		DATA COLLECTION	
Mol. Wt.	404.62	temperature	R.T
a (Å)	11.921 (1)	total data measured	10508
b (Å)	8.237 (3)	total data unique	3437
c (Å)	13.077 (4)	total data observed	2570
α (deg .)	90.0	significance test	$F(0) > 3\sigma F(0)$
β (deg .)	99.55 (1)		
γ (deg .)	90.0		
V ($Å^3$)	1266.28	REFINEMENT	
System	Monoclinic	No. of parameters	173
Space Group	$P2_1 / a$	Final R	0.070
D (calc, g/cm^3)	2.12	Final RG	0.069
Z	4		
F (000)*	784		
Radiation	Mo Kα		
λ	0.71069 Å		
μ cm^{-1}	32.64		

[* : F(000) = No. of Electrons per Unit Cell]

TABLE A1.2 : Atomic Coordinates for [4-Cl-C_6H_4CNSSN][AsF_6]

Atom	X/A	Y/B	Z/C
As	0.40690 (6)	0.13818 (8)	0.14463 (5)
F(1)	0.47160 (69)	0.27725 (69)	0.22582 (50)
F(2)	0.33527 (69)	0.00148 (72)	0.06222 (62)
F(3)	0.40138 (80)	0.01833 (83)	0.24595 (52)
F(4)	0.40709 (80)	0.25568 (83)	0.04093 (44)
F(5)	0.52621 (55)	0.04782 (114)	0.13279 (60)
F(6)	0.28473 (59)	0.23120 (117)	0.15492 (65)
Cl	-0.32502 (20)	0.11619 (32)	0.38653 (16)
S(1)	0.24279 (16)	0.13453 (28)	0.84482 (17)
S(2)	0.12536 (17)	0.13240 (26)	0.93874 (15)
N(1)	0.15408 (49)	0.13828 (77)	0.73994 (47)
N(2)	0.01853 (51)	0.13325 (73)	0.84834 (44)
C(1)	0.04505 (53)	0.13458 (75)	0.75233 (50)
C(2)	-0.04548 (53)	0.13068 (76)	0.66129 (49)
C(3)	-0.02488 (67)	0.18117 (94)	0.56540 (59)
C(4)	-0.11162 (72)	0.17726 (103)	0.48127 (57)
C(5)	-0.21686 (62)	0.11926 (91)	0.49203 (56)
C(6)	-0.23599 (61)	0.06747 (102)	0.58669 (58)
C(7)	-0.15221 (60)	0.07073 (89)	0.62783 (54)

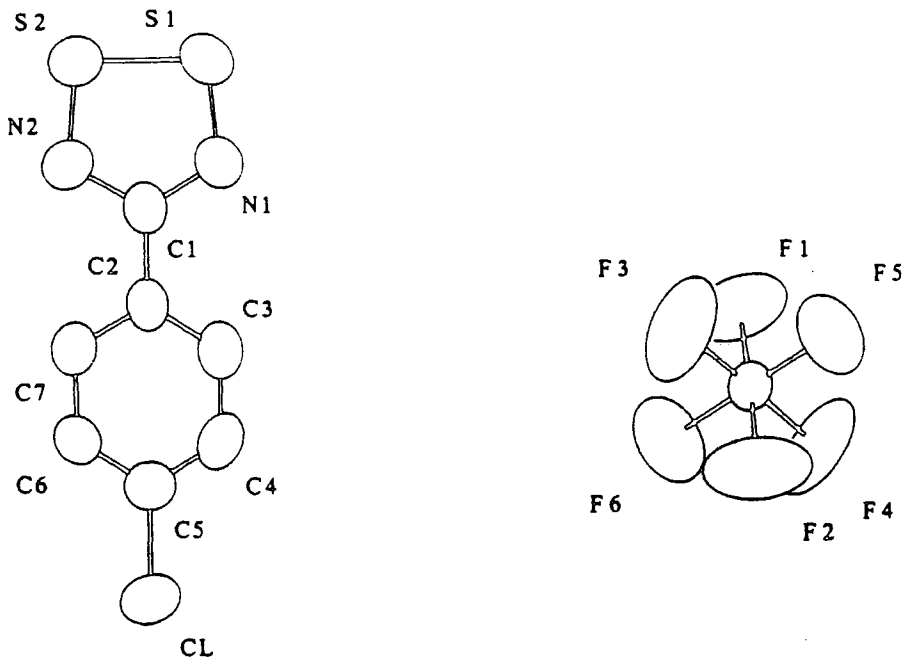

Fig. A1.1

The Asymmetric Unit of [4-Cl-C_6H_4CNSSN][AsF_6]

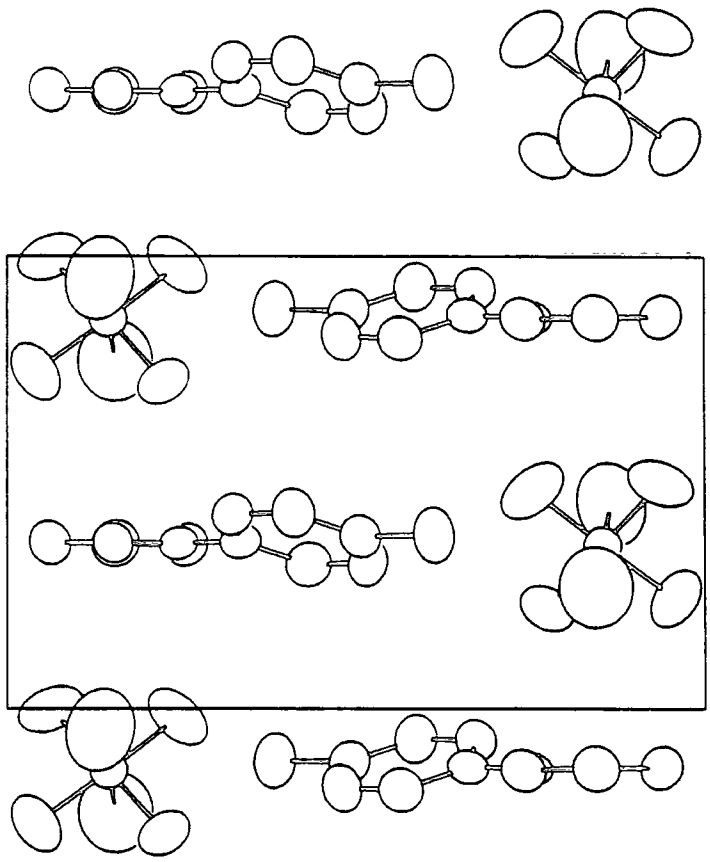

Fig. A1.2

Crystal Packing in [4-Cl-C_6H_4CNSSN][AsF_6]

TABLE A1.3 :Bond Lengths (Å) for [4-Cl-C_6H_4CNSSN][AsF_6]

F(1) - As	1.662 (7)	F(2) - As	1.689 (7)
F(3) - As	1.662 (7)	F(4) - As	1.666 (7)
F(5) - As	1.635 (8)	F(6) - As	1.671 (8)
C(5) - Cl	1.725 (9)	S(2) - S(1)	2.010 (5)
N(1) - S(1)	1.587 (8)	N(2) - S(2)	1.587 (8)
C(1) - N(1)	1.337 (9)	C(1) - N(2)	1.345 (9)
C(2) - C(1)	1.469 (10)	C(3) - C(2)	1.381 (10)
C(7) - C(2)	1.396 (10)	C(4) - C(3)	1.380 (11)
C(5) - C(4)	1.371(12)	C(6) - C(5)	1.364(11)
C(7) - C(6)	1.376(11)		

TABLE A1.4 : Bond Angles (deg .) for [4-Cl-C_6H_4CNSSN][AsF_6] (Excluding AsF_6^-)

N(1)-S(1)-S(2)	95.5 (3)	N(2)-S(2)-S(1)	95.7 (3)
C(1)-N(1)-S(1)	114.6 (6)	C(1)-N(2)-S(2)	114.3 (6)
N(2)-C(1)-N(1)	119.8 (7)	C(2)-C(1)-N(1)	120.1 (7)
C(2)-C(1)-N(2)	120.1 (7)	C(3)-C(2)-C(1)	120.8 (7)
C(7)-C(2)-C(1)	118.7 (7)	C(7)-C(2)-C(3)	120.5 (7)
C(4)-C(3)-C(2)	119.6 (8)	C(5)-C(4)-C(3)	120.2 (8)
C(4)-C(5)-Cl	119.9 (7)	C(6)-C(5)-Cl	120.4 (7)
C(6)-C(5)-C(4)	119.7 (8)	C(7)-C(6)-C(5)	121.9 (8)
C(6)-C(7)-C(2)	118.0 (8)		

TWIST ANGLE BETWEEN RINGS (Deg .) : 21.86 (18)

TABLE A1.5 : Anisotropic Thermal Parameters (Å x 10^4)

for [4-ClC_6H_4CNSSN][AsF_6]

The anisotropic temperature factor exponent takes the form

$-2\pi^2 (h^2a^*2U_{11} +...+2hka^*b^*U_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As	567 (4)	460 (3)	488 (3)	-8 (3)	48 (3)	0 (3)
F(1)	2089 (73)	713 (36)	1209 (48)	-209 (34)	-602 (47)	-238 (42)
F(2)	2000 (74)	746 (39)	1832 (70)	-325 (43)	-988 (58)	-195 (44)
F(3)	2727 (99)	1114 (51)	1136 (50)	615 (42)	634 (58)	-133 (58)
F(4)	2865 (99)	1128 (49)	698 (35)	383 (35)	344 (48)	45 (57)
F(5)	920 (44)	2413 (93)	1638 (65)	-368 (63)	248 (43)	775 (54)
F(6)	1045 (51)	2266 (93)	1914 (76)	-154 (68)	315 (50)	836 (56)
Cl	850 (14)	1075 (18)	634 (12)	-79 (12)	-142 (10)	193 (13)
S(1)	565 (11)	736 (13)	830 (14)	26 (11)	-43 (9)	36 (10)
S(2)	706 (12)	667 (12)	626 (11)	-53 (10)	-54 (9)	-10 (10)
N(1)	572 (33)	629 (36)	694 (37)	67 (31)	37 (28)	19 (30)
N(2)	689 (36)	559 (34)	552 (32)	-22 (28)	-11 (27)	-46 (30)
C(1)	529 (34)	371 (29)	572 (36)	38 (28)	93 (28)	20 (28)
C(2)	530 (33)	404 (30)	557 (34)	31 (28)	126 (27)	61 (28)
C(3)	663 (46)	669 (48)	669 (45)	29 (37)	142 (37)	11 (37)
C(4)	826 (55)	786 (55)	505 (39)	63 (37)	91 (37)	91 (43)
C(5)	617 (42)	620 (44)	596 (40)	-69 (34)	-36 (33)	170 (36)
C(6)	491 (38)	829 (53)	626 (43)	-45 (39)	28 (32)	76 (37)
C(7)	628 (43)	599 (41)	549 (38)	43 (33)	99 (32)	33 (34)

APPENDIX 2

SUPERPARAMAGNETIC BEHAVIOUR OF AN UNDEFINED RHENIUM COMPLEX DUE TO CONTAMINATION BY 4-PHENYL-1,2,3,5-DITHIADIAZOLYL

A2.1 Introduction

4-Phenyl-1,2,3,5-dithiadiazolyl (PhCNSSN)· has been used as a ligand in a number of complexes involving low valency transition metals, and three X-Ray crystal structures have been determined[1-3]. There is considerable interest in the use of metal complexes of stable radicals, for example nitroxyls[4] as routes to novel magnetic materials, and thus a study of the ligation properties of the dithiadiazolyls was undertaken. During the course of this work it was established that novel magnetic properties of a dithiadiazolyl rhenium complex were in fact due to the presence of trapped dithiadiazolyl free radical, and that this residual radical could be washed out to give a diamagnetic material.

A2.2 Results and Discussion

Work by I. B. Gorrell in this laboratory[1,2,5] led to the development of a synthetic route to dithiadiazolyl complexes involving CO elimination from metal carbonyls. A number of these complexes were prepared and their magnetization properties investigated.

The complex $[Mn_2(CO)_8(PhCNSSN)]$ was prepared[5] by reaction of $Mn_2(CO)_{10}$ with $(PhCNSSN)_2$ in the presence of Me_3NO[6], and satisfactory analyses were obtained. the complex was found to be a normal paramagnet with susceptibility increasing linearly with applied field. See Fig A2.1.

The same reaction was carried out using $Re_2(CO)_{10}$ and the resulting complex (a yellow amorphous powder from toluene) gave analyses inconsistent with the rhenium analogue of the manganese complex. Table A2.1 shows typical analyses obtained for the product of this reaction and calculated analyses for possible products.

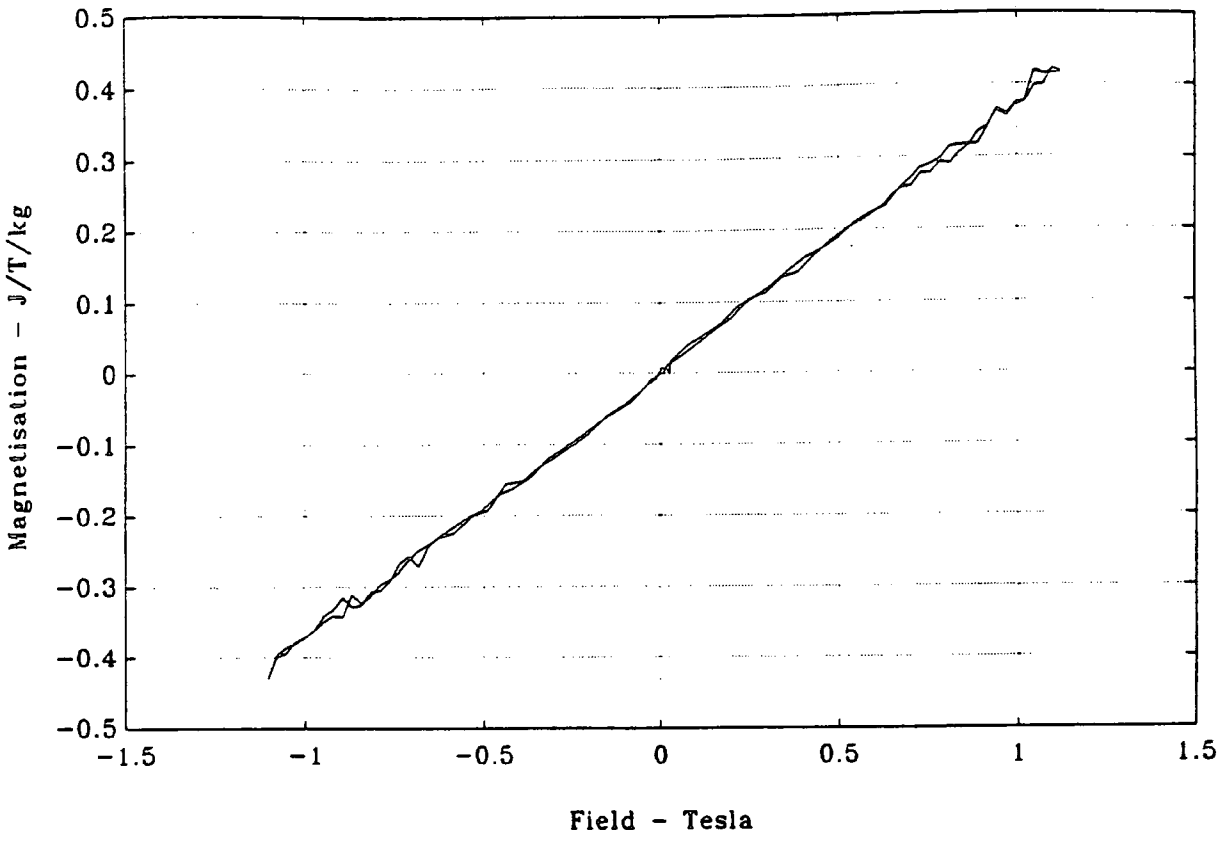

Fig. A2.1

Plot of room temperature magnetic susceptibility vs. applied field for $[Mn_2(CO)_8(PhCNSSN)]$

Table A2.1

Typical chemical analyses for the product of the reaction between $Re_2(CO)_{10}$ and $(PhCN_2S_2)_2$, and calculated analyses for possible products (Ref. 5)

	%C	%H	%N	%Re
Observed	26.84	1.92	5.35	27.32
Calc. For :				
$[Re_2(CO)_8(PhCN_2S_2)]$	23.2	0.6	3.6	47.9
$[Re(CO)_4(PhCN_2S_2)]$	27.6	1.0	5.8	38.8
$[Re(CO)_3(PhCN_2S_2)]$	26.6	1.1	6.2	41.3

Following Gorrell's initial studies the author carried out several repeat preparations and similar results were obtained. Gorrell made several suggestions as to the identity of the complex but no satisfactory structural data were obtained. The material was found to be insoluble in non-polar solvents (such as toluene and hexane), and highly soluble in more polar media such as dichloromethane and liquid sulphur dioxide, from which glassy solvates were formed.

Magnetic susceptibility measurements on this material by Gorrell from the original experiments showed a remarkable behaviour, with a rapid increase in susceptibility over a small field increment, behaviour characteristic of a superparamagnet[7-9]. This is shown in Fig A2.2.

It was decided to carry out repeat experiments in an effort to fully characterise the complex, and to reproduce the superparamagnetic behaviour seen in Gorrell's work.

Carrying out repeated preparations of the complex according to Gorrell's method yielded product which was typically diamagnetic. However, it was discovered that the magnetic

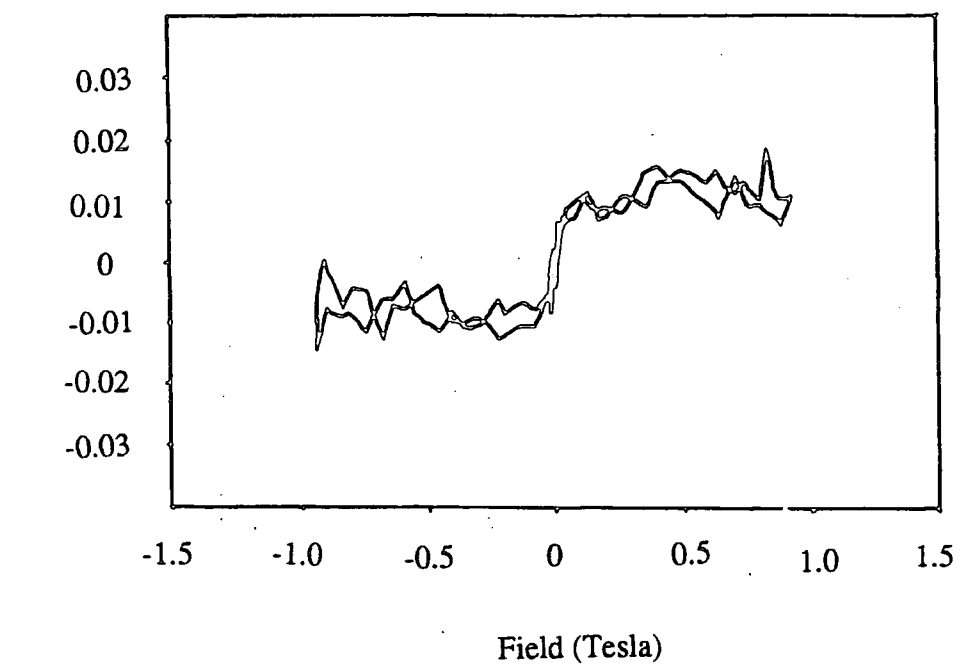

Fig. A2.2

Plot of room temperature magnetic susceptibility vs. applied field for the rhenium complex prepared by I.B. Gorrell (Ref. 5)

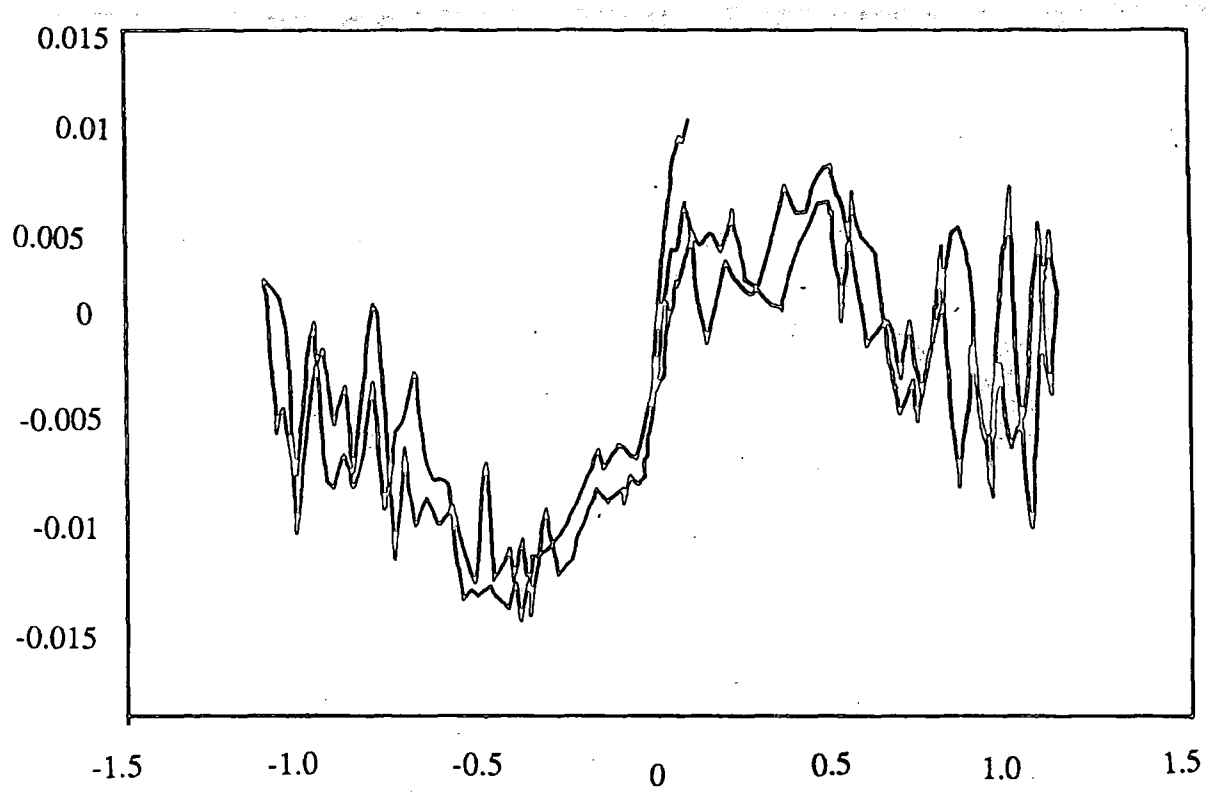

Fig. A2.3

Plot of room temperature magnetic susceptibility vs. applied field for the rhenium complex using Gorrell's method

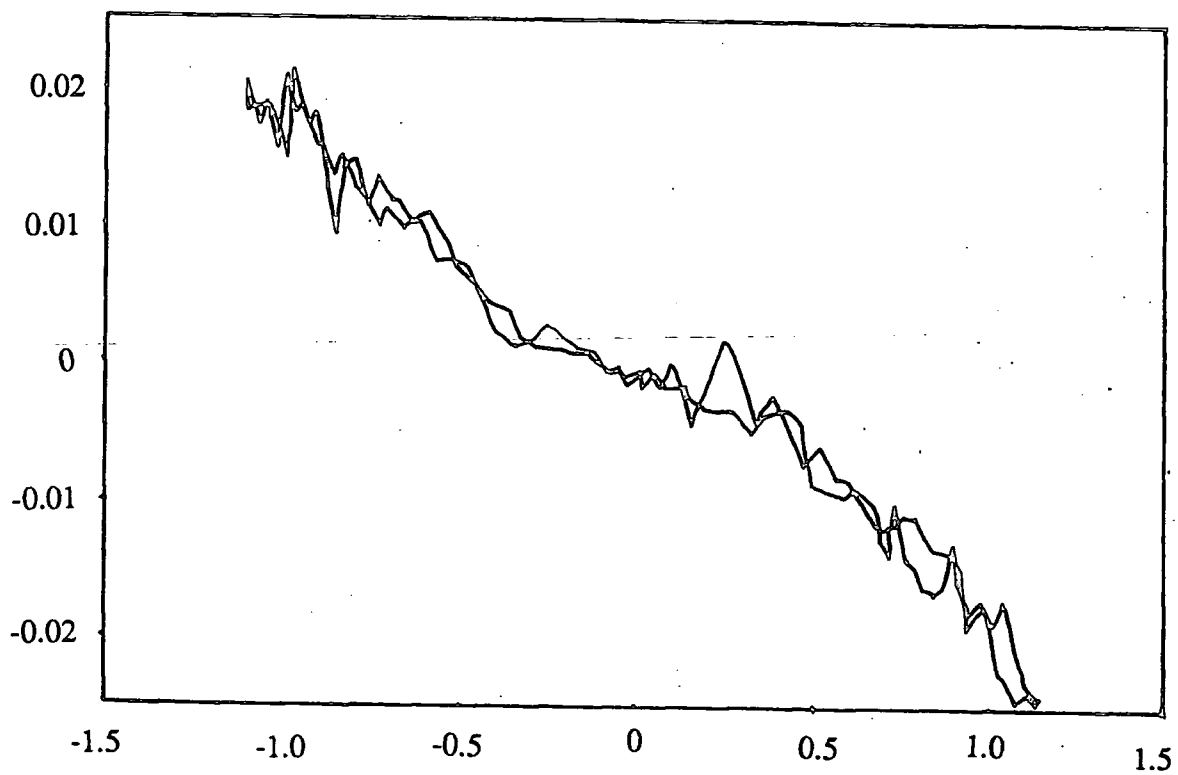

Fig. A2.4

Plot of room temperature magnetic sussceptibility vs. applied field for the same material following exhaustive washing with toluene

behaviour of the complex was dependent on the purification step ie washing with toluene. Light washing without stirring (as used in Gorrell's work) gave a product showing superparamagnetic behaviour, as shown in Fig A2.3. Exhaustive washing of this same material with stirring gave a diamagnetic material and a small amount of a dark purple residue, which gave an infrared spectrum characteristic of $(PhCNSSN)_2$. The magnetization curve for this "purified" material is shown in Fig. A2.4.

It was therefore concluded that the superparamagnetic behaviour of this material was not an intrinsic property of the material itself, but due to the presence of trapped free radicals within a diamagnetic matrix. These free radicals could be extracted out by thorough washing.

A2.3 Experimental

$Re_2(CO)_{10}$ (320 mg, 0.5 mmol) and $(PhCNSSN)_2$ (180 mg, 0.5 mmol) were dissolved in toluene (10 ml). A solution of Me_3NO (150 mg, 2.0 mmol) in dichloromethane (5 ml) was added dropwise to the reaction mixture with vigourous stirring. Reaction occurred rapidly, with an increase in temperature, evolution of gas and the formation of a fine yellow precipitate. After stirring for 24 hrs the supernatant was filtered off and the product washed with toluene (3 x 1 ml). More product was recovered from the filtrate by vigourously stirring in toluene. Yield 220 mg.

IR ν_{max} : 2100m, 2020s br, 1895s br, 1635m, 1370m, 1150m, 1055w, 1020w, 980m br, 940m, 840w, 825m, 720m, 700m, 610m, 590s, 530m, 470w cm^{-1}.

Analysis : C : 26.84 %, H : 1.92 %, N : 5.35 %, Re : 27.32 %

[From several other experiments Re content as high as 38% were recorded]

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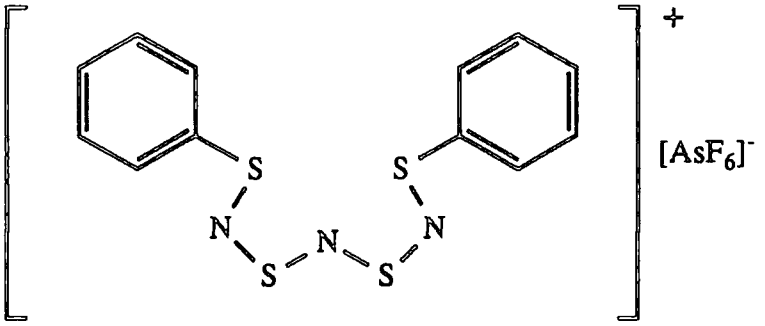
APPENDIX 3

REACTION OF [SNS][AsF_6] WITH COORDINATED CYANIDE ; REACTION WITH TETRACYANOMETALLATES (II)

A3.1 Introduction

Much of the cycloaddition chemistry of [SNS][AsF_6] has been studied using organic substrates, and very little is known about its behaviour with unsaturated bonds in other environments. Previous work in this laboratory[1] with [SNS][AsF_6] and PhHgCN gave the interesting chain compound 1, containing the S_4N_3 chain previously reported by Kuyper and coworkers[2,3].



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A3.2 Results and Discussion

The reaction of two equivalents of [SNS][AsF_6] with the tetrabutylammonium salts of tetracyanopalladate (II) and tetracyanoplatinate (II) gave insoluble products which, from chemical analysis and IR data, were formed with the elimination of two equivalents of [Bu_4N][AsF_6], and thus the products were of empirical formula [$M(CN)_2(CN_2S_2)_2$]. The products were both highly sensitive to moisture, and even using the glove box there was evidence of hydrolysis from infrared spectra of these materials. The insolubility of these products suggest that they are polymeric, and a possible reaction mechanism involves the cycloaddition of [SNS]+ across two coordinated CN groups to give discrete molecules of formula [$M(CN)_2(CN_2S_2)_2$] as transient species only, with the rapid formation of cross-links between dithiadiazole rings to give an extended

polymeric structure such as that shown in Fig. A3.1 for *trans*- addition of [SNS]+, or that shown in Fig. A3.2 for *cis*- addition.

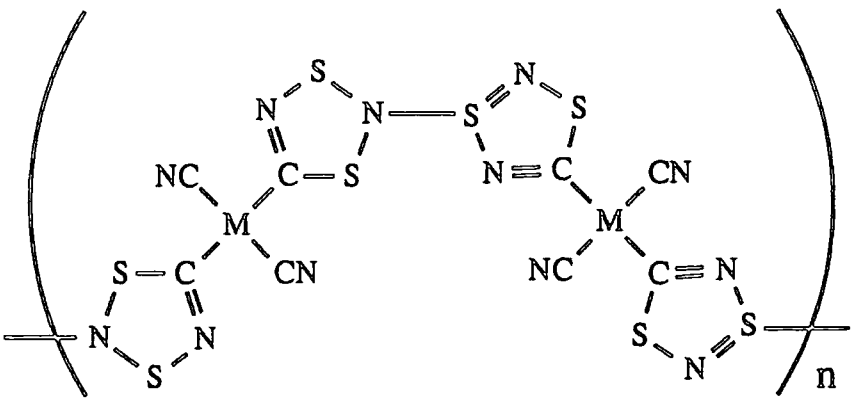

Fig. A3.1 Suggested Structure for the Product of *trans*-Addition of 2 $[SNS]^+$ to $[M^{II}(CN)_4]^{2-}$ (M = Pd, Pt)

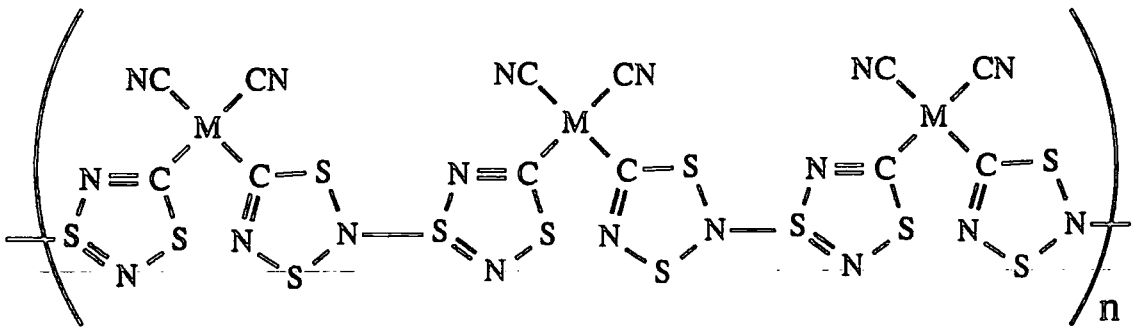

Fig. A3.2 Suggested Structure for the Product of *cis*-Addition of 2 $[SNS]^+$ to $[M^{II}(CN)_4]^{2-}$ (M = Pd, Pt)

The same reactions in 1:1 ratio also gave insoluble materials, but in very low yield, and with elemental analyses wholly inconsistent with a compound of formula $[Bu_4N][Pd(CN)_3(CN_2S_2)]$ in the case of palladium. In the reaction with the platinum-containing material a small yield of the 2:1 reaction product was obtained.

Clearly there is much to be done in the field of [SNS]+ chemistry with metal species. The reactions described here give rise to products somewhat unsuitable for full-scale characterization, but it is likely that other systems will reap richer rewards.

A3.3 Experimental

Reaction of [SNS][AsF_6] with [Bu_4N]$_2$[$Pd^{(II)}(CN)_4$] ; 2:1 Ratio

[Bu_4N]$_2$[$Pd^{(II)}(CN)_4$] (379 mg, 0.55 mmol) and [SNS][AsF_6] (293 mg, 1.10 mmol) were placed in separate legs of a "dog". SO_2 was introduced sufficient to dissolve both reagents. Upon mixing an instant reaction occurred to give a yellow-brown precipitate. Stirring was continued for 24 hrs. The supernatant was removed by filtration and the product was washed repeatedly with back-distilled SO_2. Following removal of SO_2 the product was transferred to a closed extractor and washed for 12 hrs with cycling CH_2Cl_2. Following removal of CH_2Cl_2 the product was dried *in vacuo*.

Appearance : Yellow-ochre powder, highly moisture-sensitive

Yield : 121 mg, 60%

IR (NUJOL Mull) : ν_{max} 2195s, 2140m, 2120sh, 1625wbr, 1515m br, 1500-1200sbr, 970m, 950m, 890w, 843m, 765sh, 752m, 735sh, 670w, 655m, 650sh, 595w, 577m, 527w, 470sh, 447s, 400 wbr cm^{-1}.

Analysis : Found C 14.62 %, H 0.21 %, N 22.59 % ;

$Pd(CN)_2(CN_2S_2)_2$ requires C 13.09 %, H 0.00 %, N 22.90 %

DSC : Broad decomposition profile, onset above 150°C

Reaction of [SNS][AsF_6] with [Bu_4N]$_2$[$Pd^{(II)}(CN)_4$] ; 1:1 Ratio

[Bu_4N]$_2$[$Pd^{(II)}(CN)_4$] (198 mg, 0.28 mmol) and [SNS][AsF_6] (75 mg, 0.28 mmol) were placed in separate legs of a "dog". SO_2 was introduced sufficient to dissolve both reagents. Upon mixing an instant reaction occurred to give a red-brown precipitate. Stirring was continued for 10 days during which time the product had changed colour,

to an ochre solid. Workup procedure was the same as for the 2:1 reaction. Yield 6 mg.

Analysis : Found C 3.36 %, H 0.19 % , N 4.41 % ;

$[Bu4N][Pd(CN)_3(CN_2S_2)]$ requires C 45.23 %, H 6.78 %, N 15.83 %

Reaction of $[SNS][AsF_6]$ with $[Bu_4N]_2[Pt^{(II)}(CN)_4]$; 2:1 Ratio

$[Bu_4N]_2[Pt^{(II)}(CN)_4]$ (204 mg, 0.26 mmol) and $[SNS][AsF_6]$ (139 mg, 0.52 mmol) were placed in separate legs of a "dog". SO_2 was introduced sufficient to dissolve both reagents. Upon mixing an instant reaction occurred to give a red-brown precipitate. Purification was the same as for the palladium compounds above.

Appearance : Red-brown powder, highly moisture-sensitive

Yield : 72 mg, 61%

IR (NUJOL Mull) : ν_{max} 2180s, 2140m, 1340wbr, 1285w, 1275w, 1030mbr, 965w, 860mbr, 772m, 730w, 720m, 700w, 657w, 470w, 447m, 410wbr cm^{-1}.

Analysis : Found C 10.77 %, H 0.28 % , N 17.49 % ;

$Pt(CN)_2(CN_2S_2)_2$ requires C 10.51 %, H 0.00 %, N 18.41 %

DSC : Broad decomposition profile, onset above 140°C

Reaction of $[SNS][AsF_6]$ with $[Bu_4N]_2[Pt^{(II)}(CN)_4]$; 1:1 Ratio

$[Bu_4N]_2[Pt^{(II)}(CN)_4]$ (297 mg, 0.38 mmol) and $[SNS][AsF_6]$ (100 mg, 0.37 mmol) were placed in separate legs of a "dog". SO_2 was introduced sufficient to dissolve both reagents. Upon mixing an instant reaction occurred to give an intense red colouration. Stirring was continued for 10 days during which no change in the appearance of the compound occurred. Purification was the same as for the palladium compounds above.

Appearance : Dark purple powder, highly moisture-sensitive.Yield : 27 mg

Analysis : Found C 10.49 %, H 0.37 % , N 15.21 % ;

$[Bu_4N][Pt(CN)_3(CN_2S_2)]$ requires C 38.75 %, H 5.81 %, N 13.56 %

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APPENDIX 4

SEMINARS AND LECTURES

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS

1st August 1988 to 31st July 1989

SCHMUTZLER, Prof. R. (Technische Universität Braunschweig) 06.10.88

Fluorophosphines Revisited - New Contributions to an Old Theme

DINGWALL, Dr. J. (Ciba - Geigy) 18.10.88

Phosphorus - containing Amino Acids : Biologically Active Natural and Unnatural Products

LUDMAN, Dr. C. J. (University of Durham) 18.10.88

The Energetics of Explosives

Von RAGUE SCHLEYER, Prof. P. (Universität Erlangen-Nürnberg) 21.10.88

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