# *Electrochemical, plasma and synthetic studies of dithiadiazolium and related compounds*

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# ELECTROCHEMICAL, PLASMA AND SYNTHETIC STUDIES OF DITHIADIAZOLIUM AND RELATED COMPOUNDS

Michael Ian Hansford

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To my mother, my father's memory and my friends

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# MEMORANDUM

The work in this thesis was carried out by me in the Chemistry Department of the University of Durham between October 1985 and November 1988. I declare that the work has not been submitted previously for a degree at this or any other university. This thesis is my original work, except where acknowledged by reference. The copyright of this thesis rests with the author. No quotation from it should be published without his written consent and information derived from it should be acknowledged. Material from this thesis has been or will be included in the following publications:

a)."Direct Insertion of a Nitrogen Atom into the S-S Link of a 1,2,3,5-Dithiadiazole Ring in a D.C. Nitrogen Glow Discharge", A.J. Banister, M.I. Hansford and Z.V. Hauptman, J.Chem. Soc. Chem. Comm. 1987, 63.

b)."Direct Insertion of a Nitrogen Atom into the S-S bond of a 1,2,3,5-Dithiadiazole Ring in a D.C. Nitrogen Glow Discharge, and X-ray Crystal Structure of 4-Methyl-1,2,3,5-Dithiadiazole, A.J. Banister, W. Clegg, M.I. Hansford, Z.V. Hauptman, and S.T. Wait, J. Chem. Soc., Dalton Trans. 1989, 1705.

c)."Novel S-N Ring Contractions using the 4-Phenyl 1,2,3,5 Dithiadiazole Dimer; the Synthesis and X-Ray Structures of $[[PhCN_2S_2]_2Cl[S_3N_3]$, $[PhCN_2S_2][S_3N_3]$ and $[PhCN_2S_2][S_3N_3]Cl$,and an *ab initio* Molecular Orbital Study of Bonding in $[PhCN_2S_2][S_3N_3]$, A.J. Banister, M.I. Hansford, Z.V. Hauptman, A. Luke, S.T. Wait, W. Clegg and K.A. Jorgensen. J. Soc. Chem. Submitted for publication.

# Electrochemical, Plasma and Synthetic Studies of Dithiadiazolium and Related Compounds

M.I. Hansford

## ABSTRACT

The crystal structure of $[\mathrm{Ph\overline{CNSSN}}]\mathrm{AsF_6}$ and $(\mathrm{Me\overline{CNSSN}})_2$ have been determined and a variety of new 1,2 and 1,3 dithiadiazolium derivatives synthesised including $[\mathrm{CH_3CH_2CH_2\overline{CNSSN}}]\mathrm{Cl}$ and $[(\mathrm{CH_3})_3\mathrm{C\overline{CNSSN}}]\mathrm{Cl}$. $[\mathrm{PhCN_2S_2}]\mathrm{AsF_6}$ has a longer S-S bond compared to $[\mathrm{PhCN_2S_2}]\mathrm{Cl}$ and has provided an insight into the molecular bonding in the three centre interactions in the latter. The crystalline methyldithiadiazole contains planar CNSSN rings. Within the dimer unit parallel monomer rings are linked via one weak S...S bond.

Enthalpies of fusion for a number of dithiadiazole derivatives were measured and found to be similar but significantly greater than for organic molecules of similar molecular weight. This together with the reduction of $[\mathrm{CH_3CH_2CH_2CN_2S_2}]\mathrm{Cl}$ and $[(\mathrm{CH_3})_3\mathrm{CCN_2S_2}]\mathrm{Cl}$ which gave new paramagnetic liquids has led to a more detailed understanding of the bonding and structure in these ring systems.

Dimeric aryldithiadiazoles $(\mathrm{R\overline{CNSSN}})_2$ (R = Ph or $p$-ClPh) were treated with atomic nitrogen, generated in a cool DC plasma, to form the corresponding dithiatriazine dimers by nitrogen insertion into the S-S bond; Alkyl derivatives (R = Me, propyl,$\mathrm{bu^t}$) gave polymeric products. Dithiadiazolium salts $[\mathrm{R\overline{CNSSN}}]^+X^-$ (R = Ph, $p$-ClPh, X = Br,I,CN or $\mathrm{S_3N_3}$) also reacted with nitrogen plasma to give high yields of the respective dithiatriazine. Structural criteria for these reactions are discussed. The electrochemistry of $(\mathrm{RCNSSN})_2$, $(\mathrm{RCNSNS})_2$, [RCNSSN]X (X=$\mathrm{Cl^-}$ or $\mathrm{AsF_6^-}$) and $[\mathrm{RCNSNS}]\mathrm{AsF_6}$ (R= Ph,$p$-ClPh,$p$-CH3Ph,$p$-CNPh,anthracene,Me, propyl,$\mathrm{bu^t}$,$\mathrm{Cl_3C}$, $\mathrm{CF_3}$) were studied by cyclic voltammetry.

A new $\mathrm{S_2N^+}$ salt, $\mathrm{S_2NCF_3SO_3}$, was synthesised from the reaction of $\mathrm{AgCF_3SO_3}$ with $(\mathrm{NSCl})_3$ and sulphur in liquid $\mathrm{SO_2}$ and its usefulness as a reagent compared to $\mathrm{S_2NAsF_6}$ and $\mathrm{S_2NSbCl_6}$. The crystal structure of $\mathrm{S_3N_2CF_3SO_3}$ was determined, crystals of which were isolated from the same reaction mixture and an equilibrium between $\mathrm{S_2N^+}$,$\mathrm{SN^+}$ and $\mathrm{S_3N_2}^{+\cdot}$ postulated.

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# CHAPTER ONE.

# INTRODUCTION

## 1.1. *Historical Development.*

A science recognisable as chemistry rather than alchemy became firmly established during the 18th century based on the work of Lavoisier, Proust, Berzelius etc. Daltons' atomic theory became widely accepted in the early 19th century, although Newtonian physicists, who like Lavoisier, believed the elements not to be fundamental, were still numerous and influential at this time. As a whole, however, the early nineteenth century witnessed a new renaissance of the physical sciences which arose out of the impetus of the industrial revolution. A Victorian technological boom, unparalled in previous history quickly followed, whilst organic chemistry in particular, fueled by the demands of a new dye industry, flourished with a whole range of synthetic colours. The synthesis of dyestuffs started in 1856, initially based on the alkaloid quinone. Within a few years the attempted oxidation of aniline to get to quinone had led instead to aniline purple, called mauvene, the imperial purple popular at the crystal palace exhibition of 1860[1,2]. This was the age of Kekule's monkeys although it was not until 1860 that Butlerov recognised the importance of molecular structures in chemistry and 1869 that Mendeleev introduced his periodic table. Nevertheless modern inorganic chemistry began here too. In 1834 the first inorganic heterocycle $(NPCl_2)_3$ was discovered by Liebig and Wöhler, whilst Gregory synthesised $S_4N_4$ for the first time in 1835[3]. However, further advances in inorganic heterocyclic chemistry were slow.

Impure $S_3N_2Cl_2$ was first prepared in 1851[4], but was not properly characterised until the 1880's by Demarcay, who also described $(NSCl)_3$, $S_4N_3Cl$ and $S_6N_4Cl_2$[5]. The possibility that inorganic compounds could have cyclic structures was only slowly accepted but became an increasingly important concept in the 1890's as a result of Stoke's work on phosphazenes.

However, there was little progress in S/N chemistry until after the 2nd world war when more modern techniques were developed. The advent of X-ray and electron diffraction techniques resulted finally in the elucidation in 1944 of the cyclic pseudo cluster structure of $S_4N_4$, more than 100 years after its first preparation[6]. The pace of discovery then rapidly accelerated after the development of much more sophisticated techniques such as infrared spectroscopy, inert atmosphere manipulation, vacuum line handling and with the use of aprotic reaction media. In recent years sulphur/nitrogen chemistry has progressed from relative obscurity to occupy a significant position in main group chemical research, interest stimulated largely by the discovery of the unusual properties of the conducting polymer $(SN)_x$[7].

Currently the unusual variety of chemical transformations and structures coupled with continued uncertainty over the nature of the bonding modes in these heterocycles still attracts both experimental and increasing theoretical interest. However, the sulphur/nitrogen branch of inorganic heterocyclic chemistry requires many specialised skills and experience and is therefore still confined to only a few laboratories about the world.

Sulphur/nitrogen literature has grown steadily since the first book to appear dealing largely with inorganic heterocycles, namely Becke-Goehrings classic monograph "Ergebnisse und Probleme der Chemie der Schwefel Stickstoffverbindungen" in 1957[8]. A definitive review of cyclic sulphur/nitrogen compounds has been recently published by the Gmelin Institute[9], whilst several authors have published review articles over the years, for example Becke-Goehring and Fluck (1966)[10], H.Heal (1972)[11], A.J.Banister (1975)[12], H.W.Roesky (1979)[13] and T.Chivers (1982,1983,1985)[14 -16]. Most recent texts are those by J.D.W. Haiduc and D.B. Sowerby, "Chemistry of Inorganic Homo- and Heterocycles" (1987)[17], H.Heal, "The Inorganic Heterocyclic Chemistry of Sulphur, Nitrogen and Phosphorus" (1980)[5] and J.D. Woollins, "Non-metal Rings, Cages and Clusters" (1988)[45].

## 1.2. *Current Trends in Sulphur/Nitrogen Chemistry.*

No sulphur/nitrogen heterocyclic thesis today seems to be complete without a reference to the leading role $(SN)_x$ research has played in providing major stimulus to S/N research in general. Indeed recent interest in S/N chemistry began in 1975 with the discovery of the quasi-one-dimensional metallic behaviour of $(SN)_x$ polymer, which becomes superconducting below 0.3K[7],[18]. $(SN)_x$ crystals are fibrous like asbestos and whose sides have a golden metallic reflectance. In view of the considerable excitment generated by the development of high temperature superconductors recently[19], it may be anticipated that further enthusiasm will fuel still more effort in devising new improved methods of synthesis of, and uses for, this polymer and in finding related materials which may have more desirable properties than $(SN)_x$ itself (for example, a degree of solubility or a higher transition temperature to a superconducting state). $(SN)_x$ exhibits some unusual behaviour and has been used in the fabrication of blue light emitting diodes[20], thought to be of potential commercial significance, and in the use of $(SN)_x$ batteries[21]. Despite all the recent activity, new synthetic routes to $(SN)_x$[18] are rare; the best way to make good quality $(SN)_x$ is either by the hazardous classical method (pyrolysis of $S_4N_4$ to $S_2N_2$ followed by the polymerisation of $S_2N_2$ to $(SN)_x$[22], or electrosynthesis from $S_5N_5^+$ salts[46]. There have also been numerous attempts to find suitable precursors to $(SN)_x$ analogues[23] which has resulted in a flood of related S/N papers.

Interesting examples include the determination of the crystal structure of $S_5N_5$+ as an azulene shaped ring[24] and the reactions of the small building block species $S_2N^+$ with various unsaturated species to give dithiazolium cations[25] which themselves may be reduced to free radicals of remarkable stability[26,27].

The advent of modern, more sophisticated experimental and theoretical techniques has resulted in the re-examination of old problems, for example the reaction of $S_4N_4$ with acetylenes[28] and the bonding[29] and pyrolysis[30] products of $S_4N_4$ and this trend is likely to continue. However it is important to emphazise that it is only by advances in techniques and technology that advances in synthetic methods can take place. Indeed, the development of S/N chemistry has been seriously hindered, for example by the absence of suitable nuclei by which NMR can be readily obtained. Fortunately this situation is now changing with the increasing use of such spectroscopic methods as $^{15}N$ and $^{14}N$ nmr[31] and esr[27] together with the wider availability and use of electrochemical methods and X ray analysis.

The use of MNDO[32], CNDO, PM3 and ab initio type calculations to obtain full molecular orbital descriptions is gaining increasing acceptance and is particularly useful in the interpretation of the various bonding modes in S/N compounds, although it is thought necessary to include d orbital functions to obtain geometries which closely fit experimental data[33,34]. This is a very recent development aided by the wide availability and considerably increased power of all computers from PC's and Vax systems to mainframes. The recognition of $S_4N_3^+$ and $S_2N_2$ as Hückel aromatic species[35] and the discovery of the $14\pi$ electron $S_5N_5^+$ were key developments in explaining electron distribution and bonding types. This lends a degree of predictabilty to the synthesis of S/N compounds, although the lability of S/N rings and cages and their unusual chemistry may alter synthesis of theoretically possible structures.

On the whole, S/N compounds tend to be electron rich; despite this and usually because of low lying SOMO's or LUMO's, S/N compounds still have extensive electron accepting properties which have been widely investigated by Chivers and co-workers[36],[37], who have also prepared a number of new binary sulphur nitrides, notable $S_3N_3^-$ and sulphur/nitrogen/phosphorus compounds.

With a trend towards ever more sophisticated equipment and techniques, it is likey that further advances in the synthetic and theoretical aspects of all active areas of research from M/S/N compounds[38],[39] to S/N/O and S/N/B[40] will be rapid.

## 1.3. *Summary of this Thesis.*

This section reviews the various chapters of this thesis and discusses the relevance of these to sulphur/nitrogen research as a whole. Chapter 3 concentrates on some synthetic studies of both 1,2 and 1,3 dithiadiazolium salts. Many of the cations may be readily reduced to the $7\pi$ electron species which are unusually persistent and stable free radicals, and some of these have the unusual property of being paramagnetic liquids at room temperature, examples of which are both novel and rather rare. The physical properties of the dithiadiazole systems were studied, using selected members, largely by differential scanning calorimetry. An X-ray crystal structure was obtained of $[PhCN_2S_2]AsF_6$ for a comparative study with $[PhCN_2S_2]Cl$, the crystal structure of which has only just been reported. Chapter 4 is concerned with the effect that a cool DC nitrogen plasma has on a variety of 1,2,3,5 dithiadiazolium salts and related dithiadiazoles and a variety of similar S/N compounds. Very little work has been carried out using nitrogen plasmas for molecular syntheses because yields are generally low[41], but this study was initiated by the observation that some 5 membered ring dithiadiazoles readily polymerised under a Tesla discharge. It was therefore thought possible to convert these rings into S/N/C analogues of $(SN)_x$ by plasma methods, the theory being that the introduction of a carbon group into an $(SN)_x$ chain would enable side chain modifications whilst maintaining reasonable conductivity. However, a novel insertion reaction was observed instead in which a nitrogen atom inserts across the disulphide bond. This led to speculation about the wider use of this reaction in nitrogen fixation. Concurrent with the physical studies (chapter 3), the redox and electrochemical behaviour of a wide range of 1,2,3,5, and 1,3,2,5 dithiadiazolium and other S/N species are reported (Chapter 5). Kinetic details for the $S_2NAsF_6$/MeCN reaction and Hammett plots for substituted aryl derivatives were obtained using cyclic voltammetry, which proved to be a powerful tool.

Over the last couple of years much interest has been shown in the $S_2N^+$ species as a proven and useful synthetic building block[42] for dithiadiazolium and dithiazolium salts. It reacts in a facile cycloaddition to many alkynes and nitrile derivatives[43]. A comparative study of the potential use of several $S_2N^+$ salts was undertaken. In this $S_2NSbCl_6$,which it was hoped would be a more accessible S/N precursor,[44] was compared with both $S_2NAsF_6$ and $S_2NCF_3SO_3$. $S_3N_2CF_3SO_3$ and $S_2NCF_3SO_3$ were synthesised in a simple preparative method, both $S_3N_2{}^+$ and $S_2N^+$ were obtained from the same reaction, suggesting that these were in equilibrium, a view consistent with previous reports[44]. The esr spectrum was measured and the X ray crystal structure is reported for $S_3N_2CF_3SO_3$. Several attempts were made to react $S_2NAsF_6$ with isonitrile compounds, metal unsaturated complexes and other S/N compounds with the aim of producing novel species; although no new compounds were obtained interesting reactions were observed and the field of unsaturated metal complexes has the potential for some interesting chemistry.

## 1.4 *Some Practical Aspects.*

The two most important factors which dominate S/N experimental chemistry are the moisture sensitivity and the lability of the S/N rings and cages. Indeed, it is this latter factor which makes S/N chemistry so varied and some reaction pathways so unexpected. Molecular frameworks of carbon, phosphorus and nitrogen tend to persist relatively unchanged through reactions. This, howez#Z::I&:not:t#p:case:with#S/N{$}ruXtures which often cleave and rearrange. This places considerable constraints on the experimental conditions and is the reason why so many synthetic reactions are carried out at room temperature. However, it should be noted that the use of heat in some preparations for example to cleave $(NSCl)_3$ in the synthesis of 1,2,3,5 dithiadiazolium salts is an advantage.

In general, moisture sensitivity is a major problem and also places severe limitations on handling techniques, see chapter 2. For example $AsF_5$ is an extremely moisture sensitive gas and thorough drying of equipment with $SF_4$ was often necessary to avoid massive hydrolysis. $S_2NAsF_6$ is also extremely sensitive and even small amounts of hydrolysis products significantly affect yields and reactions. For successful results extreme care must be taken in the purification of starting materials and solvents, in the cleaning and drying of reaction vessels and in the manipulation of reaction mixtures. A solvent particularly useful in S/N chemistry is liquid $SO_2$, being relatively inert and very easily purified. However, pressures encountered severely hinder the use of techniques routine in other areas of chemistry eg. NMR and often involve designing new equipment. These difficulties, however, are a challenge from which a chemist can learn much in overcoming.

## 1.6 *Nomenclature.*

At the time of writing there is still no internationally agreed nomenclature for sulphur/nitrogen heterocycles and there is, it appears, no solution likely in the near future. This is despite the fact that this problem has been under urgent consideration by IUPAC's Inorganic nomenclature Commission for at least the last nine years[5]. It is not surprising therefore that there is considerable confusion in this area, with groups tending to adopt many different conventions. Probably the most widely known system is that used by Chemical Abstracts. This, however, has the not inconsiderable disadvantage of being extremely cumbersome and sometimes incomprehensible to use. This is because the CA system is based on organic nomenclature systems and was built up by a succession of expedients. This means that very often compounds are named substitutively as they would be in organic chemistry, eg. ligands on inorganic heterocycles replace hydrogen atoms in hypothetical parent compounds which would probably never even exist. The easiest method and most widely understood both for written and verbal communication is the use of empirical formulae, eg. $S_3N_2Cl$ or structural formulae and trivial names, eg. $(NSCl)_3$ or (NSCl) trimer instead of trichlorotrithiatriazine, even though this is considerably better than the CA system under which this compound has the name 2,4,6,trichloro, 1,3,5,2,4,6 trithiatriazine. It is this convention of using trivial names and empirical formulae that is used throughout this thesis. The 1,2,3,5 and 1,3,2,5 dithiadiazolium derivatives will be referred to as the 1,2 and 1,3 isomers respectively throughout this thesis.

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# CHAPTER TWO

# GENERAL EXPERIMENTAL PROCEDURES

## 2.1 General Techniques:

### 2.1.1 *Manipulation of Moisture-Sensitive Materials.*

All manipulations of moisture sensitive or hygroscopic materials and all purifications and distillations of solvents were performed under an atmosphere of dry nitrogen or *in vacuo*. Bench nitrogen was taken from the departmental supply line and purified by passage through a heated copper column (300°C, to remove oxygen) and through several $P_4O_{10}$ towers (to remove moisture) before use. Other manipulations were conveniently performed under an atmosphere of dry nitrogen in a Vacuum-Atmospheres Corporation (California) glove box (type HE43-2), equipped with a recirculating pump and a mixed bed column containing Linde 13X molecular sieve and a de-oxo catalyst (HE493 DRI-TRAIN). The pressure inside the glove box was maintained above atmospheric pressure with a Pedatrol HE-63-P regulating unit and the nitrogen was supplied from a high pressure cylinder (B.O.C."white spot" grade). The water content was typically 2 ppm.

### 2.1.2. *Infrared Spectra.*

Infrared spectra were recorded on Perkin Elmer Grating Spectrophotometers, type 477 or 577. Spectra of solids were recorded as nujol mulls on KBr plates unless otherwise stated, and generally prepared under nitrogen. Gas phase spectra, especially of fluorinated or highly moisture sensitive materials were recorded using a passivated stainless steel cell fitted with AgCl windows.

### 2.1.3 *Raman Spectra.*

Raman spectra were recorded on a Cary 82 Spectrophotometer (Spectra Physics 125 laser, 6328Å exciting line or Spectra Physics 164 laser, 5154Å exciting line), or a Ramanlab spectrophotometer (Spectra Physics

125 laser, 5154Å exciting line). Samples were sealed in capillaries.

### 2.1.4 *Nuclear Magnetic Resonance Spectra.*

Both $^{13}C$ and $^{1}H$ nuclear magnetic resonance spectra were obtained on a Brüker AC 250 spectrometer at 62.896 and 250.134 MHz respectively. In both cases chemical shifts were measured in ppm relative to $(CH_3)_4Si$ (TMS) internal reference at 0 ppm. The upfield direction was taken as negative. The $^{1}H$ spectra samples were sealed in 5mm OD tubes, the remainder in 10mm OD tubes.

### 2.1.5 *Mass Spectra.*

Mass spectra were recorded on a VG 7070E Mass Spectrometer at 120-180° C at 70eV with an accelerating voltage of 8 kV. Samples were introduced by direct insertion into the ion source and run in both the chemical ionisation (CI) and electron impact (EI) modes.

### 2.1.6 *X-Ray diffraction data.*

X-ray powder diagrams were obtained using a Debye-Scherrer camera and Cu-K radiation (nickel filter). The image was recorded on Agfa-Gevaert Osray M3 X-ray film. The samples were ground to a powder and sealed in thin walled capillaries (0.3mm O.D. Lindemann glass or quartz). Oscillation and Weissenberg photographs were recorded on the same film with 1-2h and 15-24 h exposures respectively using a Nonius integrating Weissenborg goniometer with a Philips X-ray generator Type PW 1009 130. This was fitted with a Cu anode and a Ni filter and run at 42kV and 16mA. Full X-ray crystal structure determinations were carried out at Newcastle University by Dr. W. Clegg on a Siemens AED2 diffractometer with a graphite monochromator using MoK$\alpha$ radiation ($\lambda$ = 0.71073Å).

Programs (SHELTXL and local software) were run on a Data General Model 30 computer.

### 2.1.7 *Elemental Analysis.*

Except where stated otherwise, elemental analysis were performed in this department by Mr. R.Coult (S,N,As,Cl) and by Mrs. M.Cocks (C,H,N,S,F).

Carbon, hydrogen, nitrogen and some sulphur analys~~i~~es were determined by micro combustion in a Carlo Erba 1106 Elemental Analyser. Sulphur and chlorine were also obtained by oxygen flask combustion followed by $BaClO_4$ titration for sulphate ions and potentiometric $Ag^+$ titration for chloride ions. Arsenic was determined by atomic absorption spectroscopy using a Perkin Elmer 403 Atomic Absorption Spectrometer.

### 2.1.8 *Glassware.*

Pyrex flasks and sinters fitted with either conical ground glass joints or J.Youngs' Teflon stemmed greaseless valves (further referred to as Youngs taps) were either placed in an oven (*ca.*120°C) for 3-4 hours or were gently flamed with a hand torch (*ca.*500°C) in a flow of nitrogen before use. The procedures for using more specialized glassware are described where appropriate.

### 2.1.9 *Vacuum lines.*

For general purpose manipulation of solvents and reagents, a double pyrex vacuum/nitrogen manifold fitted with both high vacuum ground glass taps and Youngs taps leading to Viton fluoroelastomer rubber "O"-ringed S19 ball joints was used - a vacuum as good as to $10^{-3}$ Torr could be achieved with the use of a mercury diffusion pump backed by an Edwards (No.2) two stage rotary oil pump.

Connection to reaction vessels was via either rubber tubing and tap adaptors, or 1/4" ground glass with 1/4" / 1/4" Swagelok unions to Youngs S19 cup connectors. For high vacuum sublimations a good vacuum was essential to lower the temperature of the sublimation and hence lessen thermal decomposition of the compounds under investigation. A high vacuum manifold, (designed and constructed by Z.V.Hauptman), was made from pyrex. Using a silicone oil diffusion pump and an Edwards (M8) rotary backing pump, with Youngs taps and rubber "O" ringed joints, pressures of $6 \times 10^{-7}$ Torr could be achieved; slight greasing of the valves and "O"-rings gave the best results.

For the manipulation of condensable and toxic gases, eg ClCN, and particularly for $SO_2$ and $AsF_5$ it was found convenient to use a vacuum manifold made of stainless steel and equipped with stainless steel Whitey Valves (1KS4) and a Bourdon pressure gauge. Attachment of vessels to the manifold was via Swagelok 1/4" O.D. compression fittings furnished with teflon ferrules. Vacuum as good as $10^{-3}$ Torr was regularly achieved. The steel line had the advantage that it could be dried by flame or by heating tape whilst under dynamic vacuum or passivated and dried with $SF_4$, which was found to be particularly effective.

### 2.1.10 *Temperature control.*

Various heating devices were used, such as a silicone oil bath and stirrer hotplate, or electric heating tapes connected to a variable transformer. Both on the high vacuum line and the plasma apparatus it was possible to control the temperature to within 1/2°C by the use of a Eurotherm 821 Controller unit and either a resistive wire-wound electric furnace (built by Z.V.Hauptman) or a silicone oil bath and stirrer hotplate.

Cooling below room temperature to as low as -40°C was achieved by the use of a Haake F3 Bath Circulator with methylated spirit as coolant, the temperature being controlled to within 1°C.

### 2.1.11 *Differential Scanning Calorimetry. (D.S.C.).*

A Mettler FP80 Control Unit coupled to a Mettler FP85 TA Thermal Analysis Cell and a Vitatron 2001 series Y-t chart recorder were used to obtain melting point values, decomposition temperatures and enthalpies of fusion and sublimation where appropriate. Samples were hermetically sealed under dry nitrogen in aluminium capsules by cold welding.

## 2.2. Specialized Techniques.

### 2.2.1 *Two Bulbed Reaction Vessels.*

A typical vessel (called a dog) is illustrated in Fig. 2.1 and has been described previously[1]. The bulbs (generally 25ml) are separated by a No.3 porosity sintered glass frit and each may be isolated with a Youngs tap. For larger scale reactions a vessel with 200ml bulbs was used. The dog could be attached to the metal vacuum line via 1/4" O.D. ground glass fittings. These vessels are particularly useful for working with moisture sensitive materials. They may be rigorously flame dried whilst under dynamic vacuum. The size lended itself to gravimetric studies and thus losses or additions to the system under investigation could be detected. Finally as a closed system they were very useful for working with solvents with vapour pressures greater than atmospheric, (typically $SO_2$, *ca.* 3atm. ClCN, *ca.*6 atm.). Similarly, accurately weighed aliquots of gaseous reagents could be introduced into the reaction mixtures. Separation of soluble from insoluble products was achieved by a combination of filtration and washing with back distilled solvent.

Products were conveniently recovered after removal of solvent by cutting the bulbs with a glass knife and hot spotting the cut to remove the bulbs, usually under a dry nitrogen atmosphere. The vessels could then be re-used after re-attachment of the bulbs and annealing in an oven up to 580°C.

### 2.2.2. *NMR Tubes.*

It was found that some reactions could be conveniently monitored by nuclear magnectic resonance spectroscopy. Ten millimetre pyrex tubes were fitted with Youngs taps. The tubes could then be connected to the metal vacuum manifold and volatile solvents or reagents were condensed into the tubes from the vacuum line. The tubes could be accurately weighed, so a precise record of reagents and products could be kept.

### 2.2.3. *Closed Extractors.*

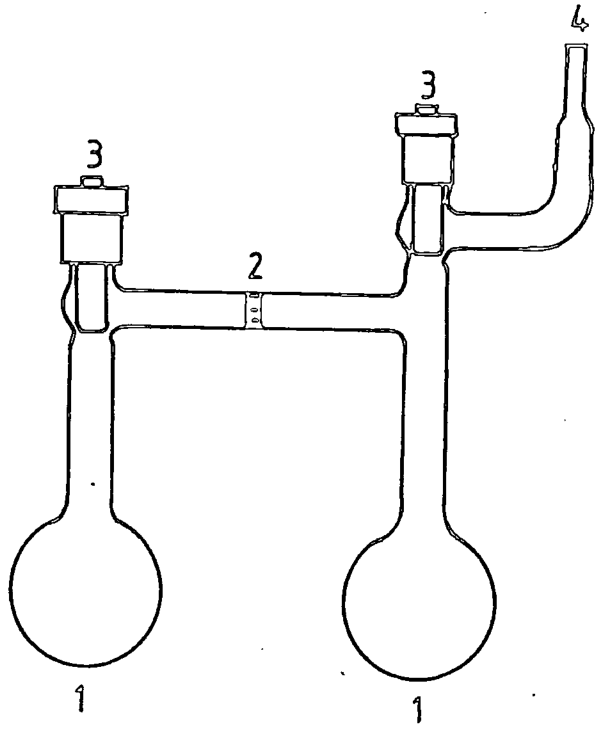
This type of apparatus has already been described in the literature[2]. The closed extractor (designed by Dr. Z.V.Hauptman) can be used for the exhaustive or partial extraction of moisture sensitive materials with relatively volatile solvents, eg. $SO_2$, $CCl_4$, or $CH_3CN$. It may also be used in conjunction with a dog for the slow addition of relatively insoluble reagents by means of continous washing.

## 2.3. Electrochemical Techniques.

### 2.3.1. *Cyclic Voltammetry.*

Cyclic voltammograms were recorded using a BioAnalytical Systems Potential Ramp Generator (type CV-1B) and a Linseis LY17100 XY chart recorder. Unless otherwise stated the solvent was acetonitrile doubly distilled from $CaH_2$ and finally passed through an alumina (Woelm B super 1) column.

Figure 2.1. A "Dog".



1. Reaction Bulb 25ml or 200ml.

2. No. 3 glass sinter frit.

3. Youngs tap.

4. 1/4" Ground glass.

All distillations and experiments were performed with strict exclusion of moisture and oxygen under an atmosphere of dry nitrogen in a specially airtight three electrode cell (See Figure 2.3.).
The working electrode was a platinum disc (0.002cm$^2$) pressure molded in FEP (= tetrafluoroethylene hexafluoropropylene co-polymer). The supporting electrolyte, $Bu_4NBF_4$, was prepared by metathesis from $Bu_4NHSO_4$ (Labkemi AB, Sweden) and $KBF_4$ (BDH ltd.), purified by double crystallisation from ethyl acetate/diethyl ether mixture and finally vacuum dried ($10^{-5}$ Torr) at 125°C. All solutions and cells were prepared and sealed under nitrogen in a glove box.

### 2.3.2. *Reference Electrodes.*

In general it was found convenient to use either 0.1M $Ag^+/Ag$ or 0.01M $Ag^+/Ag$ reference electrodes, made up in anhydrous acetonitrile for experiments carried out in both acetonitrile and $SO_2$. The potential of these was always checked before and after use against a standard saturated calomel electrode (s.c.e.) to which all results were converted. The potentials of the electrodes used were remarkably stable over a period of many months.

(i). In acetonitrile; The reference solution comprised of a 0.01M solution of $AgBF_4$ (0.2 mol dm$^{-1}$ $Bu_4NBF_4$) in MeCN sealed in a FEP tube (designed and built by Z.V.H.) with silver wire connected to 1/4" stainless steel for use in the 1/2"/1/4" Swagelok system which facilitated a vacuum tight seal. It could also be used in a Quickfit thermometer screw compression fitting. A quartz thread wick sealed at the opposite end in teflon dipped into the solution under investigation. This maintained a potential of 0.252V ± 0.005V.

(ii) In $SO_2$; For pressurised systems, an adaption of a reference electrode previously described was used[1].

This was designed and built by Dr. Z.V. Hauptman and its advantage over the previous design was that it was easily refillable with fresh $AgBF_4$ solution (0.1M in MeCN). The electrode itself comprised of a glass sintered frit in a thin glass tube which lead up to a 1/4" smooth glass section.(see Figure 2.2). The tube was sealed with a Youngs tap, which had previously been drilled through to accommodate the silver metal tip. The tube could then simply be filled with the $AgBF_4$ solution required through the side arm. Any bubbles that formed through de-gassing etc. could be then be released and the liquid level topped up from the reservoir. This maintained a potential of 0.33 V $\pm$ 0.005V.

As the glass electrode was used in liquid $SO_2$, it was found that slow diffusion of $SO_2$ across the frit occurred into the electrode causing a fine white precipitate to form very slowly (possibly $Ag_2SO_4$). However, this did not appear to affect the potential of the electrode over a period of a month or so. Both electrodes were stored under nitrogen with the tip immersed in a solution of a relevant concentration of $AgBF_4$ in actonitrile.

### 2.3.3. *Other electrodes.*

For bulk electrolysis, platinum sheets or platinum coiled wire was used, although sometimes sacrificial zinc sheet could be used. In CV experiments the anode was always a coiled platinum wire. Platinum cathodes were polished in a slurry of alumina and concentrated nitric acid before use.

**Figure 2.2.** Ag/Ag$^+$ Glass reference electrode for pressurised systems.

1. Pyrex sinter porosity no.4.
2. 1/4" O.D. smooth glass for air tight Swagelok connection.
3. 0.1M AgBF$_4$ solution in MeCN.
4. Ag metal attched to central through rod.
5. Knife edge to 4. for a tight seal against teflon tap.
6. PTFE stem of Youngs' greaseless tap.
7. Side arm of Youngs' tap down to 1/4" ground glass.
8. Brass ring around PTFE stem to prevent yielding through axial compression.
9. Washer.
10. Stainless steel (or Monel rod), 1/8" diameter, with 5BA thread both ends centrally bored through PTFE stem.

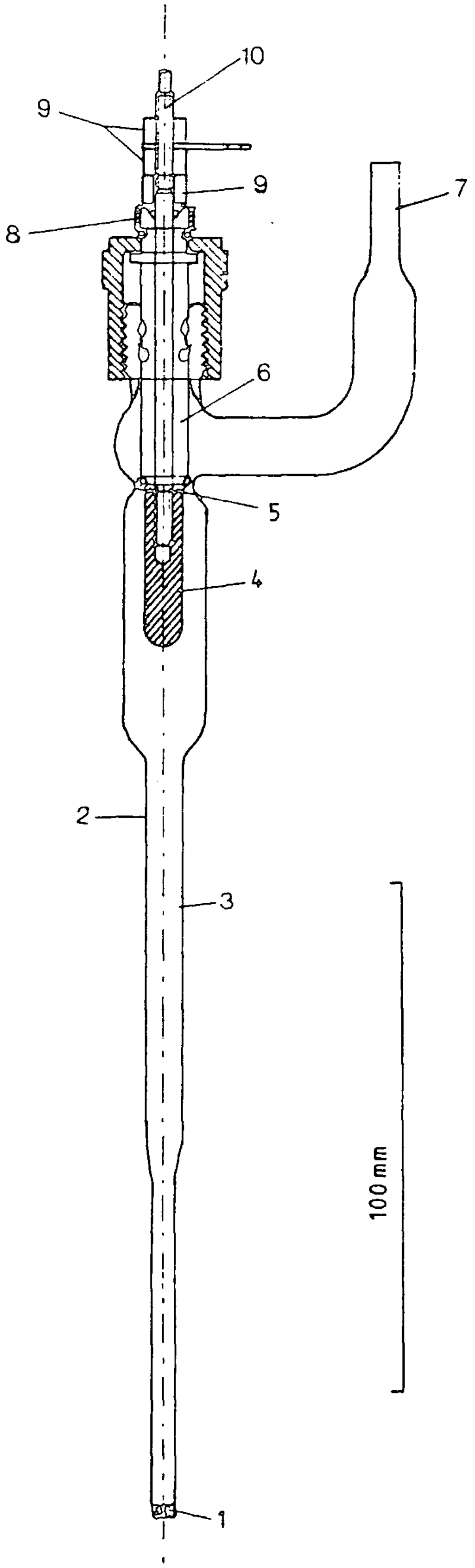
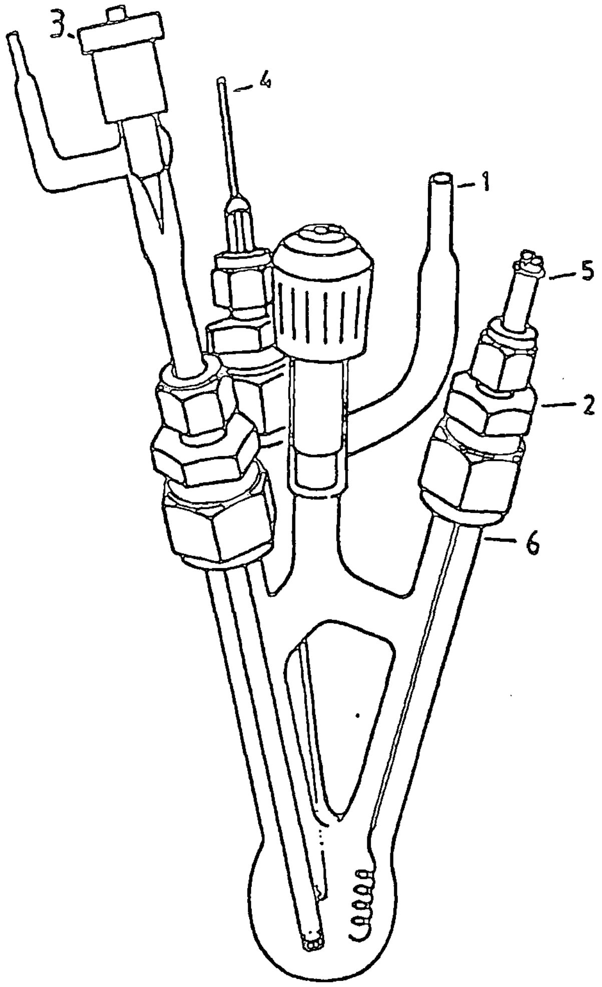


Figure 2.3. Three limbed electrochemical cell used for Cyclic Voltammetry.



1. 1/4" Ground Glass connection.
2. Swagelock 1/2" to 1/4" reducing union.
3. Reference electrode.
4. Platinum microelectrode.
5. platinum Auxiliary electrode.
6. 1/2" precision O.D. smooth glass.

### 2.3.4. *Elecrochemical Cells.*

For all CV work a 3 limbed one compartment cell was used, see Figure 2.3. For bulk electrolysis a 2 compartment cell proved useful. The electrodes were introduced *via* reamed out Swagelok 1/2" to 1/4" compression fittings. Although initially 1/2" ground glass tubing was used for the limbs of the vessels, it was found that a more effective seal could be obtained by the use of smooth 1/2" precision glass tubing.

## 2.4. Sulphur - Nitrogen Starting Materials.

### 2.4.1. $S_3N_2Cl_2$.- *Chlorothiodithiazyl Chloride.*

This is prepared following the method described by Jolly and Maguire[3], but with modifications developed by Dr. Z.V.Hauptman. Ammonium chloride (100 g, oven dried, 1.87 mols), $S_2Cl_2$, 100 ml (1.24 mols) and powdered sulphur (20 g, 0.078 mols) were placed in a specially designed 500ml round bottom flask fitted with two air condensers ( 50 cm x 3 cm) placed one on top of the other and terminating in a calcium chloride drying tube open to the air. All joints were fitted with teflon sleeves and the flange was lubricated with Kel-F grease. The mixture was brought to reflux, and the reflux point inside the condensers was controlled by means of a jet of compressed air which locally cooled the condenser. The reflux point was initially set close to the top of the condenser, where after a short while red brown crystals of $S_3N_2Cl_2$ formed. After the initial formation of a ring of crystals inside the condensor, the jet of compressed air was gradually lowered, thus leaving behind a continous and substantial crust of crystalline $S_3N_2Cl_2$. The reaction was complete after approximately 6 h when all the $S_2Cl_2$ had been consumed. The lower air condenser was removed to a twin necked round bottom flask, fitted with a tap adaptor and stopper.

The crude $S_3N_2Cl_2$ was then pumped on to remove volatile impurities, in particular $SCl_2$ and $S_2Cl_2$, and the crystals were then scraped into the flask against a counter current of dry nitrogen. These were further pumped on before storing in a sealed container in the glove box. Yields of up to 20 g $S_3N_2Cl_2$ were obtained by this method and the reaction pot could be re-used up to 5 times simply by re-charging with further aliquots of $S_2Cl_2$. Infrared spectrum, $\nu_{max}$ 1010s, 933vs, 826w, 710s, 579s, 459s, 403vs, 381ms $cm^{-1}$.

### 2.4.2. $(NSCl)_3$.- *Trithiazyltrichloride.*

This was prepared by the chlorination of $S_3N_2Cl_2$ according to the method described by Jolly and Maguire[3]. $S_3N_2Cl_2$, placed in a round bottom flask reacted with chlorine gas (dried by passage through a $P_4O_{10}$ column) with release of $SCl_2$. Complete conversion and removal of $SCl_2$ from the mixture was helped considerably if the crystalline mass was broken up several times during chlorination. The solid extract was eventually exhaustively extracted with cold $CCl_4$ in a scaled up version of the closed extractor described earlier. The $(NSCl)_3$ dissolved to give a bright yellow solution and bright yellow crystals leaving only a small amount of white residue solid on the frit (probably some $NH_4Cl/NH_4SO_4$). Virtually quantitative conversion was obtained by this method. Infrared spectrum (CsI plates) $\nu_{max}$ 1020vs, 835sh, 701s, 622w, 498vs, 441w, 390vs, 360vw, 347sh, 320sh $cm^{-1}$

### 2.4.3. $S_3N_2Cl$ - *Thiodiathiazyl chloride.*

There are two methods of bulk preparation of this compound. The first according to Jolly and Maguire[3] requires the heating of $S_3N_2Cl_2$ *in vacuo* for 8 - 10 h. The conversion by this method is incomplete and the product is generally contaminated with $S_4N_3Cl$. The second method produces much purer $S_3N_2Cl$ and is an altogether simpler procedure.

It involves the dechlorination of $S_3N_2Cl_2$ by $SO_2$ by stirring a suspension in $SO_2$ for several days in the presence of sunlight[2]. $S_3N_2Cl_2$ (0.5 g, 2.56 mmol) was placed into a 'dog', and $SO_2$ (25ml) condensed on to this. An orange/brown suspension is thus obtained. Over about 2 h this slowly darkens and gradually goes green. At the same time, the solid in contact with the $SO_2$ also goes green. After 3 days there is an orange solution over good dark green crystals. These are filtered off and the green solid washed several times by back distillation. (Yield = 0.36 g, 88% based on $S_3N_2Cl_2$). $S_3N_2Cl$ requires; N 17.54%, S 60.25%, Cl 22.2%. Found; N 17.65%, S 59.01%, Cl 23.8%.

### 2.4.4. $[PhCN_2S_2]Cl$ - *4-Phenyl 1,2,3,5, Dithiadiazolium Chloride.*

This was prepared by the method described by Banister et al[4] from the reaction of benzonitrile, with ammonium chloride and sulphur dichloride. Ammonium chloride (20.0 g, 0.37 mol, finely powdered and oven dried) was suspended in sulphur dichloride (100 ml, 1.58 mol) and benzonitrile (38 ml, 0.37 mol) in a 500 ml twin necked round bottom flask. The reaction was maintained at reflux at 100°-120° C for 15 hours. Initial preparations had a continous stream of dry chlorine gas passing through the solution at approximately 60 $mm^2s^{-1}$. However, it was found for later preparations that a blanket of chlorine gas over the mixture which was renewed periodically was adequate to prevent formation of $S_3N_2Cl_2$. The mixture was then cooled to -10° C and filtered. The crude orange product was washed with 4 x 50 ml aliquots of diethyl ether and then pumped on for a further 4 hours to remove any remaining $SCl_2$. The product was then placed in a large closed extractor and washed with liquid $SO_2$ (25 ml). This gave an orange solution and unreacted ammonium chloride on the frit. Evaporation of the $SO_2$ gave deep orange crystals of $[PhCN_2S_2]Cl$. Yield = 24.6 g, 31 % based on benzonitrile.

$C_7H_5N_2S_2Cl$ requires C 38.8%, H 2.3%, N 12.9%, S 29.6%, Cl 16.4%. Found C 38.4%, H 2.6%, N 12.4%, S 30.0%, Cl 17.1%. Infrared spectrum, $\nu_{max}$ = 1600w, 1390m, 1350w, 1150m, 1070m, 1028m, 1000w, 922m, 893s, 840s, 785s, 701s, 690msh, 549s, 510w, 472w cm$^{-1}$.

### 2.4.5. $(PhCN_2S_2)_2$.- *4-Phenyl 1,2,3,5 dithiadiazole.*

$[PhCN_2S_2]$ Cl (7.3 g, 33.7 mmol) and an excess of zinc/copper couple[4] were stirred together in 50 ml of THF for 4 hours at room temperature. Immediately on adding the couple to the orange solution there was immediate colour change and the solution went purple/black. The solution was then evaporated to dryness and the crude black solid placed directly into a sublimer. $(PhCN_2S_2)_2$ (yield = 3.2 g, 53 %) sublimed ($10^{-3}$ Torr, 120° C, cold finger = 10° C) to give dark green needle crystals. It was not found necessary to purify these any further. $C_{14}H_{10}N_4S_4$ requires C 46.38%, H 2.76%, N 15.46%, S 35.40%. Found C 47.1%, H 2.43%, N 15.8%, S 34.95%. Infrared spectrum, $\nu_{max}$ = 1595mw, 1320m, 1240m, 1235m, 1185w, 1175w, 1160w, 1145msh, 1140s, 1075m, 1023m, 1003w, 970br, 922w, 896w, 836m, 805s, 780vs, 772s, 720m, 690s, 686s, 655s, 510s cm$^{-1}$.

### 2.4.6. [*p* - $ClPhCN_2S_2$]Cl - *4-(4-chlorophenyl) 1,2,3,5 dithiadiazolium Chloride.*

This was prepared by the method described as above by Banister et al[4]. $NH_4Cl$ (20.0 g, 0.37 mol) was suspended in $SCl_2$ (150ml, 2.34 mol), to which 4- chlorobenzonitile (10.0 g, 0.07 mol) was added. This was refluxed for 5h (85°C) under a blanket of $Cl_2$. The mixture was then cooled to -20°C, filtered and the crude product washed with 2x 10ml aliquots of dry diethyl ether followed by continous extraction with $SO_2$. The product was then recrystallised from $SO_2$, (yield = 6.15g, 35% ).

$C_7H_5Cl_2N_2S_2$ requires C 33.5%, H 1.6%, N 11.2%, Cl 28.3%, S 25.5%. Found; C 33.37%, H 1.56%, N 11.38%, Cl 27.80%, S 25.61%. Infrared spectrum, $\nu_{max}$ = 1595br, 1412wsh, 1400w, 1283mw, 1174m, 1152ms, 1091s, 1010s, 960w, 919mw, 890s, 842vs, 733vs, 725s, 682ms, 540ms, 495m, 489w $cm^{-1}$.

### 2.4.7. $S_2NAsF_6$ - *Dithiazyl hexafluoroarsenate.*

This was prepared by the method described by Passmore et al[5] from $S_4N_4$, $S_8$ and $AsF_5$. Yields of 70 % were obtained when the crude product was recrystallised from $SO_2$. It was noted that better and purer yields were also obtained when large crystals of $S_2NAsF_6$ were allowed to grow first.

### 2.4.8. $S_4N_4$ - *Tetrasulphur tetranitride.*

This was prepared according to the method described Jolly and Villena-Blanco[6]. $S_2Cl_2$ (50 ml, 0.62 mols) was chlorinated in $CCl_4$ (1400ml) to give $SCl_2$. When this was complete, ammonia gas was passed into the solution. The flow rate was adjusted such that the temperature of the reaction was kept below 50°C.

$$6SCl_2 + 16NH_3 \xrightarrow{CCl_4} S_4N_4 + 2S + 14NH_4Cl \qquad \text{Eq. 2.1}$$

The mixture goes through a series of colour changes, from initial pale yellow,through cream and various shades of green, gradually getting darker, until a brown/red and finally a gold colour is reached, after about 2 h. The filtrate was then washed with ice cold water to remove most of the $NH_4Cl$ to leave green coloured $S_4N_4$ which was then air dried for several days. This solid was then soxhlet extracted with dioxane (400ml) for 6h to leave behind any further $NH_4Cl$, Yield = 30 g. Further purification was then achieved by several recrystallisations from benzene. Even purer $S_4N_4$ may then be obtained by a sublimation. Analysis; $S_4N_4$ requires N 30.40%, found N 30.35%. Infrared spectrum, $\nu_{max}$ = 930s, 770w, 720m, 700s, 548s, 530w, 520w, 350s.

## 2.5. Other Starting Materials.

### 2.5.1. *Arsenic Pentafluoride.*

Commercial supplies of $AsF_5$ are not available in this country. It was therefore necessary to prepare this reagent from the burning of arsenic in fluorine gas in a modified preparation previously used in this lab. Fortunately fluorine was readily available in this Department in a 50/50 $N_2/F_2$ mixture from cylinders supplied by Mattheson. This replaced the much less reliable and hence more dangerous use of an electrochemical cell to generate $F_2$.

The apparatus, shown in Figure 2.4. consisted of a flow system in which the $N_2/F_2$ mixture was passed over lumps of arsenic (lumps were used to prevent the reaction becoming too vigorous). The $AsF_5$ produced was then swept into the first of two cold traps at liquid air temperature (to prevent the condensation of liquid $F_2$). These could be independently isolated by means of Youngs taps. The last cold trap terminated in a dual steel manifold T piece. To this was attached the Monel storage cylinder, along with a vacuum line and a supply of dry nitrogen. The T piece was arranged such that either a stream of dry nitrogen could be blown across the end vent (to disperse unreacted $F_2$ and $N_2$ carrier gas) or a vacuum applied to the line to manipulate the volatile $AsF_5$.

The tubing consisted of 1/4" OD copper tubing throughout, all connections between metal and glass parts of the apparatus were *via* 1/4" Swagelok teflon compression fittings. The flow of gas was controlled with Monel Whitey Valves(1KS4). The reaction vessel itself consisted of 1" Monel tube, one end of which terminated with 1/4" Monel tubing to a Whitey valve (1KS4) whilst the other end was fitted with a flange and a Whitey (1KS4) valve, such that the tube could be easily opened and charged with a ceramic alumina boat loaded with the required arsenic.

The reaction vessel was wound with copper tubing for water cooling, since the extremely vigorous nature of the reaction generates a large amount of heat. The whole apparatus was connected together, Tap H closed and the system evacuated up to Tap A. The system was then let down to nitrogen, and this whole procedure was repeated several times to purge any air from the system.

Tap B was then closed and Tap A opened fully, thus the flow rate of $F_2/N_2$ from a secondary calibrated supply system, was controlled by the use of Tap B. The remaining taps were all opened except for G and F. The flow was monitored by use of the bubbler, whilst dry $N_2$ was bled across the T piece and through the bubbler.

Typically 20 g arsenic were loaded into the reaction tube. Once the $F_2/N_2$ gas reached the arsenic, the reaction proceeded rapidly, although the reaction rate could effectively be controlled by the flow rate of the gas. A white solid ($AsF_5$) very quickly collected in the first trap with a small amount being carried over to the second trap. It was important to avoid blocking the inlet and outlets on the traps and also that no liquid $F_2$ condensed.

Any $AsF_5$ escaping from the two traps or being carried through the system could easily be seen by the formation of dense white fumes of arsenic oxides. Eventually after 4 h the reaction was complete. The $AsF_5$ was purified by fractional distillation into the second cold trap. Taps D and H were then closed and the $AsF_5$ condensed across into the storage vessel.

A small cylinder of known volume (10ml) was attached to the top of the storage cylinder along with a calibrated Bourdon gauge, thus enabling small known quantities of $AsF_5$ to be dispensed (See Figure 2.5).

Figure 2.4. Flow diagram for $AsF_5$ Preparation.

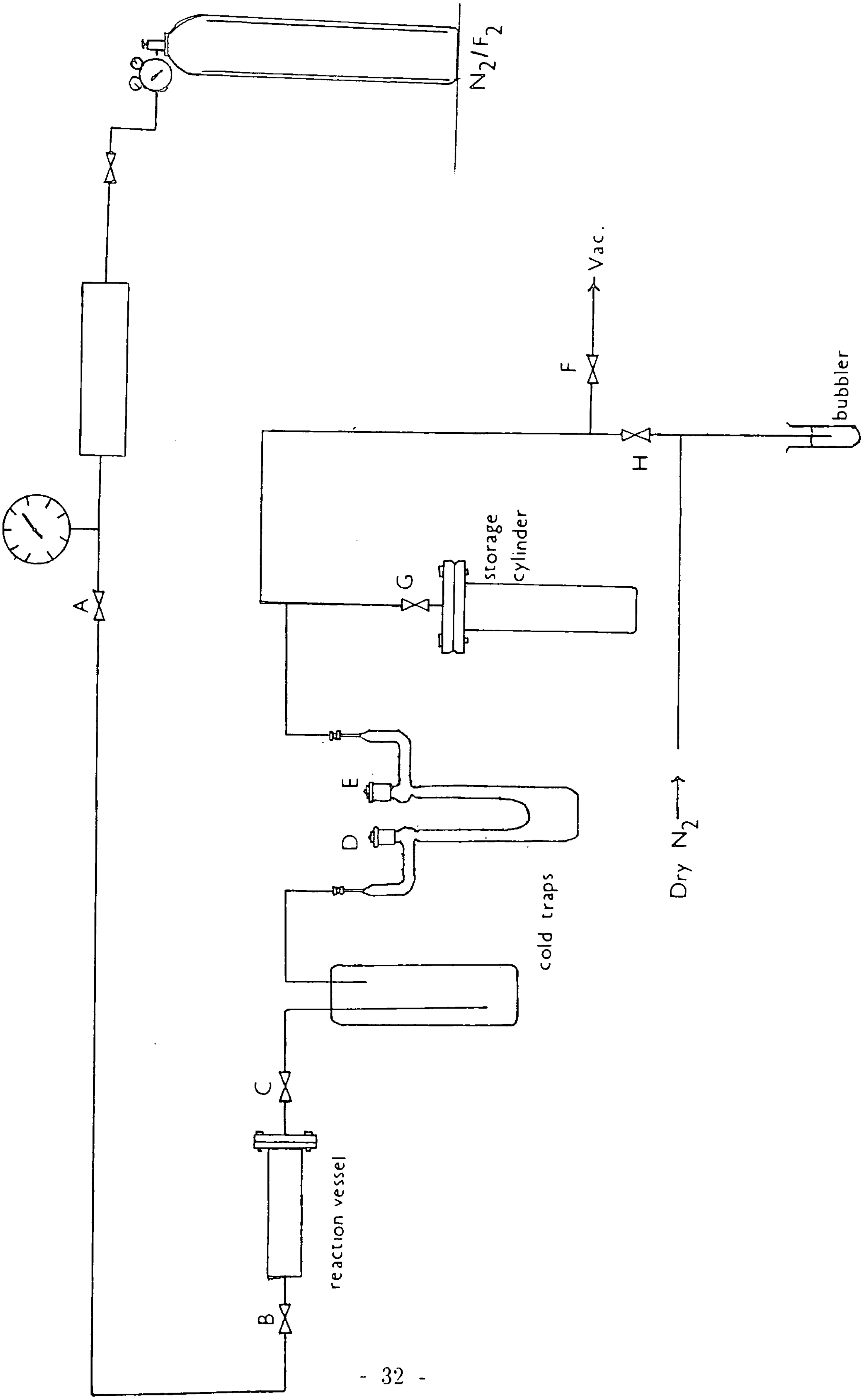
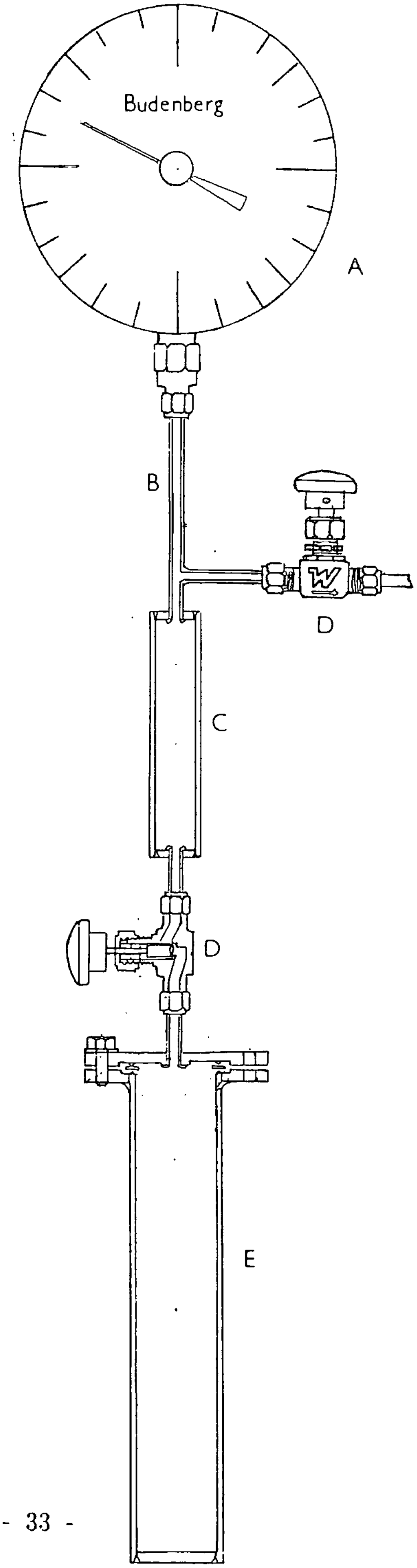


Figure 2.5. Storage vessel and Budenburg gauge.



2.5.2. ***Silver hexafluoroarsenate.*** $AgAsF_6$ - This was prepared by the direct recation of $AsF_5$ with Ag as described in the literature[1] according to equation 2.2.

$$2Ag + 3AsF_5 \xrightarrow{liq.SO_2} 2AgAsF_6 + AsF_3 \qquad \text{Equ. 2.2}$$

Powdered silver ( 8.0 g, 0.074 mol, 99% pure.) was placed in a pre-weighed glass bulb (*ca.* 200ml) fitted with a Youngs tap. $SO_2$(15ml) was condensed on top of this and after re-weighing the bulb, $AsF_5$ (total = 19 g) was also condensed into the bulb in three aliqouts. Each time the bulb was allowed to warm to room temperature. An exothermic reaction occurred to give a very slightly brown solution above the unreacted silver. The solution was shaken each time and then allowed to stand for 1/2 h. Eventually all the silver had dissolved giving a light brown solution. Removal of all the volatiles (excess $AsF_5$, $AsF_3$, $SO_2$) yielded a white crystalline solid ($AgAsF_6$). Yield = 21 g, 98%. Infrared spectrum, $\nu_{max}$ 690s, 385s.

## 2.6. Miscellaneous reagents.

**2.6.1. Sulphur Tetrafluoride,** $SF_4$ - This was used direct from the cylinder, supplied by Matheson. It was used to pacify the vacuum line and scrupuously dry the manifold and reaction cans prior to $S_2NAsF_6$ preparations.

**2.6.2. Chlorine,**$Cl_2$ - For large scale reactions this was used direct from the cylinder, supplied by Matheson, and was dried by passage through a $P_4O_{10}$ column.

**2.6.3. Fluorine, $F_2$** - Elemental fluorine was supplied by Matheson as a 50/50 mixture and used via a secondary cylinder of known volume, fitted with an accurate corrosion resistant Bourdon gauge manufactured by the Budenburg Company.

**2.6.4. Silver, Ag** - Silver powder, 99.9% pure, was supplied by B.D.H. Ltd. and used direct from the bottle.

**2.6.5. Silver tetrafluoroborate, $AgBF_4$** - This was supplied by B.D.H. Ltd. and was stored in its black polythene container in the glove box.

**2.6.6. Silver triflate, $AgCF_3SO_3$** - This was supplied by Aldrich and stored in its brown bottle in the glove box.

**2.6.7. Cyanogen, $(CN)_2$** - Supplied by Matheson, this was used direct from the cylinder.

**2.6.8. Sulphur, $S_8$** - Supplied by B.D.H. ltd., this was dried *in vacuo* before use. For the preparation of high purity $S_2N^+AsF_6^-$, 99.9999% pure sulphur was used.

**2.6.9. Sulphur dichloride, $SCl_2$** - Supplied by B.D.H. Ltd. and used direct from the bottle.

**2.6.10 Disulphur dichloride, $S_2Cl_2$** - Supplied by B.D.H. Ltd. and used direct from the bottle.

**2.6.11. Ammonium Chloride, $NH_4Cl$** - Supplied by Hopkin and Williams, this was dried at 100° C in an oven before use.

**2.6.12. Antimony pentachloride, $SbCl_5$** - This was supplied by B.D.H. Ltd. and distilled before use ( 68°C, 14 torr).

**2.6.13. Lithium bis(trimethylsilyl)amide, $((CH_3)_3Si)_2NLi$** - This was supplied by Aldrich as a 1.0M solution in THF and used direct from the bottle.

**2.6.14. Benzonitrile, PhCN** - This was supplied by Aldrich and dried over molecular sieve(grade 4A, B.D.H.Ltd.). It was then used direct from the bottle.

**2.6.15. 4 - Chlorobenzonitrile, *p* - $ClC_6H_4CN$** - This was supplied by Aldrich, and the powder used direct from the bottle.

**2.6.16. Tetrabutylammonium tetrafluoroborate (TBATFB), $nBu_4NBF_4$** - This was supplied by S.T.Wait for use in the CV work. It was synthesised by simple metathesis from $Bu_4NHSO_4$ (Lab Kemi, Sweden) and $KBF_4$ (BDH Ltd.). It was purified by double recrystallisation from an ethylacetate/diethyl ether mixture and finally vacuum dried ($10^{-5}$ Torr) at 125°C.

**2.6.17. Arsenic, As** - Granular arsenic, 99.9% pure, was supplied by Alpha Products and was used direct from the bottle.

**2.6.18. Tetramethylammonium chloride, $Me_4NCl$** - This was supplied by Aldrich and vacuum dried at 110°C ($10^{-3}$ Torr) before use.

## 2.7. Purification of Solvents.

**2.7.1. Sulphur dioxide, $SO_2$** - Sulphur dioxide, supplied by B.D.H. ltd. was stored for an initial period of 1 week over $P_4O_{10}$, and then distilled from the $P_4O_{10}$ onto $CaH_2$ over which it was stored. The storage and distillation were conveniently performed in stainless steel vessels which could accommodate 500 ml batches of $SO_2$ (designed by Dr Z.V.Hauptman).

**2.7.2. Acetonitrile, $CH_3CN$** - For general purpose use as a solvent, H.P.L.C. grade acetonitrile was distilled from $P_4O_{10}$ and stored in a pyrex vessel fitted with a Youngs tap.

For electrochemical use, a much purer solvent was required. It was found, however, that sufficient purification was achieved if Fisons DNA grade acetonitrile was refluxed and distilled from $CaH_2$ just prior to use and stored in a pyrex vessel fitted with a Youngs tap.

### 2.7.3. Solvents dried over sodium.

The following solvents were used after storing for a sufficient period over sodium wire; diethyl ether, pentane, hexane. Diethyl ether was only used after a negative peroxide test had been obtained.

### 2.7.4. Solvents dried by distillation.

The following solvents were dried by reflux and distillation from $P_4O_{10}$ followed the same process over $CaH_2$; methylene chloride, carbon tetrachloride and toluene. Toluene was then stored over sodium wire, whilst $CH_2Cl_2$ was stored over molecular sieve(grade 4A, BDH Ltd.).

### 2.7.5. Thionyl Chloride - $SOCl_2$.

This was purified by fractional distillation[7] from 10% by weight triphenyl phosphite in apparatus fitted with teflon sleeves. It was stored in the dark in a pyrex glass bulb fitted with a Youngs tap.

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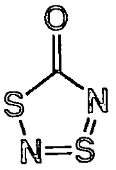
# CHAPTER THREE.

# DITHIADIAZOLIUM SALTS AND RELATED HETEROCYCLES.

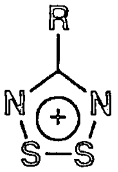
## 3.1. INTRODUCTION.

There has been considerable attention paid to the preparative methods of S/N heterocycles. Particularly in the past few years these have concentrated on various C/S/N systems with a view to their use as possible pre-cursors to organic analogues of $(SN)_x$[1].

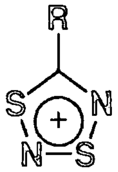
For the five membered C/S/N heterocycles of formula $CN_2S_2$ there are, however, just three known isomers:-



I.



II.



III.

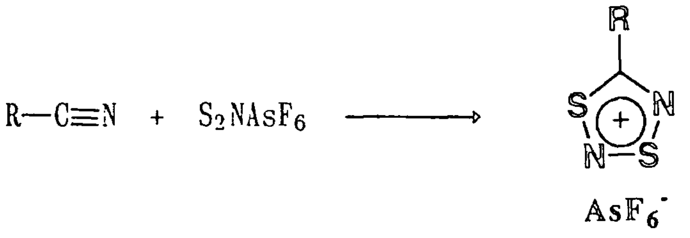
These are the 5-oxo, $1,3\lambda,2,4$, dithiadiazole (I), and the 1,2,3,5 dithiadiazolium (II) and the 1,3,2,5 dithiadiazolium (III) isomers respectively. Generally, synthetic routes are numerous and varied and very often only with rather speculative mechanistic routes. There are two main preparative routes to (II). The earliest was the reaction of $(NSCl)_3$ with an organic nitrile first reported in 1977[2,3] along with the first crystal structure of a type (II) compound, that of $(Cl_3\overset{C}{\wedge}CN_2S_2)Cl$[3,4].

$$RCN + 1/3(NSCl)_3 + 1/8S_8 \longrightarrow [RCN_2S_2]Cl. \qquad \text{Eq. 3.1}$$

The best route, however, involves the reaction of an organic nitrile with $SCl_2$ and $NH_4Cl$ under a blanket of dry chlorine[5]. The proposed mechanism for this reaction is the *in situ* formation of 'NSCl'. This is a more convenient synthetic method since $SCl_2$ is much more readily accessible than $(NSCl)_3$ and yields are generally greater.

$$RCN + 2SCl_2 + NH_4Cl \longrightarrow 4HCl + [RCN_2S_2]Cl \qquad \text{Eq. 3.2}$$

There are several other less important methods, eg. the reaction of $NaN_3$ with $RCN(NSCl)_2$ to obtain (II)[6]. The 1,3 isomer has been prepared from the reaction of $S_4N_4$ with $Br_2$ and $CS_2$ ar room temperature[7] but until the synthesis of $S_2NSbCl_6$ appeared in 1978[8], very few examples were known. The $S_2N^+$ cation, as the more useful $AsF_6$ salt[9], reacts via a simple (4 + 2) symmetry allowed cycloaddition[10] with 1,3, dipoles or Diels-Alder unsaturated organic groups, such as $RC{\equiv}N$ and $RC{\equiv}CR$.



Eq. 3.3

This reaction is an example of more general routes to cations containing the 1,3,2,5 dithiadiazolium and the 1,3,2 dithiazolium rings[11]. Both of the dithiadiazolium isomers may be readily reduced to the corresponding dithiadiazole systems - remarkably stable $7\pi$ electron free radicals. Phenyldithiadiazole, $(PhCN_2S_2)_2$, was the first reported example of such a radical, its dimer being formed by the sodium thiocyanate reduction of $[PhCN_2S_2]Cl$[12].

Esr studies showed that a solution of $(PhCN_2S_2)_2$ contains persistent free radicals, indicated by a simple 1,2,3,2,1, quintet due to interaction of an unpaired electron with two equivalent nitrogen nuclei[13]. No dimer units were detected above 250K in solution. As indicated by Mews[14], ring orbitals of the dithiadiazolium system are only marginally disturbed by radical formation and by changes in ligand, and the energy changes with conformation are only small. Fig. 3.1.

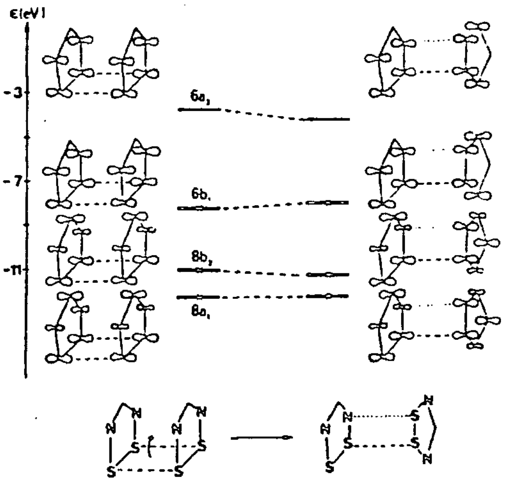


**Figure 3.1.** $\mathrm{R}\overline{\mathrm{CNSSN}}$ Orbital Energy Levels.

Indeed actual conformation depends more on subtle effects such as secondary interactions and packing forces. Further MNDO calculations[15] have shown $HCN_2S_2$ to have an $^2A_2$ ground state which explains well the above observations and the fact that the hyperfine coupling constants for the dithiadiazole radicals are practically invariant to the nature of R. This is because the $A_2$ SOMO of $HCN_2S_2$ has a vertical node bisecting the ring and which therefore prevents direct conjugative interaction between the unpaired electron and the ligand. A photoelectron spectral study of $RCN_2S_2$ has shown three distinct ionisations of electrons which correspond respectively to the low lying SOMO (7-9ev), the heterocyclic $\pi$ and $\sigma$ orbitals and finally the orbitals associated with the ligands, all of which indicates that dithiadiazoles are resonably insensitive to the ligand environment. Nevertheless, since some of the alkyl derivatives are stable paramagnetic liquids at room temperature and the aryl derivatives are dimers or polymers, the physical properties do seem to depend somewhat on the R substituent.

Known 1,2 dithiadiazolium salts are either brightly coloured, type A or purple/black, typeB, depending on the anion. The harder[29] the anion the more brightly coloured the salt, for instance, $PHCN_2S_2AsF_6$ - bright orange, $PhCN_2S_2Br$ - dark red and $PhCN_2S_2I$ - black[5].

The first crystal structure of a dithiadiazolium system, that of $[Cl_3CN_2S_2]Cl$ appeared in 1977[4] but did not present very satisfactory results because of solvent incorporation into the structure and strong cation/anion interactions. In the chlorides, for example, there are considerable chlorine/sulphur interactions as indicated by the close approach of the chloride atom to the disulphide atoms. There is increasing cation/anion 3 centre interactions in the series $Cl^-$ - $FeCl_4^-$ - $Br^-$ - $I^-$ - $CN^-$ - $NCS^-$. To minimise these effects and therefore to allow comparison with similar structures, eg. $[PhCN_2S_2]_2[S_3N_3]$[25] etc., the compound $[PhCN_2S_2]AsF_6$ was synthesised by simple metathesis and its crystal structure determined. The $AsF_6^-$ anion is relatively hard and $[PhCN_2S_2]AsF_6$ gave a crystal analysis with an R value of 2.6. In this chapter studies related to some physical measurements are reported,along with the synthesis of new dithiadiazolium salts and dithiadiazoles.

## 3.2. EXPERIMENTAL.

**3.2.1.** ***Preparation of*** $(p - ClPhCN_2S_2)_2$. - Bright orange $[p\text{-}ClPhCN_2S_2]Cl$ was prepared according to literature methods from p - ClPhCN, $NH_4Cl$ and $SCl_2/Cl_2$[5].

A suspension of $[p - ClPhCN_2S]_2$ Cl (0.964g, 3.86 mmol) was stirred with Zn/Cu couple (2.0g, 15.5mmol) in 20ml of dried THF at room temperature. On addition of the Zn/Cu couple the solution turned black/purple. After stirring for 1/2 h the THF was removed under vacuum to leave a purple/black solid, which was purified by sublimation ($10^{-6}$ Torr, 100°C which yielded a black/green solid(0.51g, 61%) similar in appearance to $(PhCN_2S_2)_2$. Found; C 38.51, H 1.79, N 13.46, S 28.78, Cl 15.96; $C_7H_4N_2S_2$ Cl requires C 38.97, H 1.86, N 12.99, S 29.74, Cl 16.4; m.s CI m/e 215 11% $(PhCN_2S_2)^+$, m/e 137 100% $(ClPhCN_2)^+$; ir $\nu_{max}$= 1590m, 1490m, 1405s, 1245mbr, 1175m, 1165w, 1155m, 1135s, 1105m, 1095vs, 1025s, 905w, 845m, 840s, 810s, 780vs, 720s, 650s, 510s, 485m.

### 3.2.2. ***Preparation of 4- Propyl - 1,2,3,5 Dithiadiazole.***

$[CH_3CH_2CH_2C\overline{NSSN}]$ Cl was prepared in an analogous manner to that of $[PhCN_2S_2]Cl$. n-Butylonitrile, $CH_3CH_2CH_2CN$, (32ml, 0.37mol, $\rho$=0.7936) was refluxed in a suspension of $NH_4Cl$ (20.0g, 0.37mol) in $SCl_2$ (120ml, 1.89mol) for 5h under a blanket of dry chlorine. After refluxing, the reaction mixture was cooled to 0°C and filtered. Orange $[CH_3CH_2CH_2CN_2S_2]Cl$ (7.1g, 10.5%) was obtained after $SO_2$ extraction of the crude solid. $[CH_3CH_2CH_2CN_2S_2]Cl$ (1.5g, 8.22mmol) was stirred with a suspension of excess Zn/Cu couple (2.0g, 15.5mmol) in liquid $SO_2$ for 6h at room temperature. The $SO_2$ was then carefully vented off, before the volatile product was fractionated through a series of U traps held at -15°C and -196°C respectively under a slight dynamic vacuum. Gentle heating was applied to the solid residue to help volatilise the product. A dark red volatile liquid condensed in the connecting tubes and finally in the first U trap. The product was a purple/red solid which on warming to room temperature melted to a red liquid (0.76g, 63%).

Found C 32.4, H 4.6, N 19.3, S 44.1; $C_4H_7N_2S_2$ requires C 32.6, H 4.76, N 19.0, S 43.6; DSC.(4°C/min) mpt. 10.0°C; m.s(CI) m/e 147 $(C_4H_7N_2S_2)^+$, 57%, m/e 69 $(C_3H_7CN)^+$ 100%.

### 3.2.3. *Preparation of 4-t-Butyl-1,2,3,5 Dithiadiazole.*

$[(CH_3)_3CCN_2S_2]Cl$, prepared according to literature[3], (0.75g, 3.8mmol) was reduced following the same procedure as in 3.2.2. (yield = 0.53g, 86%). Found C 37.12, H 5.5, N 17.97, S 40.06; $C_5H_9N_2S_2$ requires C 37.24, H 5.60, N 17.38, S 39.80. DSC.(4°C/min) mpt. 22.0°C (cf. lit.20 -21°C); esr. g=1.905, (cf.lit. g=2.0121); m.s. (CI). m/e 161 $(C_5H_9N_2S_2)^+$ 37%, m/e 64 $(S_2)^+$ 79%, m/e 57 $((CH_3)_3C)^+$ 65%.

### 3.2.4. *Preparation of 4-t-Butyl-1,3,2,5 Dithiadiazole.*

$[(CH_3)_3C\overline{NSNS}]AsF_6$ was prepared from $S_2NAsF_6$ and t-BuCN in $SO_2$ according to literature[16], (measured mpt=150.0°C, cf lit. reported decomposed above 300°C).

$[(CH_3)_3CN_2S_2]AsF_6$ (1.0g, 2.86mmol) was reduced in a similar procedure to that followed in 3.2.2. except using $SbPh_3$ (0.77g, 2.18mmol) and $Me_4NCl$ (0.56g, 5.1mmol), again according to literature[16]. The whole preparation took place in the dark. A dark brown liquid (0.41g, 89%) was obtained, a cyclic voltammogram of this was recorded immediately, and which showed ~~the presence of~~ some 1,2 isomer already present.
Mpt 0 -1°C

### 3.2.5. *Preparation and crystal structure of 4-Phenyl-1,2,3,5 Dithiadiazolium Hexafluoroarsenate.*

Recrystallised $[PhCN_2S_2]Cl$ (0.56g, 2.6mmol) was placed in one bulb of a dog with $AgAsF_6$ (0.77g, 2.6mmol) in the other. $SO_2$ was condensed onto both (2 X 15ml) and warmed to room temperature.

The $AgAsF_6$ dissolved readily, whilst the $[PhCN_2S_2]Cl$ required some stirring before it dissolved. On addition of the $AgAsF_6$ solution to the $PhCN_2S_2Cl$, a dense white flocculent precipitate formed immediately (analysed as AgCl). The bright orange solution formed was stirred for a further 4h before being carefully decanted off and filtered. Bright orange crystals of $[PhCN_2S_2]AsF_6$ (0.93g, 97%) were grown as thin rhomb like platelets by reducing the volume of $SO_2$, and a suitable one for an X ray structure determination isolated. Found C 22.36%, H 1.39%, N 7.73%, S 17.51%, F 31.2%, As 19.98%; $C_7H_5N_2S_2AsF_6$ requires C 22.69%, H 1.35%, N 7.57%, S 17.32%, F 30.80%, As 20.26%.

(ii).**Crystal Data** - $C_7H_5N_2S_2AsF_6$, $M_r$ = 370.2,
Monoclinic, Space group $P2_1/c$.
a = 13.515(2), b = 5.7573(7), c = 15.175(2)Å, $\beta$ =94.83(1)°.
U = 1176.6$Å^3$, Z = 4, $D_c$ = 2.089 $gcm^{-3}$.
F(000) = 720, $\lambda(MoK\alpha)$ = 0.71073Å (graphite monochromator), T =295°C,
$\mu$ =3.28$mm^{-1}$.

Intensity data from a crystal of dimensions 0.06 x 0.54 x 0.8 mm mounted under $N_2$ in a sealed Lindeman capillary were collected on a Siemens AED2 diffractometer ($\omega/\otimes$ scans with on-line profile fitting, $2\sigma_{max}$= 50°, no significant variation for 3 standard reflections. Semi empirical absorption corrections were applied (transmission 0.35 - 0.87), 1965 unique reflections were measured. For determination of the structure 1593 reflections were used with $F>4\sigma_c(F)$ ($\sigma_c$ based on counting statistics only).

(iii).**Structure Determination** - All non H atoms were located by direct methods and refined with anisotropic thermal parameters and with H atoms constrained to give C-H = 0.96Å on ring angles external bisectors. U(H) = 1.2eq(C).

Weights were assigned as $\omega^{-1} = \sigma^2(F) = \sigma_c^2+9-55G+216G^2-12S+4S^2+9GS$. $(G=F_0/F_{max}, S=\sin\otimes/\sin\otimes_{max})$.
An isotropic extinction parameter X was refined to $X = 7(3) \times 10^{-7}$, where $F_c{}'=F_c/(1+XF_c{}^2/\sin2\otimes)^{1/4}$. Final residues are R = 0.0462, R = 0.0434, goodness of fit = 1.07, mean and max. shift/esd were 0.004 and 0.026 and all features in the final difference synthesis were between +0.68 and -0.51 $e\text{Å}^{-3}$. Refined coordinates are given in the tables 3.1. to 3.4.

### 3.2.6. *Preparation of 4-t-Butyl-1,2,3,5 Dithiadiazolium Hexafluoroarsenate.*

$[^t\text{ButylC}\overline{\text{NSSN}}]\text{AsF}_6$ was prepared by a metathesis procedure similar to that in 3.2.5. $[(CH_3)_3CCN_2S_2]AsF_6$ (0.5g, 2.54mmol) was placed in one half of a dog with $AgAsF_6$ (0.76g, 2.54mmol) in the other. $SO_2$ was condensed into both sides and the two solutions brought together, stirred for 5h at room temperature and filtered. The $SO_2$ solution yielded an orange/yellow solid (0.85g, 96%). $[(CH_3)_3CCN_2S_2]AsF_6$ was identified by infra-red. Found C 17.26, H 2.54, N 7.61, S 18.41; $C_5H_9N_2S_2AsF_6$ requires C 17.14, H 2.6, N 7.80, S 18.30.

### 3.2.7. *Preparation of 4-Benzyl-1,2,3,5 Dithiadiazolium Chloride.*

$[PhCH_2CN_2S_2]Cl$ was prepared in an analogous manner to that described in the literature[5]. $C_6H_5CH_2CN$ (22.3ml, 0.185mmol, $\rho$=0.972) was syringed against dry nitrogen into a suspension of oven dried $NH_4Cl$ (10.0g, 0.185mmol) in $SCl_2$ (120ml). A blanket of dry chlorine was maintained in the reaction vessel and the mixture heated at reflux (110°C) for 7h. The volume was reduced by about 40ml by evacuation and the slurry cooled to RT and then to -20°C. A bright orange/red crystalline solid (7.6g, 17.5%) was obtained on extracting the solid

Table 3.1. Bond Lengths (Å) and angles (°) for $[PhCN_2S_2]AsF_6$.

| | | | |
|---|---|---|---|
| S(1)-S(2) | 2.017(3) | S(1)-N(1) | 1.581(5) |
| S(2)-N(2) | 1.575(5) | N(1)-C(1) | 1.335(7) |
| N(2)-C(1) | 1.337(8) | C(1)-C(2) | 1.466(7) |
| C(2)-C(3) | 1.384(8) | C(2)-C(7) | 1.388(8) |
| C(3)-C(4) | 1.387(8) | C(4)-C(5) | 1.375(10) |
| C(5)-C(6) | 1.372(9) | C(6)-C(7) | 1.394(8) |
| As-F(1) | 1.690(5) | As-F(2) | 1.671(6) |
| As-F(3) | 1.661(7) | As-F(4) | 1.698(6) |
| As-F(5) | 1.664(8) | As-F(6) | 1.719(5) |

| | | | |
|---|---|---|---|
| S(2)-S(1)-N(1) | 94.9(2) | S(1)-S(2)-N(2) | 95.1(2) |
| S(1)-N(1)-C(1) | 116.0(4) | S(2)-N(2)-C(1) | 116.1(4) |
| N(1)-C(1)-N(2) | 118.0(5) | N(1)-C(1)-C(2) | 121.2(5) |
| N(2)-C(1)-C(2) | 120.8(5) | C(1)-C(2)-C(3) | 119.7(5) |
| C(1)-C(2)-C(7) | 119.9(5) | C(3)-C(2)-C(7) | 120.3(5) |
| C(2)-C(3)-C(4) | 119.3(6) | C(3)-C(4)-C(5) | 120.4(6) |
| C(4)-C(5)-C(6) | 120.6(5) | C(5)-C(6)-C(7) | 119.8(6) |
| C(2)-C(7)-C(6) | 119.6(5) | F(1)-As-F(2) | 89.2(3) |
| F(1)-As-F(3) | 92.6(4) | F(2)-As-F(3) | 88.5(4) |
| F(1)-As-F(4) | 92.1(3) | F(2)-As-F(4) | 178.5(3) |
| F(3)-As-F(4) | 92.1(4) | F(1)-As-F(5) | 89.9(4) |
| F(2)-As-F(5) | 92.8(4) | F(3)-As-F(5) | 177.2(4) |
| F(4)-As-F(5) | 86.5(4) | F(1)-As-F(6) | 179.5(3) |
| F(2)-As-F(6) | 91.2(3) | F(3)-As-F(6) | 87.8(4) |
| F(4)-As-F(6) | 87.5(3) | F(5)-As-F(6) | 89.7(4) |

Table 3.2. The atomic coordinates (x $10^4$) and isotropic thermal parameters (Å$^2$ x $10^3$) for the hydrogen atoms.

| Atom | x | y | z | U |
|---|---|---|---|---|
| H(3) | 9469 | 1450 | 6881 | 56 |
| H(4) | 11137 | 2504 | 6793 | 69 |
| H(5) | 11535 | 6059 | 6184 | 68 |
| H(6) | 10287 | 8604 | 5647 | 64 |
| H(7) | 8607 | 7562 | 5705 | 59 |

Table 3.3. Atomic Coordinates (x$10^4$) for [$PhCN_2S_2$]$AsF_6$.

| Atom | x | y | z |
|---|---|---|---|
| S(1) | 6020(1) | 4249(4) | 6134(1) |
| S(2) | 6457(1) | 1105(3) | 6605(1) |
| N(1) | 7110(3) | 5206(9) | 6080(3) |
| N(2) | 7601(3) | 1618(9) | 6601(3) |
| C(1) | 7844(4) | 3733(10) | 6327(3) |
| C(2) | 8887(4) | 4404(11) | 6295(3) |
| C(3) | 9631(4) | 2908(11) | 6622(3) |
| C(4) | 10616(4) | 3537(12) | 6573(4) |
| C(5) | 10851(4) | 5640(13) | 6216(4) |
| C(6) | 10117(4) | 7135(11) | 5893(4) |
| C(7) | 9124(4) | 6524(11) | 5931(4) |
| As | 6495(1) | 5666(1) | 8881(1) |
| F(1) | 7197(3) | 4649(12) | 8096(3) |
| F(2) | 7341(5) | 4667(16) | 9656(3) |
| F(3) | 7082(5) | 8205(12) | 8934(6) |
| F(4) | 5613(4) | 6674(16) | 8113(3) |
| F(5) | 5860(7) | 3189(13) | 8845(7) |
| F(6) | 5772(3) | 6691(10) | 9675(3) |

Table 3.4. Anisotropic thermal parameters (Å x $10^3$) for [$PhCN_2S_2$]$AsF_6$.

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

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 43(1) | 71(1) | 78(1) | 3(1) | -4(1) | -2(1) |
| S(2) | 48(1) | 57(1) | 84(1) | -5(1) | 10(1) | -11(1) |
| N(1) | 46(2) | 55(3) | 62(3) | 5(2) | 0(2) | 3(2) |
| N(2) | 49(2) | 46(3) | 62(3) | -2(2) | 10(2) | -1(2) |
| C(1) | 43(2) | 45(3) | 35(2) | -3(2) | 2(2) | 0(2) |
| C(2) | 45(2) | 41(3) | 37(2) | -6(3) | 8(2) | -4(3) |
| C(3) | 49(3) | 47(3) | 45(3) | 2(2) | 9(2) | 7(3) |
| C(4) | 47(3) | 67(4) | 57(3) | 0(3) | 8(2) | 4(3) |
| C(5) | 51(3) | 62(4) | 57(3) | -8(3) | 13(2) | -5(3) |
| C(6) | 58(3) | 48(4) | 56(3) | -3(3) | 13(2) | -11(3) |
| C(7) | 51(3) | 47(3) | 49(3) | -2(2) | 3(2) | 2(2) |
| As | 38(1) | 59(1) | 51(1) | -5(1) | 5(1) | 3(1) |
| F(1) | 74(2) | 174(6) | 62(2) | -37(3) | 15(2) | 24(3) |
| F(2) | 133(4) | 226(8) | 75(3) | -16(4) | -19(3) | 102(5) |
| F(3) | 125(5) | 97(4) | 255(9) | -35(5) | 90(5) | -47(4) |
| F(4) | 89(3) | 221(8) | 91(3) | 5(4) | -11(3) | 66(4) |
| F(5) | 176(7) | 88(5) | 280(10) | -60(6) | 90(7) | -64(5) |
| F(6) | 73(2) | 120(4) | 90(3) | -27(3) | 33(2) | 6(3) |

with liquid $SO_2$. The product was identified by infra-red spectroscopy and analysis. A further recrystallisation yielded red platelets but none suitable for a X ray crystal structure determination were found.

### 3.2.8. *Preparation of 4 - Phenyl - 1,3,2,5 Dithiadiazolium Hexafluoroarsenate.*

$S_2NAsF_6$ (0.217g, 0.811mmol) was placed into one half of a dog and PhCN (0.1g,0.811mmol, 0.09ml) syringed into the other. $SO_2$ (10ml) was condensed onto the $S_2NAsF_6$ which dissolved on warming to room temperature and was transferred onto the PhCN. An immediate reaction occurred to give a blue/green solution which was stirred for a further 8h, after which the $SO_2$ was removed and the solid residue washed with diethyl ether (3x15ml). On extraction with $SO_2$ a blue/green solid (0.18g, 60%) was obtained. Found C 23.0, H 1.41, N 7.50, S 17.56; $C_7H_5N_2S_2AsF_6$ requires C 22.70, H 1.35, N 7.57, S 17.32. i.r. $\nu_{max}$ = 1598s, 1495w, 1410vs. 1349m, 1329m, 1299m, 1273w, 1220m, 1210m, 1192m, 1170w, 1105m, 1072m, 1003s, 990vs, 918s, 890s, 841m, 800vs, 779vs, 720vs,br, 680vs,sh, 650s, 613m, 590s, 580sh, 570m, 440s, 400vs, ( 720 & 400cm$^{-1}$ belong to $AsF_6^-$)

### 3.2.9. *Preparation of $(CH_3CN_2S_2)_2$ from $[CH_3\overline{CNSSN}]Cl$*[13]

$(CH_3CN_2S_2)_2$ (0.5 g, 3.2 mmol) was reduced in a similar manner as 3.2.2. The product (0.34 g, 57%), which sublimed out under dynamic vacuum into a "U" tube, was a very air and moisture sensitive red/green volatile solid. Found: C 20.3, H 2.6, N 23.3, S 53.6; $C_2H_3N_2S_2$ requires C 20.1, H 2.5, N 23.5, S 53.8.

### 3.2.10. *Crystal structure of* $(CH_3CN_2S_2)_2$[17].

(*i*). ***Crystal Growth.*** - A suitable crystal was isolated from a sealed pyrex tube containing *ca.* 60 mg of $(CH_3CN_2S_2)_2$ within which a random mass transport was driven by natural fluctuations of ambient temperature over a period of nearly a year. Numerous earlier attempts at growing crystals by controlled sublimation in experiments of shorter duration (hours or days rather than months) failed. These included *in situ* growth in evacuated sealed quartz capillaries for X-ray diffraction studies. In many instances the crystals grown were well-shaped but their diffraction pattern invariably betrayed a highly imperfect lattice, mainly due to twinning and a heavy mosaic texture. Another purpose of the long term experiment with the sealed $(CH_3CN_2S_2)_2$ was to test a suspected photosensitivity of 1,2,3,5 dithiadiazoles with small alkyl substituents at the 4 position. No photodecomposition was detected despite frequent exposure of $(CH_3CN_2S_2)_2$ to direct sunlight. A small number of very thin platelets up to 1mm formed but these were most likely crystals of acetamide, $CH_3CO.NH_2$ - a product of hydrolysis by traces of chemisorbed moisture in the pyrex tube (despite thorough prior drying).

(*ii*) ***Crystal Data.***-$C_4H_6N_4S_4$, M = 238.4,
Triclinic, space group P $\bar{1}$,
a = 11.296(1), b = 12.498(1), c = 14.647(2)Å, $\alpha$ = 72.06(1),
$\beta$ = 77.85(1), $\gamma$ = 77.30(1)°,
U = 1896.3Å$^3$, Z = 8, $D_c$ = 1.670,
F(000) = 976, $\lambda$(Cu $K_\alpha$ )= 1.54184Å(graphite monochromator),
$\mu$ = 8.74 mm$^{-1}$, T=295 k.

Intensity data from a crystal of dimensions 0.5 x 0.2 x 0.2 mm mounted under $N_2$ in a sealed quartz capillary were collected on a Siemens AED2 diffractometer ($\omega/\Theta$ scans with on-line profile fitting,

$2\Theta_{max}$ 130°, one unique hemisphere of data with $l > 0$; no significant variation for 3 standard reflections).Semiempirical absorption corrections were applied (transmission 0.11 - 0.27), 6241 unique reflections were measured. For determination of the structure 5103 reflections were used, with $F > 4\sigma_c(F)$ ($\sigma_c$ based on counting statistics only).

(*iii*). ***Structure determination.*** - All non H atoms were located by direct methods and refined with anistropic thermal parameters and with H atoms constrained to give C-H = 0.96A, H-C-H = 109.5°, $U(H) = 1.2U_{eq}(C)$. Weights were assigned as $W^{-1} = \sigma^2(F) = \sigma_c^2(F) + 1 + 35G + 10G^2 - 6S + 6S^2 - 29GS$ ($G = F_o/F_{max}$, $S = \sin\Theta/\sin\Theta_{max}$). An isotropic extinction parameter X was refined to $X = 5.3(4) \times 10^{-6}$, where $F_c' = F_c/(1 + x F^2{}_c/\sin 2\Theta)^{1/4}$. Final residues are; R = 0.040, $R' = (\Sigma\, w\, \Delta^2/\Sigma\, w\, F_o^2)^{1/2} = 0.060$, goodness of fit = 1.17; mean and max. shift/esd were 0.06 and 0.62, and all features in the final difference synthesis were between +0.16 and $-0.33eÅ^{-3}$. Refined co-ordinates are given in table 3.7.

### 3.2.11. *Reaction of Anthracene 9 - carbonitrile with $S_2NAsF_6$.*

An immediate reaction, giving a very dark green colour, occurred when an $SO_2$ solution (10ml) containing $S_2N\,AsF_6$ (0.46g, 1.72mmol) was added to a suspension of $C_{14}H_9CN$ (0.35g, 1.72mmol) in $SO_2$(15ml). After stirring for 2h the $SO_2$ was removed to leave an olive green microcrystalline solid (0.80g, 98%). Found C 37.64, H 1.92, N 5.75, S 14.0, As 16.18; $C_{15}H_9N_2S_2AsF_6$ requires C 38.29, H 1.91, N 5.96, S 13.64, As 15.95, F 24.25. m.s.(CI) m/e 78 $(S_2N)^+$, 31%, m/e 203 $(C_{14}H_9CN)^+$ 100%.i.r. $\nu_{max}$= 1618m, 1550m, 1520m, 1415s, 1310m, 1285m, 1260s, 1190w, 1160w, 1155w, 1090m, 1025m, 965m, 955s, 920s, 900s, 845m, 810s, 780s, 755m, 740s, 720vs, 700vs, 670s, 660s, 640w, 610m, 590m, 520s, 470m, 400vs.

### 3.2.12. *Preparation of 4 - Methyl - 1,2,3,5 Dithiadiazolium Hexafluoroarsenate.*

This was prepared by metathesis as in 3.2.5 from $AgAsF_6$ (0.384g, 1.29mmol) and $[CH_3CN_2S_2]Cl$ (0.2g, 1.29mmol) in liquid $SO_2$.A brown solution resulted, which on filtering and removal of $SO_2$ gave a brown solid (0.24g, 61%) identified as $[CH_3CN_2S_2]AsF_6$ by i.r. and elemental analysis. $C_2H_3N_2S_2AsF_6$ requires C 7.79, H 0.97, N 9.09, S 20.81, As 24.34, F 37.00. Found C 7.85, H 1.10, N 9.11, S 20.69, As 25.1.

Table 3.5. Final positional parameters within $(MeCN_2S_2)_2$. Bond lengths (A) and angles (°).

| | | | |
|---|---|---|---|
| S(11)-S(12) | 2.077(1) | S(11)-N(11) | 1.628(3) |
| S(12)-N(12) | 1.639(3) | N(11)-C(11) | 1.333(5) |
| N(12)-C(11) | 1.329(4) | C(11)-C(12) | 1.488(6) |
| S(21)-S(22) | 2.071(2) | S(21)-N(21) | 1.632(3) |
| S(22)-N(22) | 1.636(4) | N(21)-C(21) | 1.347(6) |
| N(22)-C(21) | 1.326(5) | C(21)-C(22) | 1.502(6) |
| S(31)-S(32) | 2.078(2) | S(31)-N(31) | 1.628(3) |
| S(32)-N(32) | 1.639(3) | N(31)-C(31) | 1.331(6) |
| N(32)-C(31) | 1.323(5) | C(31)-C(32) | 1.494(5) |
| S(41)-S(42) | 2.074(1) | S(41)-N(41) | 1.629(3) |
| S(42)-N(42) | 1.636(3) | N(41)-C(41) | 1.343(5) |
| N(42)-C(41) | 1.313(4) | C(41)-C(42) | 1.500(6) |
| S(51)-S(52) | 2.074(1) | S(51)-N(51) | 1.629(3) |
| S(52)-N(52) | 1.639(3) | N(51)-C(51) | 1.341(4) |
| N(52)-C(51) | 1.326(5) | C(51)-C(52) | 1.478(5) |
| S(61)-S(62) | 2.084(2) | S(61)-N(61) | 1.639(3) |
| S(62)-N(62) | 1.641(4) | N(61)-C(61) | 1.337(4) |
| N(62)-C(61) | 1.322(6) | C(61)-C(62) | 1.500(6) |
| S(71)-S(72) | 2.078(2) | S(71)-N(71) | 1.626(3) |
| S(72)-N(72) | 1.629(4) | N(71)-C(71) | 1.335(6) |
| N(72)-C(71) | 1.328(5) | C(71)-C(72) | 1.507(6) |
| S(81)-S(82) | 2.074(2) | S(81)-N(81) | 1.633(4) |
| S(82)-N(82) | 1.635(4) | N(81)-C(81) | 1.341(6) |
| N(82)-C(81) | 1.327(5) | C(81)-C(82) | 1.493(6) |

| | | | |
|---|---|---|---|
| S(12)-S(11)-N(11) | 95.0(1) | S(11)-S(12)-N(12) | 93.8(1) |
| S(11)-N(11)-C(11) | 114.2(2) | S(12)-N(12)-C(11) | 114.8(3) |
| N(11)-C(11)-N(12) | 122.1(3) | N(11)-C(11)-C(12) | 119.1(3) |
| N(12)-C(11)-C(12) | 118.8(4) | S(22)-S(21)-N(21) | 94.7(1) |
| S(21)-S(22)-N(22) | 94.7(1) | S(21)-N(21)-C(21) | 114.2(2) |
| S(22)-N(22)-C(21) | 114.5(3) | N(21)-C(21)-N(22) | 122.0(3) |
| N(21)-C(21)-C(22) | 118.2(3) | N(22)-C(21)-C(22) | 119.7(4) |
| S(32)-S(31)-N(31) | 94.8(1) | S(31)-S(32)-N(32) | 94.1(1) |
| S(31)-N(31)-C(31) | 113.9(2) | S(32)-N(32)-C(31) | 114.1(3) |
| N(31)-C(31)-N(32) | 123.1(3) | N(31)-C(31)-C(32) | 117.9(3) |

| | | | |
|---|---|---|---|
| N(32)-C(31)-N(32) | 119.0(4) | S(42)-S(41)-N(41) | 94.7(1) |
| S(41)-S(42)-N(42) | 94.2(1) | S(41)-N(41)-C(41) | 114.0(2) |
| S(42)-N(42)-C(41) | 114.8(3) | N(41)-C(41)-N(42) | 122.3(3) |
| N(41)-C(41)-C(42) | 117.7(3) | N(42)-C(41)-C(42) | 120.0(4) |
| S(52)-S(51)-N(51) | 94.1(1) | S(51)-S(52)-N(52) | 94.6(1) |
| S(51)-N(51)-C(51) | 115.4(3) | S(52)-N(52)-C(51) | 114.8(2) |
| N(51)-C(51)-N(52) | 121.1(3) | N(51)-C(51)-C(52) | 119.0(4) |
| N(52)-C(51)-C(52) | 119.9(3) | S(62)-S(61)-N(61) | 94.6(1) |
| S(61)-S(62)-N(62) | 94.0(1) | S(61)-N(61)-C(61) | 114.1(3) |
| S(62)-N(62)-C(61) | 114.9(2) | N(61)-C(61)-N(62) | 122.4(4) |
| N(61)-C(61)-C(62) | 118.3(4) | N(62)-C(61)-C(62) | 119.3(3) |
| S(72)-S(71)-N(71) | 94.0(1) | S(71)-S(72)-N(72) | 94.8(1) |
| S(71)-N(71)-C(71) | 114.9(2) | S(72)-N(72)-C(71) | 114.2(3) |
| N(71)-C(71)-N(72) | 122.0(4) | N(71)-C(71)-C(72) | 117.9(3) |
| N(72)-C(71)-C(72) | 120.1(4) | S(82)-S(81)-N(81) | 94.8(1) |
| S(81)-S(82)-N(82) | 94.5(1) | S(81)-N(81)-C(81) | 113.9(2) |
| S(82)-N(82)-C(81) | 114.4(3) | N(81)-C(81)-N(82) | 122.4(4) |
| N(81)-C(81)-C(82) | 117.8(4) | N(82)-C(81)-C(82) | 119.8(4) |

**Table3.6. Distances (Å) and angles (°) of MeCNSSN.** The tabulated data are averages of values pertaining to 8 dithiadiazolium rings of the assymetric unit.

| | | | |
|---|---|---|---|
| S - S | 2.076(2) | SSN | 94.5(1). |
| S - N | 1.636(3) | CNS | 114.5(3). |
| N - C | 1.324(5) | NCN | 122.2(4). |
| C - C | 1.495(6) | NCC | 118.9(4). |

Average S/S distances between two monomers.

S(1) - S(2) 3.097(3).

**Table 3.7. Final Atomic Coordinates (x $10^4$);**

| Atom | x | y | z |
|---|---|---|---|
| S(11) | 3900(1) | 6118(1) | 4352(1) |
| S(12) | 5532(1) | 6758(1) | 4036(1) |
| N(11) | 3462(2) | 6414(2) | 5392(2) |
| N(12) | 5303(2) | 7108(2) | 5058(2) |
| C(11) | 4251(3) | 6895(3) | 5630(2) |
| C(12) | 3935(4) | 7232(4) | 6553(3) |
| S(21) | 2686(1) | 8491(1) | 3193(1) |
| S(22) | 2182(1) | 8949(1) | 4482(1) |
| N(21) | 3992(2) | 8960(2) | 2908(2) |
| N(22) | 3435(3) | 9462(2) | 4371(2) |
| C(21) | 4221(3) | 9405(3) | 3569(3) |
| C(22) | 5431(4) | 9804(3) | 3399(4) |
| S(31) | 1106(1) | 3549(1) | 6260(1) |
| S(32) | -549(1) | 3564(1) | 5846(1) |
| N(31) | 1567(3) | 2184(2) | 6421(2) |
| N(32) | -277(3) | 2194(2) | 5936(2) |
| C(31) | 780(3) | 1657(3) | 6232(2) |
| C(32) | 1132(4) | 405(3) | 6339(3) |
| S(41) | 2389(1) | 3916(1) | 4072(1) |
| S(42) | 2767(1) | 2171(1) | 4248(1) |
| N(41) | 1075(3) | 4093(2) | 3708(2) |
| N(42) | 1498(2) | 2137(2) | 3894(2) |

|  |  |  |  |
|---|---|---|---|
| C(41) | 778(3) | 3128(3) | 3666(2) |
| C(42) | -434(4) | 3205(4) | 3364(3) |
| S(51) | 3755(1) | 6302(1) | 2075(1) |
| S(52) | 4358(1) | 5763(1) | 825(1) |
| N(51) | 5120(2) | 6031(2) | 2377(2) |
| N(52) | 5801(3) | 5413(2) | 985(2) |
| C(51) | 6029(3) | 5612(3) | 1765(2) |
| C(52) | 7302(3) | 5363(4) | 1971(3) |
| S(61) | 4082(1) | 8763(1) | 860(1) |
| S(62) | 5874(1) | 8400(1) | 1159(1) |
| N(61) | 4459(3) | 8389(2) | -156(2) |
| N(62) | 6467(3) | 8002(3) | 167(2) |
| C(61) | 5664(3) | 8049(3) | -389(3) |
| C(62) | 6102(4) | 7659(4) | -1293(3) |
| S(71) | 999(1) | 8055(1) | 1336(1) |
| S(72) | -683(1) | 8066(1) | 968(1) |
| N(71) | 1568(3) | 6778(3) | 1228(2) |
| N(72) | -309(3) | 6798(3) | 799(2) |
| C(71) | 815(3) | 6280(3) | 964(2) |
| C(72) | 1292(4) | 5106(4) | 826(4) |
| S(81) | 1936(1) | 9222(1) | -762(1) |
| S(82) | 2513(1) | 7636(1) | -1025(1) |
| N(81) | 576(3) | 9406(3) | -1058(2) |
| N(82) | 1222(3) | 7614(3) | -1351(2) |
| C(81) | 373(3) | 8530(3) | -1318(2) |
| C(82) | -869(4) | 8592(4) | -1551(3) |

### 3.2.13. *Preparation of 4-Methyl-1,3,2,5 Dithiadiazolium hexafluoroarsenate.*

This was prepared in a modification of the literature method[18]. $S_2NAsF_6$ (0.41g,1.53mmol) was reacted with excess MeCN (2ml) in liquid $SO_2$. The solution was stirred for 1h, and after removal of the $SO_2$ and the excess MeCN under vacuum left a light brown residue (0.463g, 98%) which was identified as $[CH_3\overline{CNSNS}]AsF_6$ by i.r.

### 3.2.14. *Preparation of 4-Trichloromethyl-1,3,2,5 Dithiadiazolium Hexafluoroarsenate.*

$Cl_3CCN$ (0.175g,1.2mmol, $\rho$=1.44) and $S_2NAsF_6$ (0.324g, 1.2mmol) were reacted together in liquid $SO_2$. Although no immediate colour change was observed, the solution turned cherry red after stirring for 48h. On removal of the $SO_2$, the residual solid was washed with a little (5ml) diethyl ether. Pale red/brown crystals were obtained after the solid was pumped on for 6h. Under a microscope this proved to contain a small quantity of unreacted $S_2NAsF_6$ as yellow micro-crystals (identified by infrared spectroscopy), which were easily removed by Pasteur separation from the major product. $[Cl_3CCN_2S_2]AsF_6$ requires C 6.01, N 6.96, S 15.70, Cl 17.34, Found C 5.83, N 6.80, S 15.58, Cl 17.23.

### 3.3. General DSC Procedures.

All differential scanning calorimetry (DSC) measurments were made on a mettler FP80 control unit connected to a Mettler FP85 TA Thermal Analysis cell. For melting points and evaluation of enthalpies of fusion of both liquids and solids the sample was hermetically cold sealed in a pre-weighed aluminium capsule in a glove box where a 5 figure balance was available for accurate determination of weight. A trace over a range of temperature from -20°C to 400°C was possible by surrounding the analysis cell with a cooling coil connected to a Haake F3 bath circulator and insulating it with polystrene. Traces were usually run at 4°/min and a chart speed of 10mm/min. For accurate determination of $\Delta H_f$, it was necessary to standardise the chart before use with an indium sample of known weight and thermal capacity, (Enthalpy of fusion = 28.5 J/g)[31].

It was also found possible to obtain some enthalpies of evaporation for those samples whose vapour pressure was sufficiently great. This technique involved quickly piercing a capsule at thermal equilibrium at a given temperature. The instrument quickly returned to a new equilibrium set by the rate of evaporation of the sample through the pin hole, see Figure 3.2. The trace would return to the original equilibrium when all the sample had evaporated giving a measure of the total heat input. A flow of argon through the cell prevented hydrolysis of the sample.

This method is the basis of the Knudsen method of determination of relative molar masses, where the rate of loss of mass from a container through a small hole is proportional to the vapour pressure and is dependent on Grahams' law of diffusion:-

$$Z_wA_o = {}^{\rho.A_o}/(\pi mkT)^{1/2}$$

$Z_w$ = collision frequency, $\rho$ = Vapour pressure,

$A_o$ = Area of small hole, T = Temperature

m = relative molar mass, k = Boltzman constant.

### 3.3.1. Thermal study of 1,2,3,5 $(RCN_2S_2)_2$,(R = t-Butyl,Propyl,Ph,Me,$CF_3$)

The thermodynamic data ~~is~~ are summarised in Table 3.~~11~~ 12. and Figure 3.3 shows a typical DSC trace for a dithiadiazole. A very clear endothermic peak was generally observed which corresponded to a sharp melting point. There was no indication of decomposition, which would be an exothermic process and thus shift the trace in the opposite direction. For many of these dithiadiazoles the exact onset and peak temperature varied slightly ( ± 1.0°C) and appeared to depend on thermal history. This was particularly noticeable for the t-butyl and propyl derivatives since the rate of cooling of the sample to the start temperature seemed to influence the amount of dimerisation which occurred on freezing. The dithiadiazole ring is remarkable for its thermal stability, eg. thermal decomposition temperatures for tbutyl$CN_2S_2 \geq 170°C$, Ph$CN_2S_2 \geq 190°C$. Below these temperatures each sample gave very reproducible results indicating that no reaction occurred with the aluminium of the capsule, which has been found to occur with other S/N compounds, eg. $S_5N_5Cl$[19]. The products of pyrolysis appeared to consist of mixtures of polymer and parent nitrile detected by smell.

Figure 3.2. DSC trace for $\Delta H_{vap}$ measurements.

1. Original equilibrium
2. Hole pierced
3. New equilibrium
4. This area corresponds to total heat input

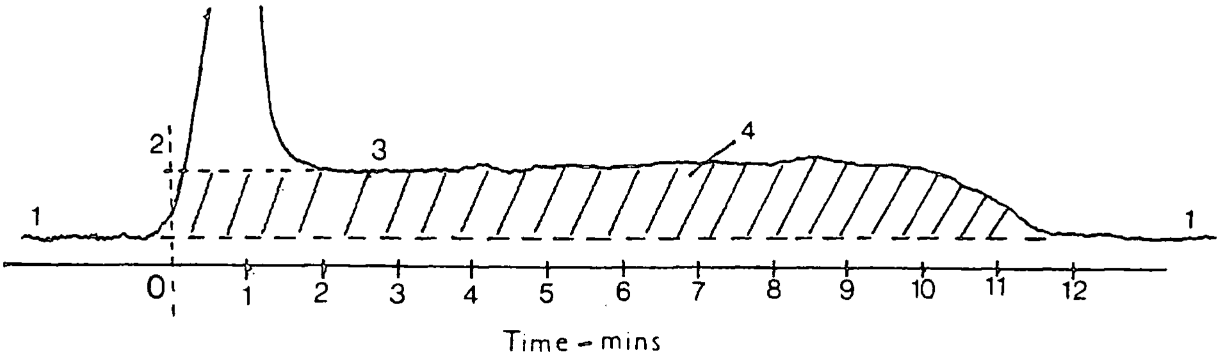
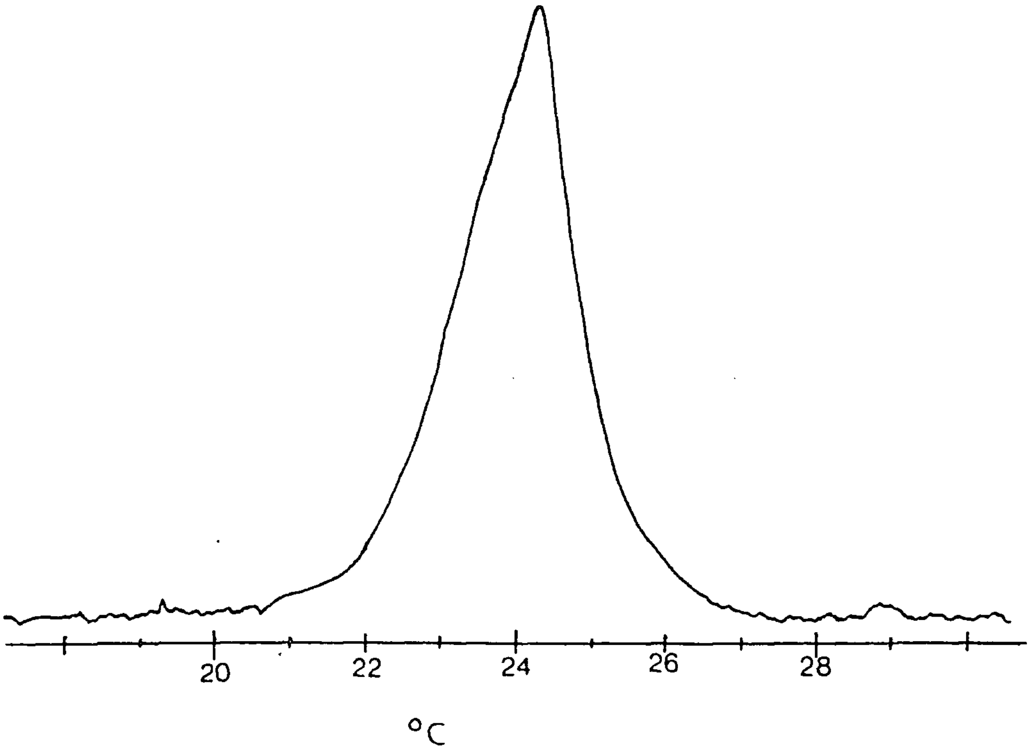


Figure 3.3. Typical DSC trace for $\Delta H_{fus}$ measurements - $\text{t-Bu}\overline{\text{CNSSN}}^{\cdot}$

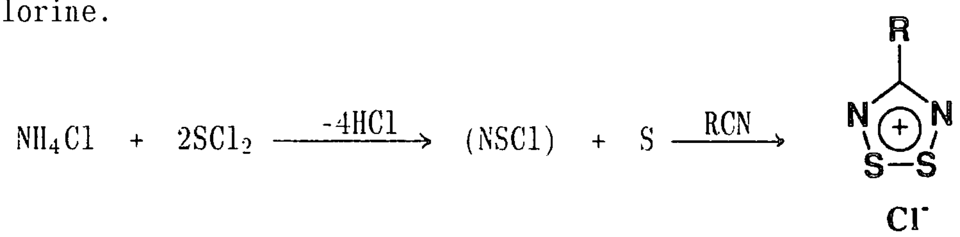


To evaluate $\Delta H_{vap}$ the evaporation of $(RCN_2S_2)_n$ ($n \leq 2$, R = t-butyl, propyl) in the liquid state at 423.2K through an orifice area *ca.* 0.0125cm$^2$ into an atmosphere of flowing argon (linear flow rate = 1cm$^{-1}$S$^{-1}$) obeyed an expected zero order kinetics, dn/dt = k.

## 3.4. RESULTS AND DISCUSSION.

### 3.4.1 *Preparation of novel dithiadiazolium/dithiadiazole rings.*

The two new derivatives, propyl and benzyl-1,2,3,5-dithiadiazolium chloride, were prepared. These were synthesised by the usual reaction of the nitrile with the $NH_4Cl/SCl_2/Cl_2$ mixture[5]. The previous failure of attempts to obtain phenyl derivatives with the electron withdrawing groups, CN- or $NO_2$-, in the para position by this route hinted at the mechanism[20]. The rate determining step is believed to be nucleophilic attack by the nitrile on $SCl_2$ to give an ionic intermediate - $[RCNSCl]^{+}Cl$ which then cyclises with NSCl with loss of chlorine.



Eq.3.4

Previous attempts to obtain dithiadiazolium salts from nitriles with *α* H atoms failed because these activated H atoms also reacted with the (NSCl)[20]. The products from these reactions were intractable black polymeric solids. Indeed if the above reaction mixtures were left to reflux for the normal time this was also found to be the case in the present study. By halving the reaction time, however, it proved possible to isolate both 4 - propyl 1,2,3,5 and 4 - benzyl 1,2,3,5, dithiadiazolium chlorides, though in reduced yields. The propyl derivative was prepared in order to compare the physical properties of its radical with those of other dervatives eg. tbutyl, Ph, Me, $CF_3$.

It was hoped that a crystal study of the benzyl compound might prove useful in comparison with the 1,2,3,5 $[PhCN_2S_2]AsF_6/Cl$ crystal structures. Unfortunately it proved impossible to obtain crystals large enough in the time available. $[4\text{-}PhCH_2CN_2S_2]Cl$ was deep red in colour indicating that it was a type A salt[5] and that therefore there was little cation/anion charge transfer. These compounds were used to collect cyclic voltammetry data on the dithiadiazolium system, which was also a useful indicator of their purity.

$[p\text{-}ClPhCN_2S_2]Cl$ had been previously reported in the literature[5]. In an attempt to extend the plasma reaction (Chapter 4) and by analogy with $(PhCN_2S_2)_2$ this salt was reduced with Zn/Cu couple. The chosen solvent was liquid $SO_2$. As expected a green/purple solid was obtained very similar in appearance to $(PhCN_2S_2)_2$, and which sublimed to yield small rhomb-like crystals in contrast to the long needles obtained for $(PhCN_2S_2)_2$. Infrared spectroscopy of $(p\text{-}ClPhCN_2S_2)_2$ revealed the same S/N ring absorbances at 1139, 805, 655 and 511 $cm^{-1}$.

The synthesis of various novel 1,2,3,5 dithiadiazolium hexafluoroarsenate salts by metathesis enabled a more detailed study of their redox behaviour to be carried out, whilst new 1,3,2,5, dithiadiazolium derivatives were obtained by the direct and facile reaction of $S_2NAsF_6$ with nitriles. The reaction occurs in the expected 4+2 cycloaddition described in the literature[10]. These are all strongly ionic compounds which give reasonably strong $RCN_2S_2^+$ peaks in otherwise complicated mass spectra. These complications are attributed to ions apparently derived from the neutral species produced on dissociation:-

$$Y^+AsF_6 \longrightarrow YF + AsF_5 \longrightarrow \text{etc.}$$

The neutral fluorides were not detected in the mass spectra, but fragments derived from them were (eg. $AsF_4^+$, $Y^+$). The mass spectra for 1,3 $MeCN_2S_2+$ showed a strong peak attributed to $CH_3CS+$, m/e 59, which did not appear in the 1,2 isomer; this does not contain a C-S bond.

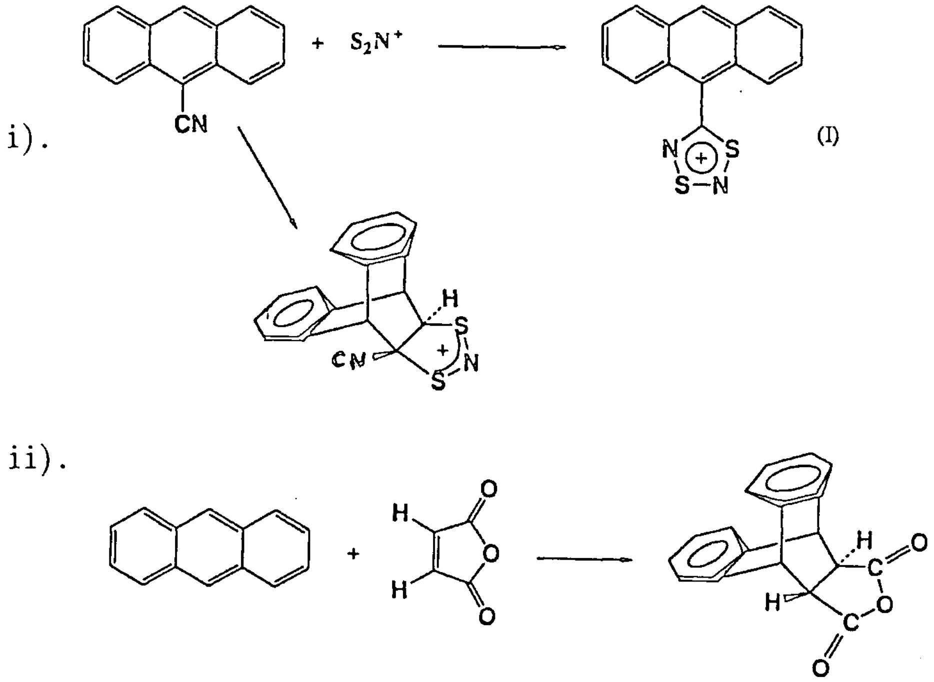
All the 1,2 compounds, however, give very strong peaks corresponding to the nitrile $RCN^+$. As might be expected nitriles with increasingly electronegative groups became increasingly unreactive towards $S_2N+$. For example, most nitriles reacted almost immediately with $S_2N^+$ but $Cl_3CCN$ took several days for incomplete reaction (approx. 40%). The fact that it does react at all is an indication of the highly favourable reaction energetics associated with the cycloaddition (MNDO calculations showed $\Delta H_{reac.}$ with RCN to be of the order of 200 $KJmol^{-1}$). Generally 1,3,2,5 $[RCN_2S_2]$ compounds are highly coloured, R=$Cl_3C$-,cherry red, t-Butyl -,chocolate brown, Ph -,green. They are very sensitive to moisture, more so than the analogous 1,2 isomer $AsF_6$ salts. Consequently problems were experienced, after a few days, in handling both $[t\text{-}ButylCNSNS]AsF_6$, which went white, and $[PhCNSNS]AsF_6$, which went brown, probably due to a poor glove box atmosphere. Although these compounds still gave identical infrared spectra to the corresponding parent compound; CV plots contained only very broad peaks. Hydrolysis usually led to the parent nitrile or an amidinium derivative, as was found to be the case with hydrolysis of the 1,2 isomers.

An attempt to obtain some conducting structures containing stacked planar groups led to the synthesis of 4- anthracene 1,3 dithiadiazolium hexafluoroarsenate. A reduction and photo-isomerisation[21] to the 1,2 isomer was envisaged. Previous attempts to obtain the 1,2 isomer direct from the reaction of $C_{14}H_9CN$ with $NH_4Cl/SCl_2$ gave a simple chlorination product with consequential deactivation to further reaction.

It appeared that a complex reaction occurred between $S_2N+$ and anthracene carbonitrile. When $S_2NAsF_6$ was used, the reaction was rapid and proceeded to the expected product (I). However, when the $SbCl_6^-$ salt was used, then not only was the reaction much slower but a mixture of dark green products was obtained.

Infra-red spectroscopy revealed, in addition to the S/N ring modes, the persistence of the nitrile group throughout the reaction. It is known that anthracene itself readily undergoes dienophile cycloaddition reactions across the 9 and 10 position carbon atoms, eg with cis butenedioic anhydride:-

Scheme 3.1.



It is possible therefore that the dienophile $S_2N^+$ also added across the carbons. Attempts to reduce the product (I) with both $SbPh_3/Me_4NCl$ and $Zn/Cu/Me_4NCl$ in $SO_2$ failed to provide recognisable products. The major product from sublimation and solvent extraction of the residue led only to isolation of pure anthracene or anthracene carbonitrile and this was taken as an indication of the instability of the S/N ring.

$\sigma_p$, the para substituent constant values (Table 3.8) are a measure of side group conjugation with benzene and hence of nitrile nucleophilicity[22,23]. Hence a brief survey of the reactivity of various para subtituted nitriles to $S_2N^+$ was carried out with a subsequent examination of how these effect electron transfer processes.

It proved possible to synthesise by the RCN/$S_2N^+$ reaction a number of 1,3 [$\rho$-XPhCN$_2$S$_2$]$^+$ salts ( X = $CH_3$,Cl, H, CN), which were subsequently examined by CV. This revealed a linear free energy relationship between them, indicating that a common electron transfer mechanism operated across the series. Previous attempts to obtain the 1,2, cyano derivative failed presumably because of the negative inductive effect.

Table 3.8. Some Values of $\sigma_p$. [22,23]

| Substituent | $\sigma_p$ |
|---|---|
| -OMe | -0.27 |
| -$CH_3$ | -0.14 |
| -H | 0.00 |
| -$CH_2$CN | +0.01 |
| -Cl | +0.23 |
| -CN | +0.66 |

### 3.4.2. *Crystal structure of 1,2 [$PhCN_2S_2$]$AsF_6$.*

Although [PhCN$_2$S$_2$]Cl was first reported in1977[2], a full crystal structure determination has only just been published[24]. The main problem encountered was disordered incorporation of solvent molecules which prevented good R values being obtained. The only structure determined before current investigations was that of [Cl$_3$CCN$_2$S$_2$]Cl[4]. Strong cation/anion interactions have been shown to occur in these compounds and to involve a triangular arrangement between the disulphide link and the halide ion. They have been found not only in organic dithiolium and 1,2,4 dithiazolium salts[30], but also in salts of S/N cations such as $S_3N_2Cl^+Cl^-$ and $S_4N_3{}^+Cl^-$. The interactions take the form of short disulphide to anion distances. In the case where the anion is chloride the sum of the van der Waals radii should be 3.7Å and from table 3.~~9~~10. it can be seen that all the S-Cl distances in [PhCN$_2$S$_2$]Cl, [PhCN$_2$S$_2$]$_2$Cl[S$_3$N$_3$][25], [PhCN$_2$S$_2$]Cl[S$_3$N$_2$][25], $S_4N_3Cl$, $S_3N_2Cl$ and [Cl$_3$CCN$_2$S$_2$]Cl lie within this distance and must therefore involve some covalent interaction.

In nearly all the crystal structures the anion is also involved in secondary interactions, indicated by the fact that the anions lie very nearly directly over the rings of adjacent cations and that many of these inter-molecular rings distances are again shorter than the sum of the van der Waal radii.

Although the $AsF_6$ anion is much harder than the chloride, anion/cation interactions have also been found in the 1,3 dithiadiazolium salts[11] (anion = $AsF_6^-$).

**Figure 3.4.** The Crystal Structure of $[PhCN_2S_2]AsF_6$.

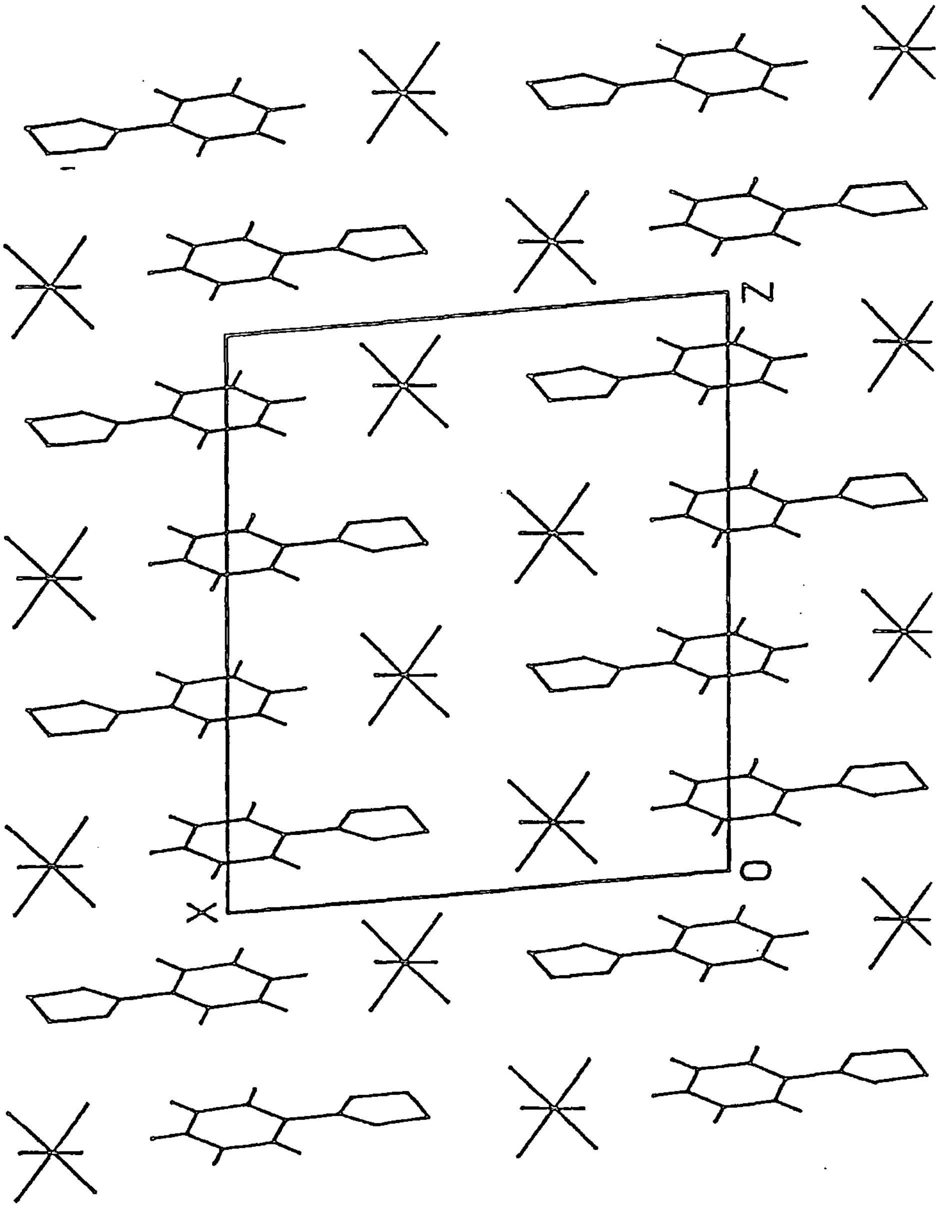
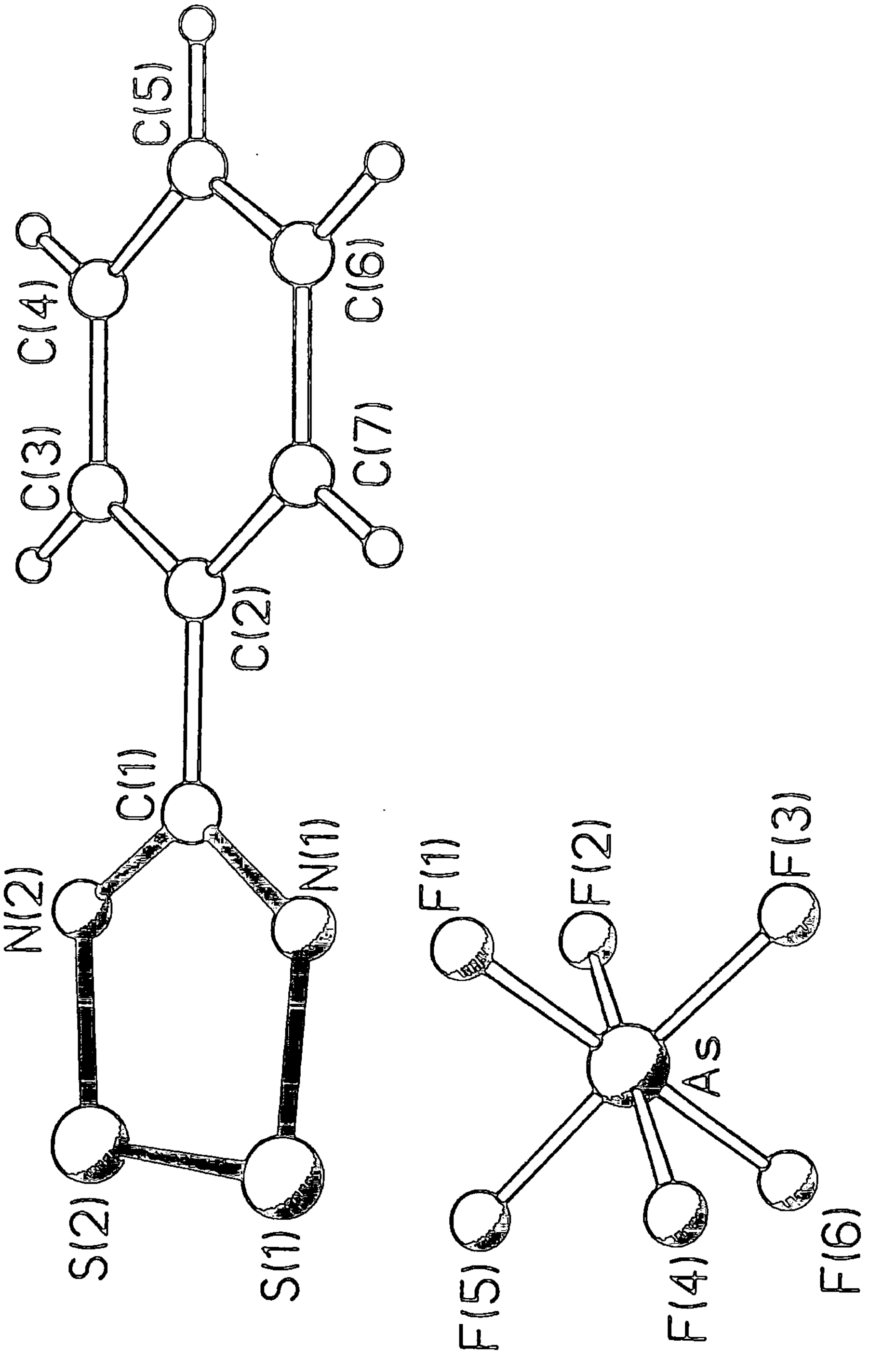


Figure 3.5. [$PhCN_2S_2$]$AsF_6$



The geometry about the $AsF_6$ anion is that of a disturbed octahedron, but no significant correlation can be made between the As-F bond length and the strength and number of fluorine/cation contacts because of large standard deviations in the F positions. The van der Waal's radii total for $S — F$ is 3.30Å and although $[CH_3\overline{CNSNS}]AsF_6$ has significant interactions, there appears to be only one $S \cdots F$ contact in $[PhCN_2S_2]AsF_6$ (See table 3.10). This is in marked contast to 1,3, dithidiazolium salts and to $[PhCN_2S_2]Cl$. This is probably a reflection of the hardness of the $AsF_6$ anion. Figure 3.5. shows the unit cell of $[PhCN_2S_2]AsF_6$ to be a simple stack arrangement, all the phenyl groups lie above each other, although not quite parallel. Each $CN_2S_2$ ring alternates with an $AsF_6$ unit and is surrounded by 3 of these.

The $[PhCN_2S_2]Cl$ structure contained disordered toluene molecules. There are only 3 ion pairs in the asymmetric unit compared to 4 in $[PhCN_2S_2]AsF_6$ which may be a simple reflection of the presence of the solvent. There are several other important differences to be noted, the principal one being the shortness of the S-S link. $[PhCN_2S_2]Cl$ has a shorter S-S bond (1.99Å) than that found in the $AsF_6$ salt. This strengthening of the SS bond in $[PhCN_2S_2]Cl$ is due to Cl interaction, or more specifically to Cl donation. The main SS contribution to the LUMO of the $PhCN_2S_2^+$ ring is antibonding and in the z direction - see Table 3.9. The lone pair of electrons on the Cl atom lie in the xy plane of the ring and cannot therefore interact with the LUMO. However, the next anti-bonding orbital (MO no.15) has a strong SS $p_x$ contribution which is also bonding with respect to the SS bond and which is of the correct symmetry such that Cl donation into it can occur. This leads to a three centre interaction which has a strong covalent bonding character to it and which strengthens the SS bond resulting in the observed decrease in bond length. The $AsF_6^-$ anion is harder and cannot interact in this way.

In $[\mathrm{PhCN_2S_2}]\mathrm{AsF_6}$ the positive charge would be drawn to the more electronegative $\mathrm{C}\langle^{\mathrm{N}}_{\mathrm{N}}$ section of the ring.

Table 3.9. Atomic coefficients of $\mathrm{HCN_2S_2}^+$ for the LUMO (MO no.14) and MO no.15.

| | LUMO (-9.1ev) | | | | MO no.15 (-8.09ev) | | | |
|---|---|---|---|---|---|---|---|---|
| | s | $p_x$ | $p_y$ | $p_z$ | s | $p_x$ | $p_y$ | $p_z$ |
| $S_1$ | 0 | 0 | 0 | +0.49 | +0.09 | +0.66 | +0.03 | 0 |
| $S_2$ | 0 | 0 | 0 | -0.50 | +0.09 | +0.66 | -0.03 | 0 |
| $N_3$ | 0 | 0 | 0 | +0.51 | -0.70 | -0.16 | -0.10 | 0 |
| $N_4$ | 0 | 0 | 0 | -0.50 | +0.70 | -0.17 | -0.10 | 0 |
| C | 0 | 0 | 0 | 0 | 0 | +0.16 | 0 | 0 |

Table 3.10. Summary of bond lengths and atomic distances.

| Compound | C-N | C-S | S-N | S-S | S...X<br>(X=Cl) | Ref. |
|---|---|---|---|---|---|---|
| $S_3N_2Cl_2$ | / | / | 1.543,1.617<br>1.580,1.615 | 2.136 | 3.04<br>2.93 | 26. |
| $S_4N_3Cl$ | / | / | 1.565,1.564<br>1.572,1.532<br>1.523,1.574 | 2.078 | 2.806<br>2.921 | 26. |
| $Cl_3CN_2S_2Cl$ | 1.308<br>1.329 | / | 1.587<br>1.579 | 2.009 | 2.884<br>2.864 | 4. |
| $[PhCN_2S_2]Cl$ | 1.340 | / | 1.590 | 1.990 | 2.906 (mean) | 24 |
| $D_2Cl[S_3N_3]$ | | / | 1.611<br>1.597 | 2.034 | 2.904,3.082<br>2.964,2.897 | 25 |
| $DCl[S_3N_3]$ | | / | 1.618<br>1.613 | 2.055 | 3.100,2.907<br>3.134,2.954 | 25 |
| $CH_3CNSNS^+$<br>$AsF_6^-$ | 1.32 | 1.77 | 1.63<br>1.59<br>1.57 | / | (X=F),<br>2.97,3.13,3.13<br>2.98,3.01,2.89<br>2.87. | 11 |
| $[PhCN_2S_2]^+$<br>$AsF_6^-$ | 1.337<br>1.335 | / | 1.575<br>1.581 | 2.017 | 3.147,3.760<br>4.183,3.264 | this work. |
| $S_6N_4AsF_6$ | / | / | 1.610,1.545<br>1.599,1.575 | 2.147 | | 26 |

D= 1,2 $[PhCN_2S_2]$

The effect of the positive charge is, however, most dramatically highlighted when $(PhCN_2S_2)_2$ is compared with $[PhCN_2S_2]AsF_6$ with S-S bond lengths of 2.08 and 2.017Å respectively.

### 3.4.3. *The* $(MeCN_2S_2)_2$ *molecule.-*

The dithiadiazole $(PhCNSSN)_2$ previously described[5] crystallises in an eclipsed conformation with two S--S interactions between the rings. In contrast, isoelectronic $S_6N_4Cl_2$ has a trans arrangement of the two rings, thereby minimising anion/anion repulsions. The compound $[CF_3CNSSN]_3Cl$ crystallises as a combination of $[CF_3CNSSN]$ Cl , with the chloride co-planar with the ring, and dimer $(CF_3CNSSN)_2$ with eclipsed rings (as in $(PhCN_2S_2)_2$ ). MNDO calculations[14] have, in fact, shown that for most dithiadiazole derivatives the energy difference between conformations is only very small, at about 5 $kJmol^{-1}$ which indicated that the molecular geometries of $(PhCN_2S_2)_2$ and $(MeCN_2S_2)_2$ would probably be similar. Table 3.11. gives a summary of the X ray crystal data for both $(PhCN_2S_2)_2$ and $(MeCN_2S_2)_2$ and an MNDO minimum energy calculation for $CH_3CNSSN$[13].

The methyl derivative, like $(PhCN_2S_2)_2$, contains parallel rings within the dimer unit. See Figure 3.6. However, there is only one S--S link of 3.08Å between the rings and the methyl groups are offset nearly 90° compared with the nearly eclipsed form (offset by 7°) of the phenyl groups in $(PhCN_2S_2)_2$[12].

There are also weak S/N and S/S secondary interactions between adjacent dimer units (with the S/N and S/S distances typically 3.0Å). When the lattice is viewed parallel to the a axis, the crystal appears composed of 'sheet polymers' parallel to the (011) plane, completely interwoven by dimer to dimer close van der Waals contacts concentrated

Figure 3.6. The dimeric unit of $MeCN_2S_2$

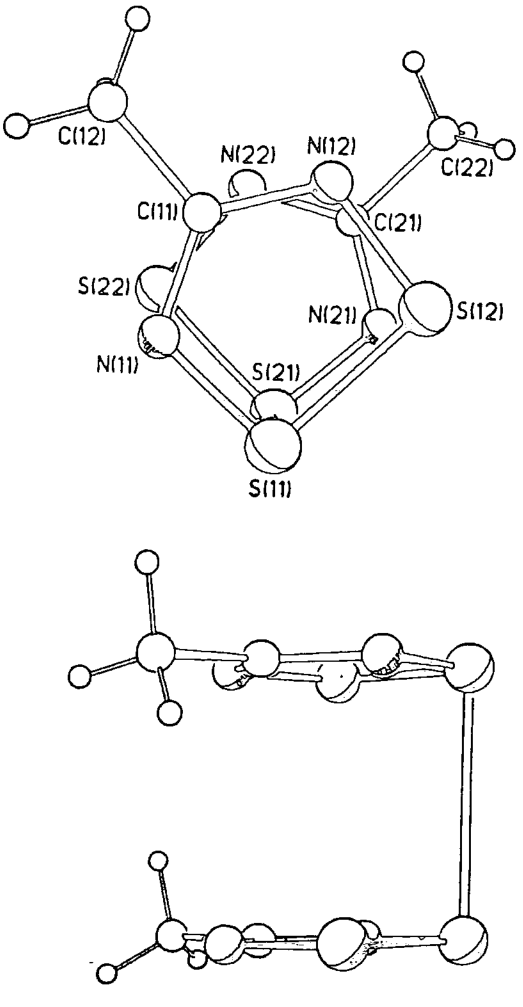


Figure 3.7. The dimeric unit of $(PhCN_2S_2)_2$.

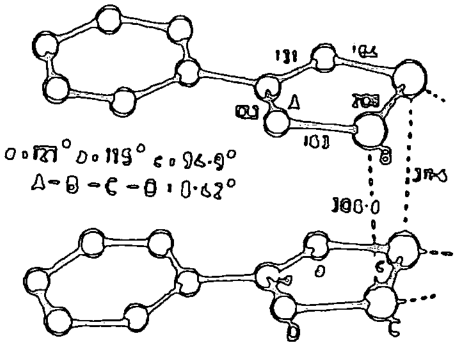
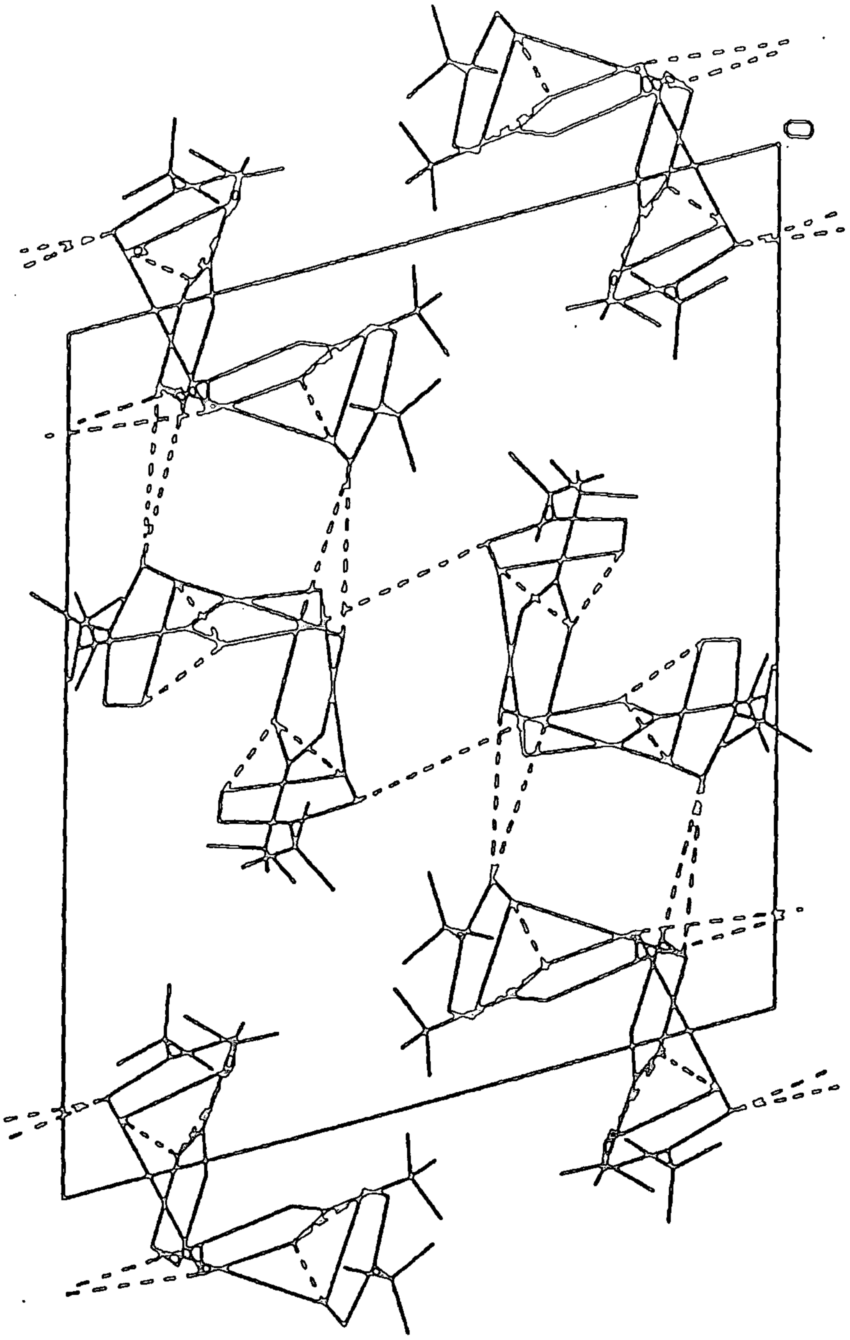


Figure 3.8. The lattice packing of $(MeCN_2S_2)_2$.



around the central plane of the sheet, while the methyl groups are pointing away from the central plane. This stacking arrangement thus creates a periodicity of high and low density regions as well as relatively weak bonding between the polymer layers. This in turn accounts for an easy glide movement in the (011) plane and the pronounced tendency for twinning.

**Table 3.11. Crystal data for $(CH_3CN_2S_2)_2$ and $(PhCN_2S_2)_2$.**

| | $(CH_3CN_2S_2)_2$ | | $(PhCN_2S_2)_2$ |
|---|---|---|---|
| (Å/°) | Observed[17] | Calculated[13] | Observed[12] |
| S-S | 2.076 | 2.069 | 2.089 |
| S-N | 1.636 | 1.605 | 1.625 |
| N-C | 1.324 | 1.364 | 1.334 |
| C-C | 1.495 | 1.516 | 1.473 |
| SSN | 94.5 | 94.0 | 94.1 |
| SNC | 114.5 | 113.6 | 115.1 |
| NCN | 122.2 | 119.0 | 121.1 |
| $\alpha$. | | 179.3 | 0 |

The CN, SN, and SS bond distances within each ring differ very little from those found in (1) except for the S--S inter-ring interaction which is slightly longer in the methyl case( 3.108Å against 3.08Å), possibly due to steric factors. MNDO calculations[13] predicted that the methyl groups would be slightly out of the plane but this does not appear to be the case. The difference is probably negligible. In fact apart from the S/S inter ring distances which do vary appreciably, the R substituent appears to have very little effect on the S/C/N ring distances and angles which is as expected since MNDO calculations have indicated that the substituents have very little effect on the energy of the orbitals in dithiadiazoles[14],[26]. Because of this and steric considerations, a trans configuration might have been expected similar to that of $S_6N_4Cl_2$. However, here it appears that in $S_6N_4Cl_2$ sulphur/chloride interactions are the determining factor in the conformation adopted; the distance from the $Cl^-$ ion to the unique sulphur is 3.152Å (less than the sum of the van der Waals radii, 3.7Å). It should also be noted that these cation/anion interactions are of considerable importance for the structures of $[PhCN_2S_2]Cl$ and $[PhCN_2S_2]_2Cl$[25] etc.

### 3.4.4. *Thermal studies.*

It was found that both $((CH_3)_3CCN_2S_2)$ and $(CH_3CH_2CH_2CN_2S_2)$ had uncharacteristically low melting points of 22°C and 10°C respectively and it was possible therefore to measure $\Delta H_{fus}$ and $\Delta H_{vap}$ for these radicals. As shown in Table 3.11.,however, the $\Delta H_{fus}$ are very similar for a whole variety of dithiadiazoles; a reflection not only of the inherent stability of the $7\pi$ five membered ring but also that the thermodynamics depends largely on the heterocyclic ring since the inductive and steric properties of the R group appear to have little effect. The propyl derivative seems to be the exception because of its unusually low $\Delta H_{fus}$ of $13.5KJmol^{-1}$. This may be a reflection of the small size of the molecule and some entropy effects.

The following series may be observed for decreasing $\Delta H_{fus}$, Ph > Me > 1,2,tBu. > $CF_3$ >propyl which exactly matches the melting points, Ph 119.7, Me 95.5, 1,2tBu 22.0, $CF_3$ 21.0, propyl 10.0, but which does not follow their molecular masses, Ph 181, Me 119, tBu 161, $CF_3$ 173, propyl 147. There is also a significant difference between the first two members of the series Ph and Me, which have considerably higher $\Delta H_{fus}$ and melting points than the remainder, and both of which are solid dimers at room temperature. Normally the lowest melting point would be expected for $(MeCN_2S_2)_2$ since this has the lowest molecular weight. So if dimerisation is an energetically favoured process for all these compounds then steric factors and possibly significant entropy gains prevent the rest, R=tBu,Propyl,$CF_3$, from dimerising. The strong electronegativity of the $CF_3$ group in $CF_3CNSSN$ might prevent dimerisation through electronic effects, but this is unlikely to be the cause since it is well established that the ring orbitals are relatively unaffected by the ligand environment. Experimentally it was observed that at RT or above RCNSSN (R=tbutyl,$CF_3$,) existed as distinctly purple/red liquids almost dichroic in behaviour, these compounds on freezing formed greenish semi crystallites similar in appearance to hoar frost amongst the red solid. This was taken as an indication that on freezing some dimerisation occurred. Indeed the unexpectedly low values of enthalpy obtained for the propyl derivative, for which no such effect was observed on freezing, supports this. A small $\Delta H_{fus}$ would be obtained if the disorder in the solid propylCNSSN was not greatly different from that of the liquid. A change in phase behaviour is therefore observed between Ph,Me and the remainder of the series.

Two $\Delta_{vap}$ values have been obtained, for the methyl derivative, by Dr Z.V.Hauptman, using an all glass sealed spring gauge, and for the $^tBu$ derivative by direct evaporation from a calorimetry cell. It should also be noted that the methyl derivative had a significantly greater $\Delta H_{fus}$ which is presumably due to the greater degree of dimerisation in MeCNSSN. No direct comparison, however, can be made between the two $\Delta H_{vap}$ values obtained for the $^tBu$ and Me derivatives since in the determination of the methyl value the equilibrium

$$(MeCN_2S_2)_2(S) \rightleftharpoons (MeCN_2S_2)_2(V)$$

was assumed[13]. This was because a linear Clausius/Clapeyron relationship was established and dissociation into monomer or thermal decomposition would have led to a curved graph. Nevertheless, it is now thought that the vapour phase species is monomeric for all these compounds and although the triple point for $(MeCN_2S_2)_2$ is 95.5°C, the same as the melting point,it would not be valid to extrapolate the $\Delta H_{vap}$

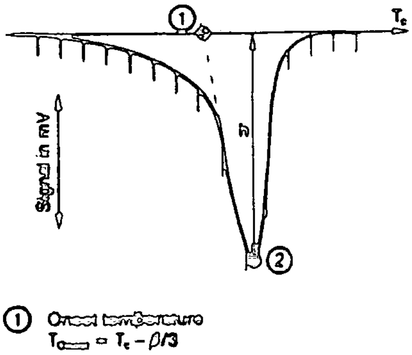
figure for the liquid/vapour equilibrium from this. It should also be noted that the $\Delta H_{fus}$ and hence the $\Delta S_{fus}$ for these $\overline{RCNSSN}$ compounds are very much higher than values for many other compounds.eg.$H_2O$. $\Delta S_{fus}$=22.0[27], benzene $\Delta S_{fus}$=38.0 $Jmol^{-1}deg^{-1}$ again an indication of considerable structural ordering. Propyl$\overline{CNSSN}$ has a $\Delta H_{fus}$ comparable with many organic compounds indicating that $PrCN_2S_2$ lacks the structural order found in other $RCN_2S_2$ compunds. However, the $\Delta H_{vap}$ for the two compounds measured,$(MeCN_2S_2)_2$ and $Bu^tCN_2S_2$ is high compared to other compounds, eg. $\Delta H_{vap}$ $H_2O$=40.7. benzene=30.8 $KJmol^{-1}$. It is also high when their molecular weight is considered, eg. $I_2$ $M_r$=254, $\Delta H_{vap}$=41.8 $KJmol^{-1}$. Presumably this is because of dimerisation, although in the case of the tBu this ordering may well take the form of a spin pairing mechanism rather than formal S-S dimers.

Table 3.12.Measured values of $\Delta H_{fus}$ and $\Delta H_{vap}$ for some dithiadiazoles

| Compound | Mr | Mpt.°C | $\Delta H_{fus}$ | $\Delta S_{fus}$ | $\Delta H_{vap}$ |
|---|---|---|---|---|---|
| $(PhCN_2S_2)_2$ | 181 | 119.7 | 59.0 | 35.3 | / |
| $(MeCN_2S_2)_2$ | 119 | 95.5 | 43.0 | 27.9 | 55.2 |
| $tBuCN_2S_2$ | 161 | 22.0 | 35.3 | 28.6 | 65.6 |
| $CF_3CN_2S_2$ | 173 | 21.0 | 21.61 | 17.5 | / |
| $ProCN_2S_2$ | 147 | 10.0 | 13.6 | 11.48 | / |
| $CF_3CSNSCF_3$ | 240 | 1.8 | 23.1 | 20.1 | 38.1[b] |

Pro=$CH_3CH_2CH_2$.
$\Delta H_{fus}$=$KJmol^{-1}$ $\Delta S_{fus}$=$calmol^{-1}deg^{-1}$ $\Delta H_{vap}$=$KJmol^{-1}$

**Determination of temperature**

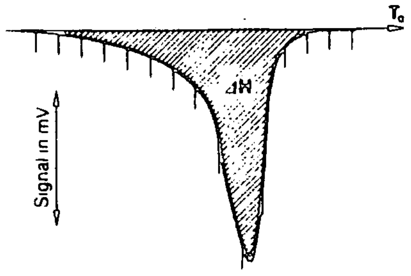


① Onset temperature
$T_{onset} = T_c - \beta/3$

② Sample temperature
$T_{sample} = T_c - \beta/3 - h/35$ (endo)
$= T_c - \beta/3 + h/35$ (exo)

$\beta$ = Heating rate [°C/min]
h = Peak height in [mV]
T = Temperature [°C]
$T_c$ = Cell temperature (marks and display)

**Determination of heat quantity $\Delta H$**



$$\Delta H = \frac{\text{Weight of cut out peak [mg]} \cdot F \cdot G}{E_{cal}}$$

$\Delta H$ = Heat quantity, enthalpy change [mJ]
F = Calibration factor [mJ/mg chart]
= . . (see operating instructions page 62)
G = Correction for measuring range and chart speed (see table)
$E_{cal}$ = Temperature dependent calorimetric sensitivity (see table)
$T_c$ = Cell temperature (marks and display)

**Table of calorimetric sensitivity $E_{cal}$ as a function of temperature:**

| T, [°C] | $E_{cal}$ | T, [°C] | $E_{cal}$ | T, [°C] | $E_{cal}$ |
|---|---|---|---|---|---|
| −20 | 1,447 | 130 | 1,058 | 280 | 0,789 |
| −10 | 1,417 | 140 | 1,037 | 290 | 0,775 |
| 0 | 1,388 | 150 | 1,015 | 300 | 0,762 |
| 10 | 1,360 | 160 | 0,995 | 310 | 0,749 |
| 20 | 1,332 | 170 | 0,975 | 320 | 0,737 |
| 30 | 1,304 | 180 | 0,955 | 330 | 0,725 |
| 40 | 1,277 | 190 | 0,936 | 340 | 0,714 |
| 50 | 1,251 | 200 | 0,918 | 350 | 0,703 |
| 60 | 1,225 | 210 | 0,900 | 360 | 0,693 |
| 70 | 1,199 | 220 | 0,882 | 370 | 0,684 |
| 80 | 1,175 | 230 | 0,865 | 380 | 0,675 |
| 90 | 1,150 | 240 | 0,849 | 390 | 0,666 |
| 100 | 1,126 | 250 | 0,833 | 400 | 0,658 |
| 110 | 1,103 | 260 | 0,818 | | |
| 120 | 1,080 | 270 | 0,803 | | |

**Table of correction factor G:**

| Chart speed [mm/min] | Measuring range [mV] 50 | 100 | 200 |
|---|---|---|---|
| 60 | 0.5 | 1 | 2 |
| 20 | 1.5 | 3 | 6 |
| 10 | 3 | 6 | 12 |

Example calculation of $\Delta H_{fus}$ for $^{t}BuCNSSN^{\cdot}$ radical - Figure 3.3.

Weight of area(paper) under DSC trace = 0.04972g

weight of sample = 0.00487g = $1.51 \times 10^{-5}$ mol (of dimer)

Range = -15° to + 32° C. $\beta = 2^{o}/\mathrm{min}$.

Sensitivity = 200mV. Chart speed = 10mm/min

$$\Delta H_{fus} = \frac{1.4263 \times 49.72 \times 200/100 \times 50/10}{1.318 \times 1.51 \times 10^{-5}}$$

### 3.4.5. *Isomerisation.*

Free radicals are generally associated with kinetic and thermodynamic instability, and indeed the 1,3 dithiadiazoles are thermodynamically unstable with respect to the 1,2 disulphide isomer. However, the 1,2 isomer itself exhibits remarkable stability for a S/N heterocycle both as a pure compund and in solution, although there is a photodecomposition with high energy UV light[28]. $R\overline{CNSNS}$ radicals undergo photochemical isomerisation in which a concerted process via a head to tail $\pi^{*}$- $\pi^{*}$ dimeric intermediate is indicated[10]. Rearrangement in this way can then be achieved with the minimum of spatial adjustment and the energetics of this process are reflected in the bond energy changes, the S-S and C-N bonds formed (305 +427 $KJmol^{-1}$) being stronger than the S-C and S-N bods broken(301 + 209 $KJmol^{-1}$). A study of the MO's both occupied and unoccupied show there to be a centre of symmetry in both the 1,3, and the 1,2 dimers (if the 1,2 isomer adopts a trans configuration) which is then retained throughout the rearrangement. The isomerisation is thermally forbidden because there is a correlated crossover (between 1,3 and 1,2) involving an occupied MO with an unoccupied one. This isomerisation has been studied[21] by esr, for example $Me\overline{CNSNS}$ gives a simple three line spectrum which decreases with time to give the five line spectrum of MeCNSSN. This method has shown this process to have second order kinetics and to be concentration dependent. Previous reports of rapid isomerisation of the 1,3 to the 1,2 isomer, which was almost quantitative after just five days, were confirmed by exposing a sample of 1,3 t-BuCNSNS to gentle heat(40°) and strong artificial light (1h) when a peak due to the 1,2 isomer became quite pronounced in a CV plot, ( a later report suggested >90% conversion after just 30 min.in sunlight[28]). Similar isomerisations have been reported to occur within a few seconds, when R=$CF_3$ for example and therefore also appear to depend on the nature of R.

### 3.5. *Conclusion.*

The synthesis of 1,2,3,5 dithiadiazolium salts by the RCN/$SCl_2$/$NH_4Cl$ route has been extended to $[CH_3CH_2CH_2CN_2S_2]Cl$ and $[PhCH_2CN_2S_2]Cl$ by careful control of reaction conditions to reduce the competing $\alpha$ H extraction reaction. 1,2,3,5 $[PhCN_2S_2]AsF_6$, 1,2,3,5 $[{}^tButylCN_2S_2]AsF_6$ and 1,2,3,5 $[MeCN_2S_2]AsF_6$ were obtained by metathesis from the corresponding chloride and $AgAsF_6$, a useful reagent in $SO_2$. $S_2NAsF_6$ was reacted with a series of increasingly deactivated aryl nitriles, XPhCN (X=$CH_3$,Cl,CN) to give the 1,3,2,5 dithiadiazolium salt. The reduction products of 1,2,3,5 $[CH_3CH_2CH_2CN_2S_2]Cl$ and 1,2,3,5 $[{}^tButylCN_2S_2]Cl$ were found to be paramagnetic liquids at room temperature, which were stable over a period of months. An esr study gave a g value of 1.998, close to that expected for a 1 electron species. The isomerisation of 1,3 $({}^tButylC_2S_2)^{\cdot}$ also a liquid at room temperature was also followed. A report concerning this and 1,2 $({}^tButylCN_2S_2)^{\cdot}$ appeared in the literature while this work was being carried out[16].

A variety of dithiadiazoles were shown to have similar $\Delta H_{fus}$, all greater than similar organic compounds and this has been taken to indicate considerable structural ordering in both the solids and the liquids. The change in physical properties between the methyl and phenyl derivatives (both solid dimers at room temperature) and the rest of the series ($CF_3$,$^t$Butyl,propyl, all liquid radicals at room temperature) was also reflected in the $\Delta H_{fus}$ and $\Delta H_{vap}$ measurements.

The crystal structure $[PhCN_2S_2]AsF_6$ shows that the small anion/cation interactions leads to a longer S-S bond than that found in $[PhCN_2S_2]Cl$. The crystal structure of $(MeCN_2S_2)_2$ shows that the preferred conformation for these dimers is cis despite MNDO calculations indicating very little difference in energy between conformations, although there is no obvious explanation for the single S-S intermolecular interaction.

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# CHAPTER FOUR.

# THE EFFECT OF A COOL DC NITROGEN PLASMA ON SELECTED S/N HETEROCYCLES.

## 4.1. INTRODUCTION

### 4.1.1. *Plasma reaction.*

In general, plasmas contain electronically excited ions and atoms and vibrationally and electronically excited molecules. Spectroscopic studies have identified a number of species in nitrogen discharges[1], the more exotic ones,eg. $N_4^+$ still attract attention[2]. However, the main species is the ground state nitrogen atom ($^4S$), from the dissociation of $N_2$, which lies at 12.139ev[3]. See Figure 4.1.

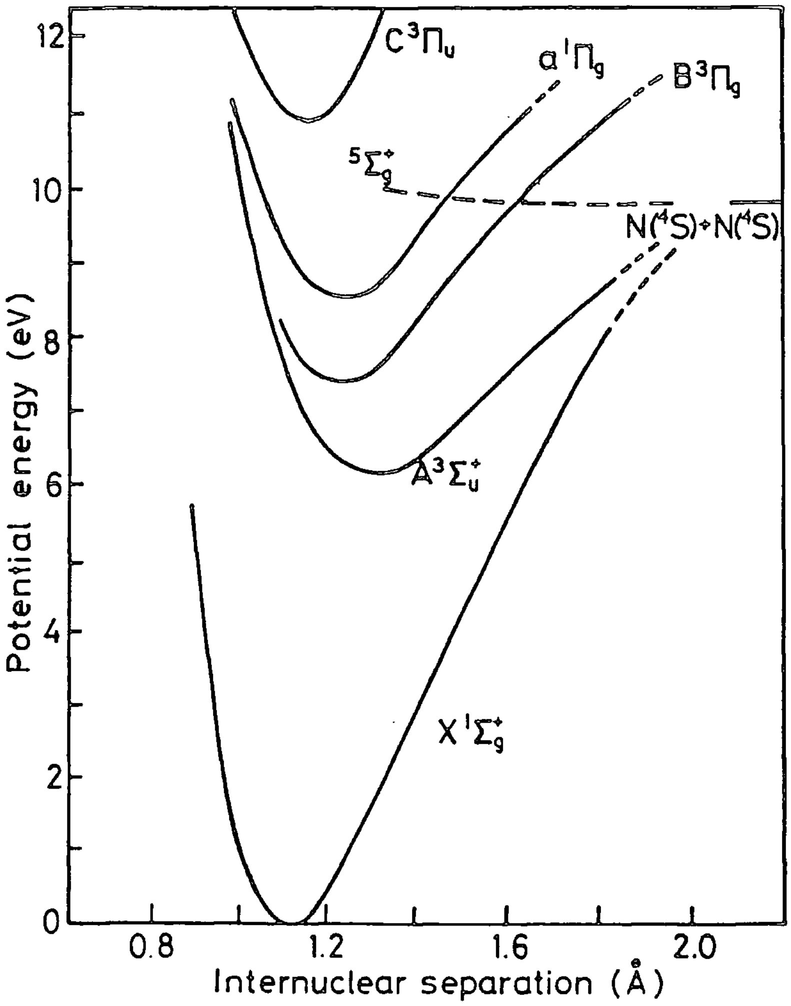


Figure 4.1. Potential Energy Diagram for the Nitrogen Molecule.

It is the $^4S$ nitrogen atoms that are the chemically active species[3] in free radical active nitrogen reactions. Electronically excited atoms and molecules and vibrationally excited molecules have a lower concentration and the longest lived excited molecular state, the $A^3\Sigma_u^+$ state, has a life time of only $10^{-2}$ s. Furthermore at these relatively high pressures ( $p \approx 1 - 4$ Torr ) $^4S$ nitrogen atoms tend to quench out the other excited atoms, eg.,

$$N(^2P) + N(^4S) \longrightarrow 2N(^4S).$$

In this work it has been assumed that an equilibrium between $^4S$ nitrogen and $N_2$ molecules is maintained whilst the discharge continues and that the chemically active species are $^4S$ nitrogen atoms.

From studies of the afterglow[1], it has been found that the $N(^4S)$ atoms have a relatively long lifetime due to their decay being a three body recombination, although catalytic decay does take place at surfaces.

**Scheme 4.1.** Recombination of atomic nitrogen;

$$N(^4S) + N(^4S) + M \longrightarrow N_2(^5\Sigma_g^+) + M.$$

$$N_2(^5\Sigma_g^+) + M \longrightarrow N_2(B^3\Pi_g) + M.$$

$$N_2(B^3\Pi_g) \longrightarrow N_2(A^3\Sigma_u^+) + h\nu$$

For this process: $-d(N)/dt = 2k(N)^2(M)$ and the rate $K_1$ is $2.1 \times 10^{-32}$ $cm^6$/molecule-sec.[1]

When an electric current (d.c.) discharge is passed through nitrogen gas at low pressure (*ca.* 1 Torr) a characteristic pink/purple glow is observed. This is largely the positive column which fills about 3/4 of the tube and is due to electronically excited $N_2$ molecules. Very often striations are observed in this column, as in the present study, which may be either moving or stationary and which are due to very complex interactions of ion and electron oscillations. If the current is turned off, a yellowish afterglow was sometimes seen (the Lewis-Rayleigh afterglow) under certain conditions. This is itself a much studied phenomenon and is due to the three body recombination of atomic nitrogen.

The main feature of the afterglow spectrum is the first positive band -$N_2$ ($B^3\Pi_g$ - $A^3\Sigma_u^+$). This is also observed in the discharge itself along with the second positive band - $N_2(C^3\Pi_u$ - $B^3\Pi_g)$ transition. Figure 4.1.

Ionisation also takes place in plasmas but the reports[1],[3] of the degree vary enormously from 0.1% to 100% and is largely dependent on how the discharge is generated. However, because of the large amount of UV radiation given off in a DC discharge it has been inferred that vibrationally excited molecules may also take part in some chemical reactions[3]. An experiment was therefore carried out under identical conditions, but instead of igniting the discharge, the sample and the tube were irradiated with high energy (6.5 ev and above) UV light to stimulate the formation of vibrationally excited $N_2$.

This was also repeated under static conditions. In both instances no uptake of nitrogen was observed and the sample remained unchanged. It was concluded therefore that the reactions primarily involve atomic $^4S$ nitrogen and not vibrationally excited $N_2$ molecules.

Nitrogen plasmas have been little used for molecular synthesis because yields are usually low. However, they have been used for the preparation of pyrrole from buta -1,3,- diene[4] and in particular in the preparation of phosphorus nitrides[5]. Furthermore, there is increasing interest in ~~its~~ their use in the fabrication of silicon nitride films for the micro-electronics industry and in polymer film formation[6].

In sulphur chemistry a few gas/gas reactions between singlet atomic nitrogen generated in a microwave discharge and various divalent sulphur compounds have been investigated[7], with a view to finding useful synthetic methods for S/N compounds. Although interesting S/N compounds were formed in this way they were either transitory or present in very low yields. Indeed significant yields were only obtained with $S_2Cl_2$ which gave $(NSCl)_3$. It appeared that whereas divalent sulphur atoms would react with atomic nitrogen, no such reaction would take place with sulphur atoms with only one lone pair of electrons available, eg. $SOCl_2$, $SO_2$, $SO_3$ (which would have a formal postive charge). The plasma method has also been used to convert $NH_3/H_2S$ and $N_2/H_2S$ mixtures to impure amorphous $(SN)_x$[8].

However, very little work has been carried out on plasma/solid synthetic reactions, particularly with regard to sulphur compounds. Therefore to assess the synthetic potential for solid/plasma reactions in S/N chemistry, a variety of 1,2,3,5 dithiadiazolium salts and their related dithiadiazoles and a variety of other similar S/N compounds were subjected to a nitrogen plasma. These were chosen as possible precursors to conductive C/S/N polymers, as various organothiazyls had been prepared in the past in as yet unsuccessful attempts to obtain highly conductive analogues of $(SN)_x$ (for which $\sigma = 1000 - 3000\ S\ cm^{-1}$)[9].

Because of the general lability of S/N heterocyclic rings, a cool d.c. nitrogen plasma was chosen because this is less energetic and hence have less destructive effect, and because it is easier to control the experimental conditions.

## 4.2. EXPERIMENTAL

### 4.2.1. *General plasma conditions.*

The two tubes used in the plasma experiments involving relatively low volatility solid starting materials are shown in Figures 4.2 and 4.3. (pages 86 and 87). Tube 4.2 was used generally for exploratory work and small scale synthesis whilst tube 4.3 proved useful in later work for scaling up reactions and modifying the system.

The whole apparatus for 4.3 is shown in Figure 4.5 (page 89) (that for tube 4.2 is a slight modification of this). $N_2$ was taken from the bench line and further dried by passage through a -196°C cold trap. 1/4" stainless steel tubing and 1/4" to 1/4" Swagelok unions were used throughout except where indicated. The pyrex discharge tube was connected to the nitrogen supply line via a 1" to 1" Swagelok union. The nitrogen flow was controlled with stainless steel Whitey valves (1KS4). The reaction tube itself consisted of a pyrex glass tube (2.5" OD, 30cm long). At one end, through which the tube was loaded in a glove box, this reduced to 1" OD ground glass to fit the swagelok union whilst at the other there was a sealed tungsten/glass insert.

The whole $N_2$ line upto tap C was evacuated and then let down to nitrogen several times to purge any air that may have entered the system. The nitrogen line was assumed to be at or slightly greater than atmospheric pressure upto the inlet tap A. The -196°C trap was removed from the line, drained and oven dried before each experiment. It was found convenient to balance the bleed rate against the pumping speed of an Edwards M5 pump with this tap, tap B being used for fine adjustment. The flow rate was usually set at 70 Torr $cm^3$ $S^{-1}$ as measured on a pre-calibrated flow meter. This rate thus allowed a residence time of an average of 2 seconds within the discharge tube, which proved adequate for most reactions.

Figure 4.2. Apparatus for the small scale reaction of solids with a d.c. nitrogen plasma.
1). Quartz discharge tube, 2). Pyrex to quartz graded joint, 3). and 4). anode and cathode - both solid tungsten rod, 6.35mm diameter. 5). demountable vacuum feed through, 6). Quartz boat, 7). *ca.* 1mm bore capillary, 8). transparent resistance heater, 9). volatiles trap, 10). Youngs' greaseless joint.

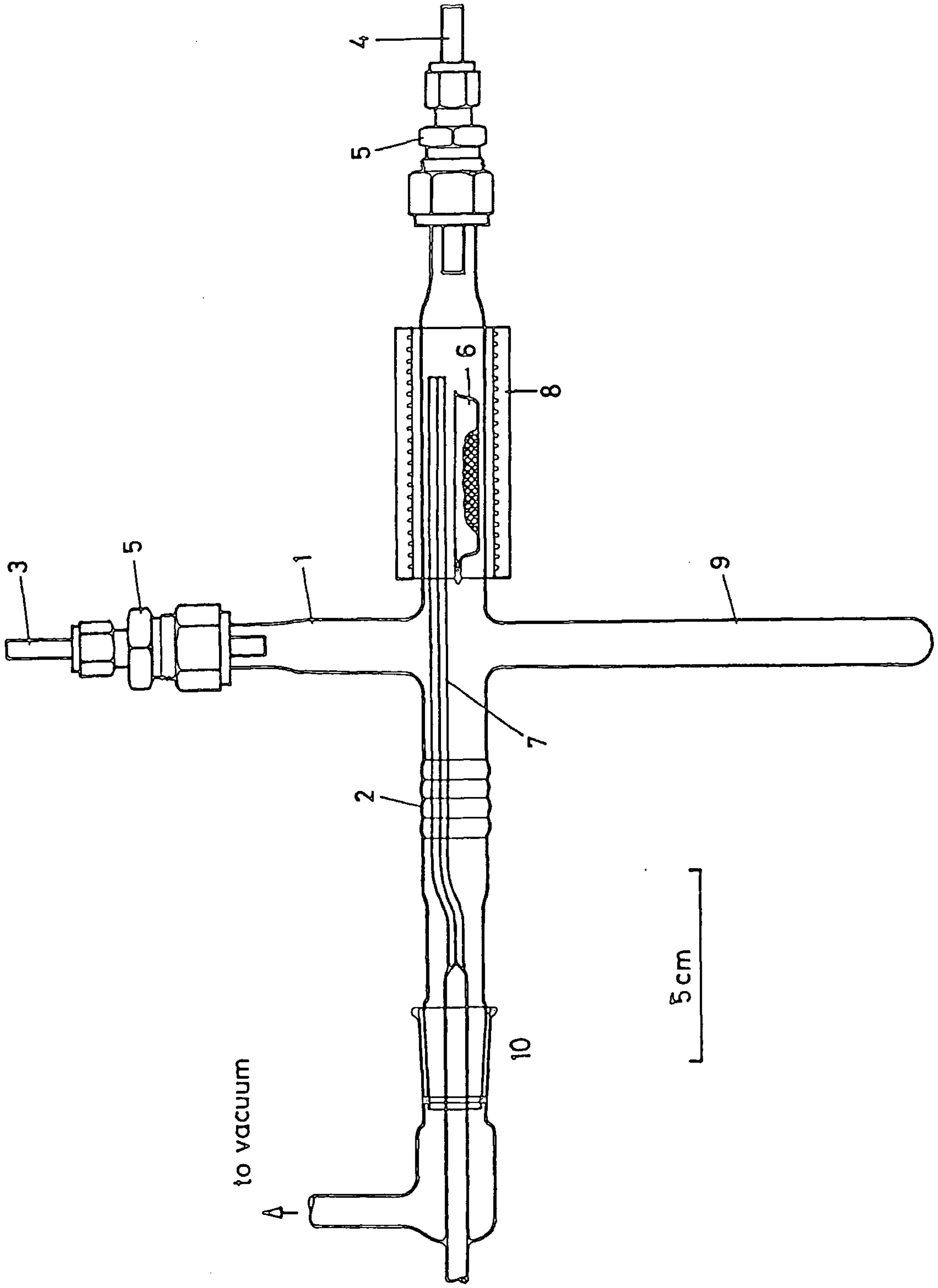


Figure 4.3. Large Reaction Apparatus

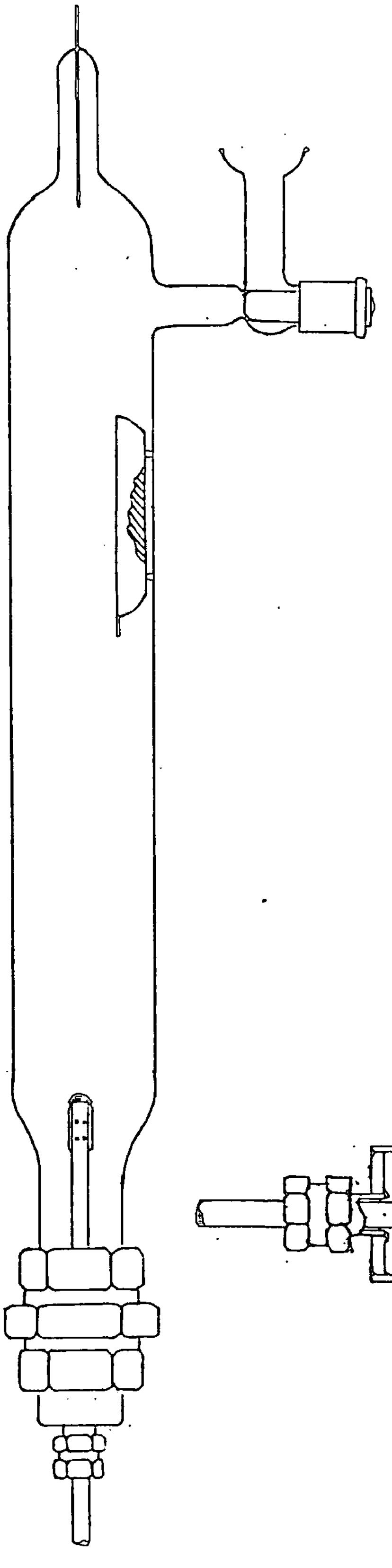
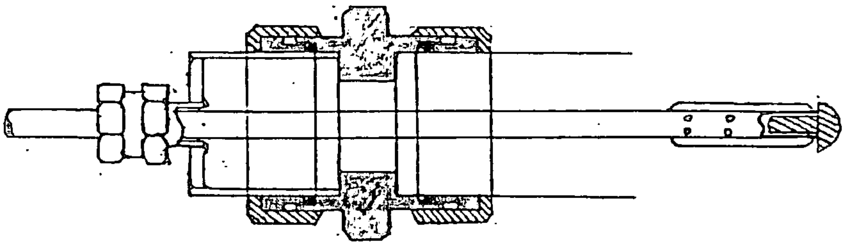


Figure 4.4.



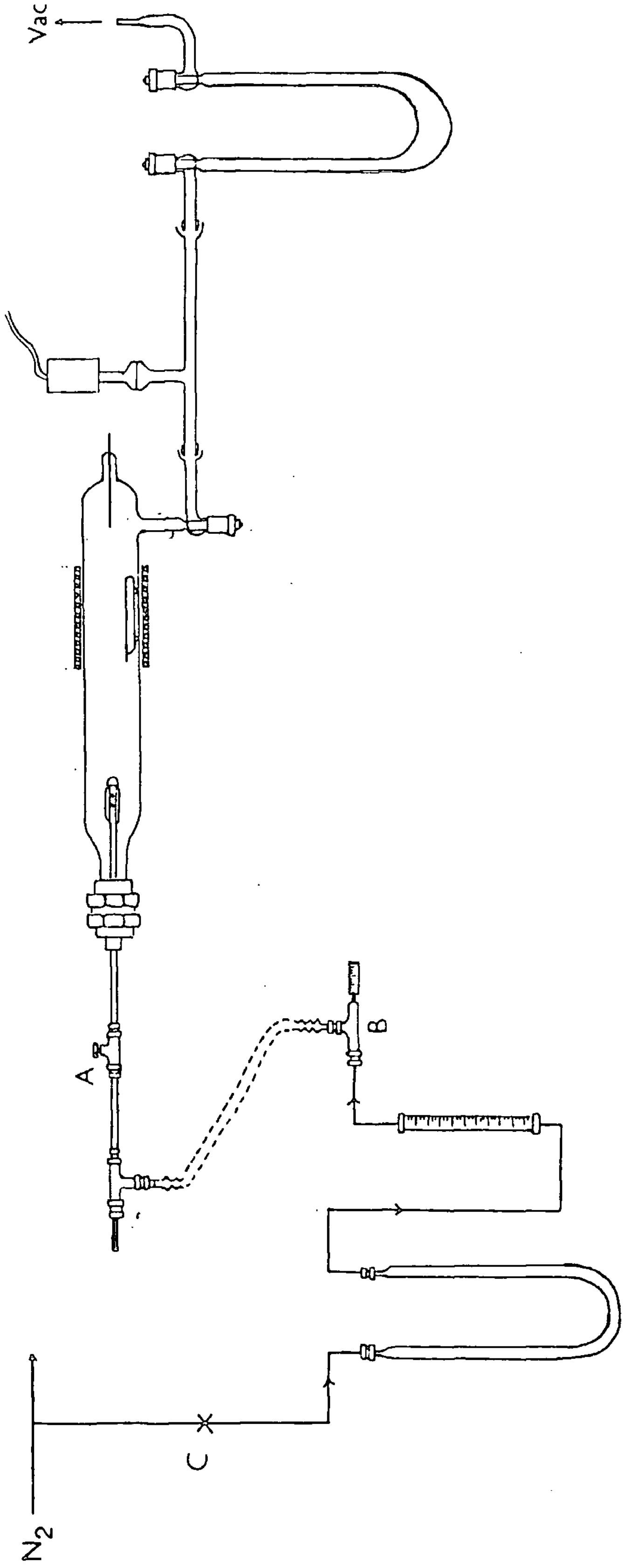
This effectively maintained a pressure of about 1 Torr (8 x$10^{-1}$ to 1.0 Mbar) in the tube as measured on an Edwards Pirani PRE 10K gauge head connected to a Pirani 502 control unit. For both tubes a current of 2 MA was used, which required about 900 to 1000 V across the electrodes. The electrodes used were of tungsten metal either as simple glass/metal lead throughs or, as in later designs, as simple tungsten rod as in Figure 4.4. (page 87). For low temperature reactions it was necessary to design an alternative tube (see Figure 4.6., page 91), for which the electrodes in Figure 4.7. (page 91) were made (designed and made by Z.V.H.). It was found that at the current density used very little sputtering of the electrodes occurred and electrode heating was kept to a minimum.

The heat naturally generated by the discharge usually maintained the temperature of the tube 1a at about 35°C. Further heating to reaction temperatures above this were achieved with an external heater, either as a simple heating tape or as a short nichrome wire wound pyrex resistive furnace (designed and built by Z.V.H) connected to a Eurotherm 821 Controller unit. Any volatile products were caught in the second cold trap which was fitted with Youngs' taps and hence sealable. The products could then be removed and examined spectroscopically.

### 4.2.2. *The preparation of* $(\mathit{Ph}\overline{\mathit{CNSNSN}})_2$.

$(\mathrm{Ph}\overline{\mathrm{CN_2S_2N}})_2$ (0.25 g, 0.7 mmol) was transferred to the plasma tube, Figure 4.2., in a glove box and loosely heaped in a quartz boat, which was then immersed in the positive column of the discharge. Nitrogen was bled in via a needle valve through a capillary (0.5 mm I.D.) into the discharge tube. The optimum reaction temperature (45°C) was maintained during the reaction by a resistive heater. Under the above conditions the reaction was normally complete in about 10 h. The crude buff coloured product consisted of air stable $(\mathrm{PhCN_3S_2})_2$ and a small amount of black polymer.

Figure 4.5. Nitrogen and Vacuum lines for Discharge Tubes.



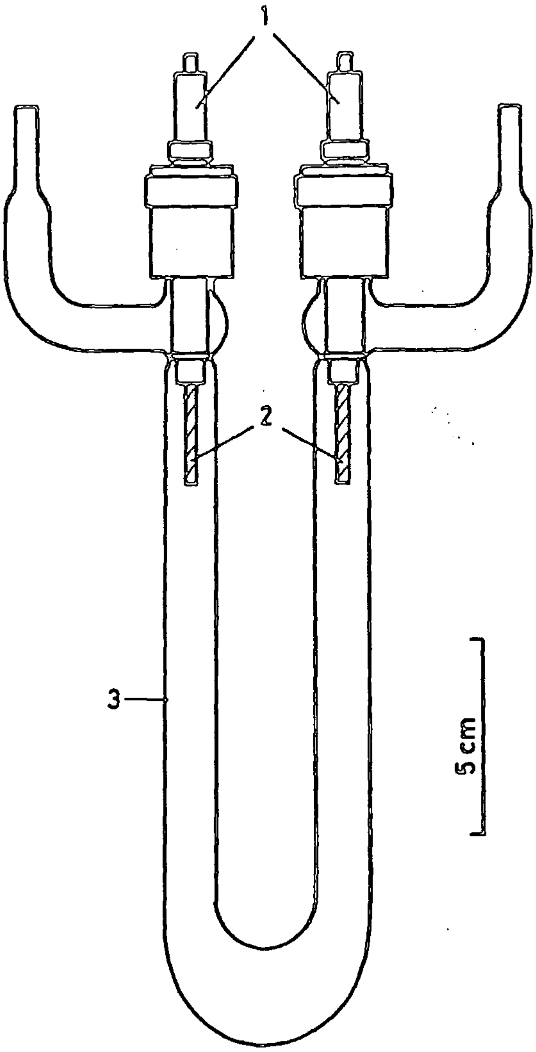
A very thin continous polymeric film also formed on the walls of the discharge tube. The pure product is largely insoluble in liquid $SO_2$ and so unreacted $(PhCN_2S_2)_2$ was washed from the product with liquid $SO_2$ using a closed extractor.[10] Typical yields of $(PhCN_3S_2)_2$ were 0.22 g (80%), and thus the energy consumption was $1.3 \times 10^8$ J $mol^{-1}$ (i.e. 92 kWh $kg^{-1}$) of the product. Found: C 42.8, H 2.1, N 21.2, S 32.9; $C_7H_5N_3S_2$ requires C 43.0, H 2.6, N 21.4, S 32.8;mass spectrum (CI), m/e 181 $(PhCNS_2)^+$, amd m/e 195 $(PhCN_3S_2)^+$ relative abundance 76% and 68% respectively. Typical composition of the concomitant polymer was $C_3H_{2.5}NS$; C 41.4, H 3.0,N 18.0; S 37.5; DSC (4°C/min), m.p.118°C (sharp endotherm), *cf.*m.p.115°C.[11], followed by immediate decomposition 123°C (sharp exotherm) leaving a purple melt. The comparison of the infrared spectra of $(PhCN_2S_2)_2$ before and after nitrogenation is shown in Figure 4.8.

The unit cell parameters of $(PhCN_3S_2)_2$ given by Boeré *et al*[11] were used to calculate the X-ray powder pattern.[12] This agreed very well with the observed pattern, (h,k,l) $d_{hkl}$/Å(obs), $d_{hkl}$/Å(calc); (001) 11.47, 11.51; (010) 10.22, 10.21; (011) 6.62, 6.60; ($\bar{1}01$) 5.82, 5.81; (021) 5.40, 5.40; (022) 4.70, 4.70.

### 4.2.3. *UV irradiation of $(PhCN_2S_2)_2$.*

(1) *In the solid state.*- The apparatus was set up as before except that a quartz lens was used in place of the cathode insert. Nitrogen was bled into the system via a T piece placed between the window and the tube. $(PhCN_2S_2)_2$ was loaded into a quartz boat and placed at the focal point of the UV beam produced using the 200W Hg/Xe setting of an Oriel 8500 power supply connected to an Oriel 6135 lamp. $(PhCN_2S_2)_2$ was then irradiated with UV light of 190 nm and above for 36 hours. The flow rate was adjusted to 70 Torr $cm^3s^{-1}$ and the sample heated to 45°C. This experiment was repeated under static conditions with a pressure of 1 Torr of nitrogen maintained in the tube. There was no observable change in the solid.

Figure 4.6. Apparatus for the plasma reaction of liquids and solids at low temperature.
1). High tension feed through (adapted Youngs' tap), 2). Solid tungsten rod, 3.2mm diameter. 3). Pyrex discharge tube with widened U bend.



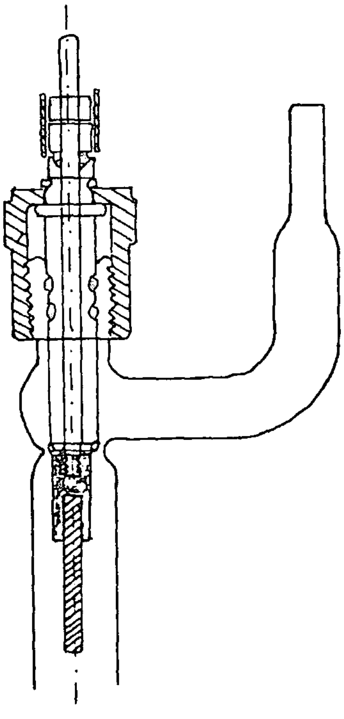


Figure 4.7

(2). *In solution.*- A solution of $(PhCN_2S_2)_2$ (0.18 g, 0.5 mmol) in 10 $cm^3$ of dry MeCN ( UV cutoff <200 nm) contained in a fused silica tube (12.7 mm O.D) was irradiated in a photochemical reactor ( Rayonet, model RPR - 208 giving approximately 120 watts of 253.7 nm UV energy) for 36 h.

During the irradiation, nitrogen ( pre-saturated with MeCN vapour ) was bubbled through the solution via a fine disperser at a rate of *ca.* 10 $cm^3$ (at STP) per minute with an overpressure of *ca.* 2 bars inside the tube. The temperature of the solution inside the UV reactor was 35°C. At the end of this experiment there was a noticeable fading of the original deep purple colour of the solution but this was restored on standing for a few hours. On evaporation of the MeCN the solid residue analysed as $(PhCN_2S_2)_2$.

### 4.2.4. *Preparation of* $(p\text{-}ClC_6H_4\overline{CNSNSN})_2$.

$(p - ClPhCN_2S_2)_2$ was prepared and purified as reported in Chapter 3. The dark green powder (0.25 gm, 1.15 mmol), again in a quartz boat, was immersed in the positive column of the discharge tube in the same way as in 4.2.2. above. The optimum reaction temperature was 60°C and the reaction took about 12 h. The dark brown air-stable crude product ($p$ - $ClPhCN_3S_2$) was purified as for ($PhCN_3S_2$). Found: C 36.7, H 1.5, N 18.1, S 27.4, Cl 15.1; $C_7H_4N_3S_2Cl$ requires: C 36.6, H 1.7, N 18.3, S 27.8, Cl 15.4 ; m.s. (CI): m/e 230 $[p\text{-}ClC_6H_4CN_3S_2]^+$, 29%; m/e 215 $[p\text{-}ClC_6H_4CN_2S_2]^+$,71%; DSC (4°C/min), 114.5°C (endotherm) followed by decomposition at 118.2°C. Infrared spectra of ($p$ - $ClPhCN_2S_2)_2$ and ($p$ - $ClPhCN_3S_2$) are shown in Figure 4.8.

### 4.2.5. *Preparation of* $[PhCN_2S_2]CN$.

$[PhCN_2S_2]Cl$ (0.76 g, 3.5 mmol) was placed in one bulb of a dog with a slight excess of silver cyanide (0.50 g, 3.73 mmol) in the other.

$SO_2$ was condensed onto both solids (8 ml, 12.0 g. in each) and left for 1 day. Although $[PhCN_2S_2]Cl$ is readily soluble in $SO_2$, AgCN is only slightly so giving a very pale solution. The orange $[PhCN_2S_2]Cl$ solution was then brought over onto the AgCN when the whole solution went immediately very dark brown. The resulting suspension was stirred for 3 days. After this time the solution was carefully decanted off and filtered. After several back washings of $SO_2$, a white $SO_2$ insoluble solid was left (largely AgCl, from analysis and infrared). On removal of the $SO_2$, a dark brown crystalline solid was obtained. Yield = 0.69 g, 95% based on $[PhCN_2S_2]Cl$. This solid (0.45g ) was further purified by transferring to an extractor and washing with $SO_2$ for 2 hours. This left a trace amount of AgCN (0.005 g), identified with infrared, on the frit. The $SO_2$ was evaporated leaving again a brown crystalline product. $C_7H_5N_3S_2$ requires; C 46.35, H 2.41, N 20.28, S 30.96. Found; C 45.1, H 2.46, N 18.9, S 31.14.

### 4.2.6. *Preparation of $(RCN_3S_2)_2$ from $[RCN_2S_2]$ X (R = Ph, p -$ClC_6H_4$ X = $CN^-$, $Br^-$, $I^-$).*

i). For X = $I^-$, $Br^-$; Compounds $[RCN_2S_2]$ X (typically, 1 mmol) were placed in the positive column of the discharge under the same flow conditions and current densities as for 4.2.1. The temperature was maintained with a Eurotherm 821 controller. When X = $I^-$ the reaction temperature was found to be 35°C and reaction was complete in 8 h. Typical yields were 47%. A thick coating of polymer also formed on both the discharge tube walls and the boat. Iodine was identified in the cold trap by infrared and Raman spectra. With X = $Br^-$ reaction occurred at 47°C and was complete in about 12 h. Typical yields here were 55%. Bromine in the cold trap was again identified spectroscopically.

ii). For X = $CN^-$; Again using tube 4.3. $[PhCN_2S_2]^+CN^-$ (0.1 g, 0.5 mmol) was subjected to a nitrogen plasma.

No external heating was applied, but within minutes a thick black polymer film built up. Reaction temperature was about 35°C and was complete in about 12 h, leaving a dark brown solid in the boat. Yield = 0.067 g. This was loaded into an extractor and washed with $SO_2$ leaving red/brown $(PhCN_3S_2)_2$ (0.049 g) on the frit, according to infrared spectroscopy. The solid obtained from the $SO_2$ fraction (0.018 g, 18% of original) gave infrared bands corresponding to $[PhCN_2S_2]Cl$, but with broad polymer bands.

### 4.2.7. *The effects of a nitrogen plasma on* $[PhCN_2S_2]Cl$.

$[PhCN_2S_2]Cl$ (0.5 g, 2.31 mmol) was exposed to a nitrogen plasma. The temperature was raised in 10°C steps every 1 h, from room temperature over a period of 18 h to 110°C. However, over this temperature range there was no appreciable change in the starting material, confirmed with infrared spectroscopy. Only very small amounts of polymer formed.

### 4.2.8. *Reaction of* $(RCN_2S_2)_2$ *with a nitrogen DC plasma* ( $R = Pr, Bu^t$ ).

Both these dervatives are liquids at room temparture and are presumably largely present as free radical monomers[13]. The discharge apparatus was modified (Figure 4.6.). Because a pressure of only approx. 1 Torr is generally maintained in the discharge tube, it was found necessary to cool or freeze the dithiadiazole to prevent too much escaping into the gas phase. Typically 5ml of liquid were syringed into the bulb which was sealed in the glove box. This was then removed and connected to the nitrogen line and the discharge apparatus. The whole bulb and side arm were then immersed in a cold bath cooled to -10°C. With a nitrogen flow of 50 Torr $cm^3s^{-1}$ the discharge was ignited at a pressure of 1 Torr. At -10°C a small amount of brown polymer formed on the walls of the discharge tube, whilst some red monomer collected in the cold trap. As the temperature was raised to 0°C an increasing amount of polymer formed.

After about 8 h there was no remaining liquid in the bulb and a dense coating of a brown film had formed which infrared spectra revealed to be polymeric with broad ill-defined absorptions.

### 4.2.9. *Reaction of $[RCN_2S_2]\ X$ ( $R$ = Pr,t-Bu, $X$ = I-,Br-) with a DC nitrogen discharge.*

Using the discharge tube in Figure 4.6. 0.5 g of $[\text{alkylCN}_2\text{S}_2]^+\ \text{X}^-$ was placed in the bulb and cooled to -5°C. Using a flow rate of 50 Torr $\text{cm}^3\text{s}^{-1}$ and maintaining a current of 2.5 mA, the discharge was ignited. After 5 h the temperature was raised to 0°C. The reaction was complete in a further 8 h. A heavy coating of polymer had formed on the discharge tube walls and the trapped halogen ($I_2$ or $Br_2$) was identified with infrared and Raman spectra.

### 4.2.10. *Preparation of $[Ph\overline{CNSSN}][S_3N_3]$ and its reaction with nitrogen plasma.*

It is most easily prepared by a simple metathesis;

$$\underset{(1)}{[\text{PhCN}_2\text{S}_2][\text{AsF}_6]} + \underset{(2)}{[\text{Pr}_4\text{N}][\text{S}_3\text{N}_3]} \xrightarrow[\text{rt}]{\text{CH3CN}} \underset{(3)}{[\text{PhCN}_2\text{S}_2][\text{S}_3\text{N}_3]} + [\text{Pr}_4\text{N}][\text{AsF}_6]$$

Compound (1) was prepared by the reaction of $(\text{PhCN}_2\text{S}_2)_2$ with $\text{AgAsF}_6$ in $\text{SO}_2$ and (2) was prepared according to literature[14].

(1) (0.114 g, 0.308 mmol) and (2) (0.10 g, 0.32 mmol) were placed together in a Schlenk. On addition of 10 $\text{cm}^3$ of $\text{CH}_3\text{CN}$ a deep red solution and a green precipitate formed. After stirring for 1 day the solution was filtered off and the green solid was sublimed (70°C, 4 x $10^{-7}$ Torr), giving green crystals with a metallic sheen. They are only moderately air sensitive. (Yield = 0.058 g, 58%). $\text{C}_7\text{H}_5\text{N}_5\text{S}_5$ requires; C 26.31, N 21.92, H 1.57. S 50.18. Found; C 26.40. N 22.09, H 1.52, S 50.07.

(3) (0.030 g, 0.094 mmol) was acted on by the nitrogen plasma. The reaction proceeded without any additional heating (ie. at *ca.* 35°C inside the discharge tube) to give ($PhCN_3S_2$). A thick black polymer film also quickly formed.

### 4.2.11. *Preparation of* $[Ph\overline{CNSSN}]_2Cl$.

$(PhCN_2S_2)_2$ (0.0418 g, 0.115 mmol) and $[PhCN_2S_2]Cl$ (0.05 g, 0.231 mmol) were placed in an agate mortar. On grinding the mixture became sticky but eventually a brown powder resulted. The powder was then heated to 160°C for 10 minutes. The absence of peaks in an infrared due to reactants was taken to indicate an almost quantitative yield. $C_{14}H_{10}N_4S_4Cl$ requires; C 42.24, N 14.08, H 2.51, S 32.2. Found; C 42.55, N 14.12, H 2.58. S 33.18.

### 4.2.12. *Reaction of* $(PhCN_3S_2)_2$ *with* $SO_2Cl_2$.

$(PhCN_3S_2)_2$ (0.5 g, 1.28 mmol) was placed into one bulb of a dog and an excess of dry $SO_2Cl_2$ (20ml) syringed onto the solid against a counter current of dry nitrogen. After about 10 mins all the solid had dissolved giving a yellow solution which was filtered off. Fine yellow needlelike crystals of $PhCN_3S_2Cl_2$ (identified by infrared spectroscopy and elemental analysis) grew on reduction of the volume of $SO_2Cl_2$. The remaining liquid was decanted into the first bulb and all the $SO_2Cl_2$ removed under vacuum to leave a yellow powder also shown to be $PhCN_3S_2Cl_2$. First yield of crystals = 0.491 g (72%). Total yield = 0.67 g, (98%). $C_7H_5N_3S_2Cl_2$ requires C 31.58, H 1.88, N 15.79, S 24.10, Cl 26.65; Found C 31.57, H 1.89, N 15.77, S 24.0, Cl 26.81. Infra red $\nu_{max}$ = 1590m, 1345s, 1297s, 1182s, 1165m, 1095m, 1069m, 1028s, 1003w, 915s, 790s, 705vs, 667m, 530s, 499s, 478s, 425s, 407m, 380s.

### 4.2.13. *Reaction of $PhCN_3S_2Cl_2$ with $(Me_3Si)_2NCN$.*

$PhCN_3S_2Cl_2$ (0.5 g, 1.88 mmol) was dissolved in 50ml of MeCN in a Schlenk and cooled to 0° C. $(Me_3Si)_2NCN$ (0.5 ml, 1.88 mmol) dissolved in 10 ml of MeCN was added dropwise to the $PhCN_3S_2Cl_2$ over 1 h. On warming slowly to room temperature, the solution gradually went a deep red colour, before a brick red precipitate formed. This was filtered off and dried before being exhaustively extracted with liquid $SO_2$ in a closed extractor. This yielded a $SO_2$ insoluble solid which infrared showed to be polymeric, whilst the $SO_2$ soluble fraction also yielded a brown powder, but which was identified as $PhC_2N_5S_2$ by chemical analysis, m.s. and infrared spectroscopy. Yield of $PhC_2N_5S_2$ = 0.15 g, (34%). $C_8H_5N_5S_2$ requires C 40.83, H 2.13, N 29.77, S 27.27; Found C 41.00, H 2.21, N 29.75, S 27.30. Infrared $\nu_{max}$ = 1340s, 1290m, 1172s, 1150s, 1100w, 1072m, 1025m, 1010m, 1000s, 980m, 935w, 925m, 850w, 820m, 778s, 723s, 706s, 688m, 675s, 650w, 575s, 514s, 508s, 495s, 470m. m.s. m/e 235 $PhC_2N_5S_2+$ (9%), 195 $PhCN_3S_2+$ (51%), 103 PhCN+ (100%), 40 $CN_2+$(2%)

### 4.2.14. *Cyclic voltammetry.*

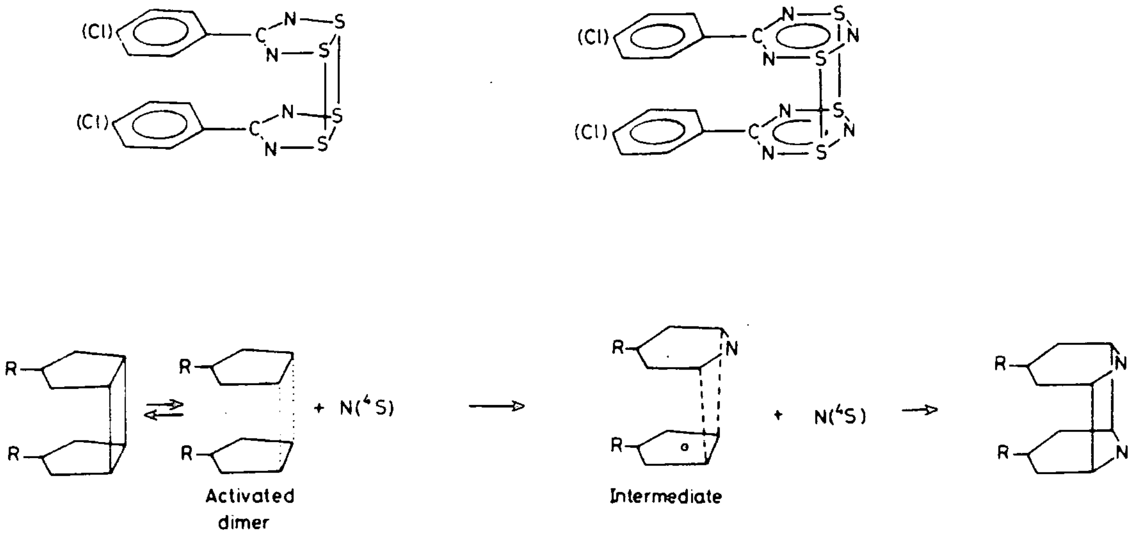
All electrochemical measurements were carried out under strict exclusion of moisture and oxygen in a specially designed airtight three limbed electrode cell described elsewhere[15]. Cyclic voltammograms were recorded using a Bioanalytical System Inc. CV-1B instrument and a Linseis LY17100 XY chart recorder. The working electrode was a platinum disc (0.002 $cm^2$) pressure moulded in FEP (= tetrafluoro - ethylene hexafluoropropylene co-polymer ). The reference electrode used was $Ag/Ag^+$ (0.1 mol $dm^{-3}$ $AgBF_4$, 0.2 mol $dm^{-3}$ $Bu_4NBF_4$ in MeCN), its potential vs. S.C.E. +0.32 V remained stable ±0.002v over a period of several months. The solvent was acetonitrile doubly distilled over $CaH_2$ and finally passed through an alumina (Woelm B-super 1) column. All distillations and experiments were performed under an atmosphere of dry nitrogen.

The supporting electrolyte, $Bu_4NBF_4$, was prepared by metathesis from $Bu_4NHSO_4$ (Labkemi AB, Sweden) and $KBF_4$ (BDH Ltd.), purified by double crystallisation from ethylacetate/diethyl ether and finally vacuum dried ($10^{-5}$ Torr) at 125°C. All solutions and cells were prepared and sealed under nitrogen in a glove box.

(i). *Cyclic voltammogram of PhCNSNSN* - $PhCN_3S_2$ (0.0053 g, 0.014 mmol) was dissolved in 10 $cm^3$ of dry $CH_2Cl_2$ and 5 $cm^3$ MeCN with tetrabutylammonium tetrafluoroborate (0.43 g, 1.3 mmol). Voltammograms run at +5.0°C showed an oxidation half-wave potential ($E^{ox}_{p/2}$) at +1.3V and a reduction half wave-potential ($E^{red}_{p/2}$. at -0.52V).

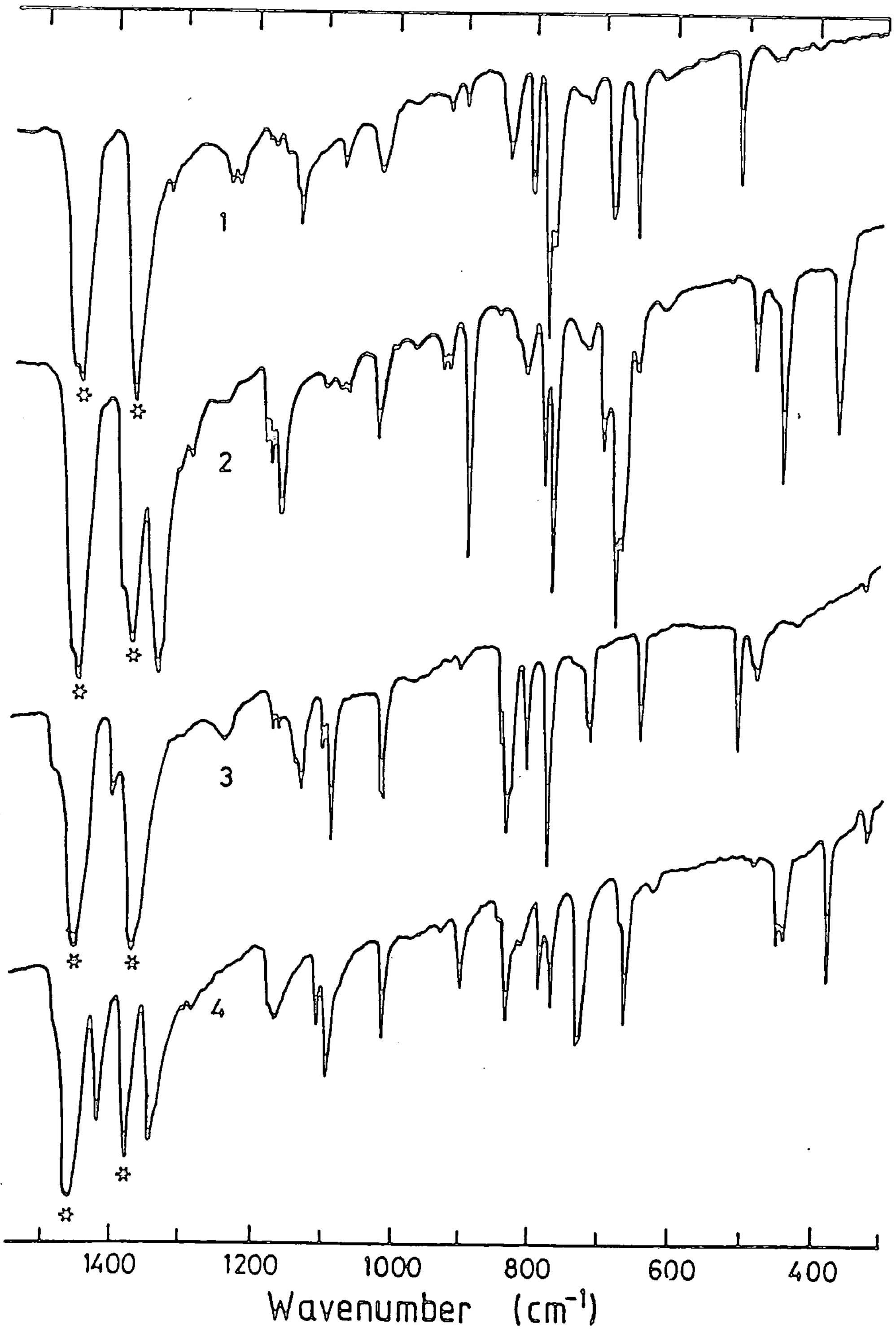
## 4.3. RESULTS AND DISCUSSION.

The unique insertion of atomic nitrogen, generated in a DC plasma, into the disulphide link of the five membered 1,2 dithiadiazole $RCN_2S_2$ ( R = Ph, p-ClPh) has been reported previously[16]. Scheme 4.2.



Scheme 4.2.

Figure 4.8. Comparison of infrared spectra of $(PhCN_2S_2)_2$ and $(p - ClPhCN_2S_2)_2$ before (spectrum 1 & 3) and after (spectrum 2 & 4) plasma nitrogenation, (CsI plates).



These reactions are reported in more detail along with analogous reactions with $RCN_2S_2$ ( R = Me, Pr, $Bu^t$) and with $RCN_2S_2^+ X^-$ ( R = Ph, p-ClPh, Pr,$Bu^t$, X = $Cl^-$ , $Br^-$ , $I^-$ ). Structural criteria which facilitate the nitrogenation reaction are discussed with particular regard for $(CH_3CN_2S_2)_2$ for which the X-ray data has been given in Chapter 3.

MNDO calculations[17] and e.s.r studies have indicated that the odd electron in $PhCN_2S_2$ lies in a SOMO distributed over the NSSN fragment of the ring and dimerisation occurs through $\sigma$ overlap of the z components at the sulphurs. (See Table 4.1, page 101, Figure 4.9 shows SOMO and dimer structure)[18]. Our own MNDO calculations show that, perpendicular to the ring, the p orbital contribution at sulphur and nitrogen are roughly 1:1.

Further e.s.r. studies have shown $PhCN_2S_2$ to consist largely of dimer units in the solid state, but with a very small proportion (< 1%) of monomer radical present. The percentage of monomer in alkyl derivatives (where R = Pr, $Bu_t$) rises considerably such that for alkyl= $Bu^t$ at room temperature the majority (> 75%) consists of monomer.[19] For the group of compounds $RCN_2S_2$ where R = Pr, $Bu^t$ which are liquids at room temperature the apparatus was slightly modified and used at -30°C to +40°C (see Figure 4.6.).

The dithiadiazole may react in two possible ways. It may react either as the monomer with atomic nitrogen in a radical/radical reaction (d), or it may react in the dimer form(c). The latter is more likely because of the very low concentration of monomer present in the solid, though reaction via the monomer must take place to some extent.

Figure 4.9. Diamgramatic representation of the SOMO and the overlap of the $P_z$ component in the $(PhCN_2S_2)_2$ dimer unit.

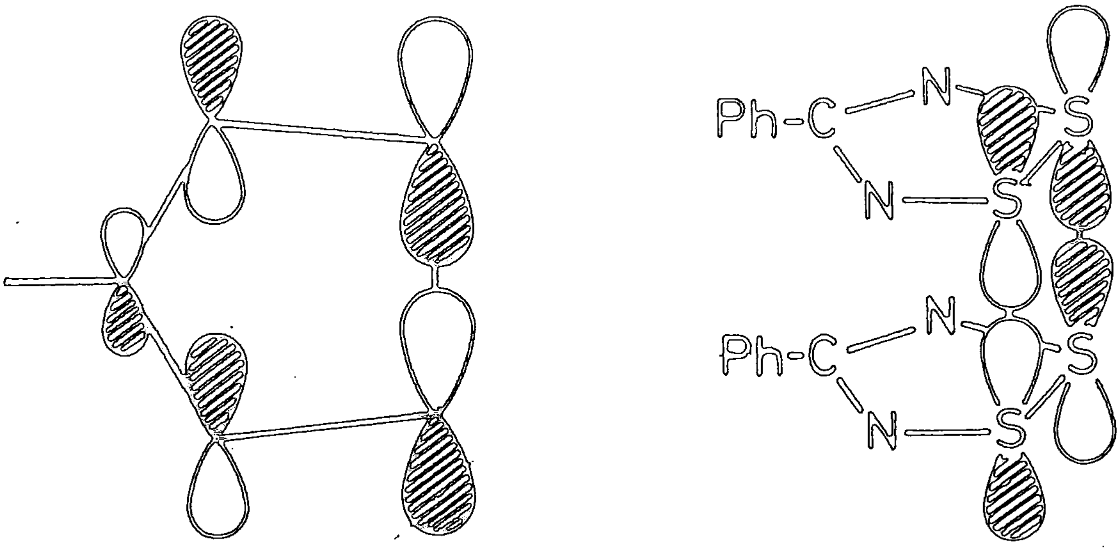


Table 4.1. HOMO/LUMO MNDO data for $HCN_2S_2^+$.

HOMO (-17.62ev)

| | s | $p_x$ | $p_y$ | $p_z$ |
|---|---|---|---|---|
| $S_1$ | 0 | 0 | 0 | -0.52 |
| $S_2$ | 0 | 0 | 0 | -0.52 |
| $N_3$ | 0 | 0 | 0 | +0.30 |
| $N_4$ | 0 | 0 | 0 | +0.30 |
| C | 0 | 0 | 0 | +0.53 |

LUMO (-9.1ev)

| | s | $p_x$ | $p_y$ | $p_z$ |
|---|---|---|---|---|
| $S_1$ | 0 | 0 | 0 | +0.49 |
| $S_2$ | 0 | 0 | 0 | -0.50 |
| $N_3$ | 0 | 0 | 0 | +0.51 |
| $N_4$ | 0 | 0 | 0 | -0.50 |
| C | 0 | 0 | 0 | 0 |

MO no.15 (-8.09ev)

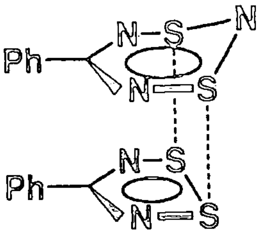
| | s | $p_x$ | $p_y$ | $p_z$ |
|---|---|---|---|---|
| $S_1$ | +0.09 | +0.66 | +0.03 | 0 |
| $S_2$ | +0.09 | +0.66 | -0.03 | 0 |
| $N_3$ | -0.70 | -0.16 | -0.10 | 0 |
| $N_4$ | +0.70 | -0.17 | -0.10 | 0 |
| C | 0 | +0.16 | 0 | 0 |

Scheme 4.

a). $[PhCN_2S_2]_2$ + $N_2$* --/--→ $[PhCN_3S_2]_2$

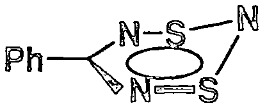
b). $[PhCN_2S_2]$ + $N_2$* --/--→ $[PhCN_3S_2]_2$

c). $[PhCN_2S_2]_2$ + N* -----→



------→

d). $[PhCN_2S_2]$ + N* -----→



--×2--→

X-ray crystal structure studies[20] have shown that for $(PhCN_2S_2)_2$ there are channels running parallel through the lattice. These have a diameter of in excess of 3.5 Å (see Figure 4.11, page 108), the atomic radius of atomic nitrogen is 1.3 Å, so that it is possible for atomic nitrogen to diffuse through the crystal structure to the reaction sites. Whole crystals when subjected to plasma nitrogen showed very definite reactant/product boundaries which were observed to move with time and so the solid state reaction may well be diffusion controlled.

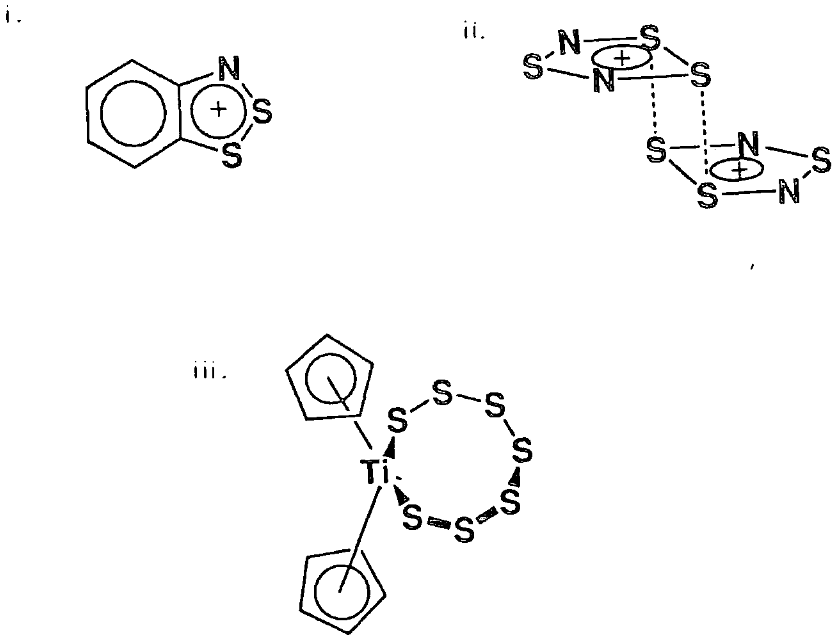
As expected, the ease of chemical and electrochemical reduction of $(RCN_2S_2)$ X increases with the atomic number of the halogen, X. Consequently the various halides ( $X = Cl^-$, $Br^-$, $I^-$)of both the aryl and the alkyl derivatives were all subjected under similar conditions to a nitrogen DC plasma discharge. For the aryl derivatives, it was observed, that the chlorides were inactive but that the bromides and the iodides both yielded the same product $Ar\overline{CNSNSN}$ with release of halogen. As expected, the iodides required the lower reaction temperatures.

In the case of the alkyl derivatives, however, the corresponding halogen was again released, but with almost complete conversion to brown polymer. Presumably because their radicals are monomeric, the alkyl derivatives are too volatile and are quickly lost into the gas phase where they are subjected to the vigorous conditions of the plasma with consequent molecular fragmentation and conversion to a non-stoichiometric polymer. Thus no compounds alkyl$CN_3S_2$ were obtained from the cations and free radicals, only non-stoichiometric polymer. The polymers obtained from both aryl and alkyl dithiadiazoles were all air stable, and adhered strongly to the surface of the quartz boat and glass discharge tube.

The mechanism of these nitrogen insertion reactions involving dithiadiazolium salts is uncertain. However, for the cation reactions the most likely first step is the electron transfer to give the neutral radical $[\mathrm{R}\overline{\mathrm{CNSSN}}]^{\cdot}$. This electron may either come from the pool of free electrons in the plasma or it may come from the anion through bombardment with the nitrogen atoms (which would explain the correlation between reactivity and the ionization potential of the halide ion). Clearly the energies required for the ionisation of $X^-$, the reduction of $RCN_2S_2^+$, as well as for molecular/lattice re-organisation and bond formation must have their source in the plasma.

A further contributory factor to the ease of the reaction of the cations, however, must be the high electron affinity. Since the LUMO of $\mathrm{R}\overline{\mathrm{CNSSN}}^+$ is antibonding with respect to both the SS bond and the SN bonds the first electron provision will weaken both bond types, see Table 4.1, page 101. Formation of the new SN bond (stronger than the SS bond they replace, SS = 264kJmol$^{-1}$, SN = 243kJmol$^{-1}$ single bond order, or 301 kJmol$^{-1}$ for bond order 1.5) completes the process.

Further S/N compounds were also subjected to plasma nitrogen including $S_8$, $S_4N_4$, $S_3N_2Cl_2$, $S_4N_3Br$. It was thought that, in particular, the structural similarities of $S_3N_2Br$ or $C_6H_4NS_2^+Br^-$ (Scheme 4.4.) would facilitate the insertion of nitrogen. Other SS bonded species such as $S_4N_3Br$, and various transition metal complexes containing the disulphide group such as $Cp_2TiS_7$ and $Pt(N_2HS_2)(PPh_3)\ BF_4$[21] were also placed in a nitrogen discharge. In all these cases, however, the sample was either left unchanged or, particularly in the case of the sulphur rich compounds, varying amounts of $(SN)_x$ were obtained as thin films coating the walls of the discharge tube. The related compound $[Ph\overline{CNSSN}]_2Cl$ was also placed under a nitrogen plasma. No reaction was observed until externally heated to 100°C when very quickly a black polymer film formed, leaving pseudomorphs of the original black needle crystals. On mulling, these powdered to a brown/orange solid which, from infra-red spectra, was almost entirely $[PhCN_2S_2]Cl$.



Scheme 4.4.

However, the compound $[PhCNSSN][S_3N_3]$ which, like $(PhCN_2S_2)_2$ contains adjacent $PhCN_2S_2$ units, did react with atomic nitrogen to yield $(PhCN_3S_2)_2$

and at a much lower temperature than previously observed for $(PhCN_2S_2)_2$; the reaction occurred readily at room temperature. There was no observed $(SN)_x$ produced or other sulphur compounds which could be expected from the fragmentation of the $S_3N_3$ unit. It is concluded therefore that all the S/N from this is incorporated in the black C/S/N polymer layer which also forms.

### 4.3.1.*Discussion.*

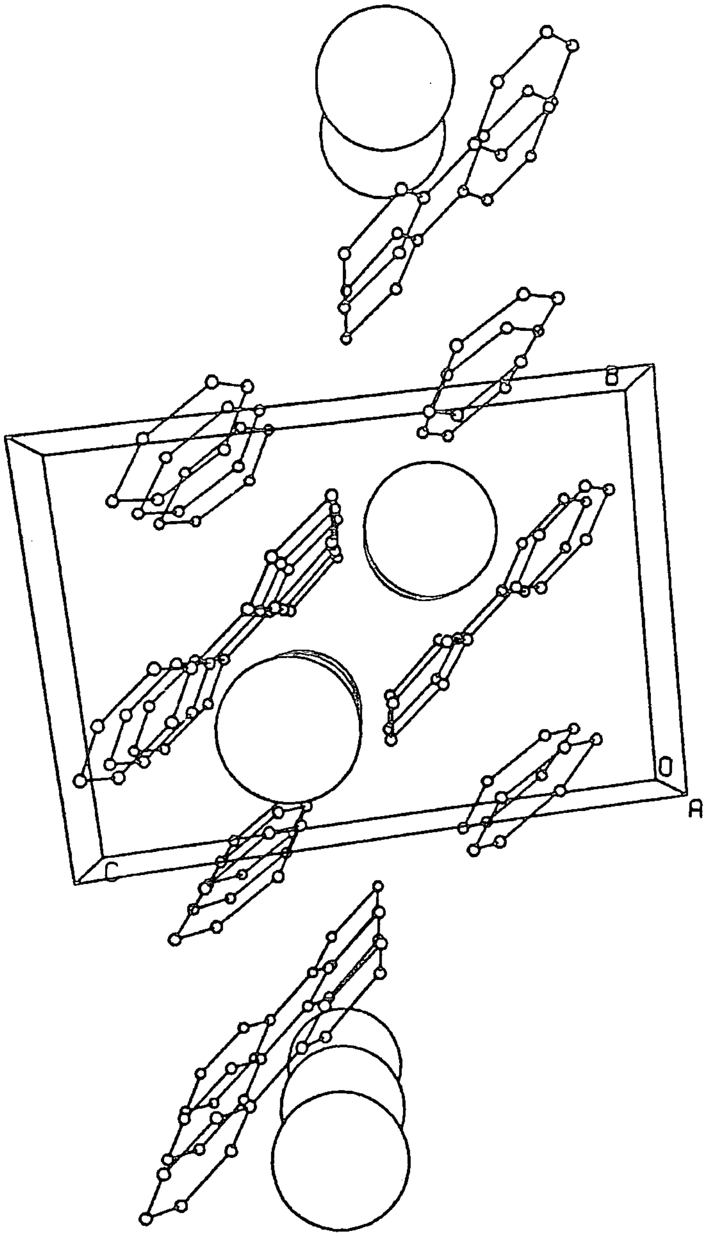
Of the 1,2,3,5 dithiadiazoles ($RCN_2S_2$) studied, it was only in the case of R = Ph or *p*-$ClC_6H_4$ that the plasma nitrogenation produced the corresponding 1,3,2,4,6 dithiatriazine ($RCN_3S_2$). The experimental results indicated several general criteria for successful nitrogen insertion into 1,2,3,5 dithiadiazoles.

(1). Since the reaction is heterogeneous (gas/solid), it is most likely controlled by the diffusion rate of the nitrogen atoms through the solid to the reaction sites.

(2). The crystal packing must be such as to permit diffusion of atomic nitrogen, whislt the packing itself is dependent on the substituent R in $RCN_2S_2$. The substituent also has a profound effect on the stability of the produced intermediate and final product (Scheme 4.1.). When R = aryl the dithiadiazole and the dithiatriazine product are dimeric and the proposed intermediate is then a mixed 5 membered/6 membered ring dimer. If, on the other hand, R = alkyl where the starting dithiadiazole, as a volatile liquid, is largely monomeric then the intermediates may also have a decreased tendency for dimeric stabilisation with consequential increased volatility.

(3). The starting material and product must be solids of low volatility and sufficiently stable in the plasma. The experimental evidence suggests that when the temperature is high enough to generate vapour at a partial

Figure 4.10. A View of the "Channels" through $[PhCN_2S_2][S_3N_3]$.



pressure comparable to that of the nitrogen in the plasma tube, polymeric films form on the reactant sample and on the discharge tube walls. This clearly is the case when R = alkyl derivatives ( R = Pr, $Bu^t$.), even when the temperature is below room temperature.

These criteria impose quite severe constraints both on suitable reactants and on reaction conditions. In an effort to ascertain just how restrictive these constraints were, we studied two special cases with similar physical properties: $(PhCN_2S_2)_2$ and $(MeCN_2S_2)_2$.

Both these are dark green/purple bichromic crystalline dimeric solids at room temperature, both melt without decomposition, $(PhCN_2S_2)_2$ at 127°C and $(MeCN_2S_2)_2$ at 95.5°C. The vapour pressure of $(MeCN_2S_2)_2$ was measured in this laboratory[22]. Unfortunately there are no vapour pressure/temperature data for $(PhCN_2S_2)_2$, but from its very low sublimation rate in vacuum at the typical nitrogenation temperature of 45°C, it has been estimated as between 0.01 and 0.1 Torr.

As mentioned above, support for a diffusion-controlled mechanism for the nitrogenation of $(PhCN_2S_2)_2$ was obtained by examining the cross section of a single crystal of $(PhCN_2S_2)_2$ at various stages of the plasma reaction. The different colours of the reactant and product made it easy to discern the boundary between the unreacted core of $(PhCN_2S_2)_2$ and the surrounding buff coloured layer of $PhCN_3S_2$. While the nitrogenation of $(PhCN_2S_2)_2$ proceeded with a readily observable rate at 25°C, an increment of just 20°C produced a steep rise in the reaction rate.

(Diffusion coefficient as a function of temperature is given by the Arrhenius relation $D = D_0\exp(-E_d/kt)$, where $E_d$ is the activation energy of diffusion and $D_0$ is the frequency or pre-exponential factor).

In contrast to $(PhCN_2S_2)_2$ there was no analogous formation of $(MeCN_3S_2)_2$ from $(MeCN_2S_2)_2$ over a range of temperature (-25°C to + 50°C).

A likely reason for this becomes clear from a comparison of molecular packing in the crystal lattices of $(PhCN_2S_2)_2$ and $(MeCN_2S_2)_2$. While the structure of $(PhCN_2S_2)_2$ has been known for some time[20], it has not previously been possible to obtain crystals of $(MeCN_2S_2)_2$. Figure 4.11.a-d juxtaposes the molecular packing in the structures of $(PhCN_2S_2)_2$ and $(MeCN_2S_2)_2$. A perspective view down the b axis of the orthorhombic unit cell ($P2_12_12_1$) of $(PhCN_2S_2)_2$ reveals sizable van der Waals regions (channels) through which atomic nitrogen can reach the S-S links.
The structure of $(MeCN_2S_2)_2$ (Figure 4.11a-d) is best represented as a projection parallel to the a axis to reveal the close S/S and S/N contacts between adjacent dimer units.

Here, the units numbered 1-2 and 5-6 form a close contact of 2.954 Å between S11 - S51, shorter than the average distance of 3.100 Å between the sulphur atoms of the opposite coplanar rings. Thus, this type of packing leaves too small van der Waals regions between the S-S ends for effective N diffusion to occur. In addition to this adverse geometric factor the diffusion will be hampered by a lower temperature in the plasma tube necessitated by a higher vapour pressure of $(MeCN_2S_2)_2$ with respect to $(PhCN_2S_2)_2$.

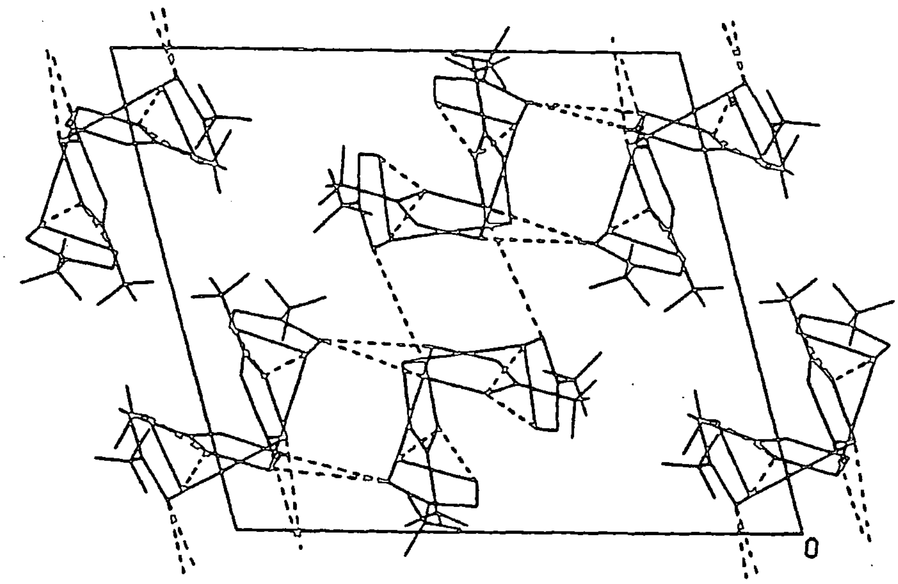
Both the geometry and the reaction temperature considerations have dealt with the kinetic aspects. It is, however, possible that an important contributory factor to the successful plasma nitrogenation of $(PhCN_2S_2)_2$ is the stabilisation energy which arises from a weak overlap of the uppermost $\pi$ orbitals of the two cofacial $PhCN_3S_2$ rings[11]. This is reflected in the considerably shorter distances, viz., 2.53 Å between the sulphur atoms of the two cofacial rings in $(PhCN_3S_2)_2$ as compared with an average distance 3.11 Å of the dimeric $(PhCN_2S_2)_2$.

Figure 4.11. Comparison of the $(MeCN_2S_2)_2$ and $(PhCN_2S_2)_2$ crystal structures.

a. Stick model projection of the $(MeCN_2S_2)_2$ structure parallel to the a axis with the close S-N intermolecular contacts shown as dashed lines.

b. Three selected dimer molecules showing shortest intermolecular distances. (the methyl groups are ommitted for clarity).

a.



b.

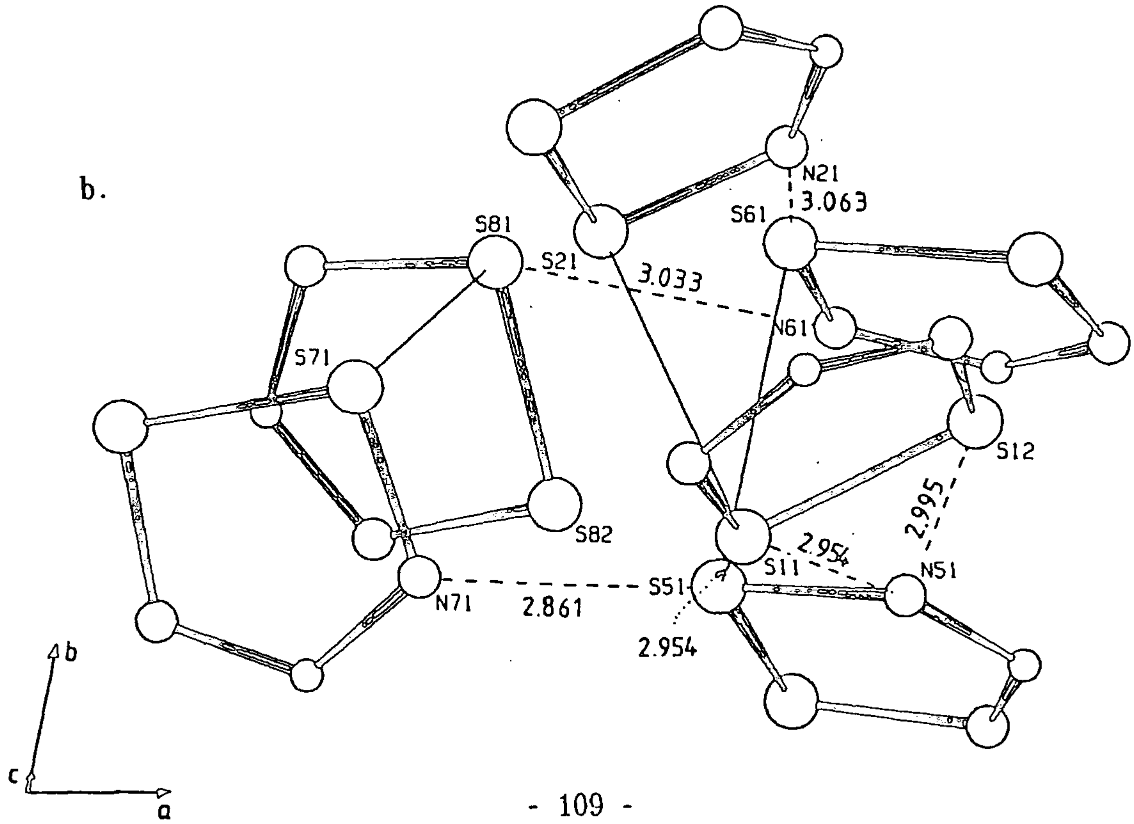
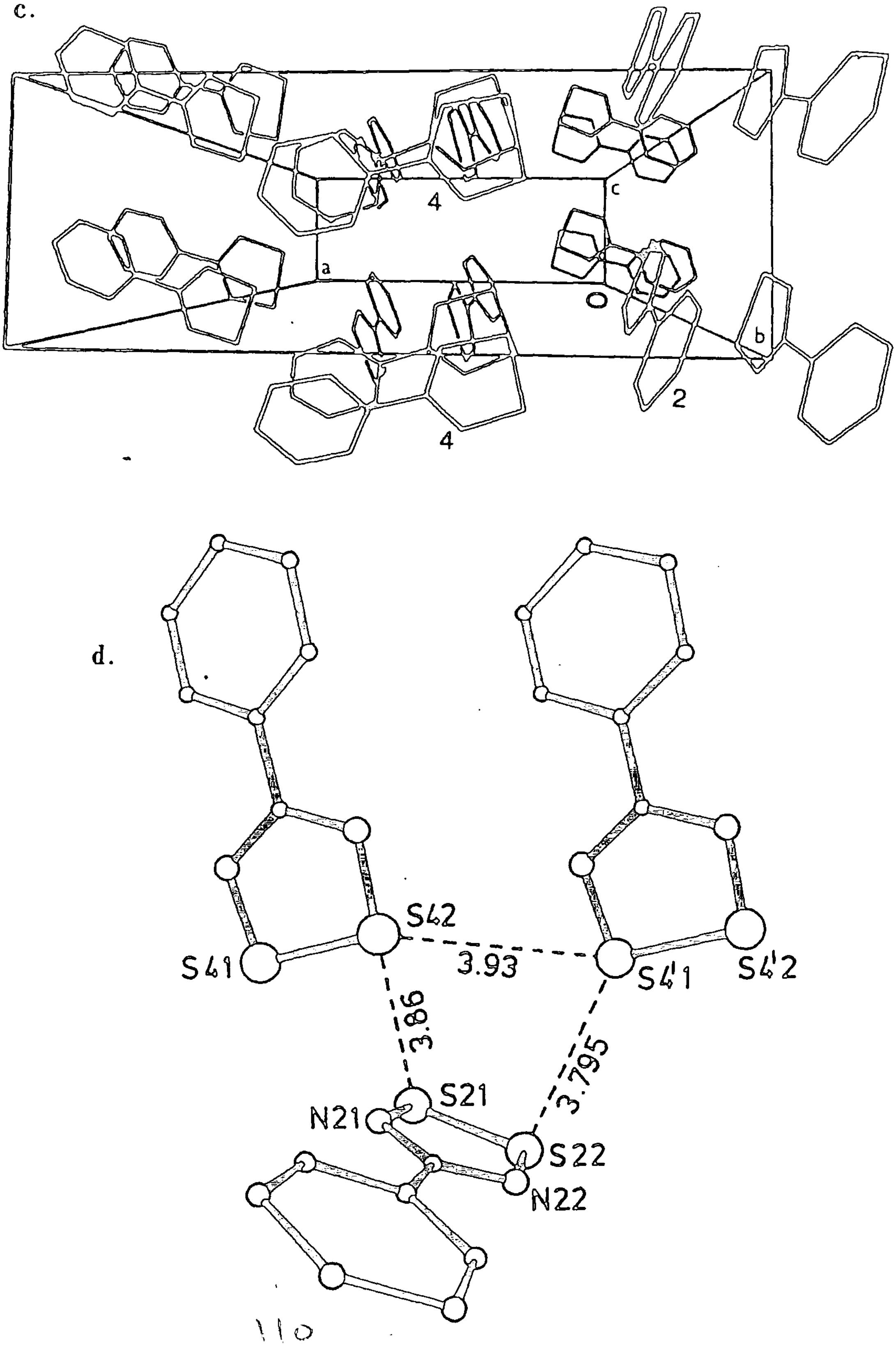


Figure 4.11. c. A perspective view down the b axis(32.98Å) of the $(PhCN_2S_2)_2$ orthorhombic unit cell, showing the van der Waals channels (cf.d.). Only the molecules filling the upper half of the unit cell are shown.

d. The 'bottle-neck' of the channels with the S-S intermolecular distances shown (corresponding to positions of three of the $(PhCN_2S_2)_2$ molecules in Figure 4.10c.. numbered 2, 4 and 4'.



There is yet another kinetic advantage to be considered, namely the 'least motion' principle. The relatively minor spatial reorganisation occurring during the conversion of $(PhCN_2S_2)_2$ to $(PhCN_3S_2)_2$results in a high degree of crystallinity of the product (as obtained by plasma nitrogenation at 45°C ). This crystallinity is seen from the well-resolved sharp X-ray powder diffraction lines. In contrast, chemically prepared $(PhCN_3S_2)_2$ according to Boeré[11] gave fewer diffused lines probably due to a high degree of subdivision. Similar differences in the resolution quality apply to the infrared spectra.

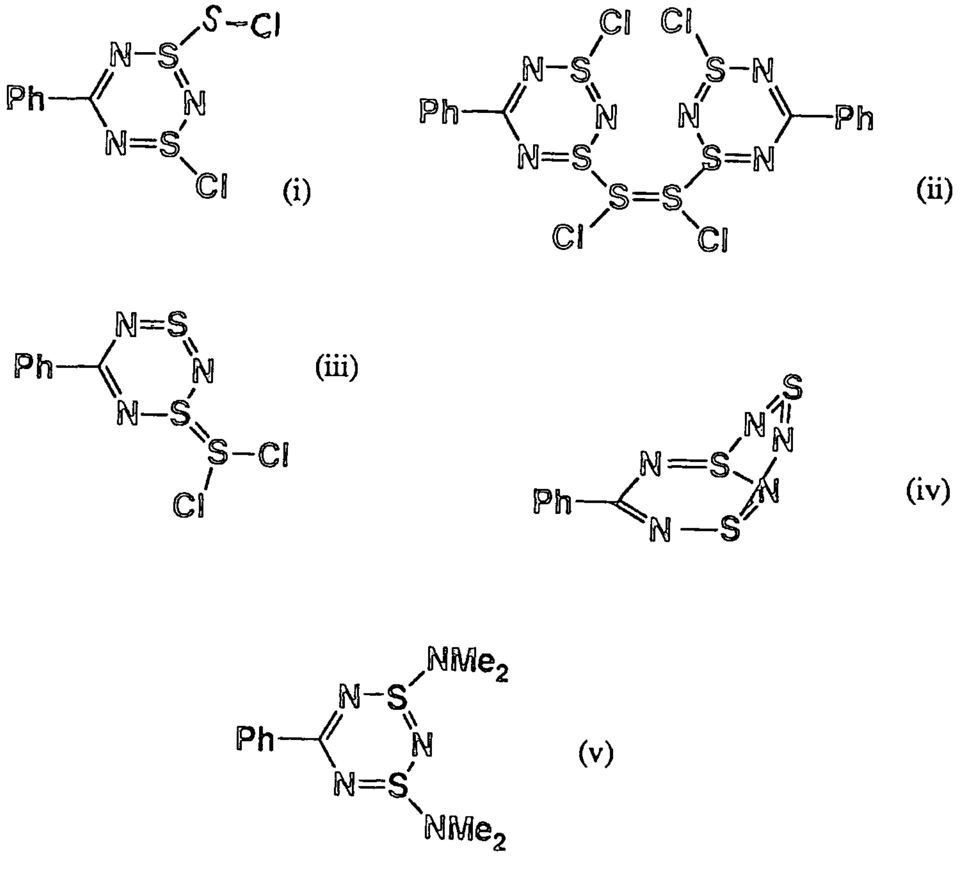
### 4.3.2. ***$PhCN_3S_2$*: CV and reactions.**

$(PhCN_3S_2)_2$is air stable and rather chemically unreactive: This stability is also reflected in the high oxidation potential, found experimentally (page 98);

$$(PhN_3S_2)_2 \longrightarrow 2(PhCN_3S_2)+ \quad + \quad 2e- \qquad E_P/_2 = +1.3 \text{ V.}$$

A reduction peak was also found with value of -0.52 V. Neither of these two process is reversible, suggesting that the cation and the anion of $PhCN_3S_2$ are unstable. This is borne out experimentally, since although it is possible to obtain the cation and dication in solution with highly polar solvents, they are always associated with cationic polymer and further attempts to isolate the solid have so far resulted only in causing further polymerisation. The dichloride derivative, $PhCN_3S_2Cl_2$[11], previously synthesised by the chlorination of $PhCN_5S_3$, can easily be prepared in very pure form by the reaction of sulphuryl chloride with $PhCN_3S_2$. These chlorines atoms are readily replaced by other groups, eg. $-NMe_2$. $(PhCN_3S_2)_2$ readily dissolves with reaction in thionyl chloride yielding yellow crystals.

Their sublimation in vacuum at *ca*. 60°C produced thin pale yellow platelets. Chemical analysis gave an empirical formula $PhCN_3S_2.SCl_2$ (Scheme 4.5), however, Weissenberg diffraction photograph indicated thermal disorder which thwarted a full X-ray structure determination. By analogy with $PhCN_3S_2Cl_2$ and $PhCN_3S_2(NMe_3)_2$, $PhCN_3S_2.SCl_2$ may have structure 4.5.(i) which would account for the thermal disorder, 4.5.(ii) is less likely since SS doble bonds are not strong, 4.5.(iii) is least likely since the $-SCl_2$ group, a strong chlorinating agent, will chlorinate the other sulphur. $(Me_3Si)_2NCN$ reacted to form the novel bicyclic compound $PhC_2N_5S_2$ with a bridging carbon atom. This is analogous to the known compound $PhCN_5S_3$ with a bridging sulphur atom in the same position.


(i) (ii) (iii) (iv) (v)

Scheme 4.5.

## 4.4 Conclusion

It is concluded that the uniqueness of the plasma nitrogenation of $(\mathrm{Ph}\overline{\mathrm{CNSSN}})_2$ and $(\mathrm{ClC_6H_4}\overline{\mathrm{CNSSN}})_2$ arises from an unusual combination of a number of structural and volatility factors not easily matched by other related compounds. This study may help in identifying other compounds siutable for further nitrogen fixation studies.

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# CHAPTER FIVE.

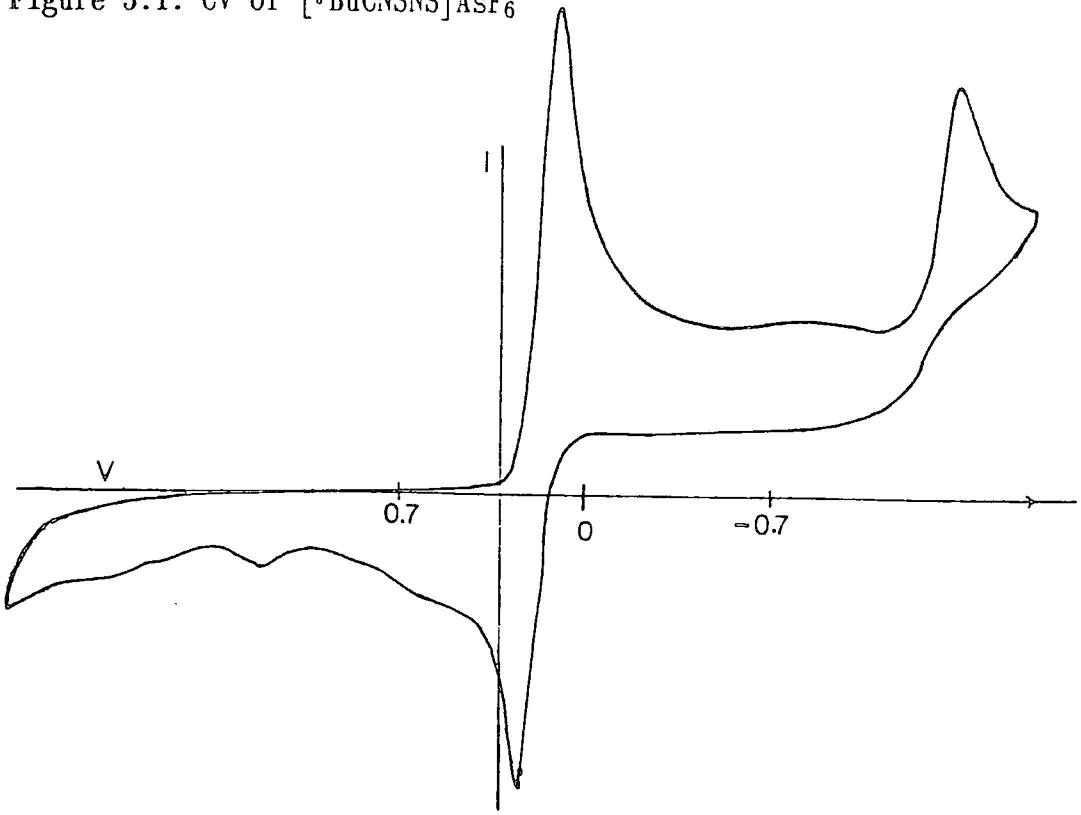
# AN ELECTROCHEMICAL STUDY OF THE 1,2 AND 1,3 DITHIADIAZOLIUM SYSTEM AND SOME S/N HETEROCYCLES.

## 5.1. INTRODUCTION.

In this chapter the redox behaviour of various 1,2,3,5 and 1,3,2,5 dithiadiazolium systems and some $S_3N_2^+$ and $S_2N^+$ salts is reported. The redox potentials of many of these systems were obtained along with some mechanistic details using cyclic voltammetry(CV); some kinetic details for the $S_2NAsF_6/CH_3CN$ reaction were also obtained from CV data.

The relationship between polarographic behaviour and the structure of organic and inorganic substances has been well established, as has the effect of various substituents on the half-wave potential[1]. CV, also known as linear sweep voltammetry, is a useful tool in studying the electrochemical properties of many compounds. In this technique the potential of the working electrode is scanned in a cyclic manner both in the anodic and the cathodic directions and involves mass transfer of the active species to the electrode by diffusion only. In this way both reduction and oxidation peaks of the sample and of reaction intermediates may be observed. The voltammogram therefore provides the electrode potential for the process and gives an indication of the stability of the intermediates. In the case where the electron transfer is fast and the product stable in the solution the CV appears reversible, as shown in Figure 5.1. (page 118) The relative peak current is a measure of stability in solution and the ratio is 1.0 in the no reaction case. Thus where the electron transfer is followed by rapid chemical reaction the CV appears non-reversible, Figure 5.2. (page 118) ie, non-reversibility is an indication of an atypical electrode process[2,3].

Figure 5.1. CV of $[{}^{t}\mathrm{Bu}\overline{\mathrm{CNSNS}}]\mathrm{AsF_6}$



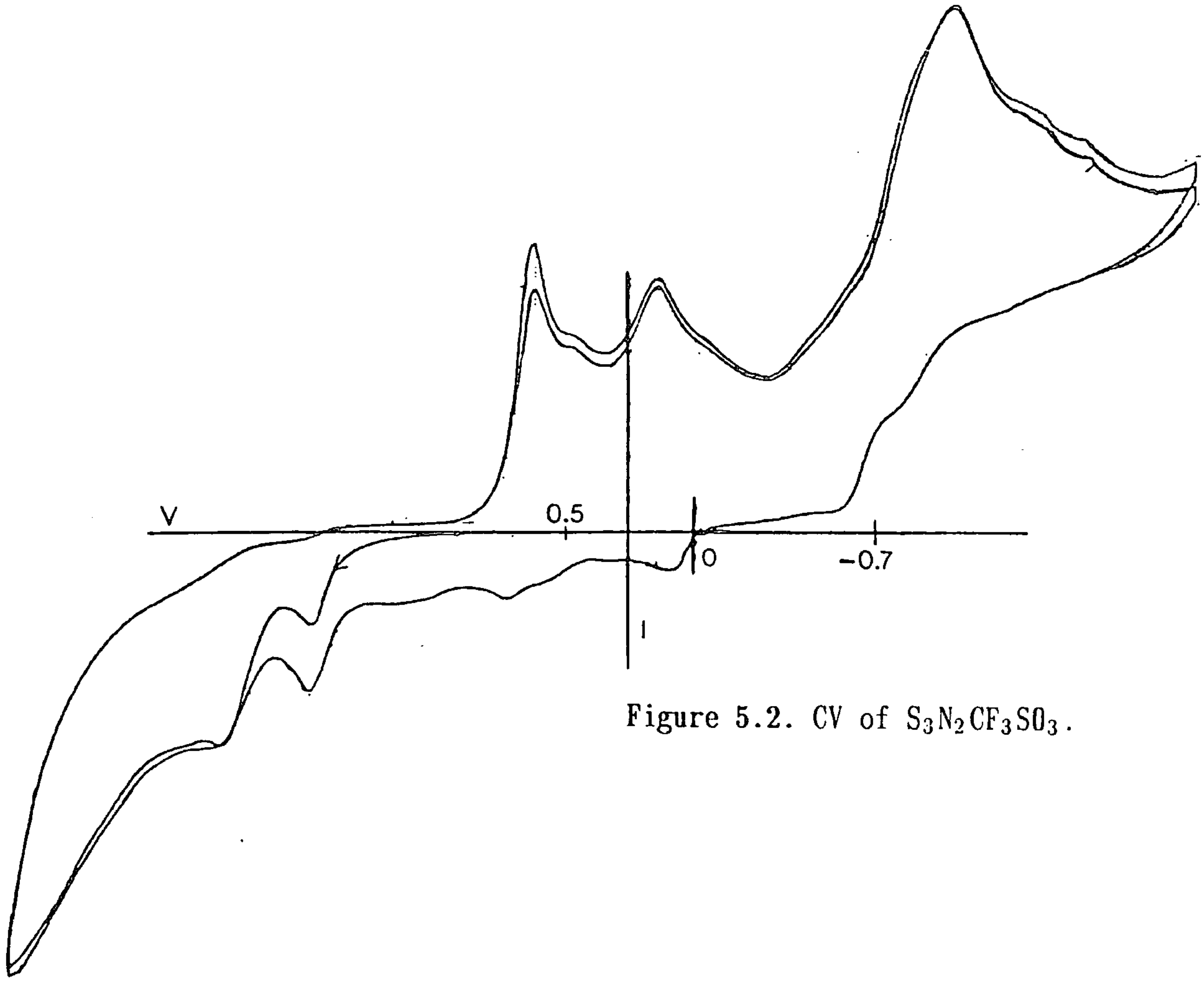


Figure 5.2. CV of $S_3N_2CF_3SO_3$.

## 5.2. GENERAL THEORY.

### 5.2.1.

The theoretical analysis of the cyclic voltammetry method is very complex and no attempt is made here to reproduce it. Instead a few simplified and relevant equations are given below.

The current passed as the voltage is swept is made up of Faradaic and capacitative components (usually associated with the double layer). For sweep rates less than 1 $Vs^{-1}$, however, the capacitative (charging) current is usually small compared to the Faradaic current, which for a reaction producing an adsorbed intermediate is given by the Butler-Volmer equation[4],[5]:-

5.2.1.1 $$I_{net} = i_o A[e^{-\alpha nF\ /RT} - e^{(1-\alpha)nF\ /RT}]$$

$i_o$ = exchange current density.

$\alpha$ = Transfer coefficient.

A = Area, $cm^2$.

= Overpotential = $E - E_{eq}$.

which itself leads to the important Tafel Equation;

$$\ln i_{net} = \ln i_o - \alpha nf\ .$$

In the three elctrode cell used the potential of the working electrode is measured against a reference, and this potential between the working electrode (we) and the reference electrode (re) is:-

5.2.1.2. $$E_{we-re} = \phi_{we-re} + \eta_{we} - \phi_{re,e} + IR_{we-re}.$$

The difference bewteen $E_{we-re}$ measured when a current flows and the value at equilibrium is:-

5.2.1.3.
$$\Delta E = \phi_{we,e} + \eta_{we} - \phi_{re,e} + IR_{we-re} - (\phi_{we,e} - \phi_{re,e})$$
$$\Delta E = \eta_{we} + IR_{we-re}.$$

I = Current, R = Resistance of cell.

$\phi$ = Potential of electrode through which the current is flowing.

$\phi_e$ = Potential at equilibrium.

$\eta$ = Over-potential.

$IR_{we-re}$ = Potential drop in the solution between working electrode and the reference electrode.

In the simplest case planar electrodes are used (as in these experiments) and then CV becomes a semi-infinite linear diffusion process. However, because the process depends on diffusion, problems may arise at slow scan rates, because of the complication of natural convection. These are minimized by the use of rapid scan techniques and as charging currents remain small scan rates between 1 - $20Vs^{-1}$ are usually sufficient.

Thus the potential of the working electrode is varied linearly with time up to the switching potential. At this peak potential the current for a reversible wave is given by the Randles-Sevcik[6,7] equation:-

5.2.1.4.
$$i_p = kn^{3/2}.AD^{1/2}.C_0V^{1/2}$$

A = electrode area, $cm^2$. k = a constant.

$i_p$ = peak current, [A]. D = Diffusion coefficient.

V = rate of potential change [$Vs^{-1}$] = sweep rate.

$C_0$ = Concentration [$moldm^{-3}$]

5.2.1.5. $\quad {}^{i_P}/_{V^{1/2}}.C = K'.$

K' = all constants from 5.2.1.4.

Thus for a reversible charge transfer, in the absence of chemical complications, the product of the peak current divided by the square root of the voltage sweep rate multiplied by the concentration of the substrate is a constant independent of the sweep rate. This expression is called the current function and when plotted versus $V^{1/2}$ gives a very convenient means of detecting follow-up chemical reactions. It also means that the current and hence the peak current is proportional to the concentration of the substrate and this relationship has been used to determine a reaction rate for the $S_2NAsF_6/CH_3CN$ reaction in section 5.3 2. (page 125).

## 5.3. GENERAL EXPERIMENTAL.

A 3 electrode Pt disc/wire system (Chapter 2, pg 23), was used in all the experiments described below. Voltammograms were recorded at a sweep rate of 196 mV/s (11.76 V/min) generally with a sensitivity of 500 mA/V for the solution of approximately $10^{-3}$ mol $dm^{-3}$ concentration. The weight of the sample under investigation was determined such that it would give this concentration in 15.0 ml of MeCN. Thus the weights were typically in the range 2 - 10 mg. The supporting electrolyte was tetrabutylammonium tetrafluoroborate,(TBATFB), usually 0.35 g (1.1 mmol) which then gave a concentration of 0.1M in 15ml of MeCN. Experiments were usually conducted in the temperature range -10° to -15° C. For those compounds, which in their neutral form were liquids at room temperature, a special teflon microsyringe was designed.

The range (window) of the potential scan that could be used, varied according to the solvent used. For instance, $SO_2$(liq.) has a limiting potential on the cathodic side of about -0.16 V, below this cathodic break down of $SO_2$ will occur to give various radical species[8],[9] eg.

$$SO_2 \longrightarrow SO_2^{-\cdot}$$

On the anodic side, however, the range stretches to approximately +3.5V. Liquid $SO_2$ is therefore a convenient solvent for the investigation of highly oxidised species. Furthermore, it is a clean, non-participating solvent, making it an attractive solvent for S/N chemistry and products are generally easy to isolate[10],[11]. Acetonitrile, on the other hand, has a limited potential range between about 2.0 and -2.0 V vs SCE. after which solvent breakdown again occurs. However, most of the important electrochemical processes occur within this range, and because there are important processes in the cathodic region for most of these heterocyclic compounds, acetonitrile was generally the solvent of choice, particularly since, unlike $SO_2$, MeCN is electro-inert. The $RCN_2S_2$ systems studied were either (i) chlorides, (ii) hexafluoroarsenates or (iii) neutral radicals. The chlorides always gave a peak corresponding to the oxidation of choride; the redox potential of the $AsF_6^-$ ion, however, lay beyond the normal scanning limits. In all subsequent discussion unspecified redox values refer to $E_{p/2}$ and have been converted to the s.c.e. scale. Formal potentials may be obtained by the formula;-

$$E_{p/2} = (E_{pa} + E_{pc})/2.$$

$E_{pa}$ = Anodic peak potential.
$E_{pc}$ = Cathodic peak potential.

usually, however, half wave potentials were obtained for each wave by using the half peak height method[4].

### 5.3.1. *Cyclic Voltammetry of $S_2NAsF_6$.*

#### *(i). CV in $SO_2$.*

An oven dried 3 limbed cell was placed in a glove box. $S_2NAsF_6$ (0.010g, 0.037 mmol) was placed in the cell with TBATFB (0.35 g, 1.1 mmol) and the cell fitted with Swagelok compression fittings. A platinum disc electrode and a coiled platinum wire counter electrode were introduced through two of the limbs along with a teflon stirring bar and the third sealed with a 1/4" OD stainless steel rod. $SO_2$ (15.0ml, 21.9g) was condensed into the cell. The solution was cooled to -15°C and against a counter current of dry nitrogen, the specially constructed glass Ag/$Ag^+$ reference electrode was inserted in place of the steel plug. Cyclic voltammograms were recorded at -10° C, maintained by an alcohol bath over a magnetic stirrer; see Figure 5.3

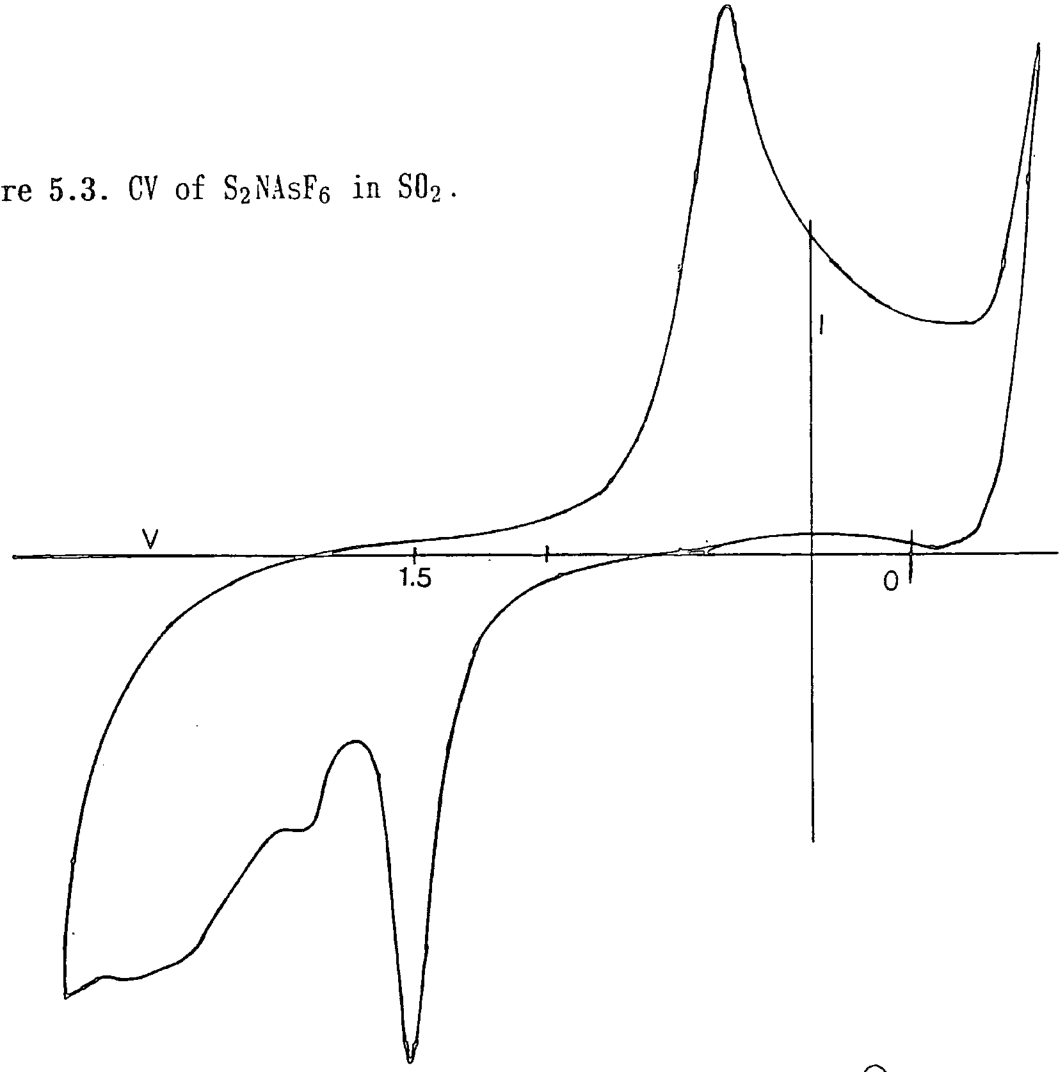
$$E_p = + 0.60 \text{ V.}$$

$$E_{p/2\,(ox)} = + 0.76 \text{ V.}$$

#### *(ii). CV in Acetonitrile.*

$S_2NAsF_6$ (0.01 g, 0.037 mmol), was placed in the 3 electrode cell with TBATFB as before. The cell was cooled to -20° C and $CH_3CN$ syringed in against a counter current of dry nitrogen. The voltammogram showed two peaks, Figure 5.4. The smaller peak at $E_p$ = + 0.08 V corresponded to the formation of 4 methyl 1,3,2,5 dithiadiazolium hexafluoroarsenate as previously established with an authentic sample. It was therefore concluded that the larger peak at $E_p$ = + 0.65 V was associated with $S_2NAsF_6$. Two repeat experiments were carried out. In the first the cell was cooled to -196° C and the $CH_3CN$ frozen as it was syringed in.

Figure 5.3. CV of $S_2NAsF_6$ in $SO_2$.



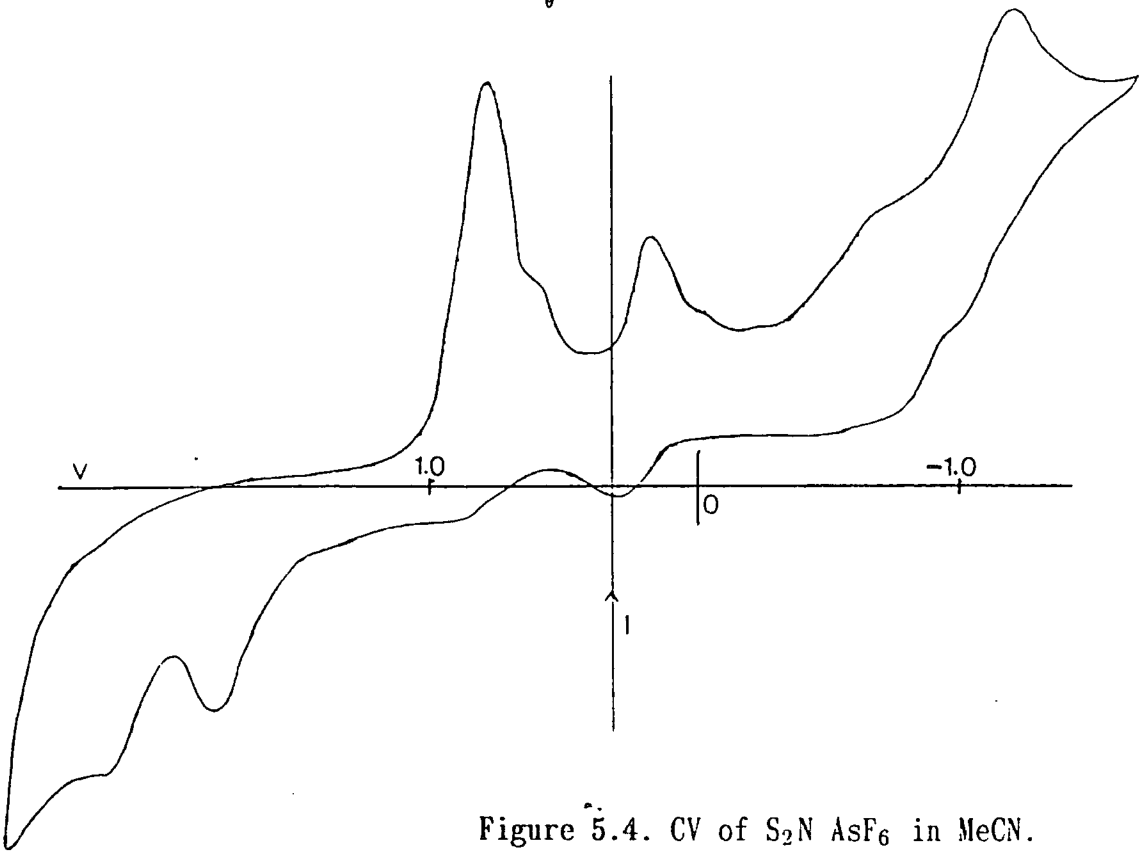


Figure 5.4. CV of $S_2N$ $AsF_6$ in MeCN.

On warming to -20° C no peak could be observed corresponding to the formation of the 4-methyl, 1,3,2,5 dithiadiazolium salt as before, suggesting that the reaction is in some way auto-catalytic. In the second experiment the $CH_3CN$ was added at room temperature to the cell. In this case no peak could be found corresponding to the $S_2NAsF_6$, and therefore the reaction must be very fast at this temperature .
The electrode potential values found for $S_2N^+AsF_6/CH_3CN$ were:-

$$E_p = + 0.65\ V$$

$$E_{p/2\,(ox)} = + 0.72\ V.$$

### 5.3.2. *Kinetic Study of $S_2NAsF_6/CH_3CN$.*

$S_2NAsF_6$ (0.01 g, 0.037 mmol) was placed in the cell as before and cooled to -20° C. $CH_3CN$ (15.0 ml) was slowly syringed onto this against dry nitrogen and a stop watch started immediately. Voltammograms were then recorded at regular intervals over a 4 h period. The initial measurements were made every minute for the first 15 minutes, every 5 minutes for the next 1 h 45 minutes and then finally every 20 minutes. An "infinity value" was obtained after about 6 h, when the reaction appeared to be complete. The peak height was measured in mm above the base line. See Figure 5.5.

### 5.3.3. *Cyclic Voltammetry of the $S_3N_2^{+\cdot}$ cation.*

(i). $S_3N_2AsF_6$ in MeCN. - This is a brown crystalline solid only moderately soluble in MeCN. However, a solution of $S_3N_2AsF_6$ (0.010g, 0.012mmol) in MeCN was prepared as in 5.3.1.(ii) above and voltammograms were recorded at -10° C. See Figure 5.6. The general nature of these voltammograms meant that it was difficult to measure the half wave potentials, so only peak potentials are given.

Two large non reversible peaks were observed on the reduction side and a third non reversible peak was obtained on the oxidation side.

$E^1{}_p$ = + 0.58V [cf. $S_2N^+$ $E^1{}_p$=+0.66V

$E^2{}_p$ = + 0.16V $E^2{}_p$=+0.08V]

(ii). $S_3N_2AsF_6$ in liquid $SO_2$. - $S_3N_2AsF_6$ appeared much more soluble in liquid $SO_2$. A similar voltammogram to that in MeCN was obtained, although the $E_p$ values were shifted to slightly higher oxidative potentials. This is a common feature when comparing these two solvents.

$E^1{}_p$ = +0.7V

$E^2{}_p$ = +0.24V

(iii). $S_3N_2Cl$ in liquid $SO_2$. - This black/green compound is largely insoluble even in $SO_2$. However, it was possible to get sufficient into solution in $SO_2$ to obtain a weak voltammogram. This had general characteristics similar to those of $S_3N_2AsF_6$. $E_p$ values were very close to those previously obtained, and in one instance it proved possible to measure an $E_{p/2}$.

$E_p$ = +0.68V

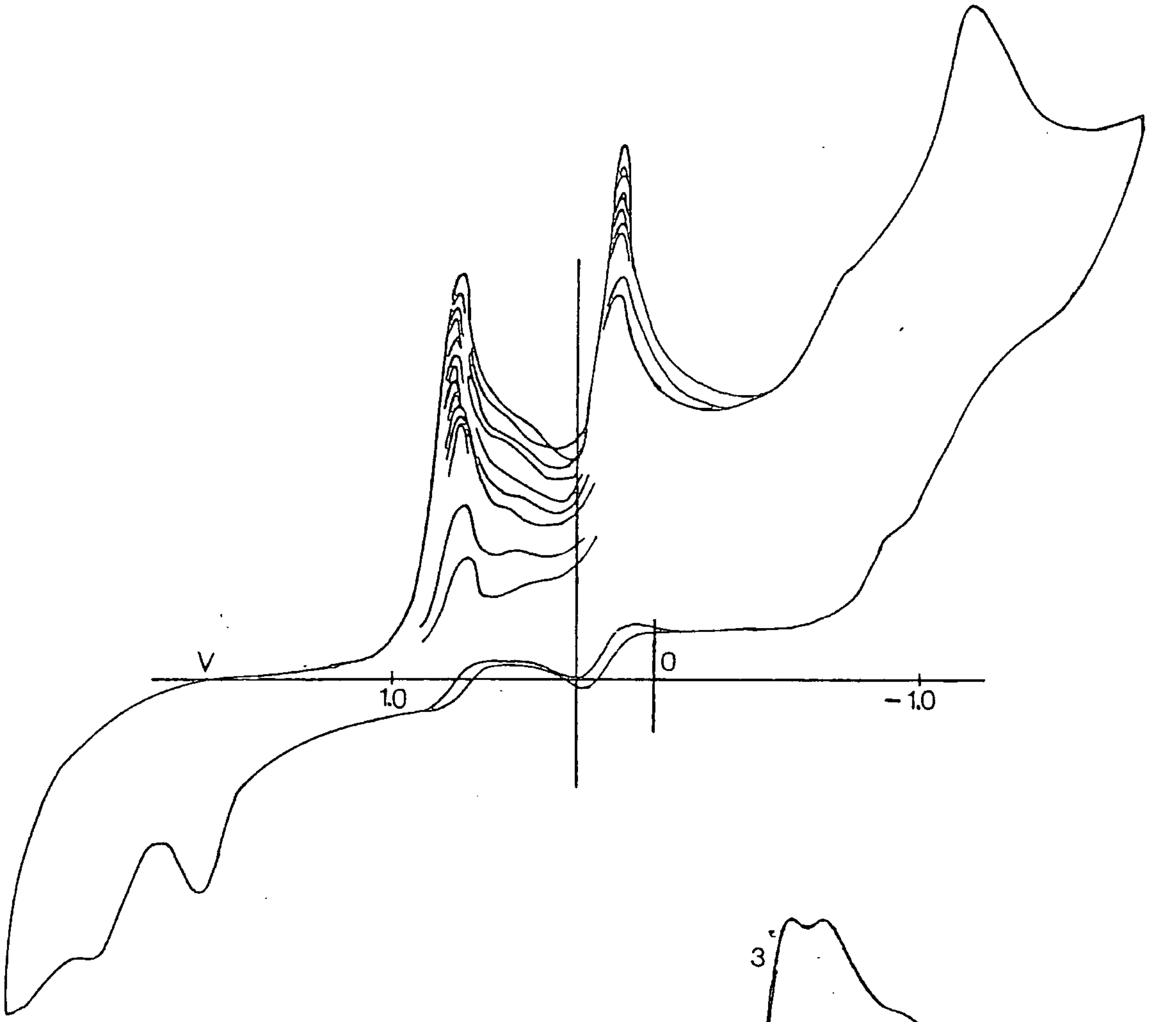
$E_{p/2}$ = +0.85V

(iv). $S_3N_2CF_3SO_3$ in MeCN. - The preparation of this black/blue crystalline solid is decribed in chapter 6, page 160. Again a very similar voltammogram to that of $S_3N_2AsF_6$ was obtained with again a third peak observed at +1.49V.

$E^1{}_p$ = +0.62V

$E^2{}_p$ = +0.15V

Figure 5.5. CV of the reaction between $S_2NAsF_6$ and MeCN



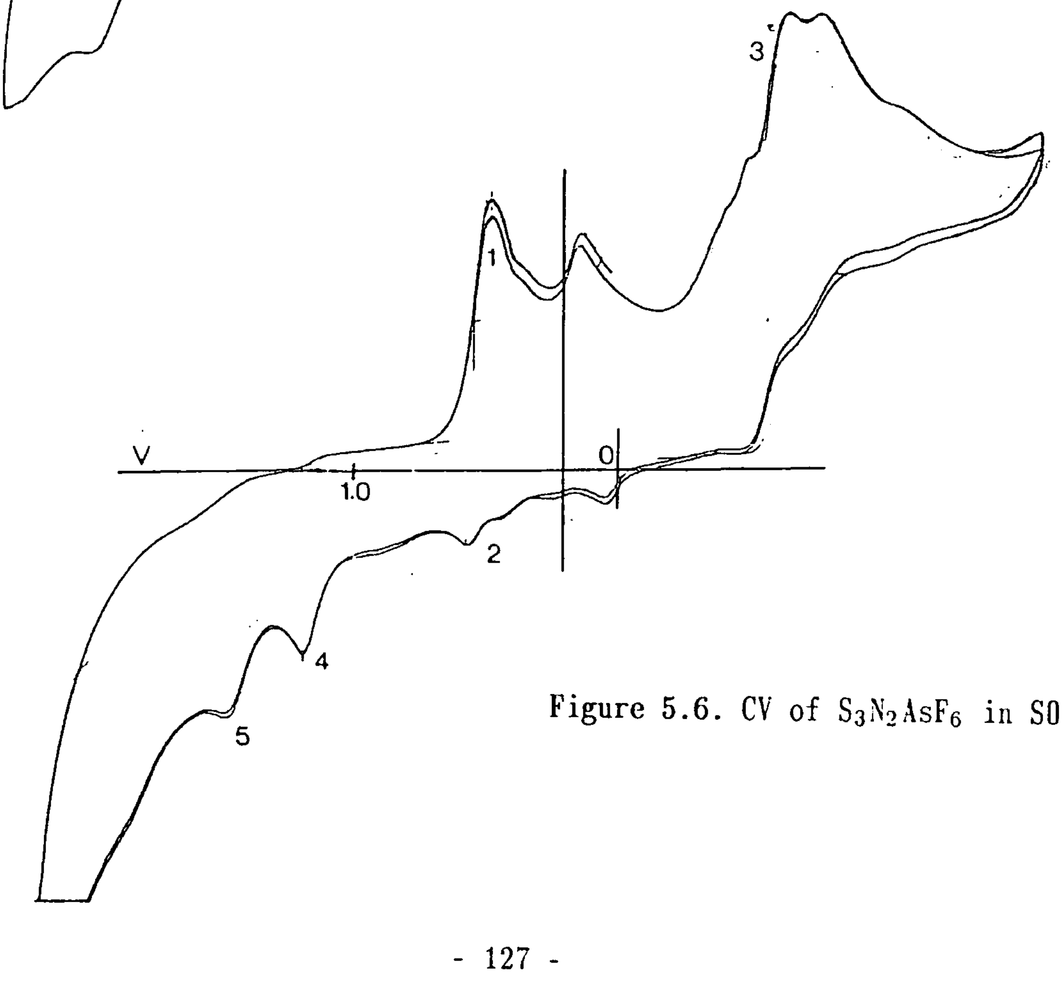


Figure 5.6. CV of $S_3N_2AsF_6$ in $SO_2$

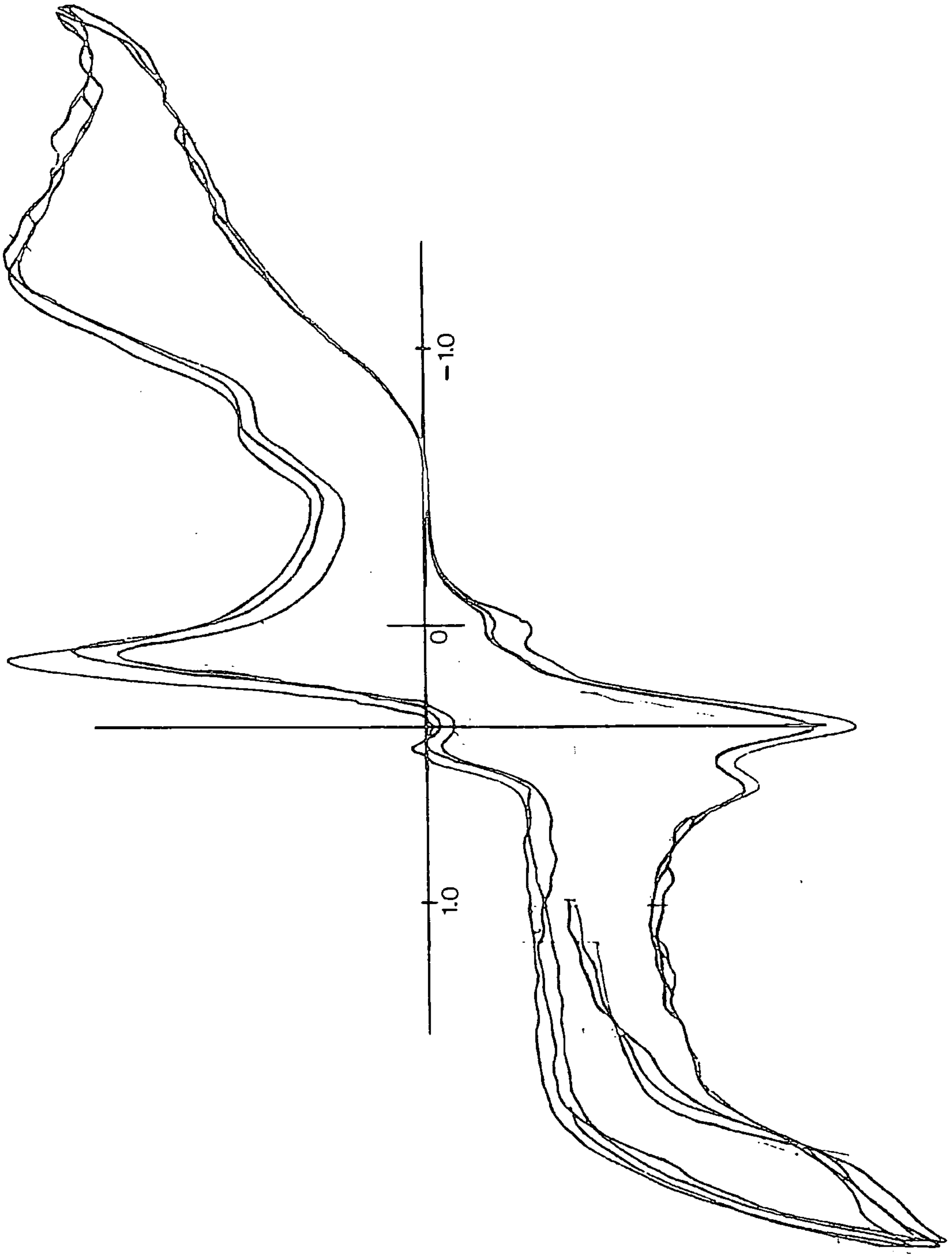


Figure 5.7. The Isomerisation of "1,3", $^{t}$ButylCN$_2$S$_2^{\cdot}$ to "1,2", $^{t}$ButylCN$_2$S$_2^{\cdot}$

### 5.3.4. *Cyclic Voltammetry of 4-t-butyl 1,3,2,5* dithiadiazole, $(CH_3)_3C\overline{CNSNS}\cdot$

A prepared 3 limbed cell was placed in a glove box. Freshly prepared 1,3 t-butyl dithiadiazole (0.02g, 0.12mmol) was quickly transfered via a special teflon micro syringe to the cell which was wrapped in foil. To ensure complete exclusion of moisture, MeCN (15.0ml) was also added whilst in the glove box. As far as possible all manipulations were carried out in the dark, although short periods of artificial light were necessary. The cell was transferred to the voltammetry unit and cooled to -15°C and its CV recorded. The total time for this operation was approximately 25 mins. See Figure 5.7. (page 128).

$E^1{}_p = +0.38V$ $\quad E^2{}_p = +0.32V$

$E_{p/2} = +0.47V$ $\quad E_{p/2} = +0.18V$

$E^1 = 1,2(CH_3)_3C\overline{CNSSN}$

$E^2 = 1,3(CH_3)_3C\overline{CNSNS}$

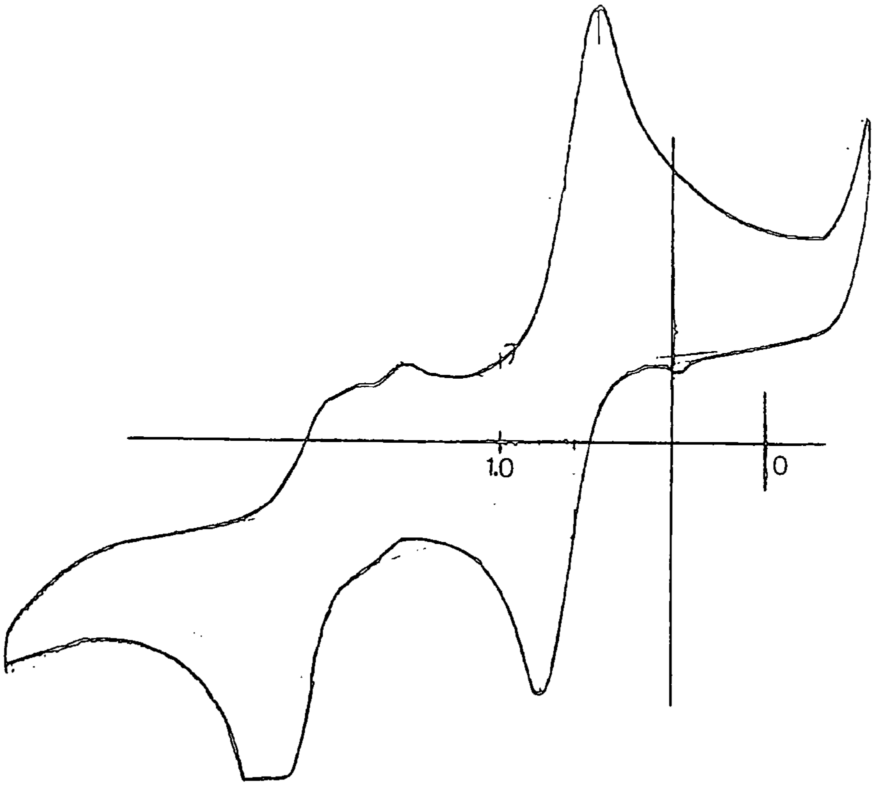
### 5.3.5. *Cyclic Voltammetry of 4-Phenyl 1,2,3,5 dithiadiazolium chloride.*

Using the above procedure, (5.3.1. (i)) $[PhCN_2S_2]Cl$ (0.01g, 0.046mmol) and TBATFB (0.35g, 1.1 mmol) were placed into a cell with $SO_2$ and warmed to RT to give a yellow solution. This was then cooled to -10°C at which temperature voltammograms were recorded. This was repeated with (0.004g, 0.018mmol) $[PhCN_2S_2]Cl$ in 15.0 ml MeCN and the same result was obtained.

$E_p = +0.52V$

$E_{p/2} = +0.60V$

Figure 5.8. CV of 1,2,3,5 $[PhCN_2S_2]Cl$.



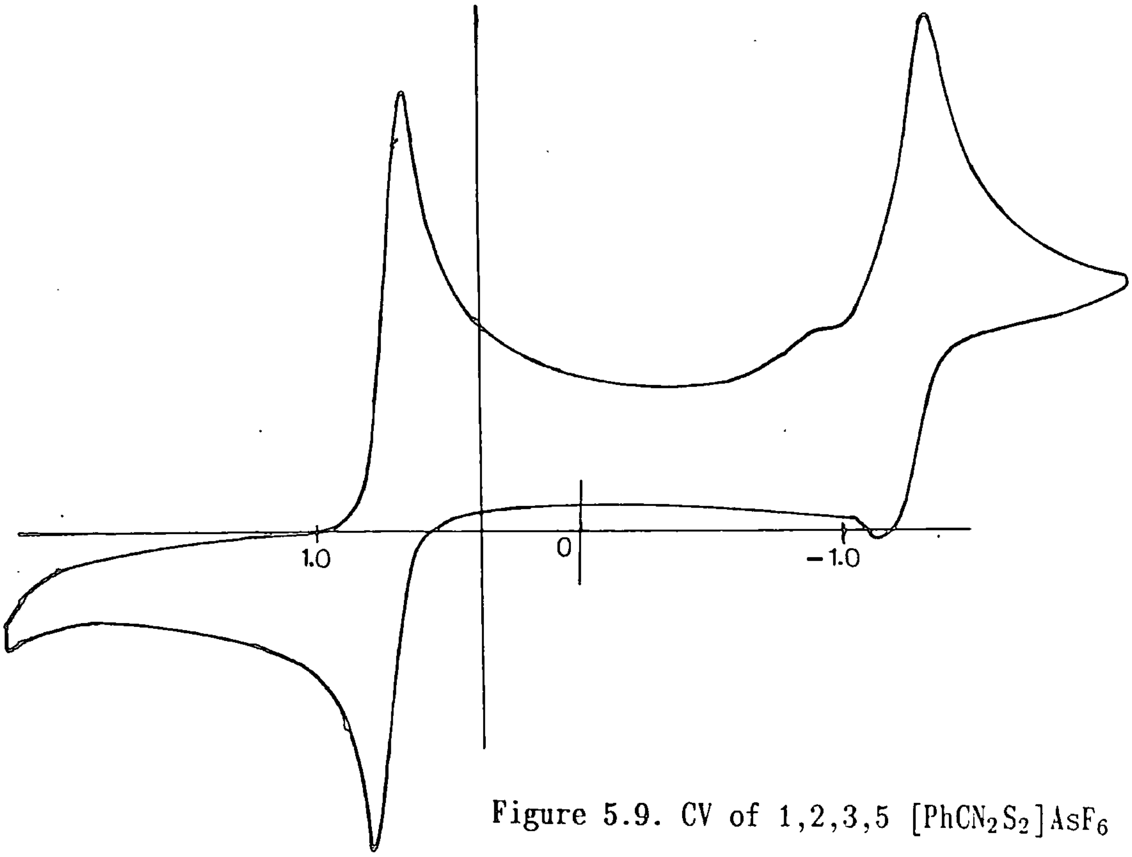


Figure 5.9. CV of 1,2,3,5 $[PhCN_2S_2]AsF_6$

Figure 5.8. shows a good reversible CV. Peak 2 is the oxidation peak for the chloride ion[12]. A corresponding reduction peak for the chlorine is not observed either because the gas was lost from the solution or that it was too reactive to remain for long.

$$Cl^- + e^- \longrightarrow 1/2\ Cl_2. \qquad E_{p/2} = 1.32\ V.$$

### 5.3.6. *Cyclic Voltammetry of 4-Phenyl 1,2,3,5 dithiadiazolium hexafluoroarsenate.*

The above procedure was repeated using bright orange $[PhCN_2S_2]AsF_6$ (0.006g, 0.016mmol) which readily dissolved in MeCN (cf. $[PhCN_2S_2]Cl$). Furthermore the system was very clean and clearly showed a sharp quasi reversible 2nd electron process. Figure 5.9.

$E_p = +0.46V$

$E_{p/2} = +0.51V$

### 5.3.7. *Cyclic Voltammetry of 4-P-Chlorophenyl 1,3, dithiadiazolium hexafluoroarsenate.*

Again the procedure in 5.3.2(ii) was followed using (0.007g, 0.017mmol) $[p\text{-}ClPhCNSNS]AsF_6$. The CV run at -10°C showed a reasonably clean system, but noticeably there is now no sharp peak correspong to a 2nd electron process. The broad peak at - 1.46V indicates chemical complications and was entirely irreversible.

$E_p = +0.19V$

$E_{p/2} = +0.28V$

## 5.4. RESULTS AND DISCUSSION.

### 5.4.1. *The Redox Potentials of the Dithionitronium and $S_3N_2^{+\cdot}$ cations.*

(i) $S_2NAsF_6$ in liquid $SO_2$.

The experiments described in this chapter were made possible by use of developments (by Z.V.H.) which overcame many of the serious problems, like low electrolyte solubility, encountered in earlier attempts to apply CV to $SO_2$ solutions. Indeed it was not until 1979 that Bard et al[9] found that tertiary butyl ammonium salts act as suitable background electrolytes in $SO_2$. They also used Ag/Ag+ as a quasi-reference electrode, but had difficulty in reproducing the potential (only 50mV) of the reference electrode in each experiment. Furthermore an experimental temperature of -40°C was required to reduce the vapour pressure of $SO_2$ sufficiently for their cone and socket electrochemical cell. Since at ambient temperatures $SO_2$ develops pressures up to 3 atmospheres, a new cell was constructed by us with Swagelok compression fittings. This had the added advantage that experiments with both $SO_2$ and MeCN could be conducted under moisture free conditions. The reference electrode was completely filled with MeCN and so could be used in pressurized systems, because of the virtual incompressability of liquids.

A typical CV of $S_2NAsF_6$ in $SO_2$ is illustrated in Figure 5.3. (page 124). Since this is a simple system, the major reduction peak at E = +0.76V can be assigned unambiguously to the reduction of the $S_2N+$ ion. This high value compared with most of the dithiadiazolium rings reflects the ease of electro-reduction and the electrophilic behaviour of $S_2N+$ in many of its reactions. It is also consistant with recent measurements of the redox potential of $SN^+$ at $E_{p/2}^{red} \geq +0.8V$[13] and $S_3N_2^{+\cdot}$ at $E_{p/2}^{red} = +0.66V$ (MeCN). As expected $SN^+$, behaving like a pseudo-metal atom, is the most oxidising, having a value similar to that for Ag/Ag+, $Fe^{3+}/Fe^{2+}$, $Hg^{2+}/Hg$ and $NO_3^-/NO_2$[14]. The trend continues in line with increasing size and increasing number of low energy electron-accepting LUMOs.

An oxidation peak also occurs in the voltammogram at $E^{ox}_{1/2}$ = +1.52V, but is unlikely to be the reverse of the process at E=+0.76V since the half peak potential difference is 0.76V, compared to 59/n mV at 25 °C potential difference allowed for a reversible process[15]. Indeed its value is very close to that for $S_4N_2+$ ( $E_{p/2}$= 1.43V)[16]. The formation of this species can be explained in the following sequence:-

Scheme 5.1.

$$
\begin{aligned}
S_2N^+ + e^- &\longrightarrow S_2N^{\cdot}\\
S_2N^{\cdot} + S_2N^+ &\longrightarrow S_4N_2{}^+
\end{aligned}
$$

or

$$S_2N^{\cdot} + S_2N^{\cdot} \longrightarrow S_4N_2 \xrightarrow{-e^-} S_4N_2{}^+$$

Neither of these processes appears to be reversible. Previous workers[17] expected to see the formation of $S_3N_2{+}^{\cdot}$ via the mechanism in scheme 5.2. Although there is no correlation with the voltammogram of $S_3N_2{}^{+\cdot}$ obtained independently from authentic samples, the fact that $S_3N_2{}^+$ may be obtained from an $S_2N^+$ reaction mixture may be evidence for an $S_3N_2{}^{+\cdot}/S_2N^+$ equilibrium.

Scheme 5.2.

$$
\begin{aligned}
S_2N^+ + e^- &\longrightarrow S_2N^{\cdot}\\
S_2N^{\cdot} &\longrightarrow SN^{\cdot} + S\\
SN^{\cdot} + S_2N^+ &\longrightarrow S_3N_2{}^{+\cdot}
\end{aligned}
$$

It is possible that both $S_2N^{\cdot}$ and $SN^{\cdot}$ are too reactive to remain in solution long enough to be detected by the returning sweep. However, on prolonged electrolysis of a $S_2NAsF_6$ /$SO_2$ solution at +0.70V, a third peak at $E_p{}^{red}$= +1.34V did appear after about 10 minutes, but it had decomposed by the second sweep. It was unclear as to what species this might belong.

It is also worth noting that it has been established[10] that in solution $S_3N_2^{2+}$ is in equilibrium with $SN^+$ and $S_2N^+$.

$$S_3N_2^{2+} \;\text{———}\; SN^+ + S_2N^+$$

### (ii) *The $S_2NAsF_6$/MeCN Reaction.*

In MeCN, $S_2NAsF_6$ gave a more complex CV due to the appearance of a second major reduction peak at $E_p^{red} = +0.08V$. This was assigned to the chemical reaction[18];


(I)

4 methyl 1,3 dithiadiazolium$^+AsF_6^-$

This was confirmed by the fact that the peak grew in height with time whilst the $S_2N+$ peak diminished, see Figure 5.5, and that an authentic sample of (I) gave a peak at $E_p^{red} = +0.07V$.

This enabled some kinetics of the reaction to be followed. From expression 5.2.1.5 (page 121) it could be shown that the peak height is proportional to concentration for a reversible process. The previous CV of an authentic sample of (I) had shown that this indeed was a reversible process and therefore it was possible to follow the reaction by observation of the growth of this peak. The general expression for this analysis is:-

$$\frac{d(a - x)}{dt} = -k(a - x)(b - x).$$

$$\equiv \frac{dx}{dt} = k(a-x)(b-x)$$

Since the acetonitrile is the solvent, it is present in large excess and therfore its concentration can be considered constant. The reaction thence becomes pseudo 1st order.

$$b \gg x, \quad (b-x) \approx \text{constant } c.$$

$$\Longrightarrow \frac{d(a - x)}{dt} = -k.c.(a - x).$$

$$\Longrightarrow d\ln(a - x) = -kdt.$$

$$\Longrightarrow \ln(a - x) = -kt + I$$

It is possible therefore to plot either $\ln(A_t - A_\infty)$ vs. t for the $S_2N+$ peak or $\ln(A_\infty - A_t)$ vs. t for the product peak. In practice it is easier to obtain the $A_\infty$ value for the product and so it was this that was plotted. See Graph 5.1.

(i) From the hand drawn graph:- slope $= \frac{\Delta y}{\Delta x} = \frac{0.944}{1475} = 6.4 \times 10^{-4}$.

$$\Longrightarrow k = 6.4 \times 10^{-4}.$$

(ii). From linear regression programme - all points.

$$\Longrightarrow k = 6.58 \times 10^{-4}. \qquad (r = 0.976)$$

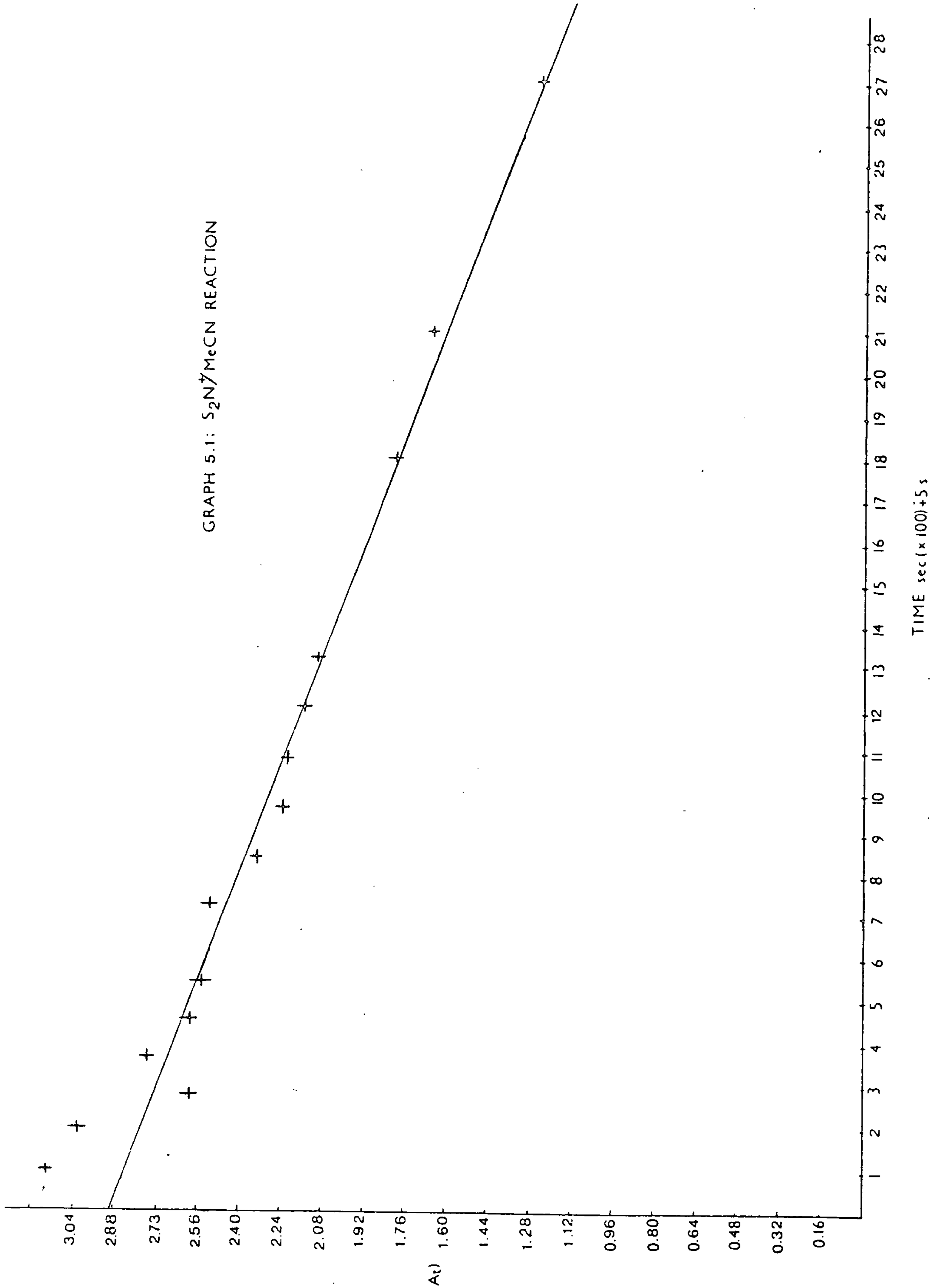
(Intercept = 2.98).

[Value obtained by missing out anomolous point.

$$k = 6.76 \times 10^{-4} \qquad (r = 0.982)$$

(intercept = 3.02)].

As can be seen from graph 5.1. a very reasonable straight line can be obtained which justifies the use of this method. A full study would involve determining the various rate constants at different temperatures and so obtain the energy of activation from Arrenhius' equation.



GRAPH 5.1: $S_2N^+$/MeCN REACTION

(iii) The $S_3N_2^{+\cdot}$ cation. - $S_3N_2Cl$ is only slightly soluble in $SO_2$ and it proved necessary to use the $S_3N_2AsF_6$ salt which, although more soluble, is still only moderately so. The several peaks obtained in $SO_2$ were superficially similar to those obtained for $S_2N^+$ in MeCN, Figures 5.4. & 5.6. (pages 124 & 127) but when compared to those of $S_2N^+$ in $SO_2$ are clearly different; they were reproduced almost exactly in MeCN. There were 2 major reduction peaks and 3 oxidation peaks, none of which have been assigned unambiguously. This CV plot is illustrated in Figure 5.6 the major oxidation peak is $E^1$, and the reduction peak $E^2$ may be the reverse of this.

$E^3$ may be a 2nd electron transfer process but is more likely to belong to another unidentified species, whilst $E^4$ and $E^5$ remain unassigned.

$E^1_p = +0.60V$ (MeCN) $E^1_{red\ P/2} = +0.66V$

[$E^1_p = +0.74V$ (SO2)]

$E^2_p = +0.69V$ $E^3_p = +0.18V$

$E^4_p = +1.45V$ $E^5_p = +1.78V$

The reduction product from $E^1$ will be $S_3N_2^\cdot$ which is an $8\pi$, anti-aromatic species and unlikely therefore to be stable. It would therefore decay rapidly possibly accounting for the small size of $E^2$. There is also a superficial similarity in Figure 5.11 to the CV for $S_2N$+/MeCN but since $S_3N_2AsF_6$ also gives 2 major reduction peaks in $SO_2$ it is unlikely that there is a connection, though the following is a possibility for $S_3N_2^{+\cdot}$;

$$S_3N_2^{+\cdot} \rightleftharpoons S_2N^+ + SN^\cdot$$

The compounds $S_3N_2Cl$ and $S_3N_2CF_3SO_3$ gave very similar CV plots.

### 5.4.2. *Hammett Plots for some Substituted Phenyl Dithiadiazolium Hexafluoroarsenate Salts.*

It was possible for a small number of dithiadiazolium systems studied to obtain Hammett $\sigma_p$ values[19,20]. These were therefore plotted against the $E_{1/2}$ values to see if a linear free energy relationship did exist between them.

The Hammett equation is; $\quad \mathrm{Log}\ {}^{k}/_{k_o} = \sigma\rho$

$k_o$ = Rate or equilibrium constant for X = H. k = Constant for group X.

$\rho$ = a constant for a given reaction under a given set of conditions.

$\sigma$ = a constant charateristic of the group X.

Strictly these $\sigma_p$ values apply only to substituents of phenyl rings para to the electroactive group, in this case the $\overline{\mathrm{CN_2S_2}}$ ring. The compound under consideration is therefore $XC_6H_4\text{-}CN_2S_2$ where X is any group. The Hammett equation is a linear free energy relationship, and in the case of equilibrium constants:-

$\Delta G = -\mathrm{RTln}k$ for the unsubstituted case.

and;

$\Delta G = -\mathrm{RTln}k_o$. Then the Hammett equation may be written:-

$$\ln k - \ln k_o = \sigma\rho$$

so that,

$$\frac{-\Delta G}{2.3RT} + \frac{\Delta G_o}{2.3RT} = \sigma\rho$$

$$-\Delta G = \sigma\rho.2.3RT - \Delta G_o$$

For a given reaction, under a given set of conditions $\rho$,R,T, and $\Delta G_o$ are all constants, so that $\sigma$ is linear with $\Delta G$.

This treatment is generally successful provided the mechanism is the same within a given reaction series. Indeed this may be extrapolated from the nature of the graph obtained. Values for $E_{P/2}$, $\sigma_P$ and $\sigma_P^+$ are given in Table 5.1. Generally $\sigma_P^+$ values relate to a developing positive charge and so were plotted against $E_{P/2}$ (ox) valves, whilst $E_{P/2}$(red) values were plotted against $\sigma_P$ to obtain the two graphs 5.4.2. Small deviations occur for H in $\sigma_P^+$ vs $E_{P/2}$(ox) and for Me in $\sigma_P$ vs $E_{P/2}$(red) but both are within experimental error.

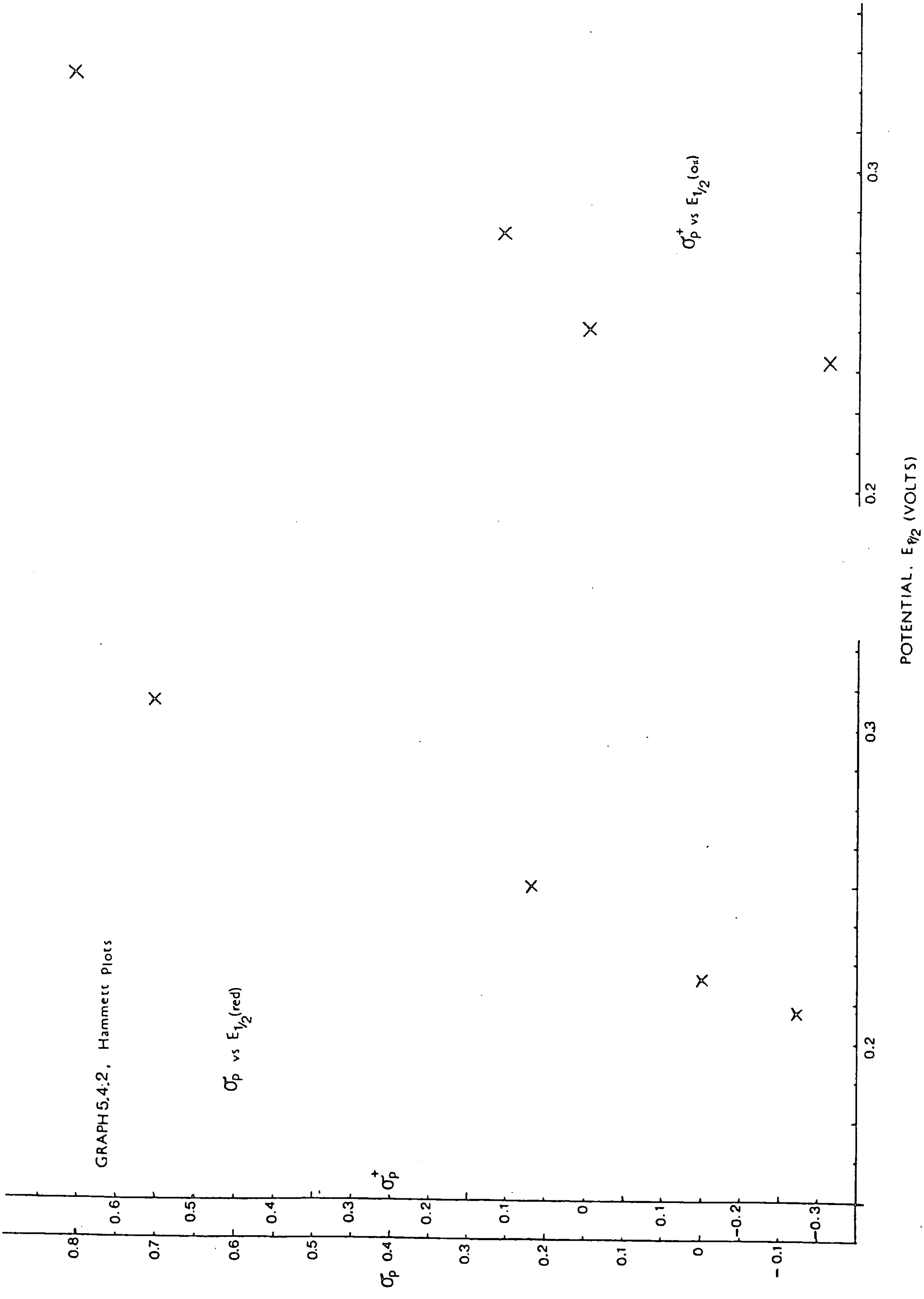
From this it can be seen that reasonably good straight lines may be drawn through the points supporting the hypothesis that the same electron transfer mechanism occurs in this series.

Table 5.1.

| Compound $\overline{RCNSNS}^+$ | $E_{P/2}$(ox) | $E_{P/2}$(red) | $\sigma_P$ | $\sigma_P^+$ |
|---|---|---|---|---|
| R | V(± 0.005) | | | |
| $\rho$-$CH_3C_6H_4$- | 0.24 | 0.21 | -0.14 | -0.31 |
| $\rho$-$HC_6H_4$- | 0.25 | 0.22 | 0.0 | 0.0 |
| $\rho$-$ClC_6H_4$- | 0.28 | 0.25 | 0.24 | 0.11 |
| $\rho$-$CNC_6H_4$- | 0.33 | 0.31 | 0.7 | 0.66 |

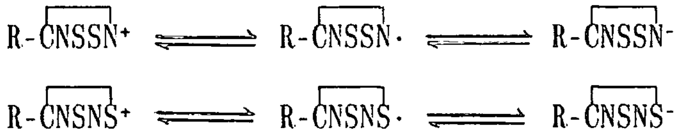
Although no strict conclusions may be drawn for the bulk of the remainder of the 1,3 substituents, qualitatively it is likely that a similar mechanism will operate throughout. It is not possible to say much about the actual mechanism for electron transfer and a wider study including other substituents would be required to see how the graphs vary.

GRAPH 5.4.2, Hammett Plots



### 5.4.3. *General considerations.*

The results are presented in Tables 5.2.- 5.5. In general these correspond to one or other of the following processes:-



$$R\text{-}CNSSN^{+} \rightleftharpoons R\text{-}CNSSN\cdot \rightleftharpoons R\text{-}CNSSN^{-}$$

$$R\text{-}CNSNS^{+} \rightleftharpoons R\text{-}CNSNS\cdot \rightleftharpoons R\text{-}CNSNS^{-}$$

Several factors concerning the system under investigation may be obtained from a consideration of the general form of a voltammogram. Obviously the number of peaks reflects the number of electron transfer processes that occurs over the potential range covered. However, it is important to remember that behaviour of a particular system will vary with changes in, for example, solvent and supporting electrolyte. A theoretical treatment is not attempted here as it is far too complex.

Table 5.2. Measured $E_{p/2}$ Values for 1,2 $RCNSSN^{+}$ Chlorides and Hexafluoroarsenates.

| **Compound, R.** | **1st e Transfer** | | **2nd e Transfer.** | |
|---|---|---|---|---|
| Chloride salts | $E_{p/2}$(ox) | $E_{p/2}$(red) | $E_p$(ox) | $E_{p/2}$(ox) |
| $PhCH_2$- | 0.78 | 0.72 | -0.94 | / |
| Ph- | 0.60 | 0.61 | -0.86 | / |
| $Cl_3C$- | 0.53 | 0.47 | -0.72 | -0.60 |
| $CH_3$- | 0.28 | 0.29 | -1.12 | -0.95 |
| $CH_3CH_2CH_3$- | 0.45 | / | / | / |
| $(CH_3)_3C$- | 0.33 | 0.28 | -1.06 | -0.93 |
| $AsF_6$ salts. | | | | |
| Ph- | 0.51 | 0.50 | -0.92 | -0.77 |
| $(CH_3)_3C$- | 0.45 | 0.43 | -1.12 | -0.99 |
| $CH_3$- | 0.46 | 0.47 | -0.88 | -0.84 |

Table 5.3. Measured $E_{p/2}$ Values for 1,3, RCNSNS$^+$AsF$_6$ salts.

| Compound R | $E_{p/2}$(ox) | $E_{p/2}$(red) | $E_P$(ox) | $E_{p/2}$(ox) |
|---|---|---|---|---|
| Anthra- | 0.29 | 0.23 | -1.57 | -1.53 |
| $\rho$-ClPh- | 0.28 | 0.25 | / | / |
| Ph- | 0.25 | 0.22 | -1.35 | -1.23 |
| $\rho$-CNPh- | 0.33 | 0.31 | / | / |
| $CH_3$- | 0.16 | 0.16 | / | / |
| $(CH_3)_3C$- | 0.18 | 0.18 | -1.41 | -1.33 |
| $\rho$-$CH_3Ph$- | 0.25 | 0.23 | / | / |

Table 5.4. Measured $E_{p/2}$ Values for 1,2, RCNSSN$^\cdot$ Radicals.

| Compound R | $E_{p/2}$(ox) | $E_{p/2}$(red) | $E_P$ | $E_{p/2}$(ox) |
|---|---|---|---|---|
| Ph- | 0.60 | 0.58 | -0.75 | -0.72 |
| $\rho$-ClPh- | 0.53 | 0.50 | -0.90 | -0.80 |
| $CF_3$- | 0.80 | 0.76 | -0.68 | -0.54 |
| $(CH_3)_3C$- | 0.44 | 0.50 | -1.18 | -1.03 |
| $CH_3CH_2CH_2$- | 0.52 | 0.74 | -1.12 | / |
| (1,3 $(CH_3)_3C$-) | 0.16 | 0.18 | / | / |

Table 5.5. Measured $E_{p/2}$ Values for other Dithiazolium rings.

| Compound | $E_{p/2}$(ox) | $E_{p/2}$(red) | $E_P$ | $E_{p/2}$(ox) |
|---|---|---|---|---|
| $CF_3CNSNCCF_3$ | 0.48 | 0.56 | / | / |
| $CF_3CNSNCCF_3AsF_6$ | 0.50 | 0.49 | / | / |
| $H(CH_3)CSNSC(CH_3)H^+$ $AsF_6^-$ | 0.35 | 0.31 | / | / |

Table 5.6. Measured $E_{p/2}$ Values for various S/N Species.

| Compound | | $E_{p/2}$(ox) | $E_{p/2}$(red) | $E_P$(ox) | $E_P$(red) | $E^3{}_P$ | $E^4{}_P$ | $E^5{}_P$ |
|---|---|---|---|---|---|---|---|---|
| $S_2NAsF_6$ | $SO_2$ | 0.76 | 1.52 | 0.60 | 1.62 | / | / | / |
| | MeCN | 0.72 | 1.45 | 0.65 | 0.08 | / | 1.47 | / |
| $S_3N_2AsF_6$ | $SO_2$ | / | / | 0.74 | 0.86 | 0.28 | 1.56 | 1.88 |
| | MeCN | 0.66 | / | 0.58 | / | 0.16 | 1.45 | 1.78 |
| $S_3N_2CF_3SO_3$ | | | | | | | | |
| | $SO_2$ | / | / | / | / | / | / | / |
| | MeCN | 0.70 | / | 0.62 | / | 0.14 | 1.49 | / |
| $S_3N_2Cl$ | $SO_2$ | 0.86 | / | 0.78 | / | 0.27 | / | / |
| | MeCN | / | / | / | / | / | / | / |

## 5.4.4. *The Redox Potentials of the 1,3, and 1,2 Dithiadiazolium system $RCN_2S_2$ X where X = $AsF_6$ or $Cl^-$.*

(i). From Figures 5.1 - 5.11, 5.13 - 5.14 it may be seen that generally the most important peak under consideration is the first electron transfer reduction peak which, for these compounds, is usually a reversible process. That this corresponds to the complete transfer of one electron was proved by coulometric experiments.

The readiness of S/N heterocycles to participate in electron transfer processes, and particularly as electron acceptors, is in part due to the presence of relatively low energy LUMO's[21],[22]. As mentioned in section 5.3.4. the electroactive part of these molecules is the $\overline{\mathrm{CN_2S_2}}$ ring; the electrochemical process occurs for the whole of that ring and therefore there is no change in the oxidation state of the S atoms. Indeed the stability of the dithiadiazolium five membered ring with both 6$\pi$ and 7$\pi$ electrons is reflected in the integrity of the ring throughout many reactions and the existence of stable paramagnetic free radical liquids[23] - see chapter 3.

The second electron process was also observed. In most cases, however, it was not generally a reversible one, indicating the presence of further chemical complications (though curiously when the starting material for the voltammetric study was a neutral radical, eg $^{t}\mathrm{butyl}\overline{\mathrm{CNSSN}}\cdot$ then the 2nd electron reduction became reversible). It is already well established that S/N heterocycles, although readily reducible to S/N anions, (again electron accepting properties are due to low energy LUMOs), undergo further chemical changes rather easily.

For instance[24], $S_4N_4 + e^- \longrightarrow S_4N_4^- \longrightarrow S_3N_3^- \longrightarrow S_2N^{2-}$.

or[25,26] $S_3N^- \longrightarrow S_2N^-$.

The anion $RCN_2S_2^-$ would be an $8\pi$ electron system and therefore anti-aromatic, and this may account for its instability; it has not proved possible to isolate the anion electrochemically and the only product obtained and identified so far has been the parent nitrile RCN. A salt containing the anion has recently been reported with the very strong electron donating (18 crown - 6) $Na^+$ [33].

(ii). It is apparent from the voltammograms Figures 5.10.& 5.11. that electron transfer is relatively faster for the $AsF_6^-$ salts than for the chloride salts. This may be ascertained qualitatively from the fact that generally $AsF_6^-$ salts give appreciably sharper peaks than do the $Cl^-$ salts both for the 1st and the 2nd reduction peaks. This is probably due to the relative degrees of solvation of the respective anions; the high charge density on a $Cl^-$ ion leads to greater solvation particularly in a solvent like acetonitrile which has a fairly high dielectric constant($\epsilon = 37$). Also chloride ions show a strong tendency for cation/anion pairing and other ion/ion interactions and disengagement of $Cl^-$ from $RCN_2S_2^+$ will slow down the redox process. The important electron transfer processes for CV measurements occur at the electrode surface and in the electrical double layer. Presumably, in chloride solutions the diffuse double layer becomes larger and relatively more important because of solvation effects and so electron transfer processes will also occur here.

The exact nature of the IHP (inner Helmholtz plane) largely depends on a number of factors; the solvent, the potential and nature of the electrode itself, and the concentration of other ions present.

The charge of the electrode will be associated with this inner Helmholtz plane (IHP). The layer in direct contact with the metal will consist largely of acetonitrile molecules with their dipoles partially orientated towards the metal surface; interspersed with these will be various ions although thses are usually anions. Anions with a relatively low solvation energy (eg. $AsF_6^-$) or a strong adsorptive affinity for the metal will therefore have a net tendency to exchange for an acetonitrile molecule close to the metal surface. Conversely more strongly solvated ions (eg. $Cl^-$) will be less able to approach the electrode surface closely. If more $AsF_6^-$ anions ( compared to $Cl^-$) are adsorbed onto the electrode surface or into the IHP then the attraction for $PhCN_2S_2^+$ is better and there is a lower activation barrier.

At higher concentrations of electrolyte, the concentration of adsorbed ions increases and the diffuse double layer becomes compressed. The concentration of the supporting electrolyte is much greater than that of the electroactive species of interest, but in these cases this is a constant effect across all the measurements and therefore may be omitted from the discussion.

(iii).Furthermore from the Table 5.7. it may be seen that for the same cations the $AsF_6$ salts generally give more positive $E_{P/2}$ [Ox] values than do the chlorides, the exception being the phenyl derivative.
This shows the importance different anions can make to measurements and the importance of being consistent in constructing a series.
The reasons for the higher values obtained may be similar to those mentioned in 5.4.4.(ii). with a faster electron transfer being an important factor. A more positive $E_{P/2}$ [Ox] value means that the compound is easier to reduce (ie. to add an electron), a more diffuse double layer or a large number of extra electron processes which would be associated with greater ion pairing for example within it would hinder this

Table 5.7. Comparison of $E_{P/2}$ values according to isomer and salt type.

| Salt | 2,$Cl_3C$- | 2,Pro- | 2,$^tBu$- | 3,$^tBu$- | 2,Me- | 3,Me- | 2,Ph- | 3,Ph- |
|---|---|---|---|---|---|---|---|---|
| $AsF_6^-$ | / | / | 0.45 | 0.18 | 0.46 | 0.16 | 0.52 | 0.24 |
| $Cl^-$ | 0.53 | 0.48 | 0.33 | / | 0.28 | / | 0.60 | / |

2 = 1,2,3,5, isomer.

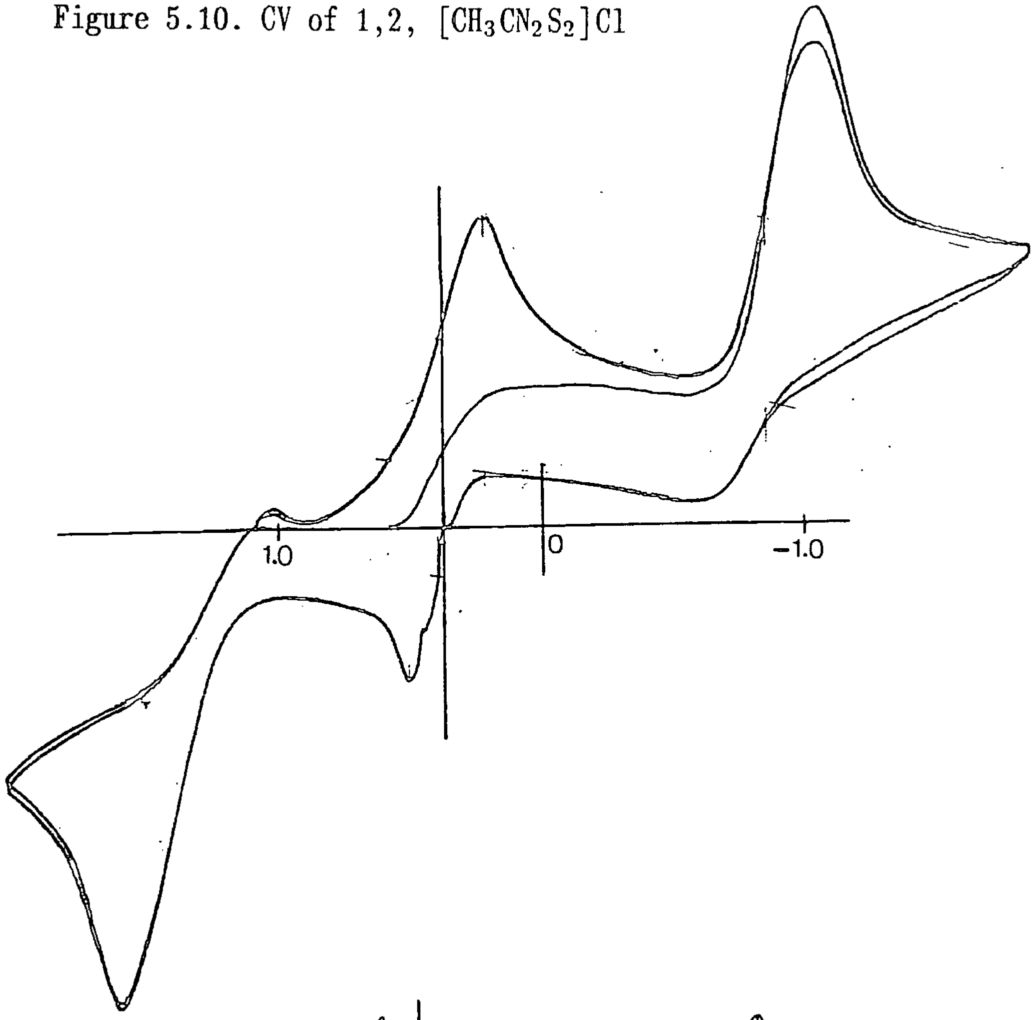
3 = 1,3,2,5, isomer.

The exception to this observed trend is the value obtained for the $[PhCN_2S_2]Cl/AsF_6$ system. Not only are the values much closer together but they are also reversed. $[PhCN_2S_2]Cl$ has a more positive $E_{P/2}$ [Ox] value than $[PhCN_2S_2]AsF_6$ (0.60 and 0.52V respectively), although a value of 0.7V might be expected of $[PhCN_2S_2]AsF_6$. This clearly means that a slightly different mechanism is at work, and that other factors come into play. Double peaks are observed in the voltammogram and one explanation may be a coupled chemical reaction, in this case, the formation of dimer units in the double layer even though esr indicates the bulk solution to be largely monomeric. A higher concentration of $PhCN_2S_2^+$ would be expected in the double layer than in the bulk solution.

$$[PhCN_2S_2]^+ \rightleftharpoons (PhCN_2S_2)^{\cdot} \rightleftharpoons (PhCN_2S_2)_2$$

It is well established that $RCN_2S_2^{\cdot}$ is a particularly stable free radical, frequently observed for a range of R substituents. However, the dimeric unit $(RCN_2S_2)_2$ is less often seen, though still known for a range of R groups eg. $CF_3$[27], Me[28], Ph[29], $\rho$-ClPh. The particular structure of $(PhCN_2S_2)_2$, moreover, seems to be almost unique amongst these compounds the other dimer compounds are usually linked by one S-S interaction.

Figure 5.10. CV of 1,2, $[CH_3CN_2S_2]Cl$



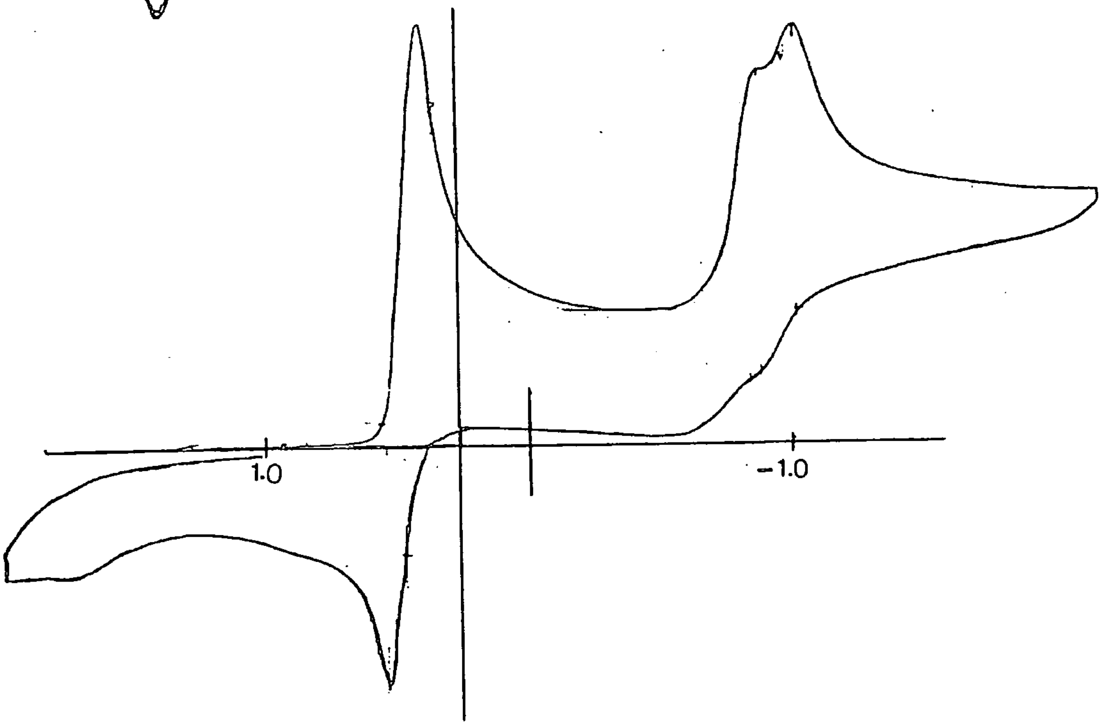


Figure 5.11. CV of 1,2, $[CH_3CN_2S_2]AsF_6$

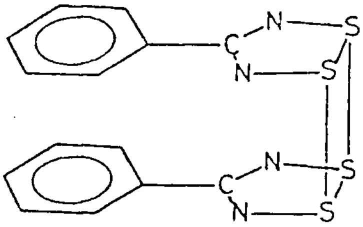


**Figure 5.12.** Dimer structure of $PhCN_2S_2$

For all three compunds $[PhCN_2S_2]Cl$, $[PhCN_2S_2]AsF_6$ and $(PhCN_2S_2)_2$ the process $PhCN_2S_2^+ \rightleftharpoons PhCN_2S_2^{\cdot}$ is the same and it is therefore to be expected that they would have similar or identical potentials. It is by no means clear how dimerisation might complicate the mechanism, but it is possible that since the $[PhCN_2S_2]AsF_6$ system is relatively unhindered by solvation effects, dimerisation would be easier. Once dimerisation had occurred reversal of the process (ie oxidation) back to the monomeric cation would then become that much harder. In the chloride system, there are solvation effects and cation/anion interactions to take into account; dimerisation here therefore would be a relatively slower process, and hence there would be more $PhCN_2S_2$ radicals still left on the return voltage sweep.

(iv).Another feature worth noting is that the voltammograms of the various neutral species, $^{t}$BuCNSSN,$p$-Cl-PhCNSSN, Figures 5.13.& 14. show not only very clear 2nd e$^-$ processes but also that these are reversible, or nearly so. That these systems show these features may be explained by the fact that they lack any interfering anions.

In several cases, eg. where R = $^{t}$butyl, the reversibility for the process is striking particularly in the voltammograms of the neutral species tBu$\overline{\text{CNSSN}}$ and Ph$\overline{\text{CNSSN}}$. The reversibility of a CV or at least its closeness to it seems to depend largely on the R group. The more the R groups interact with the electroactive group the more nearly reversible the system becomes. For a reversible process the peak potential difference should be 56mV or less. Most of the dithiadiazole systems studied had a peak potential difference of only 20-30 mV and some had no measurable difference at all.

(v).Finally from Table 5.7., it should be noted that in every case when comparing the $AsF_6$ salts (values are not available for the chlorides), the 1,2, isomers always give much higher potential values than the corresponding 1,3 isomers. This phenomenon is probably due to the relative energy levels of the LUMO/SOMO orbitals on the ring. The implication is that the LUMO is lower in energy and the HOMO/SOMO(LUMO) energy gap is smaller in the 1,2 isomer where there is considerable orbital overlap on the two adjacent sulphur atoms, than in the 1,3 isomer, where this overlap is not possible.

This conclusion seems to be borne out by theoretical (MNDO) calculations. See Figure 5.13. Because the 1,3 and 1,2 isomers have such different values for the same R group, and because the 1,3 isomer is thermodynamically unstable with respect to the 1,2 isomer[30], it should be possible to observe an isomerisation between the two. This phenomenon can clearly be seen in Figure 5.7. where a CV was taken 10 minutes after the preparation and isolation of the brown liquid 1,3 $^{t}$butyl dithiadiazole, a process which itself takes 1-1.5h. This compound reportedly photochemically isomerises to the 1,2 isomer at room temperature over a few days[30].

However, a very pronounced peak corresponding to the 1,2 isomer occurs indicating that in fact isomerisation occurs very rapidly even at only slightly elevated temperatures and when exposed to just a small amount of light, a conclusion supported independently[31].

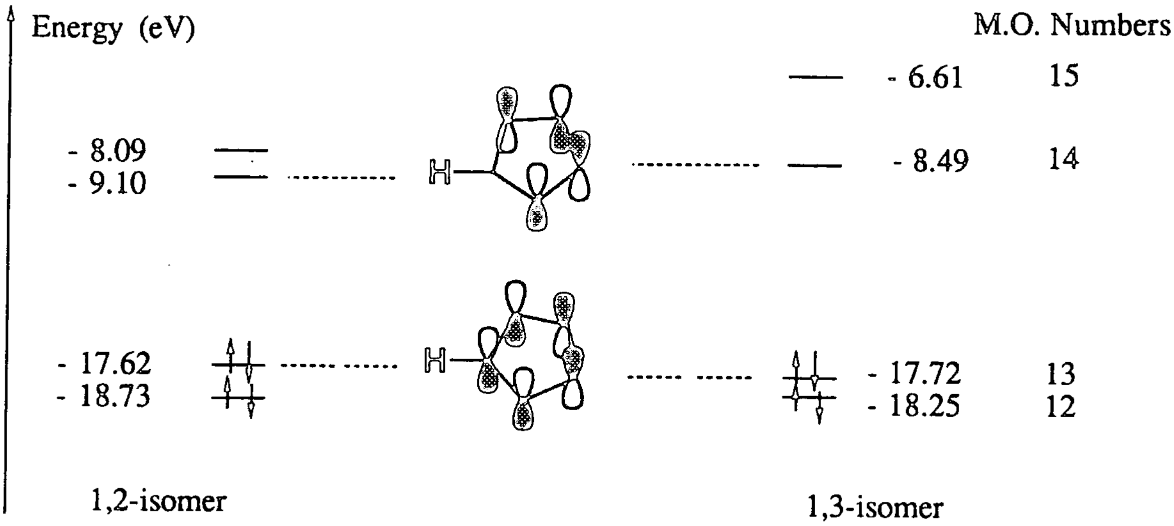


**Figure 5.13.** HOMO/SOMO(LUMO) energy levels of 1,2 and 1,3 dithiadiazoles..

**Scheme 5.4.** Redox Series.

(i). 1,2, Radicals; $CF_3$ > Ph > *p*-ClPh > propyl > $^{t}$butyl > $CH_3$.

(ii) 1,2, Chlorides; $CF_3$ > $CH_2Ph$ > Ph > $Cl_3C$ > propyl > $^{t}$butyl >$CH_3$.

(iii). 1,2, $AsF_6$ salts; $Cl_3C$ > Ph > $^{t}$butyl, $CH_3$.

(iv). 1,3, $AsF_6$ salts; $Cl_3C$ > anthr> *p*-CNPh> *p*-ClPh> Ph>*p*-$CH_3$Ph>$^{t}$bu, Me

(v). EN values[32]; $Cl_3C$, 2.65; propyl, -0.115; $^{t}$Bu, -0.3; Ph, 0.46;

Figure 5.14. CV of ${}^{t}$buCNSSN$^{\cdot}$ showing reversible 2nd e process.

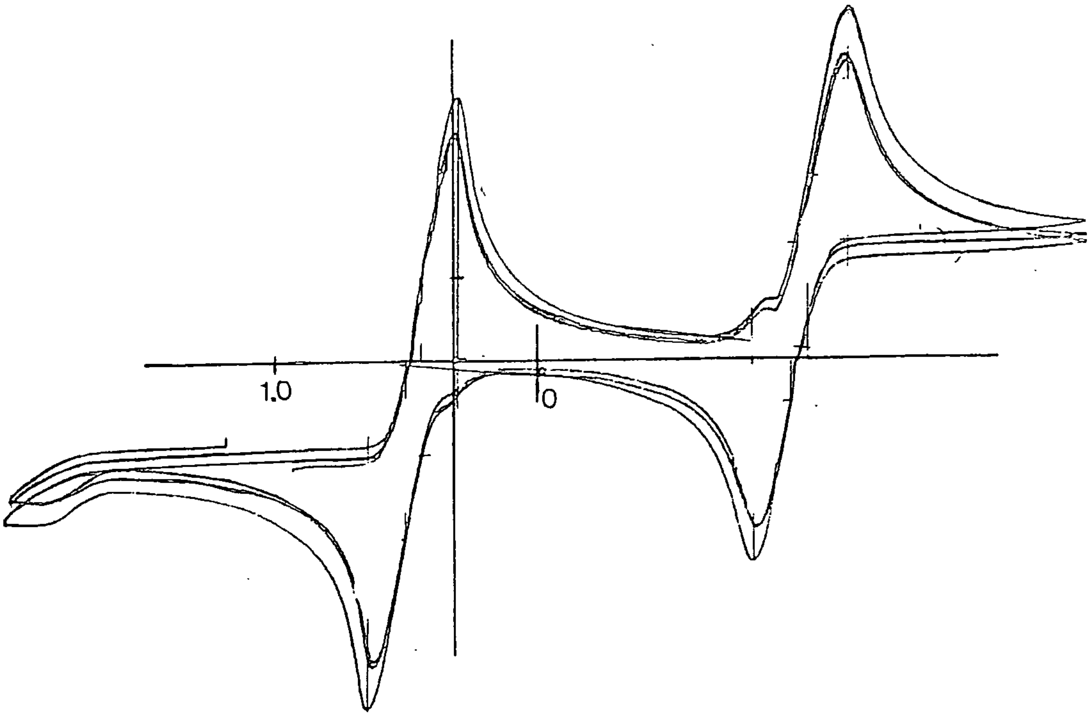
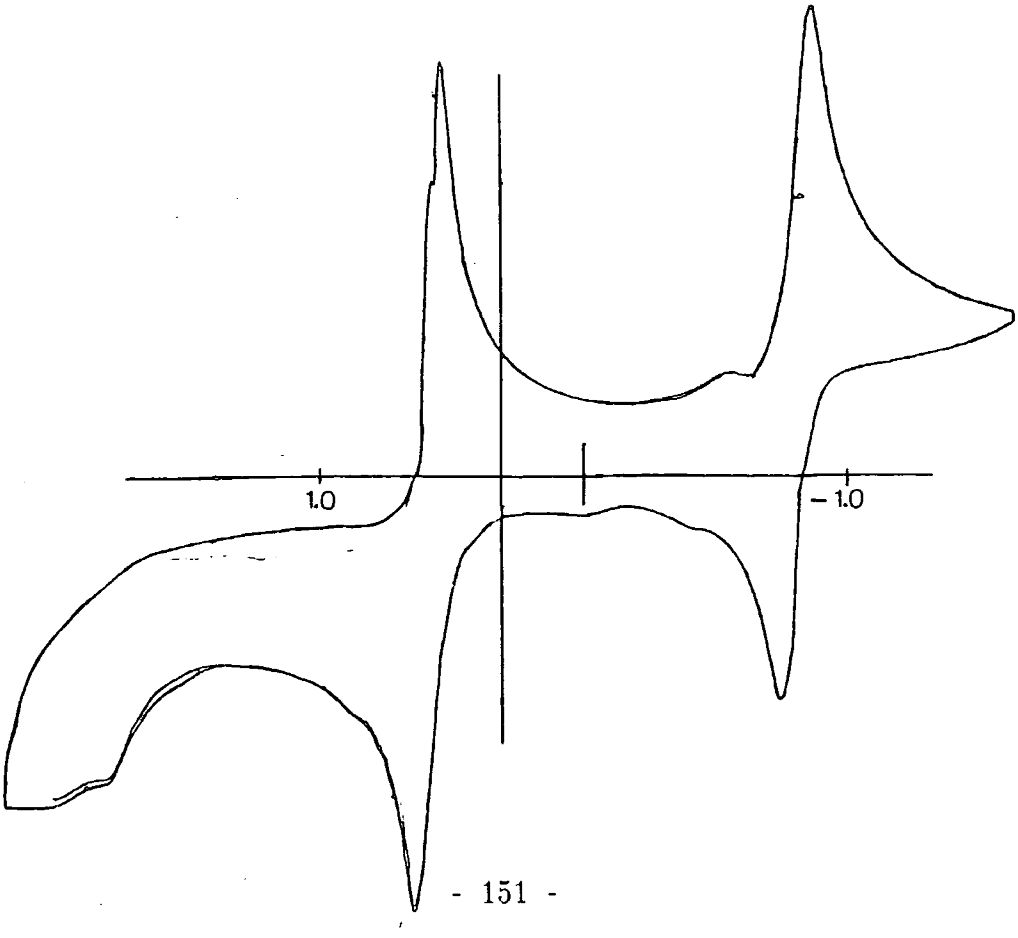


Figure 5.14. CV of 1,2, ($\rho$-ClPhCN$_2$S$_2$)$_2$



Scheme 5.4 gives the relevant oxidation series for the different systems studied. In general these are as expected with the groups with higher electronegativities producing more positive $E_{P/2}$(ox). Thus when R=$CF_3$, the oxidation peak is +0.80V. However, meaningful electronegativity values are not always available and there are some unexpected results, for example in 5.4.(ii). both phenyl and benzyl derivatives have E(ox) values above that obtained for $Cl_3C$. This can probably be explained in terms of steric factors, in the benzyl compound the bulky phenyl section may "swing away" from the electroactive area, whilst in the straight phenyl compound electron exchanges are stabilised by delocalisation into the ring and the steric factor is minimised by the planar configuration of the ring. All the alkyl derivatives give E values below the aryl compounds (they are harder to reduce ie. add an electron) and largely follow electronegativity values with the exception of the methyl derivative. See Table 5.8. Broadly speaking the pattern is the same across all four sequences, with the highly electronegative groups coming above the aryl derivatives which themselves come above the alkyl groups. Indeed in the sequences (i)-(iii) the pattern is identical and only for the 1,3 isomers is the sequence varied. Thus $Cl_3C$- falls below phenyl in the 1,2 chlorides but above it in the 1,3 $AsF_6$ salt. This is an indication of a mesomeric effect associated with the 1,2 phenyl dithiadiazolium chloride whilst electronegativity appears more important in the 1,3 salts. This is supported by the values obtained in the para- substituted phenyl sequence with both $\rho$-CN and $\rho$-Cl having a positive inductive and a strong conjugative effect over phenyl whilst the $\rho$-$CH_3$ group has a negative inductive effect and no possibilty of conjugation. It is also worth noting that within a sequence the alkyl compounds all have fairly close $E_{P/2}$(ox) values. This is attributed to their similar structure and similar electronegativities.

Figure 5.16.

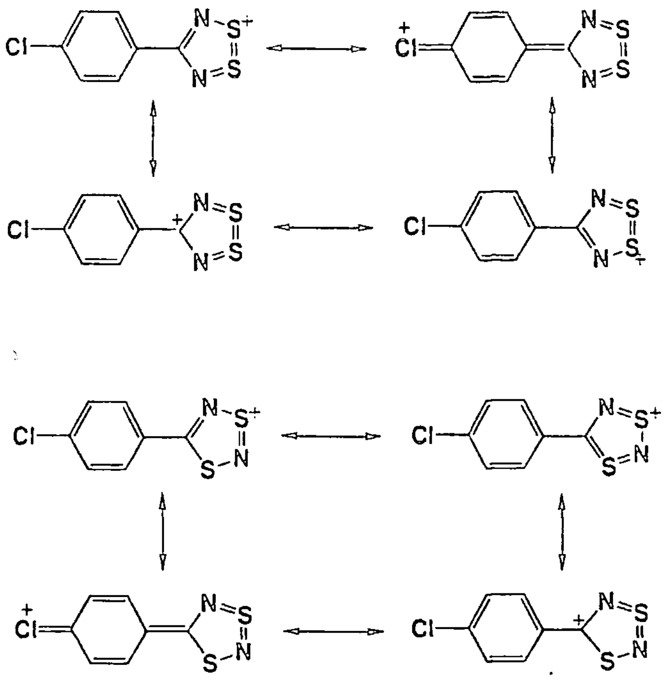


Table 5.8. Correlation of EN with $E_{P/2}$ for the alkyl derivatives.

| | $CH_3$ | $^tBu$ | $Pr^n$ | $Cl_3C$ |
|---|---|---|---|---|
| $E_{P/2}$(ox). | 0.28 | 0.33 | 0.48 | 0.53 |
| EN. | 0 | -0.30 | 0.113 | 2.65 |
| Es[29] | -1.24 | -2.78 | -1.6 | -3.3 |

$Pr^n$=propyl

EN=Electronegativity

Es=Steric factor

However, with Es, which takes steric factors into account there is no obvious correlation, which indicates that other factors such as electronegativity and inductive effects are important.

## 5.5. *Conclusion.*

CV is a useful tool in the study of S/N compounds because of their general ability to undergo electron transfer processes, particularly on the reduction side due to their good electron accepting properties.

Although the redox potentials of $RCN_2S_2$ are relatively similar within a series the R group still has a significant effect. Because the electroactive part is the $CN_2S_2$ ring, inductive and conjugative effects must be important particularly with the more electronegative groups. Steric factors, although still significant, are less important.

The redox potential for $S_2N+$ is in keeping with those found for $SN^+$ and $S_3N_2^{+\cdot}$. The Hammett plots obtained, albeit over a limited range of compounds suggest a similar electron transfer mechanism for all these types of compounds, as is indicated by the striking similarity of the CV's themselves. This may also seen between the 1,2 and the 1,3 isomeric forms suggesting a similar mechanism acts across these two rings as well.

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# CHAPTER SIX

# SOME REACTIONS OF THE DITHIONITRONIUM CATION.

## 6.1. INTRODUCTION.

The $S_2N^+$ cation was first prepared in 1978 as the $S_2NSbCl_5$ salt[1] by the reaction of $S_7NH$, $S_7NBCl_6$ or 1,4 - $S_6N_2H_2$ with $SbCl_6$ in liquid $SO_2$, but it was not until the synthesis of $S_2NAsF_6$ in 1980[2] that its usefulness as a synthetic building block was fully realised. There is a good deal of literature about the cycloaddition reactions of $S_2N^+$ with alkenes, alkynes and nitriles[3,4]. However, very little work appears to have been carried out with other unsaturated compounds, such as isothiocyanates, nitrosyls etc., nor with alkynes in unfamiliar environments eg. as ligands in transition metal complexes. Some reactions therefore of this nature were investigated and are reported in this chapter. Some results, however, proved inconclusive. Nevertheless this is an area of work ripe for further and interesting developments.

The synthesis, described below, of a new $S_2N^+$ reagent, $S_2NCF_3SO_3$, provided an insight into the solution equilibria of the $S_2N^+/S_3N_2^{+\cdot}$ system. A comparative study of the synthetic utility of various $S_2N^+$ reagents, namely $S_2NAsF_6$, $S_2NSbCl_6$ and$S_2NCF_3SO_3$ was also carried out. The crystal structure of $S_3N_2CF_3SO_3$ was first reported in 1980[5] but it contained solvent of crystallisation. This structure has been redetermined with no solvent of crystallisation and it is reported later.

## 6.2. EXPERIMENTAL.

### 6.2.1. *Preparation of $S_2N\ CF_3SO_3$.*

In a typical reaction, $SO_2$ (15ml) was condensed onto a mixture of $(NSCl)_3$ (0.634g, 2.6mmol) and silver triflate (2.0g, 7.78mmol), placed together with a teflon coated stirring bar in one side of a "dog". An immediate reaction occurred resulting in a yellow solution and a white flocculent solid. After stirring this for 1/2 h sulphur (0.0311g, 7.78mmol) was added to the pre-cooled (-15°C) solution against a counter current of dry nitrogen. This gave an olive green solution which was stirred for a further 4h at room temperature. The solution gradually turned bright yellow over this time. The solution was then carefully filtered into the empty bulb and the volume of liquid reduced severely until small thin yellow platelets formed; no further precipitate formed on cooling to -15°C. The remaining liquid was decanted off and the crystals were washed several times by back condensing $SO_2$. This left bright yellow crystals (0.65g, 37% based in silver triflate), whilst removal of the $SO_2$ from the decanted liquid left a sticky red oil, (unidentifed), but which contained crystals of $S_2NCF_3SO_3$(0.09g) and $S_3N_2CF_3SO_3$ (0.04g). The crystals of $S_2NCF_3SO_3$ were extremely moisture and oxygen sensitive and even slowly decomposed when exposed to the atmosphere of the glove box for any length of time. $S_3NCF_3O_3$ requires C 5.28%, N 6.2%, S 42.3%. Found C 5.26%, N 6.0%, S 41.5%; Infrared spectrum, $\nu_{max}$ = 1250 sbr, 1220 sbr, 1180 sbr, 1030 sbr 760 s, 635 vs, 580 m, 520 m, 440 s, 380cm$^{-1}$ s; m.s.(CI)m/e 78 (53%) $S_2N^+$, 227 (8%) 149 (8%) $CF_3SO_3^-$.

### 6.2.2. *Reaction of $S_2N$ $CF_3SO_3$ with $CH_3CN$.*

$S_2NCF_3SO_3$ (0.25 g, 1.1 mmol) was placed in one bulb of a dog. This was cooled to -196°C and dry MeCN (1.0ml, 0.019mmol, 14x excess) was syringed in on top of the solid against a counter current of dry nitrogen. The MeCN was then frozen and the vessel evacuated. Liquid $SO_2$ (15ml) was condensed onto the mixture and the whole solution stirred for 24h at room temperature. The remaining unreacted $S_2NCF_3SO_3$ was filtered off (0.175g) and the solvents removed under vacuum. This yielded dark green crystals, which were transferred to a closed extractor, washed briefly with $SO_2$ and identified by infrared spectroscopy as $[CH_3\overline{CNSNS}]CF_3SO_3$. Yield = 0.085g (30% based on $S_2NCF_3SO_3$). Infrared spectrum, $\nu_{max}$ $cm^{-1}$;1250 s, 1220 vs, 1180 vs, 1030 vs, 980 s, 760 s, 740 s, 630 s, 580 s, 520 s, 440 s, 380 s, 360 s; Analysis; $C_3H_3S_3N_2F_3O_3$ requires; C 13.4, H 1.1, N 10.4, S 35.86; found C 12.4, H 0.74, N 9.68, S 35.17.

### 6.2.3. *Reaction of $S_2N$ $CF_3SO_3$ with Benzonitrile.*

Yellow $S_2NCF_3SO_3$ (0.35g, 1.6mmol) was placed into one half of a dog with PhCN (0.17g, 1.6mmol) syringed into the other. After $SO_2$ (15ml) was condensed onto both sides and warmed to room temperature, the two solutions were brought together and stirred for 2h. Over this time the solution turned brown/red which, on removing the solvent, yielded a brown solid (0.38g, 74% based on $S_2NCF_3SO_3$) identified by infrared spectroscopy as $[PhCNSNS]CF_3SO_3$. $C_8H_5S_3N_2F_3O_3$ requires C 29.08, H 1.5, N 8.48, S 29.13, F 17.26, O 14.54. Found C 29.20, H 1.47, N 8.56, S 30.0, F 17.12.

### 6.2.4. *Preparation of $S_3N_2AsF_6$.*

Green $S_3N_2Cl$ (0.5g, 3.13mmol) was loaded with a teflon stirring bar into one side of a dog with $AgAsF_6$ (0.93g, 3.13mmol) in the other. $SO_2$ (20g) was condensed onto the $S_3N_2Cl$ and (10g) onto the $AgAsF_6$. The solutions were allowed to warm to room temperature, when the $AgAsF_6$ dissolved completely, whilst the $S_3N_2Cl$ gave a dark green solution over undissolved solid. On addition of the $AgAsF_6$ solution to the $S_3N_2Cl$ the solution turned brown immediately and after stirring for 8h a white solid had precipitated out. This solid (AgCl, identified by analysis) was filtered off. The solution yielded dark brown $S_3N_2AsF_6$ (0.96g, 98%) identified by infrared spectroscopy and purified by recrystallisation from $SO_2$.

$S_3N_2AsF_6$ requires S 30.71, N 8.94, As 23.95, F 36.4. Found S 30.65, N 8.78, As 24.16.

### 6.2.5. *Preparation of $S_3N_2CF_3SO_3$ and Crystal Structure.*

**(i) Crystal growth.** - $S_3N_2CF_3SO_3$ could be isolated, under slightly different conditions, by a similar reaction used to obtain $S_2NCF_3SO_3$. $SO_2$(15ml) was condensed onto a mixture of $(NSCl)_3$ (0.634g, 2.6mmol) and $AgCF_3SO_3$ (2.0g, 7.78mmol) in a dog. After stirring for 1/2h, a slight excess of sulphur was added (0.05g, 0.2mmol) to the pre-cooled vessel. Tiny green platelets formed in the resulting olive green solution, which were isolated in small yield by decanting off the solution at this stage, and washed by back condensing $SO_2$. The green metallic crystals (0.11g, 15% based on $(NSCl)_3$), identified by infrared spectroscopy and elemental analysis, were extremely moisture sensitive. However, a crystal suitable for X-ray analysis was picked.

**(ii). Crystal Data.** - $S_3N_2CF_3SO_3$, Mr = 273.27,
System: Monoclinic, Space group = P21/n,
a = 8.632(4), b = 10.614(8), c = 8.387(6)Å,
$\alpha = 90.0$, $\beta = 90.79(5)^\circ$, $\gamma = 90.0$.
U = 768.34$Å^3$, Z = 4, $D_c$ = 2.36 g/cm.
F(000) = 540, $\lambda(Mo,k\alpha) = 0.71069$.
$\mu = 12.17cm^{-1}$, T = 208k.

A crystal of dimensions 0.3 x 0.1 x 0.1 mm was mounted under $N_2$ in a sealed quartz Lindeman capillary. 1340 unique reflections were measured and for determination of the structure 1180 reflections were used, with $F_o > 3$. Final residues are; $R = (F)/(F_o) = 0.0248$, $R_g = 0.0358$.

### 6.2.6. *Reaction of $S_2NAsF_6$ with N-Piperidine thionitrosyl.*

On bringing a solution of $S_2NAsF_6$ (0.1g, 0.37mmol) in $SO_2$ into contact with a slight excess of N-Piperidine thionitrosyl (0.42ml, 0.40mmol) in $SO_2$ an immediate reaction took place to give a blood red solution. On removal of the $SO_2$ a red oil was obtained.

**Table 6.1. Bond Lengths (Å) and angles (°) for $S_3N_2CF_3SO_3$**

| | | | |
|---|---|---|---|
| S(4)-S(3) | 2.146(3) | N(2)-S(4) | 1.614(4) |
| N(2)-S(2) | 1.566(4) | S(3)-N(1) | 1.612(4) |
| N(1)-S(2) | 1.569(4) | S(1)-O(1) | 1.432(3) |
| S(1)-O(2) | 1.452(3) | S(1)-O(3) | 1.437(3) |
| S(1)-C | 1.828(5) | F(1)-C | 1.325(4) |
| F(2)-C | 1.326(4) | F(3)-C | 1.327(4) |

| | | | |
|---|---|---|---|
| S(4)-N(2)-S(2) | 119.3(2) | N(2)-S(4)-S(3) | 96.8(2) |
| S(4)-S(3)-N(1) | 96.9(2) | S(3)-N(1)-S(2) | 119.3(2) |
| N(2)-S(2)-N(1) | 107.6(2) | O(3)-S(1)-O(1) | 116.3(2) |
| O(2)-S(1)-O(1) | 114.6(2) | O(3)-S(1)-O(2) | 113.3(2) |
| C-S(1)-O(1) | 103.6(2) | C-S(1)-O(2) | 103.0(2) |
| C-S(1)-O(3) | 103.8(2) | F(1)-C-S(1) | 111.0(3) |
| F(2)-C-S(1) | 110.7(3) | F(2)-C-F(1) | 107.7(3) |
| F(3)-C-S(1) | 111.3(3) | F(3)-C-F(1) | 107.9(3) |
| F(3)-C-F(2) | 108.1(3) | | |

**Table 6.2. Selected Non-Bonded Distances (Å).**

Intramolecular:

| | | | |
|---|---|---|---|
| F(1)-S(1) | 2.614 | F(2)-S(1) | 2.610 |
| F(3)-S(1) | 2.620 | O(2)-O(1) | 2.427 |
| O(3)-O(1) | 2.437 | C-O(1) | 2.574 |
| F(1)-O(1) | 3.003 | F(2)-O(1) | 2.895 |
| O(3)-O(2) | 2.413 | C-O(2) | 2.577 |
| F(1)-O(2) | 2.897 | F(3)-O(2) | 3.011 |
| C-O(3) | 2.581 | F(2)-O(3) | 3.025 |
| F(3)-O(3) | 2.899 | F(2)-F(1) | 2.141 |
| F(3)-F(1) | 2.144 | S(2)-F(1) | 3.218 |
| N(2)-F(1) | 3.150 | F(3)-F(2) | 2.148 |
| S(3)-S(2) | 2.745 | S(4)-S(2) | 2.745 |
| S(4)-N(1) | 2.834 | N(2)-N(1) | 2.530 |
| N(2)-S(3) | 2.834 | | |

Intermolecular:

| | | | |
|---|---|---|---|
| S(3)-S(1a) | 3.888 | S(4)-S(1c) | 3.986 |
| S(2)-S(1b) | 4.169 | S(4)-S(1d) | 3.795 |
| S(3)-S(1d) | 4.033 | S(2)-S(1e) | 3.539 |
| F(3)-S(1e) | 3.358 | S(4)-O(1f) | 3.387 |
| N(1)-S(1e) | 3.770 | S(4)-O(2d) | 2.650 |

|  |  |  |  |
|---|---|---|---|
| S(3)-O(1a) | 2.966 | S(2)-O(2e) | 3.045 |
| S(2)-O(1b) | 3.173 | S(4)-O(3c) | 2.871 |
| S(3)-O(2d) | 2.705 | S(2)-O(3e) | 2.956 |
| F(3)-O(2e) | 3.313 | S(4)-F(1d) | 3.155 |
| N(1)-O(2e) | 3.097 | S(4)-O(2e) | 3.302 |
| N(2)-O(3c) | 3.202 | S(3)-F(1f) | 3.479 |
| S(2)-F(2f) | 3.372 | S(4)-S(3i) | 2.971 |

key to symmetry operations;

(a). x,-1,0+y,z (b). 2,0-x,1,0-y,-z
(c). 1,0-x,1,0-y,-z (d). -1,0+,
(e). 2,0-,-,- (f). 2,0-,-,1,0-

**Table 6.3. Atomic Coordinates ($x10^4$) for $S_3N_2CF_3SO_3$**

| Atom | x | y | z |
|---|---|---|---|
| S(1) | 7694.5(7) | 6352.4(6) | -1582.1(8) |
| O(1) | 8382.0(2) | 7100.0(2) | -340.0(2) |
| O(2) | 8745.0(2) | 5998.0(2) | -2843.0(2) |
| O(3) | 6202.0(2) | 6756.0(2) | -2166.0(2) |
| C | 7294.0(3) | 4851.0(3) | -604.0(3) |
| F(1) | 8596.0(2) | 4280.0(2) | -166.0(2) |
| F(2) | 6461.0(2) | 5028.0(2) | 649.0(2) |
| F(3) | 6515.0(2) | 4078.0(2) | -1566.0(2) |
| S(2) | 8518.5(7) | 1314.8(6) | 630.3(8) |
| N(1) | 8292.0(2) | -151.0(2) | 541.0(3) |
| S(3) | 6650.4(7) | -751.3(6) | 1029.6(8) |
| S(4) | 5557.1(7) | 981.1(6) | 1703.7(8) |
| N(2) | 7002.0(3) | 1894.0(2) | 1326.0(3) |

This red oil was only partially characterised and did not lend itself to either $^1H$ nmr or purification and extraction. Both analysis and infrared spectroscopy indicated that the product was impure. $C_5H_5N_3S_3OAsF_6$ requires C 14.70, H 1.22, N 10.29, S 23.56, O 3.92, As 18.37, F 27.93; Found S 29.73, N 13.1, H 1.81, C 14.58.

## 6.3. RESULTS AND DISCUSSION.

### 6.3.1. *Preparation of $S_2NCF_3SO_3$.*

Several synthetic routes to this compound were tried before a successful one was found. Previous routes have involved use of hazardous Lewis acids such as $AsF_5$ and $SbCl_5$. $S_2NSbCl_6$ was originally prepared in unspecified yield by the reaction of $S_7NH$, $S_7NBCl_2$ or 1,4- $S_6N_2H_2$ with

$SbCl_5$ in liquid $SO_2$[1]. $S_2NAlCl_4$ has also been isolated in unspecified yield from the reaction of $S_4N_4$ with $AlCl_3$ in $CH_2Cl_2$[6], whilst $S_2NAsF_6$ may be prepared according to equations 6.1 & 6.2. in liquid $SO_2$[2]. The yields were 20% and 77% respectively, though in the absence of traces of bromine, the yield for equation 6.2. was only 30%.

$$S_8(AsF_6)_2 + NaN_3 \longrightarrow S_2NAsF_6 + NaAsF_6 + N_2 + 3/4\ S_8 \qquad \text{Eq. 6.1.}$$

$$1/2S_8 + S_4N_4 + 6AsF_5 \longrightarrow 4S_2NAsF_6 + 2AsF_3 \qquad \text{Eq. 6.2.}$$

$$SN^+AsF_6 + S \longrightarrow S_2NAsF_6 \qquad \text{Eq. 6.3.}$$

The reaction according to equation 6.3 has also been shown to produce $S_2NAsF_6$[7] in 50% yield, but has the disadvantage of requiring the previous isolation of extremely moisture sensitive $SNAsF_6$. All these routes involve the use of hazardous chemicals, eg. $S_4N_4$, $NaN_3$ and $AsF_5$. $AsF_5$ cannot be bought in this country and therefore must be made by burning arsenic in fluorine, whilst $AgAsF_6$ is hazardous to prepare and expensive to buy. A more convenient preparation of $S_2NSbCl_6$[7] made use of the reaction of a stoichiometric amount of sulphur added to an *in situ* source of $SN^+$ to give $S_2N^+$. This principle has been utilised before in the preparations of $S_5N_5^+$[8] and $N(SCl)_2^+$[9], see Scheme 6.1. The participation of $SN^+$ in these reactions was confirmed by the isolation of $S_5N_5AsF_6$ and $N(SCl)_2AsF_6$ from the reactions of $SNAsF_6$ with $S_4N_4$ and $SCl_2$ respectively[10]. Reactions of Lewis acids with $(NSCl)_3$ have been extensively studied[11]. **Scheme 6.1:-**

$$(NSCl)_3 + 3MCl_3 \longrightarrow 3'NSCl.MCl_3'$$

$$'NSCl.MCl_3' + S_4N_4 \longrightarrow S_5N_5MCl_4.$$

M = Fe, Al[8].

$$(NSCl)_3 + 3MCl_3 \longrightarrow 3'NSCl.MCl_3'$$

$$'NSCl.MCl_3' + SCl_2 \longrightarrow N(SCl)_2MCl_4$$

M = Fe, Al[9].

In the reaction of $SbCl_5$ with $(NSCl)_3$ the overall reaction becomes chlorine extraction.

Scheme 6.2.

$$(NSCl)_3 + SbCl_5 \longrightarrow 3\text{'}NSCl.SbCl_5\text{'}$$

$$\text{'}NSCl.SbCl_5 + S \longrightarrow S_2NSbCl_6,$$

Besides $S_2NSbCl_6$, $S_3N_2Cl^+SbCl_6^-$ was also isolated, in fact when the weaker Lewis acids, eg $FeCl_3$[12] were used in the same reaction instead of $SbCl_5$, the major product then became $[S_6N_4][FeCl_4]_2$. This was rationalised on the basis of the weaker Lewis acidity of $FeCl_3$ towards the chloride. A unknown intermediate was suggested, S N SCl, which reacted with any $S_2NFeCl_4$ formed Scheme 6.4.

$$\left.\begin{array}{l} 1/3\ (NSCl)_3 + FeCl_3 + S \longrightarrow [S_2NFeCl_4] \\ 1/3\ (NSCl)_3 + S \longrightarrow [S\quad N\quad SCl] \end{array}\right. \longrightarrow 1/2[S_6N_4][FeCl_4]_2 + 1/2S_2Cl_2$$

The use of a strong chloride ion acceptor suggested the mechanism of removing the chlorine as a volatile or insoluble organic or inorganic chloride. Initial experiments made use of a silyl reagent, since silyl reagents have been used to great effect elsewhere in S/N chemistry[13-16].

$$3Me_3SiCF_3SO_2 + (NSCl)_3 + 3S \longrightarrow 3\ S_2NCF_3SO_3 + 3Me_3SiCl \qquad \text{Eq.6.4.}$$

$$3LiCF_3SO_3 + (NSCl)_3 + 3S \longrightarrow 3\ S_2NCF_3SO_3 + 3LiCl \qquad \text{Eq.6.5.}$$

$$3AgCF_3SO_3 + (NSCl)_3 + 3S \longrightarrow 3\ S_2NCF_3SO_3 + 3AgCl \qquad \text{Eq.6.6.}$$

$Me_3SiCF_3SO_3$ was reacted with $(NSCl)_3$ in both $CH_2Cl_2$ at reflux and $SO_2$ but in both cases a black oily tar was the only product. This was probably due to the highly reactive chlorines on the $(NSCl)_3$ attacking the hydrogen atoms of the methyl groups.

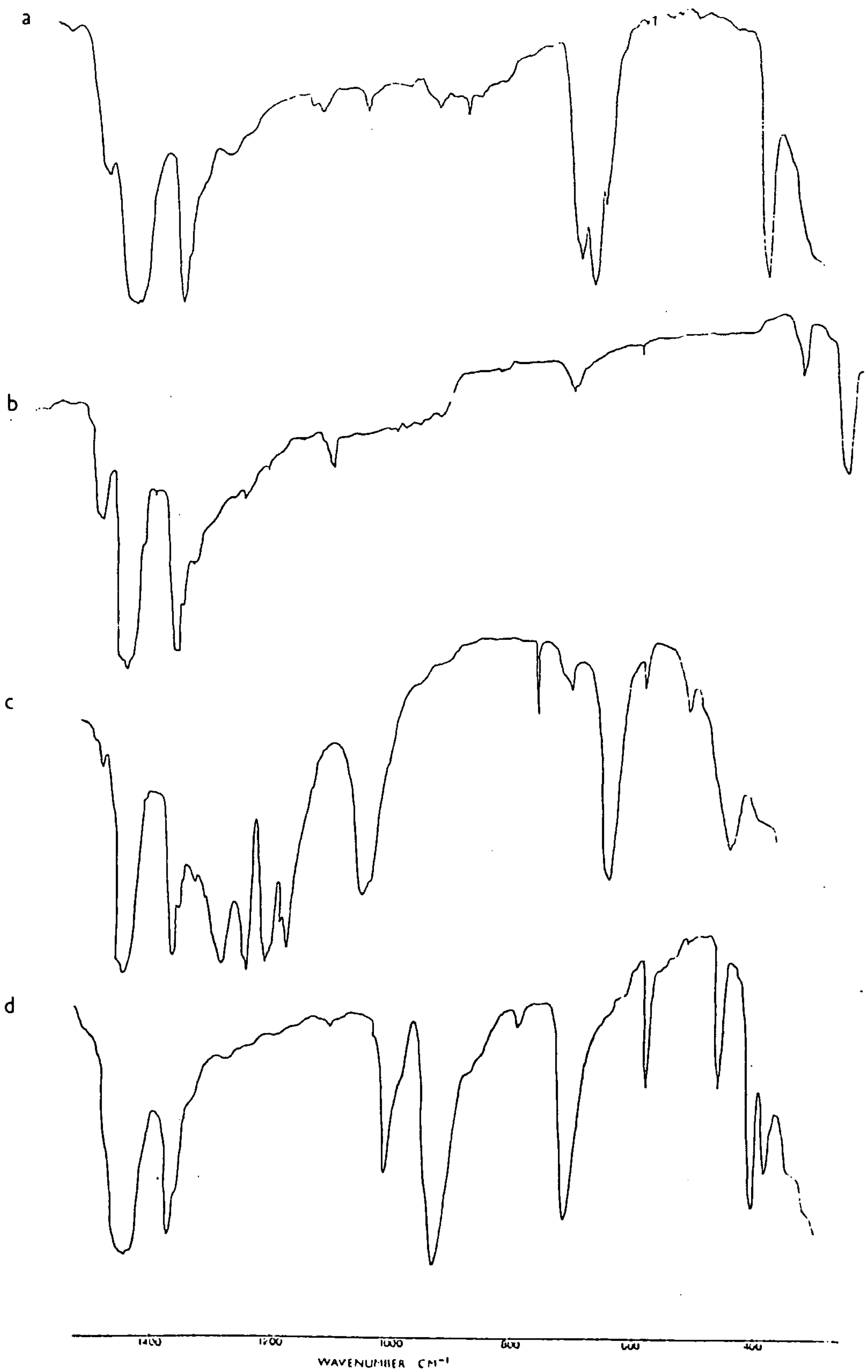
A reaction with lithium triflate in THF was tried, $LiCF_3SO_3$ being very insoluble in $SO_2$ and $CH_2Cl_2$. LiCl is also soluble in THF by coordination, but on removing the solvent only $LiCF_3SO_3$ was obtained. The only successful route found was that using $AgCF_3SO_3$. The use of silver salts in liquid $SO_2$ in reactions in which AgCl is precipitated out has been used successfully elsewhere, eg.

$[PhCN_2S_2]Cl + AgAsF_6 \longrightarrow AgCl(s) + [PhCN_2S_2]AsF_6$.

Although $AgCF_3SO_3$ is only sparingly soluble in $SO_2$, AgCl is even less so, and the reaction $AgCF_3SO_3\ (s) + SO_2 \rightleftharpoons AgCF_3SO_3\ (solv)$ proceeds to the right. On addition of $AgCF_3SO_3$ to $(NSCl)_3$ in $SO_2$ a bright yellow solution resulted, with a flocculent precipitate of AgCl. No attempt was made to isolate the intermediate, presumed to be $SNCF_3SO_3$, since $SN^+$ compounds are notoriously moisture and air sensitive. The olive green solution which resulted on addition of sulphur is possibly due to the formation of $S_3N_2^{+\cdot}$ species, formed from the reaction of the $S_2N^+$ product with the excess $SN^+$ in solution. As more sulphur solubilises, more $SN^+$ reacts to give $S_2N^+$ and the solution gradually turns yellow. When longer times were allowed for the reaction, the yields dropped. The red oil at the end of the experiments was almost certainly contained decomposition products, two of which were tentatively attributed to $S_4N_4$ and $S_3N_2O_2$ by comparison with products reported[11] from the reactions of $S_2N^+$. The bright yellow solution, which appeared stable over time was decanted off and the volume reduced to provide bright yellow platelets of $S_2NCF_3SO_3$, identified by infrared spectroscopy, elemental analysis and by reaction with MeCN.

The infrared spectra of $S_2N^+$ salts are very simple, Figure 6.1 a).-d)., the only peaks attributable to S/N bending/stretching modes are at 520, 1010 and 1490cm$^{-1}$ respectively and the major peaks are of the anion. Note that the high charge density on $S_2N^+$ has led to a shift to higher wave numbers compared to other S/N cations eg. $S_3N_2Cl_2$.

Figure 6.1. Infra-red Spectra of $S_2N^+$ salts. a).$S_2NAsF_6$, b).$S_2NSbCl_6$, c).$S_2NCF_3SO_3$, d).$S_3N_2Cl_2$.



### 6.3.2. *A Comparative Study of $S_2N^+$ Salts.*

The reactions of $S_2NAsF_6$ are well documented[3],[4]. There are, however, several other salts of $S_2N^+$, notably the $SbCl_6^-$ salt, which has been reported in the literature[1], and the $CF_3SO_3^-$ salt (page 159). However, $S_2NAsF_6$ is not easy to prepare and $S_2NSbCl_6$ reactions tend to be much slower and so a more convenient reagent was hoped for in $S_2NCF_3SO_3$.

$$As + F_2 \longrightarrow AsF_5 \xrightarrow{Ag} AgAsF_6 + AsF_3 \qquad \text{Eq.6.7}$$

$$AgAsF_6 + (NSCl)_3 + S_8 \longrightarrow S_2NAsF_6 + S_x(AsF_6)_2 \qquad \text{Eq.6.8}$$

In the preparation of $S_2NCF_3SO_3$ no polysulphur cationic species are found, presumably because of the low oxidising power of $CF_3SO_3^-$. Both $S_2NSbCl_6$ and $S_2NCF_3SO_3$ are easier to prepare than $S_2NAsF_6$ but yields are generally lower, 77% for $S_2NAsF_6$ compared to 30-40% for the triflate and $SbCl_6^-$ salts. Also side products become a problem, particularly with the $S_2NSbCl_6$ preparation. This may be in part due to the less rigorous drying of reaction vessels and reagents with $SbCl_5$ and $AgCF_3SO_3$, $AsF_5$ is vigorous remover of traces of water, and indeed extra care was found to be necessary in the preparation of $S_2NCF_3SO_3$. This compound is particularly sensitive and even decomposed in the glove box.

A comparison of solubilities revealed that whilst $S_2NAsF_6$ was extremely soluble in $SO_2$ and moderately soluble in most common organic solvents, $S_2NSbCl_6$ was almost the exact opposite in that it was practically insoluble in most solvents. $S_2NCF_3SO_3$ was soluble in $SO_2$ and showed some solubility in organic solvents, but to a lesser extent than the $AsF_6$ salt.

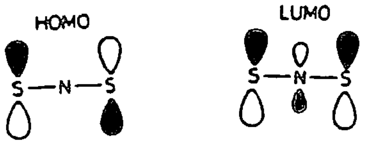
The utility of $S_2NCF_3SO_3$ as a reagent appeared to lie somewhere between $S_2NAsF_6$ and $S_2NSbCl_6$. While all three react in a similar manner, reactions were faster and cleaner for $S_2NAsF_6$ and gave higher yields. For example the reaction with MeCN took only a few hours with $S_2NAsF_6$, whilst with $S_2NCF_3SO_3$ it took 24h for an incomplete reaction. With $S_2NSbCl_6$ this reaction would take a week. and be complicated by side reactions. A particularly good example of this was encountered in the reactions of $S_2N^+$ with anthracene carbonitrile. Whilst $S_2NAsF_6$ reacted in the expected cycloaddition across the nitrile group, the $S_2NSbCl_6$ salt was apparently complicated by additions across the central carbon atoms. $S_2NCF_3SO_3$ also reacted fairly readily with benzonitrile. The products with the $CF_3SO_3^-$ anion tended to be more brightly coloured than the $AsF_6^-$ analogues, though whether this is due to some cation/anion charge transfer remains undecided.

Stability and air/moisture sensitivity seemed to be related to the hardness of the anion. Very pure $S_2NAsF_6$ may be exposed to air for short periods (1-2 mins) without too much decomposition, as may $S_2NSbCl_6$, both with relatively hard anions. $S_2NCF_3SO_3$, however, is extremely sensitive. It was concluded therefore that whilst useful for some syntheses the $S_2NCF_3SO_3$ salt does not have the utility of the $AsF_6$ derivative.

### 6.3.3. *Some Reactions of* $S_2NAsF_6$.

$S_2N^+$ salts have an extensive and diverse chemistry and are of increasing use as a building block in the synthesis of S/N and S/N/C heterocycles.

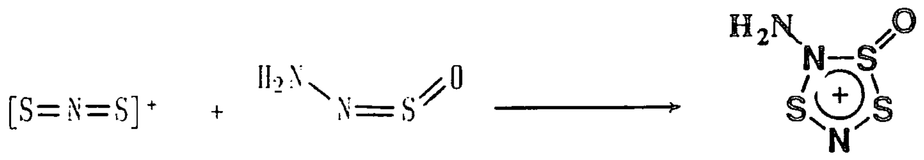
Figure 6.2.



They all appear to react in an identical manner, ie. via a concerted symmetry allowed cycloaddition[4]. This process is assisted by the large contribution of the S centres in both the HOMO and the LUMO orbitals of $S_2N^+$. This is partly due to the fact that the S centres involve not only 3p orbitals which are larger than the N 2p orbitals but are also more electropositive. The cycloaddition of S/N compounds has been shown[17] to occur via a reverse electron demand process, that is the primary interaction is donation from the HOMO of the olefin into the LUMO of the S/N species, so that for neutral S/N compounds which have relatively high energy LUMOs a strong kinetic control is imposed on reactions. Consequently neutral S/N heterocycles are only seen to react with strained or electron rich (high energy HOMO) olefins. In view of these cycloadditions it was thought that new heterocycles would be accessible by the reaction of $S_2N$+ with various unsaturated S/N compounds.

### 6.3.3.1. ***Reaction with R N S O.***

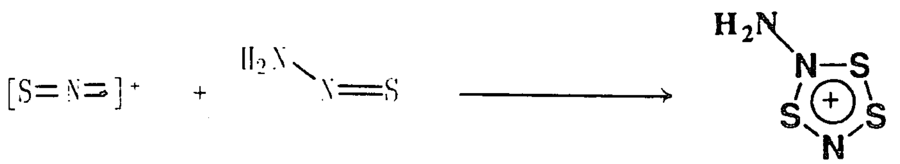
6.9.



$\Delta H_f$ 269.67 89.42 288.21

$\Delta H$ reaction = 70.88 kcal/mol.

6.10.



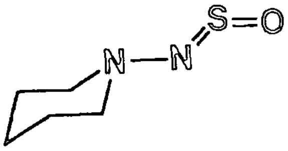
$\Delta H_f$ 269.67 79.45 294.6

$\Delta H$ reaction = 79.52 kcal/mol.

$\Delta H_f$ = Heat of formation as indicated by MNDO.

MNDO calculations suggested that both the reactions 6.9 and 6.10 should proceed easily, and the expected product should be an ionic crystalline solid. In the case of 6.9 calculations indicated that addition across the S=O bond was highly unfavourable and that ring closure would be difficult in this event.

The precursor to thiazyl derivatives R N S is usually the sulphuryl imide derivative R—N=S=O. Therefore N - piperidine sulphuryl imide (I) was chosen for an initial experiment.



(I).

N - piperidine sulphuryl imide is a stable yellow oil at room temperature and is relatively air stable. An immediate reaction occurred on addition of (I) to a solution of $S_2NAsF_6$ in $SO_2$, giving a blood red colour. On vacuum evaporation of the solvent, a red oil with a brown solid was obtained ( crude yield = 0.147g, mass loss =0.011g). An extraction with hexane gave a yellow solution, which yielded the same red oil. This was identified by its infrared spectrum and physical characteristics ( ie did not wet glass) as $S_3N_2O$. After two days $S_4N_4$ peaks were also observed in an infrared spectrum. This is a typical decomposition product of impure $S_3N_2O$. An infrared spectrum of the brown solid gave a complex absorbancy pattern, but which had peaks assignable to $AsF_6$, the sulphuryl imide (I), and $S_4N_4$. A $^1H$ nmr spectrum of this was not significantly different from (I). Several reaction pathways are possible but is complicated by the fact that $S_3N_2O$ is known to undergo further reaction with RNSO compounds[10]. Thus it appears that whilst $S_2N^+$ reacts readily with (I) to give the expected product (II), this is unstable and quickly decomposes by loss of the R group to leave $S_3N_2O$ which then reacts further with more RNSO. The ingress of moisture cannot be ruled out, although there was no evidence for NH peaks in the $^1H$ nmr which usually results from hydrolysis of S/N compounds.

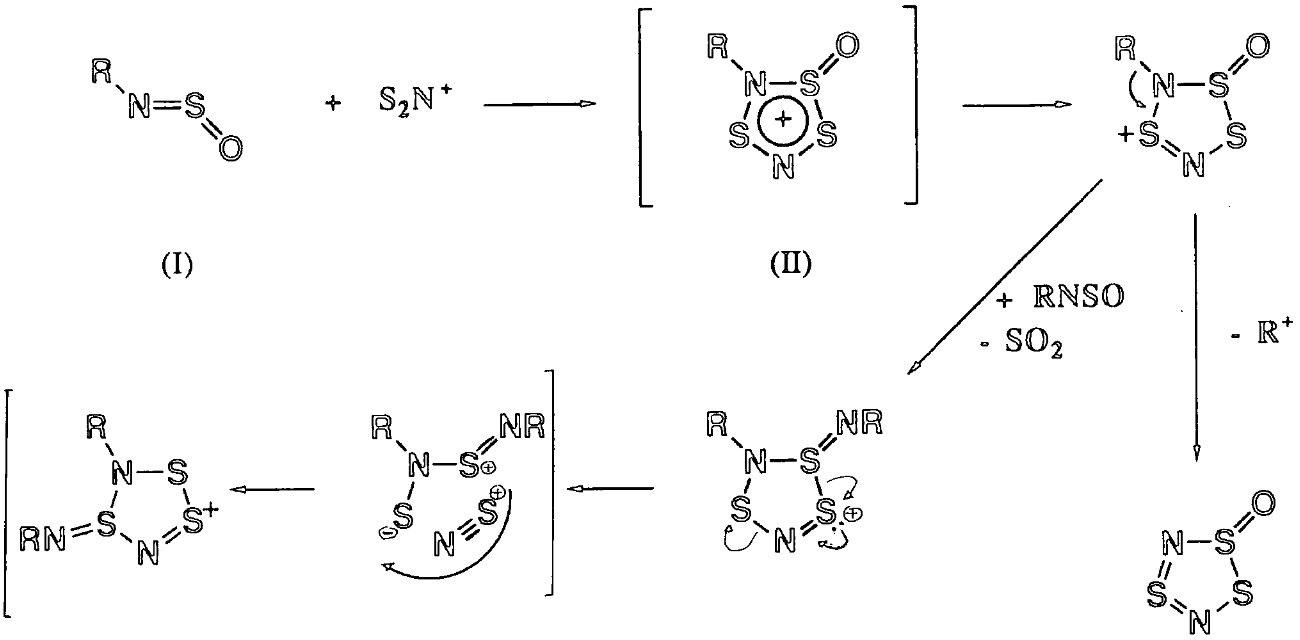


Figure 6.3.

Removal of $SO_2$ would not be sufficient to account for the small mass loss that occurred on evacuating the system, this is probably attributable to the removal of unreacted (I) and volatile products.

### 6.3.3.2. *Reactions with Hexyne, Cyclohexene and Cyclooctadiene.*

Cyclooctadiene(COD) is a common transition metal(TM) ligand and $S_2N+$ was reacted with this and hexyne and cyclohexene to investigate how $S_2N+$ would interact with TM complexes.

A 1:1 mole ratio reaction of $S_2NAsF_6$ with hexyne in $SO_2$ as a solvent yielded a pale brown crystalline solid from an orange solution. This was identified as $C_6H_{10}S_2NAsF_6$ by infrared spectroscopy, elemental analysis and mass spectroscopy. This reaction is more or less quantitative provided the hexyne is thoroughly dried over molecular sieve beforehand. Similarly a compound identified as $C_6H_{10}S_2NAsF_6$ was obtained as an almost colourless crystalline solid from the 1:1 reaction with cyclohexene, again with $SO_2$ as solvent. The integrity of the ring was established by $^1H$ nmr. An excess of cyclohexene gave a mixture of ill defined products which were hard to separate but which probably included the second addition of alkene to the $S_2N$ unit in accordance with previous literature results[4].

With COD a more complex reaction occurred. It was thought desirable to attempt to react just one double bond with $S_2N^+$ to leave one double bond free for coordination. A 1:1 mole ratio reaction, with $SO_2$ as solvent, was attempted in which the COD was syringed into the dog. Some of this, however, polymerised to a white solid on the vessel walls before getting into solution. From the resulting red solution a brown crystalline solid was obtained after a few hours. Infrared specroscopy indicated no double bonds and the solid was confirmed as $C_8H_{12}S_4N_2As_2F_{12}$ by analysis. An excess of $S_2NAsF_6$ has apparently resulted from the early polymerisation of some of the COD. Under more careful conditions, however, where the COD was introduced directly into a large volume of solvent, (again in a 1:1 reaction) a pale almost colourless solid was obtained in which, as indicated by an infrared spectrum, the $S_2N+$ had added across just one double bond .

These compounds were in all cases very moisture and air sensitive and *in situ* hydrolysis readily occurred in the reaction mixtures when the reagents were not thoroughly dried.

An order of increasing sensitivity towards moisture was qualitatively discerned going from the hexyne product through that of cyclohexene to that of COD. It was assumed that this was a reflection of decreasing thermodynamic stability with increasing carbon chain length. The enthalpy of formation will decrease with an increase in chain length as the entropy term also increases with length.

### 6.3.3.3. *Reactions with Unsaturated TM complexes.*

There are still comparatively few metallacycles and complexes containing S/N ligands. However, in recent years these have attracted increasing attention for a number of reasons. They warrant attention because they have the potential for interesting solid state properties and in forming stacking structures with potential as one dimensional conductors. A recent example of this is the synthesis of $[Pt(S_2N_2H)(PMe_3)_2][PF_6]$ which has an infinite array of ions[18],[19]. Furthermore this particular example involves a platinum or palladium atom as part of a five membered ring with $S_2N_2H^-$. M/S/N complexes and metallacycles also have the ability of stabilising otherwise unknown S/N anions, eg. $AuCl_2(S_3N)$ and providing useful S/N intermediates. The $S_3N^-$ ion is obtained by deprotonation of $S_7NH$[20],

$$S_7NH \longrightarrow S_7N^- \longrightarrow S_4N^- + 3/8S_8 \longrightarrow S_3N^- + 1/2S_8 \qquad \text{Eq.6.11}$$

Most if not all these metal complexes involve electron rich S/N ligands. Nevertheless it was thought possible to react $S_2NAsF_6$ with unsaturated ligands *in situ* in TM complexes, whilst maintaining coordination to the metal centre. The reaction site therefore should not be the site of coordination.

In order to satisfy the above criteria therefore a new TM complex was tried. $CpTaCl_2OCH_2CH{=}CH_2$ (I)[21] has a free vinyl group, coordination being through the oxygen atom.

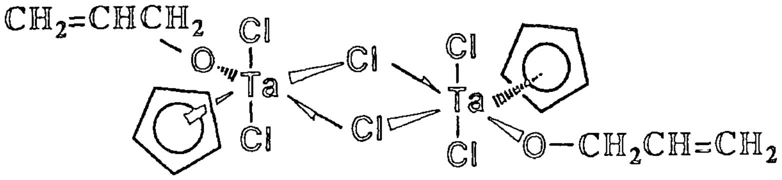
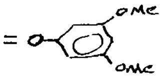


Figure 6.4. $CpTaCl_2OCH_2CH=CH_2$.

In theory the $S_2N+$ would react with the free vinyl group to give a S/N heterocycle still attached to the metal centre. Unfortunately no reaction was seen to occur, possibly because coordination had deactivated the vinyl group (by lowering the energy of the HOMO) or that the reaction was sterically hindered.

An attempt to react a second compound, $W=N\phi Me(OAr)_4$, OAr = , with $S_2NAsF_6$ was made. Reaction across the W=N bond would have led to a five membered metallacycle with tungsten similar to that formed with platinum and $S_2N_2$.

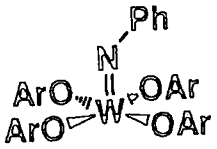


Figure 6.5. $W=NPhMe(OAr)_4$.

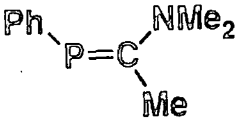
However, no reaction occurred and lack of time prevented further study. To see what effect if any $S_2NAsF_6$ would have on coordinated ligands, $S_2NAsF_6$ was placed in toluene with $(Co)_2(CO)_8$, dicobalt octacarbonyl.

After heating to reflux and stirring for ~2 days, no significant displacement of carbonyls had occurred, although a metal sheen did form on the glass walls. Although it is possible to imagine a number of complexes which might be expected to react in a similar fashion, eg cycloheptatriene chromium tricarbonyl etc.

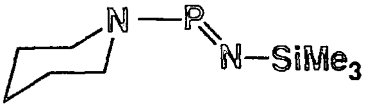
### 6.3.3.4. *Further Reactions.*

A recent development has been the synthesis of compounds of the type (I) and (II).

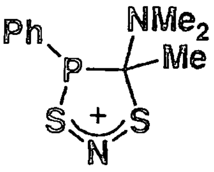
(I).



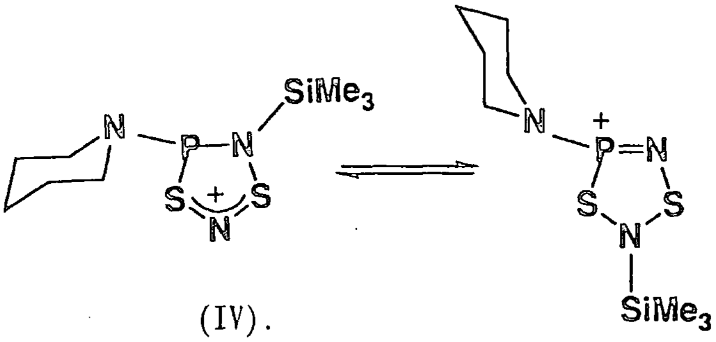
(II)



Both of these compounds should react with $S_2NAsF_6$ in typical fashion to give the products (III) and (IV) respectively.



(III).



(IV).

Initial experiments with (I) did not indicate the right conditions, and time precluded further experiments. However, since S/N/P heterocycles are already well known, it is probably simply a question of more detailed investigation and many novel heterocycles may be accessible via $S_2N^+$ reaction with eg. $R_3P{\equiv}C$ , $R{-}P{=}C{=}P{-}C$ , $C{-}N{=}P{-}C$ etc.

## 6.4. *The $S_3N_2^{+\cdot}$ Cation.*

The $S_3N_2$ ring is a member of the series of binary monocyclic thiazenes. It can be found in both neutral compounds such as $S_3N_2O$ and cationic species such as $S_3N_2Cl^+$. The neutral ring $S_3N_2$ in unknown. It would be an $8\pi$ Huckel anti-aromatic[30] with a triplet ground state and would therefore be unstable. The generation of the di-cation is more favoured.

Indeed $S_3N_2^{2+}$, a $6\pi$ aromatic cation, has recently been prepared via a symmetry cycloaddition of $S_2N^+$ and $SN^+$ [7]. The radical cation, $S_3N_2^{+\cdot}$ is a $7\pi$ species, which like many S/N compounds the exact nature of the structure and bonding remained a matter of some speculation until the past 10 years or so[22,23]. Several ionic derivatives of $S_3N_2^{+\cdot}$ in addition to the chloride and $AsF_6$ salts, have now been isolated ( with $ClS_2O_6^-$, $SO_3F^-$ $S_2O_2F^-$ and $CF_3SO_3^-$)[23]. In the solid state the radical exists almost entirely as a dimer, $S_6N_4^{2+}$, with 2 delocalised $S_3N_2$ rings in a trans configuration[13]. Monomeric salts have also been reported but these are generally early publications[23-26] and have been the subject of some dispute[23]. The monomer, however, has been shown to exist in solution. $S_3N_2AsF_6$ has been previously prepared by the oxidation of $S_4N_4$ with $AsF_5$ in liquid $SO_2$[26]. Both are hazardous chemicals and a safer preparation in higher yield was developed by the simple metathesis reaction by analogy with other silver reactions:-

$$S_3N_2Cl + AgAsF_6 \xrightarrow{\text{liq.}SO_2} AgCl(s) + S_3N_2AsF_6. \qquad \text{Eq.6.12.}$$

Silver chloride is virtually insoluble in $SO_2$ and so is easily removed by filtration. Recrystallisation gave almost pure $S_3N_2AsF_6$. The advantages of this route are (i) it gives a highly pure product, and (ii) both $S_3N_2Cl$ and $AgAsF_6$ are readily available;

$$S_2Cl_2 + NH_4Cl \longrightarrow [S_3N_2Cl]^+Cl^- + 8HCl + 5S. \qquad \text{Eq.6.13}$$

$$2[S_3N_2Cl]Cl \xrightarrow{SO_2} SO_2Cl_2 + 2S_3N_2Cl^{25}. \qquad \text{Eq.6.14}$$

It has been proposed that $S_3N_2^{2+}$ exists in solution as an equilibrium mixture containing $SN^+$ and $S_2N^+$ and this seems to have been confirmed by the reaction with hexafluorobut - 2 -yne[7].

$$S_3N_2^{2+} \rightleftharpoons SN^+ + S_2N^+ \qquad \text{Eq. 6.15.}$$

Since $S_3N_2^{+\cdot}$ was obtained from the preparation of $S_2N^+$, a similar equilibrium is proposed.

Further evidence for a complex equilibrium came from the CV studies, Chapter 4, in which $S_3N_2^{+\cdot}$ gave a number of peaks, one of which could be assigned to $S_2N^+$ and another which was tentatively assigned to $S_4N_2$. Two equilibria are therefore possible;

(i). $$S_3N_2^{+\cdot} \rightleftharpoons S_2N^+ + (SN)^{\cdot} \qquad \text{Eq. 6.16.}$$

(ii). $$\begin{array}{ccccc} S_3N_2^{+\cdot} & \rightleftharpoons & S_2N^{\cdot} & + & SN^+ \qquad \text{Eq. 6.17.} \\ & & \updownarrows & & \\ & & S_4N_2 & & \end{array}$$

Since $SN^{\cdot}$ is a reactive species and since very little $(SN)_x$ or $S_4N_4$ were detected this equilibrium may lie more to the left. However, from the preparation of $S_2N^+$ from $(NSCl)_3/S$ and $AgCF_3SO_3$ it is difficult to understand the observation that the addition of more sulphur seems to drive the reaction to $S_3N_2^{+\cdot}$ since from 6.16 and 6.17 the presence of sulphur would favour the formation of more $S_2N^+$ from any $S_3N_2^{+\cdot}$ present. Whether the product was $S_2NCF_3SO_3$ or $S_3N_2CF_3SO_3$ appeared to depend on the length of time the solution was left and on the volume of $SO_2$. However, the olive green solution always appeared first, suggesting an initial $S_3N_2^{+\cdot}$ equilibrium. The presence of both $S_2N^+$ and $S_3N_2^{+\cdot}$ has been confirmed by crystal growth and an X-ray analysis of the $S_3N_2CF_3SO_3$ obtained from the reaction mixture.

## 6.5. *The Crystal Structure of $S_3N_2CF_3SO_3$.*

The crystal structure of $S_3N_2CF_3SO_3$ was first determined by Roesky et al in 1980[5]. The salt was obtained by the reaction of triflic anhydride with $S_4N_4$ in $CH_2Cl_2$[25]. However, this contained acetonitrile as solvent of crystallisation. Since $S_3N_2CF_3SO_3$ was found in the reaction mixture for the preparation of $S_2N^+$ it was decided to redetermine the crystal structure[28] particularly since $SO_2$ tends not to be incorporated into crystal structures.

Table 6.4. Comparison of Lattice Parameters from Ref.5 and this work for $S_3N_2CF_3SO_3$

| | Ref.5 | this work. |
|---|---|---|
| Mol.wt. | 273.27 | |
| System. | Monoclinic | Monoclinic |
| Space Gp. | $P2_1/m\text{-}C_2^2n$ | $P2_1/n$ |
| Z | 4 | 4 |
| a | 7.494 | 8.632 |
| b | 23.390 | 10.614 |
| c | 6.094 | 8.8387 |
| $\beta$ | 110.94 | 90.79 |
| $D_c$ | 1.914 | 2.36 |

Figure 6.6. $S_3N_2CF_3SO_3$

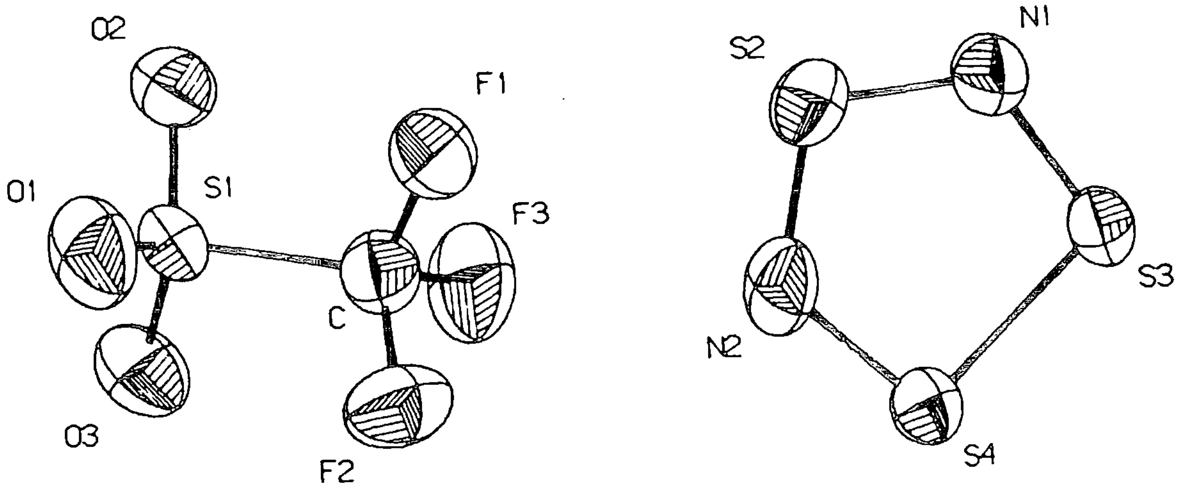


Table 6.4. compares the previous data with those from the present study in which the R value is much better. Although the previous lattice parameters are different there is good agreement between bonding distances and angles. The structure may be considered as a dimer with two $S_3N_2$ rings lying in a chair conformation linked via interactions between the two disulphide bonds. The $S_3N_2$ ring is not quite planar, being slightly puckered. The inter ring distance is 2.97Å, which seems to be typical for these type of 4 centre S/S interactions and is much less than the sum of the van der Waals radii. However, this is not the shortest intermolecular distance, there seems to be significant interactions between S(4), (and to a slightly smaller extent with S(3)), and O(2) in the $CF_3SO_3$ anion, the S(4)-O(2) distance being only 2.65Å as shown in Figure 6.8.

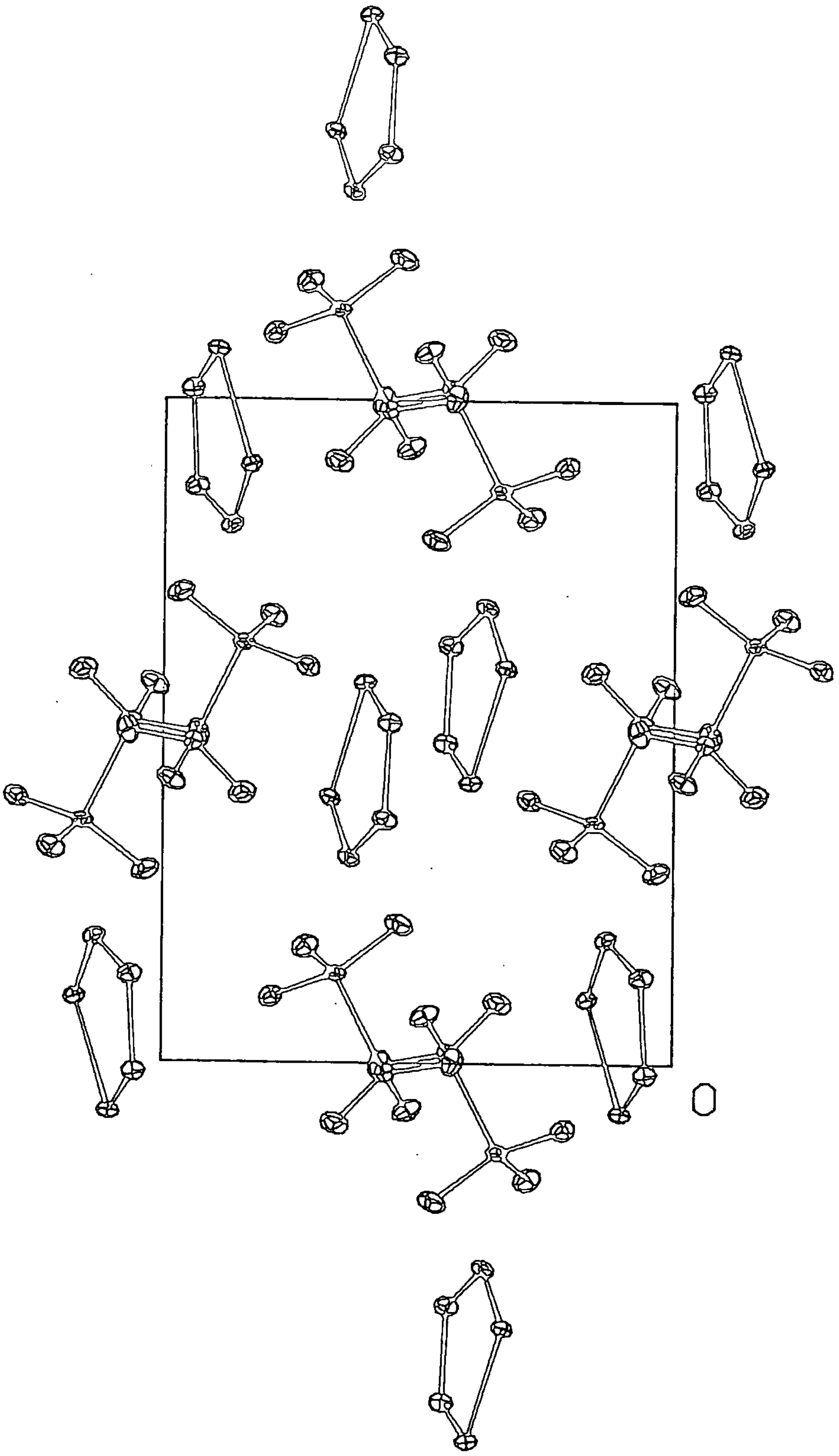
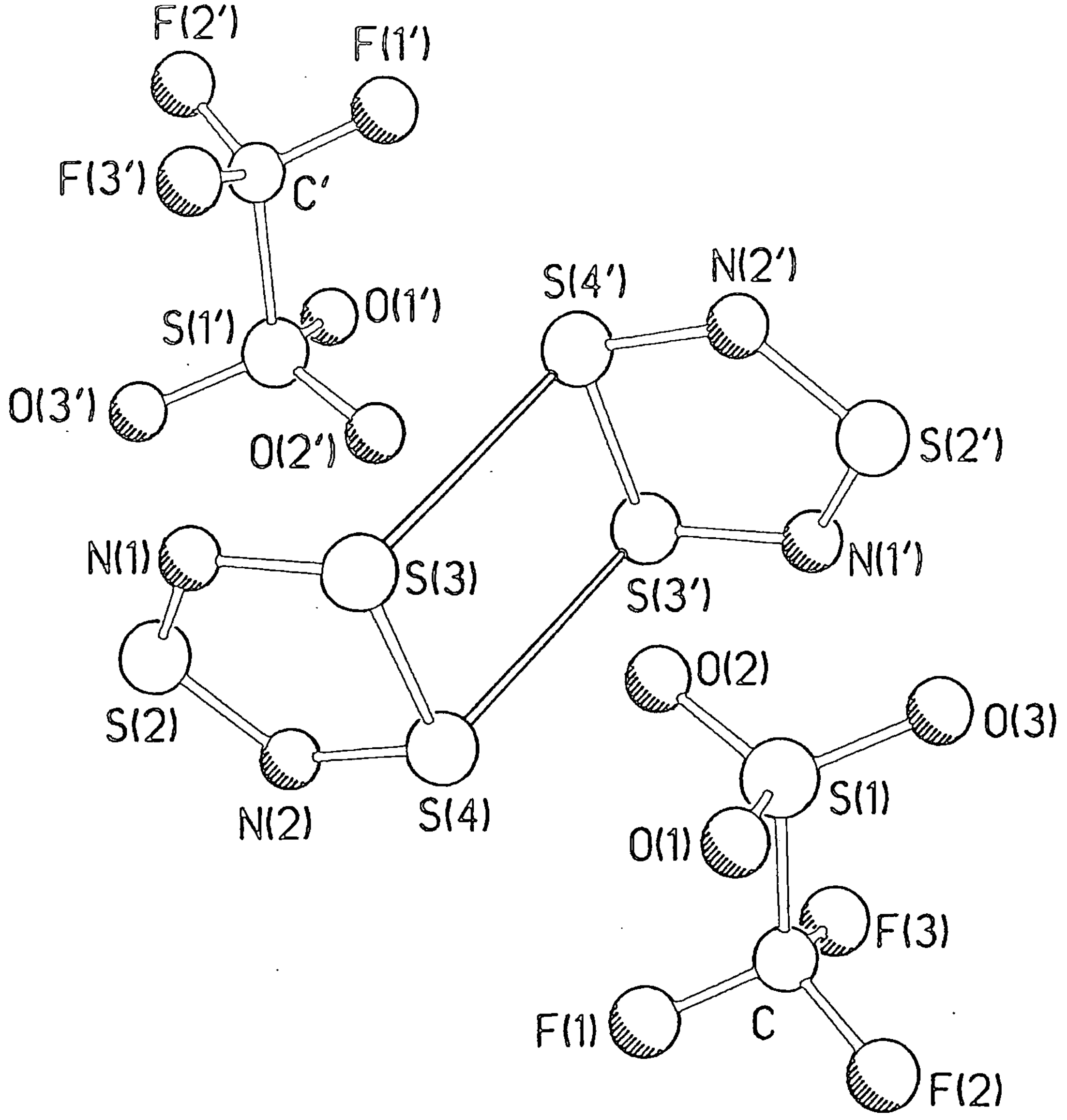


Figure 6.7. The unit cell of $S_3N_2CF_3SO_3$.

Figure 6.8. The Dimeric structure of $S_3N_2CF_3SO_3$ showing close approach of the O(3) atom,



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# APPENDIX

## DEPARTMENTAL COLLOQUIA AND DURHAM UNIVERSITY CHEMICAL SOCIETY (D.U.C.S.) LECTURES

| | |
|---|---|
| 13. 9.85 | Dr. V.S. Parmer (University of Delhi), "Enzyme Assisted ERC Synthesis". |
| 17.10.85 | Dr. C.J. Ludman (University of Durham), "Some Thermochemical Aspects of Explosions". |
| 30.10.85 | Dr. S.N. Whittleton (University of Durham), "An investigation of a Reaction Window". |
| 31.10.85 | Dr. P. Timms (University of Bristol), "Some Chemistry of Fireworks". |
| 5.11.85 | Prof. M.J. O'Donnell (Indiana-Purdue University), "New Methodology for the Synthesis of Amino Acids". |
| 7.11.85 | Prof. G. Ertl (University of Munich), "Heterogeneous Catalysis". |
| 20.11.85 | Dr. J.A.H. McBride (Sunderland Polytechnic), "A Heterocyclic Tour on a Distorted Tricycle - Biphenylene". |
| 21.11.85 | Prof. K.H. Jack (University of Newcastle), "Chemistry of Si-Al-O-N Engineering Ceramics". |
| 24.11.85 | Dr. J. Dewing (U.M.I.S.T.), "Zeolites - Small Holes, Big Opportunities". |
| 28.11.85 | Prof. D.J. Waddington (University of York), "Resources for the Chemistry Teacher". |
| 28.11.85 | Dr. S.G. Davies (University of Oxford), "Chirality Control and Molecular Recognition". |
| 28.11.85 | Dr. B.A.J. Clark (Kodak Ltd.), "Chemistry and Principles of Colour Photography". |
| 15. 1.86 | Prof. N. Sheppard (University of East Anglia), "Vibrational and Spectroscopic Determination of the Structures of Molecules Chemisorbed on Metal Surfaces". |
| 23. 1.86 | Prof. Sir J. Lewis (University of Cambridge), "Some more Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls". |

29. 1.86 Dr. J.H. Clark (University of York), "Novel Fluoride ion Reagents".

30. 1.86 Dr. N.J. Phillips (University of Technology, Loughborough, "Laser Holography".

12. 2.86 Dr. J. Yarwood (University of Durham), "The Structure of Water in Liquid Crystals".

12. 2.86 Prof. O.S. Tee (Concordia University, Montreal), "Bromination of Phenols".

13. 2.86 Prof. R. Grigg (Queens University, Belfast), "Thermal Generation of 1,3-Dipoles".

19. 2.86 Prof. G. Procter (University of Salford), "Approaches to the Synthesis of some Natural Products".

20. 2.86 Dr. C.J.F. Barnard (Johnson Matthey Group), Platinum Anti-Cancer Drug Development".

26. 2.86 Miss C. Till (University of Durham), "ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics".

27. 2.86 Prof. R.K. Harris (University of Durham), "The Magic of Solid State NMR".

5. 3.86 Dr. M. Schroeder (University of Edinburgh), "Studies on Macrocyclic Complexes".

5. 3.86 Dr. D. Hathaway (University of Durham), "Herbicide Selectivity".

6. 3.86 Dr. B. Iddon (University of Salford), "The Magic of Chemistry".

12. 3.86 Dr. J.M. Brown, "Chelate Control in Homogeneous Catalysis".

14. 5.86 Dr. P.P.R. Langridge-Smith (University of Edinburgh), "Naked Metal Clusters - Synthesis, Characterization and Chemistry".

9. 6.86 Prof. R. Schmutzler (University of Braunschweig), "Mixed Valence Diphosphorus Compounds".

23. 6.86 Prof. R.E. Wilde (Texas Technical University), "Molecular Dynamic Processes from Vibrational Bandshapes".

16.10.86 Prof. N.N. Greenwood (University of Leeds), "Glorious Gaffes in Chemistry".

29.10.86 Prof. E.H. Wong (University of New Hampshire, U.S.A.), "Coordination Chemistry of P-O-P Ligands".

5.11.86 Prof. D. Döpp (University of Duisburg), "Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes".

| | |
|---|---|
| 6.11.86 | Dr. R.M. Scrowston (University of Hull), "From Myth and Magic to Modern Medicine". |
| 13.11.86 | Prof. Sir G. Allen (Unilever Research), "Biotechnology and the Future of the Chemical Industry". |
| 20.11.86 | Dr. A. Milne and Mr. S. Christie (International Paints), "Chemical Serendipity - A Real Life Case Study". |
| 23.11.86 | Prof. H.W. Kroto (University of Sussex), "Chemistry in Stars, Between Stars and in the Laboratory". |
| 26.11.86 | Dr. N.D.S. Canning (University of Durham), "Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis". |
| 27.11.86 | Prof. R.L. Williams (Metropolitan Police Forensic Science), "Science and Crime". |
| 3.12.86 | Dr. J. Miller (Dupont Central Research, U.S.A.), "Molecular Ferromagnets; Chemistry and Physical Properties". |
| 8.12.86 | Prof. T. Dorfmuller (University of Bielefeld), "Rotational Dynamics in Liquids and Polymers". |
| 22. 1.87 | Prof. R.H. Ottewill (University of Bristol), "Colloid Science a Challenging Subject". |
| 28. 1.87 | Dr. W. Clegg (University of Newcastle-upon-Tyne), "Carboxylate Complexes of Zinc; Charting a Structural Jungle". |
| 2. 2.87 | Prof. A. Thompson (University of East Anglia), "Metalloproteins and Magnetooptics". |
| 5. 2.87 | Dr. P. Hubbersley (University of Nottingham), "Demonstration Lecture on Various Aspects of Alkali Metal Chemistry". |
| 11. 2.87 | Dr. T. Shepherd (University of Durham), "Pteridine Natural Products; Synthesis and Use in Chemotherapy". |
| 12. 2.87 | Dr. P.J. Rodgers (I.CI.Billingham), "Industrial Polymers from Bacteria". |
| 17. 2.87 | Prof. E.H. Wong (University of New Hampshire, U.S.A.), "Symmetrical Shapes from Molecules to Art and Nature". |
| 19. 2.87 | Dr. M. Jarman (Institute of Cancer Research), "The Design of Anti Cancer Drugs". |
| 4. 3.87 | Dr. R. Newman (University of Oxford), "Change and Decay: A Carbon-13 CP/MAS Study of Humification and Coalification Processes". |
| 5. 3.87 | Prof. S.V. Ley (Imperial College), "Fact and Fantasy in Organic Synthesis". |

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|---|---|
| 15. 3.87 | Prof. R.F. Hudson (University of Kent), "Homolytic Rearrangements of Free Radical Stability". |
| 17. 3.87 | Prof. R.F. Hudson (University of Kent), "Aspects of Organophosphorus Chemistry". |
| 6. 5.87 | Dr. R. Bartsch (University of Sussex), "Low Co-ordinated Phosphorus Compounds". |
| 7. 5.87 | Dr. M. Harmer (I.C.I. Chemicals and Polymer Group), "The Role of Organometallics in Advanced Materials". |
| 9. 5.87 | Prof. F.G. Bordwell (Northeastern University, U.S.A.), "Carbon Anions, Radicals, Radical Anions and Radical Cations". |
| 11. 5.87 | Prof. S. Pasynkiewicz (Technical University, Warsaw), "Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium". |
| 11. 5.87 | Dr. R.D. Cannon (University of East Anglia), "Electron Transfer in Polynuclear Complexes". |
| 12. 5.87 | Dr. E.M.Goodger (Cranfield Institute of Technology), "Alternative Fuels for Transport". |
| 24. 5.87 | Prof. S.M. Roberts (University of Exeter), "Synthesis of Novel Antiviral Agents". |
| 26. 5.87 | Dr. C. Krespan (E.I. Dupont de Nemours), "Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry". |
| 27. 5.87 | Dr. M. Blackburn (University of Sheffield), "Phosphonates as Analogues of Biological Phosphate". |
| 15.10.87 | Dr. M.J. Winter (University of Sheffield), "Pyrotechnics (Demonstration Lecture)". |
| 22.10.87 | Prof. G.W. Gray (University of Belfast), "Liquid Crystals and their Applications". |
| 3.11.87 | Dr. J. Howard (I.C.I. Wilton), "Chemistry of Non-Equilibrium Processes". |
| 4.11.87 | Mrs. C. Mapletoft (Durham Chemistry Teachers Centre), "Salter's Chemistry". |
| 5.11.87 | Dr. A.R. Butler (University of St. Andrews), "Chinese Alchemy". |
| 19.11.87 | Prof. P.G. Seebach (E.T.H. Zurich), "From Synthetic Methods to Mechanistic Insight". |
| 23.11.87 | Dr. J. Davidson (Herriot-Watt University), "Metal Promoted Oligomerisation Reactions of Alkynes". |
| 26.11.87 | Dr. D.H. Williams (University of Cambridge), "Molecular Recognition". |

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|---|---|
| 29.11.87 | Mrs. E. van Rose (Geological Museum), "Chemistry of Volcanoes". |
| 10.12.87 | Dr. C.J. Ludman (University of Durham), "Explosives". |
| 16.12.87 | Mr. R.M. Swart (I.C.I.), "The Interaction of Chemicals with Lipid Bilayers". |
| 21. 1.88 | Dr. F. Palmer (University of Nottingham), "Luminescence (Demonstration Lecture)". |
| 28. 1.88 | Dr. A. Cairns-Smith (Glasgow University), "Clay Minerals and the Origin of Life". |
| 11. 2.88 | Prof. J.J. Turner (University of Nottingham), "Catching Organometallic Intermediates". |
| 18. 2.88 | Dr. K. Borer (University of Durham Industrial Research Labs.), "The Brighton Bomb - A Forensic Science View". |
| 25. 2.88 | Prof. A. Underhill (University of Bangor), "Molecular Electronics". |
| 3. 3.88 | Prof. W.A.G. Graham (University of Alberta, Canada), "Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds". |
| 7. 3.88 | Mr. P. Lacey (Durham Chemistry Teachers Centre), "Double Award Science". |
| 16. 3.88 | L. Bossons (Durham Chemistry Teachers Centre), "GCSE Practical Assesment". |
| 7. 4.88 | Prof. M.P. Hartshorn (University of Canterbury, New Zealand), "Aspects of Ipso-Nitration". |
| 13. 4.88 | Mrs. E. Roberts (SASTRO Officer for Sunderland), "Talk - Durham Chemistry Teacher's Centre - "Links Between Industry and Schools". |
| 19. 4.88 | Graduate Chemists (Northeast Polytechnics and Universities), "R.S.C. Graduate Symposium". |
| 25. 4.88 | Prof. D. Birchall (I.C.I. Advanced Materials), "Environmental Chemistry of Aluminium". |
| 27. 4.88 | Dr. R. Richardson (University of Bristol), "X-Ray Diffraction from Spread Monolayers". |
| 27. 4.88 | Dr. J.A. Robinson (University of Southampton), "Aspects of Antibiotic Biosynthesis". |
| 28. 4.88 | Prof. A. Pines (University of California, Berkeley, U.S.A), "Some Magnetic Moments". |
| 11. 5.88 | Dr. J. Sodeau (University of East Anglia), "Durham Chemistry Teacher's Centre Lecture: "Spray Cans, Smog and Society"". |

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|---|---|
| 11. 5.88 | Dr. W.A. McDonald (I.C.I. Wilton), "Liquid Crystal Polymers". |
| 18. 5.88 | Prof. C.A. Nieto de Castro (University of Lisbon and Imperial College), "Transport Problems of Non-Polar Fluids". |
| 8. 6.88 | Prof. J.P. Majoral (University Paul Sabatier), "Stabilisation by Complexation of Short-lived Phosphorus Species". |
| 29. 6.88 | Prof. G.A. Olah (University of Southern California), "New Aspects of Hydrocarbon Chemistry". |
| 6. 7.88 | Prof. H.F. Koch (Ithaca College, U.S.A.), "Does the E2 Mechanism Occur in Solution?". |
| 29. 7.88 | Dr. M.E. Jones (Durham Chemistry Teacher's Centre), "GCSE Chemistry A Level Post-mortem". |

## FIRST YEAR INDUCTION COURSE

The course consists of a series of one hour lectures, explaining the uses and limitations of the various services available in the Department.

1. Departmental Organisation - Dr. E.J.F. Ross.
2. Safety Matters - Dr. M.R. Crampton.
3. Electrical appliances and infrared spectroscopy.
4. Chromatography and microanalysis - Mr. T.F. Holmes.
5. Atomic adsorptiometry and inorganic analysis - Mr. R. Coult.
6. Library Facilities - Mr. R.B. Woodward.
7. Mass Spectroscopy - Dr. M. Jones.
8. Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews.
9. Glass blowing techniques - Mr. R. Hart and Mr. G. Haswell.