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ELECTROCHEMICAL, PLASMA AND SYNTHETIC STUDIES OF DITHIADIAZOLIUM
AND RELATED COMPOUNDS

Michael Ian Hansford

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

October 1989



31 OCT 1990

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 $[(\text{PhCN}_2\text{S}_2)_2\text{Cl}[\text{S}_3\text{N}_3]$, $[\text{PhCN}_2\text{S}_2][\text{S}_3\text{N}_3]$ and $[\text{PhCN}_2\text{S}_2][\text{S}_3\text{N}_3]\text{Cl}$, and an *ab initio* Molecular Orbital Study of Bonding in $[\text{PhCN}_2\text{S}_2][\text{S}_3\text{N}_3]$, 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 $[\text{Ph}\overline{\text{CNSSN}}]\text{AsF}_6$ and $(\text{Me}\overline{\text{CNSSN}})_2$ have been determined and a variety of new 1,2 and 1,3 dithiadiazolium derivatives synthesised including $[\text{CH}_3\text{CH}_2\text{CH}_2\overline{\text{CNSSN}}]\text{Cl}$ and $[(\text{CH}_3)_3\overline{\text{CCNSSN}}]\text{Cl}$. $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$ has a longer S-S bond compared to $[\text{PhCN}_2\text{S}_2]\text{Cl}$ 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 $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}_2\text{S}_2]\text{Cl}$ and $[(\text{CH}_3)_3\overline{\text{CCN}_2\text{S}_2}]\text{Cl}$ which gave new paramagnetic liquids has led to a more detailed understanding of the bonding and structure in these ring systems.

Dimeric aryldithiadiazoles $(\overline{\text{RCNSSN}})_2$ (R = Ph or ρ -ClPh) were treated with atomic nitrogen, generated in a cool DC plasma, to form the corresponding dithiatiazine dimers by nitrogen insertion into the S-S bond; Alkyl derivatives (R = Me, propyl, but) gave polymeric products.

Dithiadiazolium salts $[\overline{\text{RCNSSN}}]^+\text{X}^-$ (R = Ph, ρ -ClPh, X = Br, I, CN or S_3N_3) also reacted with nitrogen plasma to give high yields of the respective dithiatiazine. Structural criteria for these reactions are discussed.

The electrochemistry of $(\overline{\text{RCNSSN}})_2$, $(\overline{\text{RCNSNS}})_2$, $[\overline{\text{RCNSSN}}]\text{X}$ (X = Cl^- or AsF_6^-) and $[\overline{\text{RCNSNS}}]\text{AsF}_6$ (R = Ph, ρ -ClPh, ρ -CH₃Ph, ρ -CNPh, anthracene, Me, propyl, but, Cl_3C , CF_3) were studied by cyclic voltammetry.

A new S_2N^+ salt, $\text{S}_2\text{NCF}_3\text{SO}_3$, was synthesised from the reaction of AgCF_3SO_3 with $(\text{NSCl})_3$ and sulphur in liquid SO_2 and its usefulness as a reagent compared to S_2NAsF_6 and S_2NSbCl_6 . The crystal structure of $\text{S}_3\text{N}_2\text{CF}_3\text{SO}_3$ was determined, crystals of which were isolated from the same reaction mixture and an equilibrium between S_2N^+ , SN^+ and $\text{S}_3\text{N}_2^{++}$ 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, unparalleled 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 (N₂Cl₂)₃ was discovered by Liebig and Wöhler, whilst Gregory synthesised S₄N₄ for the first time in 1835³. However, further advances in inorganic heterocyclic chemistry were slow.

Impure S₃N₂Cl₂ was first prepared in 1851⁴, but was not properly characterised until the 1880's by Demarcay, who also described (NSCl)₃, S₄N₃Cl and S₆N₄Cl₂⁵. 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 preparation⁶. 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-Goehring's classic monograph "Ergebnisse und Probleme der Chemie der Schwefel Stickstoffverbindungen" in 1957⁸. A definitive review of cyclic sulphur/nitrogen compounds has been recently published by the Gmelin Institute⁹, 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 excitement generated by the development of high temperature superconductors recently¹⁹, 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 diodes²⁰, thought to be of potential commercial significance, and in the use of $(SN)_x$ batteries²¹. 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 $S_5N_5^+$ salts⁴⁶. There have also been numerous attempts to find suitable precursors to $(SN)_x$ analogues²³ 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 ring²⁴ and the reactions of the small building block species S_2N^+ with various unsaturated species to give dithiazolium cations²⁵ 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 acetylenes²⁸ and the bonding²⁹ and pyrolysis³⁰ products of S_4N_4 and this trend is likely to continue. However it is important to emphasize 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 nmr³¹ and esr²⁷ together with the wider availability and use of electrochemical methods and X ray analysis.

The use of MNDO³², 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 species³⁵ and the discovery of the 14π electron $S_5N_5^+$ were key developments in explaining electron distribution and bonding types. This lends a degree of predictability 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 likely 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/B⁴⁰ 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 7π 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 low⁴¹, 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 block⁴² for dithiadiazolium and dithiazolium salts. It reacts in a facile cycloaddition to many alkynes and nitrile derivatives⁴³. 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 reports⁴⁴. 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, however, is not the case with S/N structures 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 $(\text{NSCl})_3$ 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 years⁵. 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 P₄O₁₀ 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 ^1H 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 $(\text{CH}_3)_4\text{Si}$ (TMS) internal reference at 0 ppm. The upfield direction was taken as negative. The ^1H 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 Weissenberg 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 $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{Å}$).

Programs (SHELXTL 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^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 BaClO₄ 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 6×10^{-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 SO₂ and AsF₅ 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 SF₄, 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 previously¹. 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 magnetic 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.*

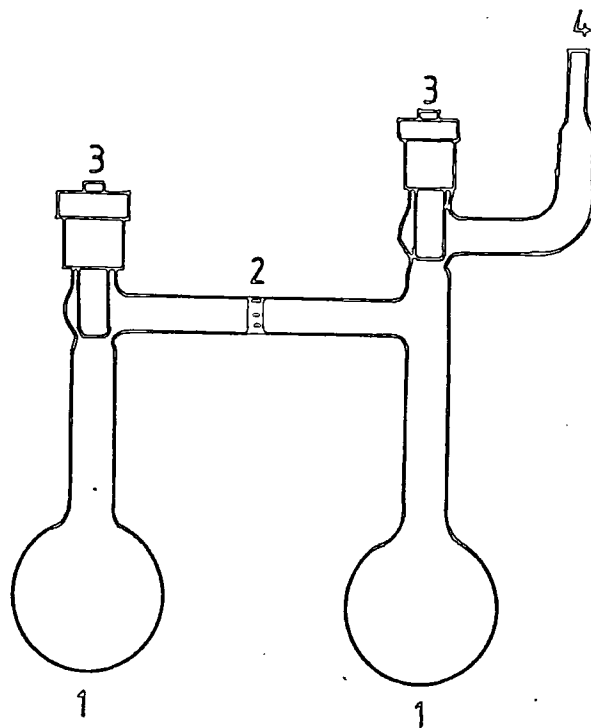
This type of apparatus has already been described in the literature². The closed extractor (designed by Dr. Z.V.Hauptman) can be used for the exhaustive or partial extraction of moisture sensitive materials with relatively volatile solvents, eg. SO₂, CCl₄, or CH₃CN. It may also be used in conjunction with a dog for the slow addition of relatively insoluble reagents by means of continuous 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 CaH₂ 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 $0.1\text{M Ag}^+/\text{Ag}$ or $0.01\text{M Ag}^+/\text{Ag}$ 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 ($0.2\text{ mol dm}^{-1} \text{ Bu}_4\text{NBF}_4$) 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 $0.252\text{V} \pm 0.005\text{V}$.

(ii) In SO_2 ; For pressurised systems, an adaption of a reference electrode previously described was used¹.

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 $0.33 \text{ V} \pm 0.005\text{V}$.

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 acetonitrile.

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 AgBF₄ solution in MeCN.
4. Ag metal attached 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.

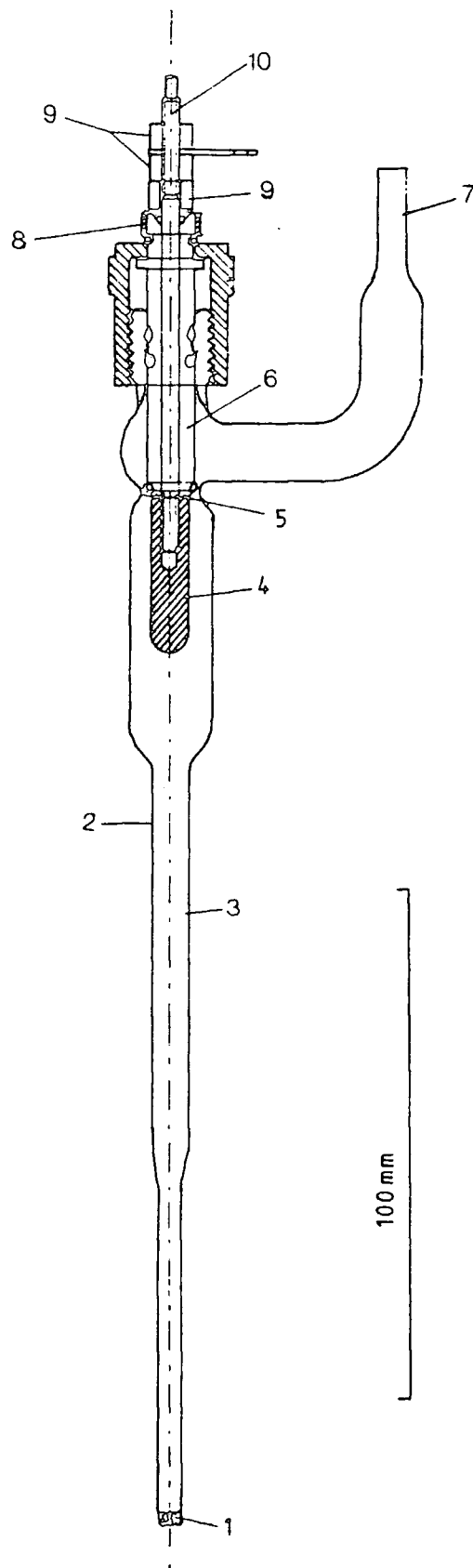
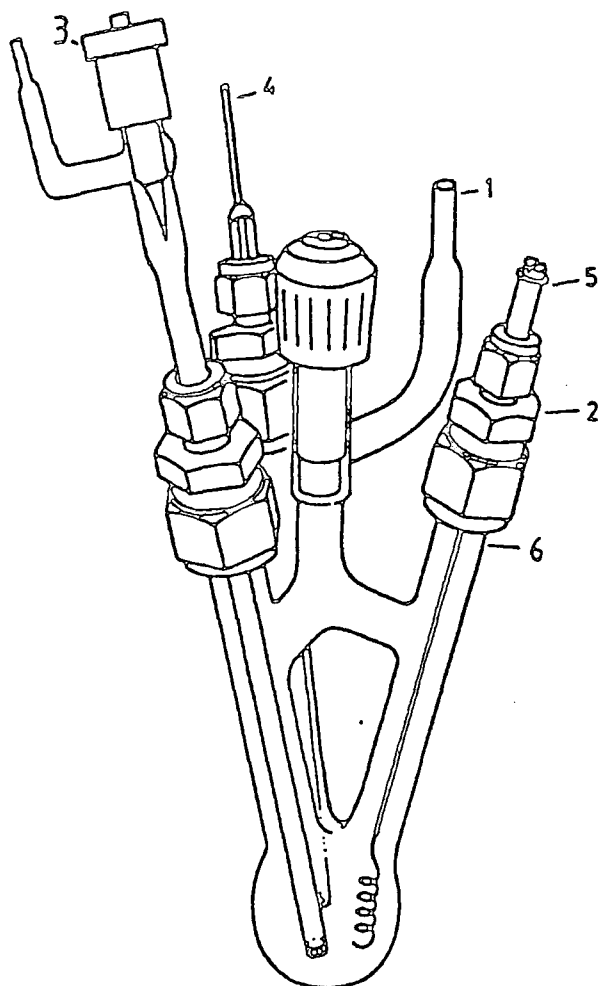


Figure 2.3. Three limbed electrochemical cell used for Cyclic Voltammetry.



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. *Electrochemical 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 Maguire³, 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 continuous 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, ν_{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 Maguire³. $S_3N_2Cl_2$, 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) ν_{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 Maguire³ 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 sunlight². $S_3N_2Cl_2$ (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 al⁴ 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 continuous stream of dry chlorine gas passing through the solution at approximately 60 mm²s⁻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, $\nu_{max} = 1600w, 1390m, 1350w, 1150m, 1070m, 1028m, 1000w, 922m, 893s, 840s, 785s, 701s, 690msh, 549s, 510w, 472w \text{ cm}^{-1}$.

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 couple⁴ 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 sublimator. $(PhCN_2S_2)_2$ (yield = 3.2 g, 53 %) sublimed (10^{-3} Torr, $120^\circ C$, cold finger = $10^\circ C$) 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, $\nu_{max} = 1595mw, 1320m, 1240m, 1235m, 1185w, 1175w, 1160w, 1145msh, 1140s, 1075m, 1023m, 1003w, 970br, 922w, 896w, 836m, 805s, 780vs, 772s, 720m, 690s, 686s, 655s, 510s \text{ cm}^{-1}$.

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 al⁴. NH_4Cl (20.0 g, 0.37 mol) was suspended in SCl_2 (150ml, 2.34 mol), to which 4-chlorobenzonitrile (10.0 g, 0.07 mol) was added. This was refluxed for 5h ($85^\circ C$) under a blanket of Cl_2 . The mixture was then cooled to $-20^\circ C$, filtered and the crude product washed with 2x 10ml aliquots of dry diethyl ether followed by continuous extraction with SO_2 . The product was then recrystallised from SO_2 , (yield = 6.15g, 35%).

C₇H₅Cl₂N₂S₂ 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%.

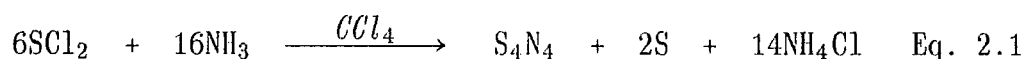
Infrared spectrum, ν_{\max} = 1595br, 1412wsh, 1400w, 1283mw, 1174m, 1152ms, 1091s, 1010s, 960w, 919mw, 890s, 842vs, 733vs, 725s, 682ms, 540ms, 495m, 489w cm⁻¹.

2.4.7. S₂NAsF₆ - *Dithiazyl hexafluoroarsenate.*

This was prepared by the method described by Passmore et al⁵ from S₄N₄, S₈ and AsF₅. Yields of 70 % were obtained when the crude product was recrystallised from SO₂. It was noted that better and purer yields were also obtained when large crystals of S₂NAsF₆ were allowed to grow first.

2.4.8. S₄N₄ - *Tetrasulphur tetranitride.*

This was prepared according to the method described Jolly and Villena-Blanco⁶. S₂Cl₂ (50 ml, 0.62 mols) was chlorinated in CCl₄ (1400ml) to give SCl₂. 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.



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 NH₄Cl to leave green coloured S₄N₄ which was then air dried for several days. This solid was then soxhlet extracted with dioxane (400ml) for 6h to leave behind any further NH₄Cl, Yield = 30 g. Further purification was then achieved by several recrystallisations from benzene. Even purer S₄N₄ may then be obtained by a sublimation.

Analysis; S₄N₄ requires N 30.40%, found N 30.35%. Infrared spectrum, ν_{\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.

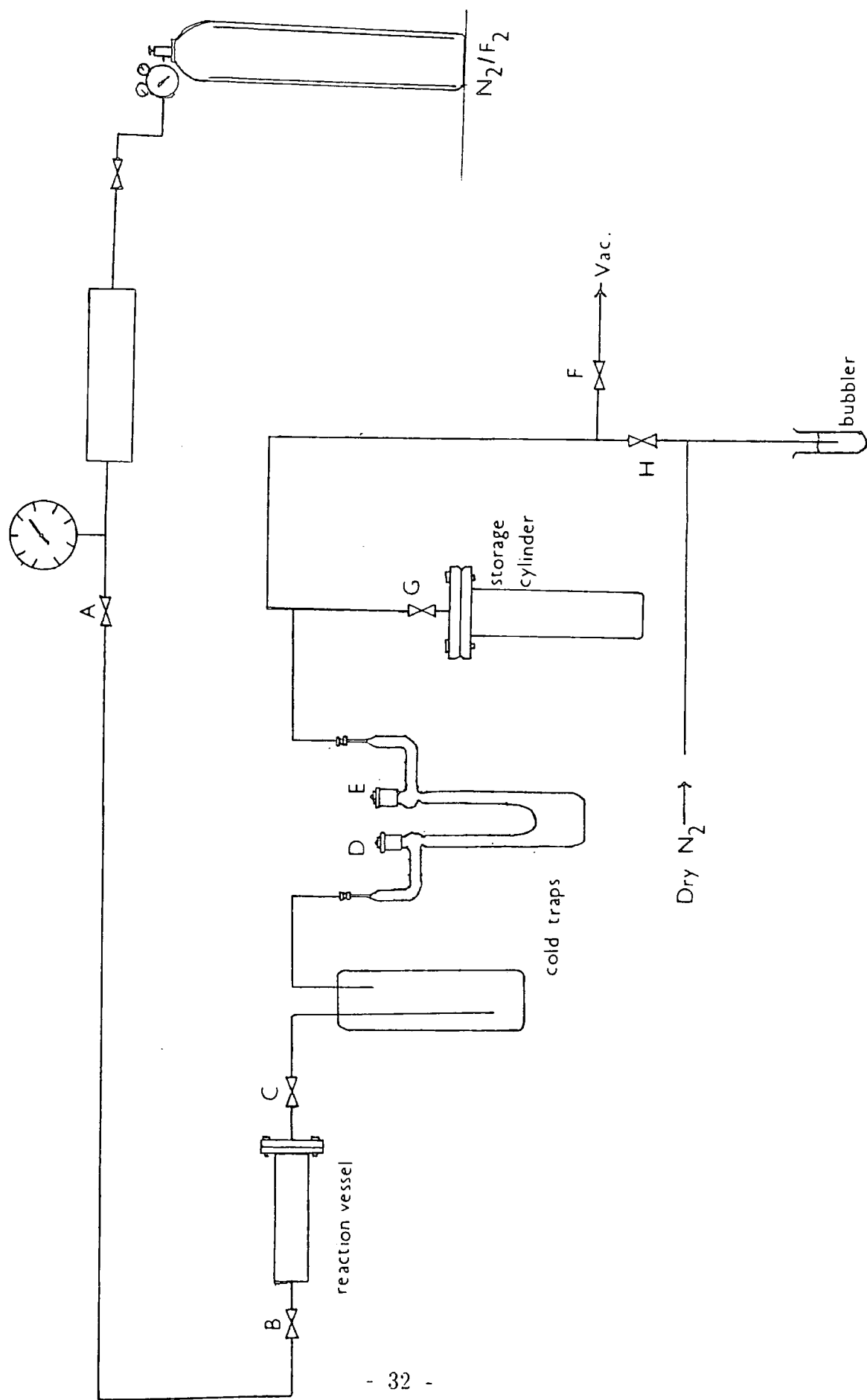
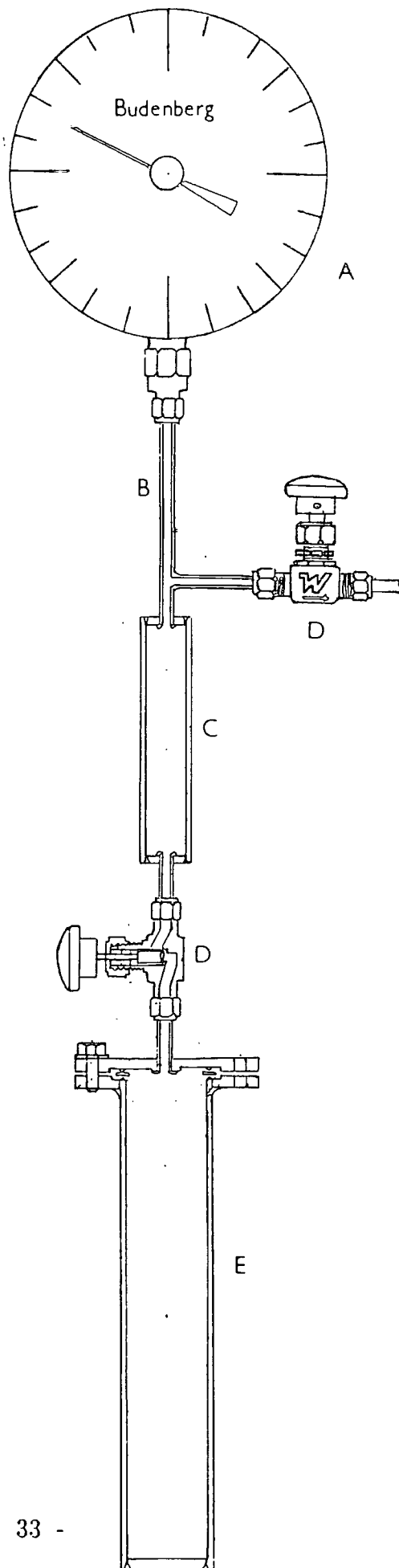
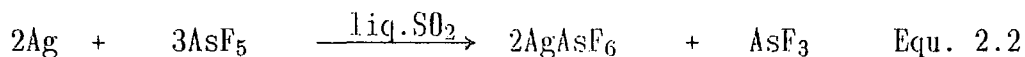


Figure 2.5. Storage vessel and Budenberg gauge.



2.5.2. *Silver hexafluoroarsenate*. AgAsF_6 - This was prepared by the direct reaction of AsF_5 with Ag as described in the literature¹ according to equation 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 aliquots. 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, ν_{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 scrupulously 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 $100^\circ C$ 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, $((\text{CH}_3)_3\text{Si})_2\text{NLi}$ - 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* - $\text{ClC}_6\text{H}_4\text{CN}$ - 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 distillation⁷ 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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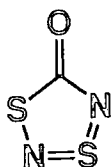
CHAPTER THREE.

DITHIADIAZOLIUM SALTS AND RELATED HETEROCYCLES.

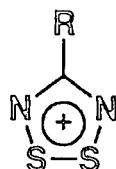
3.1. INTRODUCTION.

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 $(SN)_x^1$.

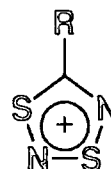
For the five membered C/S/N heterocycles of formula CN_2S_2 there are, however, just three known isomers:-



I.

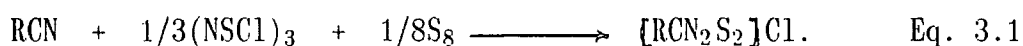


II.

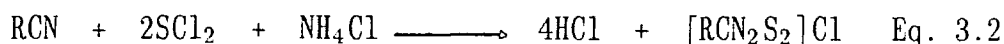


III.

These are the 5-oxo, 1,3,2,4, 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 $(Cl_3\overset{c}{C}N_2S_2)Cl^{3,4}$.



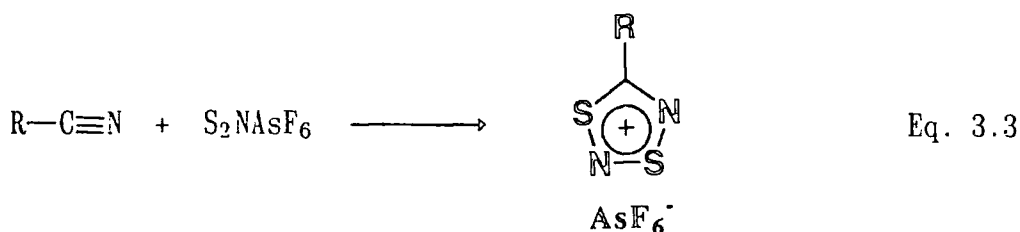
The best route, however, involves the reaction of an organic nitrile with SCl_2 and NH_4Cl under a blanket of dry chlorine⁵. The proposed mechanism for this reaction is the *in situ* formation of 'NSCl'. This is a more convenient synthetic method since SCl_2 is much more readily accessible than $(\text{NSCl})_3$ and yields are generally greater.



There are several other less important methods, eg. the reaction of NaN_3 with $\text{RCN}(\text{NSCl})_2$ to obtain (II)⁶. The 1,3 isomer has been prepared from the reaction of S_4N_4 with Br_2 and CS_2 at room temperature⁷ but until the synthesis of S_2NSbCl_6 appeared in 1978⁸, very few examples were known.

The S_2N^+ cation, as the more useful AsF_6^- salt⁹, reacts via a simple

(4 + 2) symmetry allowed cycloaddition¹⁰ with 1,3, dipoles or ^Ddiels-^Alder unsaturated organic groups, such as $\text{RC}\equiv\text{N}$ and $\text{RC}\equiv\text{CR}$.



This reaction is an example of more general routes to cations containing the 1,3,2,5 dithiadiazolium and the 1,3,2 dithiazolium rings¹¹. Both of the dithiadiazolium isomers may be readily reduced to the corresponding dithiadiazole systems - remarkably stable 7π electron free radicals. Phenyl dithiadiazole, $(\text{PhCN}_2\text{S}_2)_2$, was the first reported example of such a radical, its dimer being formed by the sodium thiocyanate reduction of $[\text{PhCN}_2\text{S}_2]\text{Cl}$ ¹².

Esr studies showed that a solution of $(\text{PhCN}_2\text{S}_2)_2$ 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 nuclei¹³. No dimer units were detected above 250K in solution. As indicated by Mews¹⁴, 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.

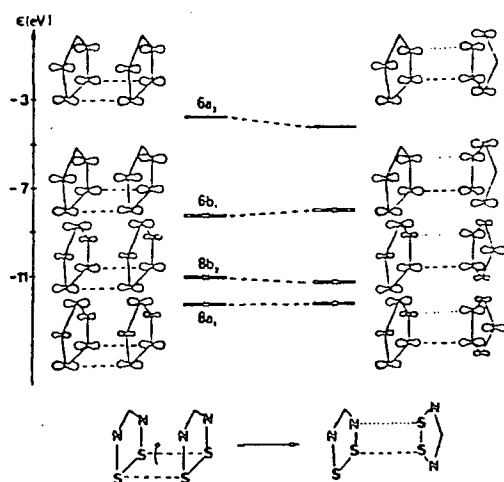


Figure 3.1. $\overline{\text{RCN}_2\text{SSN}}$ Orbital Energy Levels.

Indeed actual conformation depends more on subtle effects such as secondary interactions and packing forces. Further MNDO calculations¹⁵ 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 π and σ orbitals and finally the orbitals

associated with the ligands, all of which indicates that dithiadiazoles are reasonably 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, type B, depending on the anion. The harder²⁹ the anion the more brightly coloured the salt, for instance, $\text{PhCN}_2\text{S}_2\text{AsF}_6^-$ - bright orange, $\text{PhCN}_2\text{S}_2\text{Br}^-$ - dark red and $\text{PhCN}_2\text{S}_2\text{I}^-$ - black⁵.

The first crystal structure of a dithiadiazolium system, that of $[\text{Cl}_3\text{CN}_2\text{S}_2]^+\text{Cl}^-$ appeared in 1977⁴ 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. $[\text{PhCN}_2\text{S}_2]_2[\text{S}_3\text{N}_3]^{25}$ etc., the compound $[\text{PhCN}_2\text{S}_2]\text{AsF}_6^-$ was synthesised by simple metathesis and its crystal structure determined. The AsF_6^- anion is relatively hard and $[\text{PhCN}_2\text{S}_2]\text{AsF}_6^-$ 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 - ClPhCN₂S₂)₂*. - Bright orange $[p\text{-ClPhCN}_2\text{S}_2]^+\text{Cl}^-$ was prepared according to literature methods from p - ClPhCN, NH_4Cl and SCl_2/Cl_2 ⁵.

A suspension of [p - ClPhCN₂S]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 (PhCN₂S₂)₂. Found; C 38.51, H 1.79, N 13.46, S 28.78, Cl 15.96;

C₇H₄N₂S₂ Cl requires C 38.97, H 1.86, N 12.99, S 29.74, Cl 16.4; m.s Cl m/e 215 11% (PhCN₂S₂)⁺, m/e 137 100% (ClPhCN₂)⁺; ir ν_{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.

[CH₃CH₂CH₂CN^{SSN}] Cl was prepared in an analogous manner to that of [PhCN₂S₂]Cl. n-Butylnitrile, CH₃CH₂CH₂CN, (32ml, 0.37mol, ρ=0.7936) was refluxed in a suspension of NH₄Cl (20.0g, 0.37mol) in SCl₂ (120ml, 1.89mol) for 5h under a blanket of dry chlorine. After refluxing, the reaction mixture was cooled to 0°C and filtered. Orange

[CH₃CH₂CH₂CN₂S₂]Cl (7.1g, 10.5%) was obtained after SO₂ extraction of the crude solid. [CH₃CH₂CH₂CN₂S₂]Cl (1.5g, 8.22mmol) was stirred with a suspension of excess Zn/Cu couple (2.0g, 15.5mmol) in liquid SO₂ for 6h at room temperature. The SO₂ 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 literature³, (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.

$[(CH_3)_3CNSNS]AsF_6$ was prepared from S_2NASF_6 and t-BuCN in SO_2 according to literature¹⁶, (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 literature¹⁶. 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 $[\text{PhCN}_2\text{S}_2]\text{Cl}$ required some stirring before it dissolved. On addition of the AgAsF_6 solution to the $\text{PhCN}_2\text{S}_2\text{Cl}$, 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 $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$ (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%; $\text{C}_7\text{H}_5\text{N}_2\text{S}_2\text{AsF}_6$ requires C 22.69%, H 1.35%, N 7.57%, S 17.32%, F 30.80%, As 20.26%.

(ii). **Crystal Data** - $\text{C}_7\text{H}_5\text{N}_2\text{S}_2\text{AsF}_6$, $M_r = 370.2$,

Monoclinic, Space group $\text{P2}_1/\text{c}$.

$a = 13.515(2)$, $b = 5.7573(7)$, $c = 15.175(2)\text{\AA}$, $\beta = 94.83(1)^\circ$.

$U = 1176.6\text{\AA}^3$, $Z = 4$, $D_c = 2.089 \text{ gcm}^{-3}$.

$F(000) = 720$, $\lambda(\text{MoK}\alpha) = 0.71073\text{\AA}$ (graphite monochromator), $T = 295^\circ\text{C}$, $\mu = 3.28\text{mm}^{-1}$.

Intensity data from a crystal of dimensions $0.06 \times 0.54 \times 0.8 \text{ mm}$ mounted under N_2 in a sealed Lindeman capillary were collected on a Siemens AED2 diffractometer (ω/θ scans with on-line profile fitting, $2\sigma_{\text{max}} = 50^\circ$, 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 $F > 4\sigma_c(F)$ (σ_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 $\text{C-H} = 0.96\text{\AA}$ on ring angles external bisectors.

$U(\text{H}) = 1.2\text{eq}(\text{C})$.

Weights were assigned as $w^{-1} = \sigma^2(F) = \sigma_c^2 + 9.55G + 216G^2 - 12S + 4S^2 + 9GS$.
($G = F_0/F_{\max}$, $S = \sin\theta/\sin\theta_{\max}$).

An isotropic extinction parameter X was refined to $X = 7(3) \times 10^{-7}$, where $F_c' = F_c / (1 + XF_c^2 / \sin^2\theta)^{1/4}$. 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 $e\text{\AA}^{-3}$. 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.

[tButylCNSSN]AsF₆ was prepared by a metathesis procedure similar to that in 3.2.5. [(CH₃)₃CCN₂S₂]AsF₆ (0.5g, 2.54mmol) was placed in one half of a dog with AgAsF₆ (0.76g, 2.54mmol) in the other. SO₂ was condensed into both sides and the two solutions brought together, stirred for 5h at room temperature and filtered. The SO₂ solution yielded an orange/yellow solid (0.85g, 96%). [(CH₃)₃CCN₂S₂]AsF₆ was identified by infra-red. Found C 17.26, H 2.54, N 7.61, S 18.41; C₅H₉N₂S₂AsF₆ 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.

[PhCH₂CN₂S₂]Cl was prepared in an analogous manner to that described in the literature⁵. C₆H₅CH₂CN (22.3ml, 0.185mmol, $\rho=0.972$) was syringed against dry nitrogen into a suspension of oven dried NH₄Cl (10.0g, 0.185mmol) in SCl₂ (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 [PhCN₂S₂]AsF₆.

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 ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for the hydrogen atoms.

Atom	\underline{x}	\underline{y}	\underline{z}	\underline{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 ($\times 10^4$) for $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$.

Atom	\underline{x}	\underline{y}	\underline{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 ($\text{\AA}^2 \times 10^3$) for $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$.

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

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; $\text{C}_7\text{H}_5\text{N}_2\text{S}_2\text{AsF}_6$ requires C 22.70, H 1.35, N 7.57, S 17.32. i.r. ν_{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 & 400 cm^{-1} belong to AsF_6^-)

3.2.9. Preparation of $(\text{CH}_3\text{CN}_2\text{S}_2)_2$ from $[\text{CH}_3\overline{\text{CNSSN}}]\text{Cl}^{13}$

$(\text{CH}_3\text{CN}_2\text{S}_2)_2$ (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; $\text{C}_2\text{H}_3\text{N}_2\text{S}_2$ requires C 20.1, H 2.5, N 23.5, S 53.8.

3.2.10. Crystal structure of $(\text{CH}_3\text{CN}_2\text{S}_2)_2$ ¹⁷.

(i). *Crystal Growth*. - A suitable crystal was isolated from a sealed pyrex tube containing *ca.* 60 mg of $(\text{CH}_3\text{CN}_2\text{S}_2)_2$ 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 $(\text{CH}_3\text{CN}_2\text{S}_2)_2$ 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 $(\text{CH}_3\text{CN}_2\text{S}_2)_2$ to direct sunlight. A small number of very thin platelets up to 1mm formed but these were most likely crystals of acetamide, $\text{CH}_3\text{CO.NH}_2$ - a product of hydrolysis by traces of chemisorbed moisture in the pyrex tube (despite thorough prior drying).

(ii) *Crystal Data*. - $\text{C}_4\text{H}_6\text{N}_4\text{S}_4$, $M = 238.4$,

Triclinic, space group $P \bar{1}$,

$a = 11.296(1)$, $b = 12.498(1)$, $c = 14.647(2)\text{\AA}$, $\alpha = 72.06(1)$,

$\beta = 77.85(1)$, $\gamma = 77.30(1)^\circ$,

$U = 1896.3\text{\AA}^3$, $Z = 8$, $D_c = 1.670$,

$F(000) = 976$, $\lambda(\text{Cu } K_\alpha) = 1.54184\text{\AA}$ (graphite monochromator),

$\mu = 8.74 \text{ mm}^{-1}$, $T = 295 \text{ K}$.

Intensity data from a crystal of dimensions $0.5 \times 0.2 \times 0.2 \text{ mm}$ mounted under N_2 in a sealed quartz capillary were collected on a Siemens AED2 diffractometer (ω/θ 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 $F > 4\sigma_c(F)$ (σ_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, 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 $F_c' = F_c / (1 + X F_c^2 / \sin 2\theta)^{1/4}$. Final residues are; $R = 0.040$, $R' = (\sum w \Delta^2 / \sum w F_o^2)^{1/2} = 0.060$, 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 $-0.33e\text{\AA}^{-3}$. 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_2NAsF_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. ν_{\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 AgAsF₆ (0.384g, 1.29mmol) and [CH₃CN₂S₂]Cl (0.2g, 1.29mmol) in liquid SO₂. A brown solution resulted, which on filtering and removal of SO₂ gave a brown solid (0.24g, 61%) identified as [CH₃CN₂S₂]AsF₆ by i.r. and elemental analysis. C₂H₃N₂S₂AsF₆ 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 (MeCN₂S₂)₂. Bond lengths (Å) 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)

Table 3.6. Distances (Å) and angles (°) of MeCNS⁺SSN⁻. The tabulated data are averages of values pertaining to 8 dithiadiazolium rings of the asymmetric 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 ($\times 10^4$);

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 method¹⁸. S₂NAsF₆ (0.41g, 1.53mmol) was reacted with excess MeCN (2ml) in liquid SO₂. The solution was stirred for 1h, and after removal of the SO₂ and the excess MeCN under vacuum left a light brown residue (0.463g, 98%) which was identified as [CH₃CNSNS]AsF₆ by i.r.

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

Cl₃CCN (0.175g, 1.2mmol, ρ=1.44) and S₂NAsF₆ (0.324g, 1.2mmol) were reacted together in liquid SO₂. Although no immediate colour change was observed, the solution turned cherry red after stirring for 48h. On removal of the SO₂, 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) measurements 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 $-20^{\circ}C$ to $400^{\circ}C$ was possible by surrounding the analysis cell with a cooling coil connected to a Haake F3 bath circulator and insulating it with polystyrene. Traces were usually run at $4^{\circ}/min$ and a chart speed of $10mm/min$. For accurate determination of ΔH_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:-

$$Z_w A_o = \rho \cdot A_o / (\pi m k T)^{1/2}$$

Z_w = collision frequency,	ρ = 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 (RCN₂S₂)₂, (R = t-Butyl, Propyl, Ph, Me, CF₃)

The thermodynamic data ^{are} summarised in Table 3.1¹² 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 ($\pm 1.0^\circ\text{C}$) 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 tbutylCN₂S₂ $\geq 170^\circ\text{C}$, PhCN₂S₂ $\geq 190^\circ\text{C}$. 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. S₅N₅Cl¹⁹. The products of pyrolysis appeared to consist of mixtures of polymer and parent nitrile detected by smell.

Figure 3.2. DSC trace for ΔH_{vap} measurements.

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

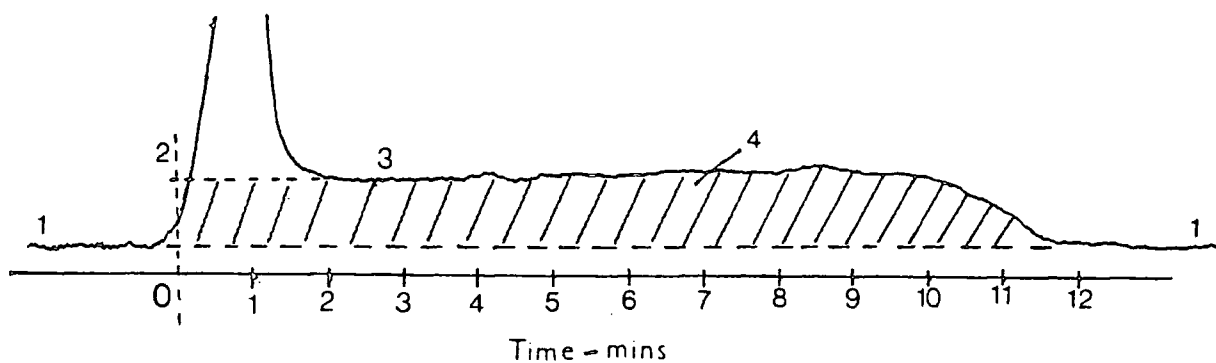
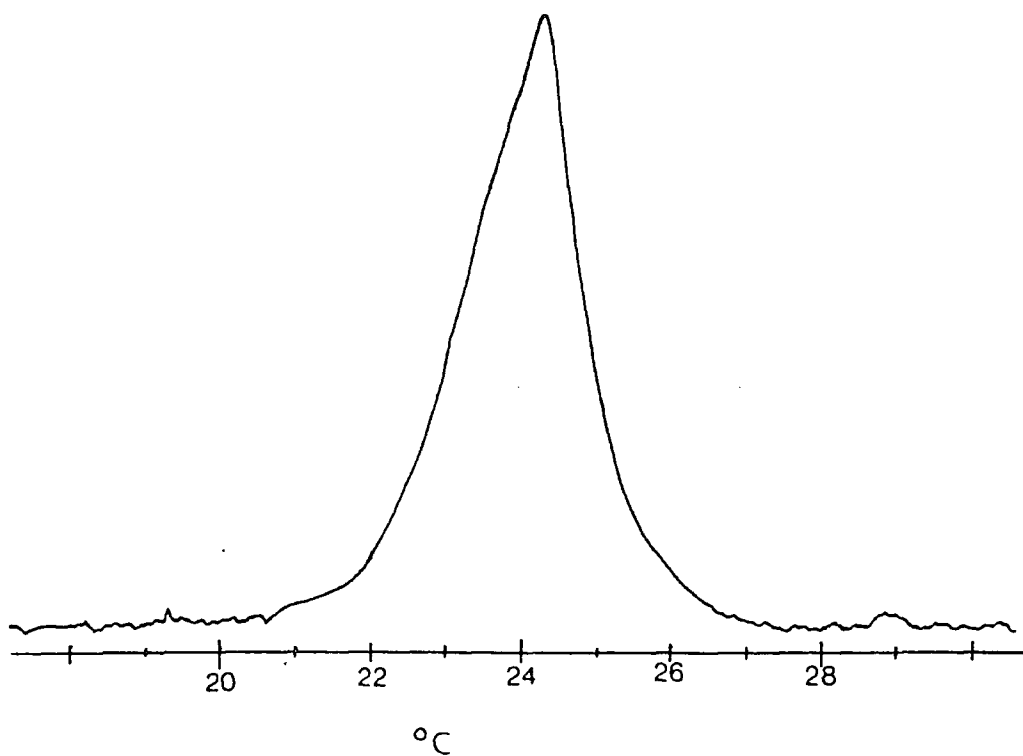


Figure 3.3. Typical DSC trace for ΔH_{fus} measurements - $t\text{-BuCNSN}$.

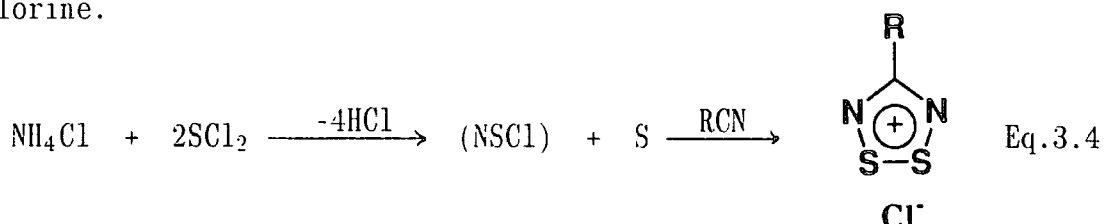


To evaluate ΔH_{vap} the evaporation of $(\text{RCN}_2\text{S}_2)_n$ ($n \leq 2$, R = t-butyl, propyl) in the liquid state at 423.2K through an orifice area *ca.* 0.0125cm^2 into an atmosphere of flowing argon (linear flow rate = $1\text{cm}^{-1}\text{S}^{-1}$) obeyed an expected zero order kinetics, $dn/dt = k$.

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 $\text{NH}_4\text{Cl}/\text{SCl}_2/\text{Cl}_2$ mixture⁵. 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 mechanism²⁰. The rate determining step is believed to be nucleophilic attack by the nitrile on SCl_2 to give an ionic intermediate - $[\text{RCNSCl}]^+\text{Cl}^-$ which then cyclises with NSCl with loss of chlorine.

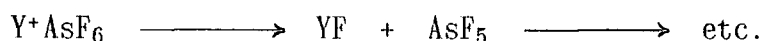


Previous attempts to obtain dithiadiazolium salts from nitriles with α H atoms failed because these activated H atoms also reacted with the $(\text{NSCl})^{20}$. The products from these reactions were intractable black polymeric solids. Indeed if the above reaction mixtures were left to reflux for the 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 derivatives 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 [PhCN₂S₂]AsF₆/Cl crystal structures. Unfortunately it proved impossible to obtain crystals large enough in the time available. [4-PhCH₂CN₂S₂]Cl was deep red in colour indicating that it was a type A salt⁵ 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*-ClPhCN₂S₂]Cl had been previously reported in the literature⁵. In an attempt to extend the plasma reaction (Chapter 4) and by analogy with (PhCN₂S₂)₂ this salt was reduced with Zn/Cu couple. The chosen solvent was liquid SO₂. As expected a green/purple solid was obtained very similar in appearance to (PhCN₂S₂)₂, and which sublimed to yield small rhomb-like crystals in contrast to the long needles obtained for (PhCN₂S₂)₂. Infrared spectroscopy of (*p*-ClPhCN₂S₂)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 S₂NAsF₆ with nitriles. The reaction occurs in the expected 4+2 cycloaddition described in the literature¹⁰. These are all strongly ionic compounds which give reasonably strong RCN₂S₂⁺ peaks in otherwise complicated mass spectra. These complications are attributed to ions apparently derived from the neutral species produced on dissociation:-



The neutral fluorides were not detected in the mass spectra, but fragments derived from them were (eg. AsF₄⁺, Y⁺). The mass spectra for 1,3 MeCN₂S₂⁺ showed a strong peak attributed to CH₃CS⁺, m/e 59, which did not appear in the 1,2 isomer; this does not contain a C-S bond.

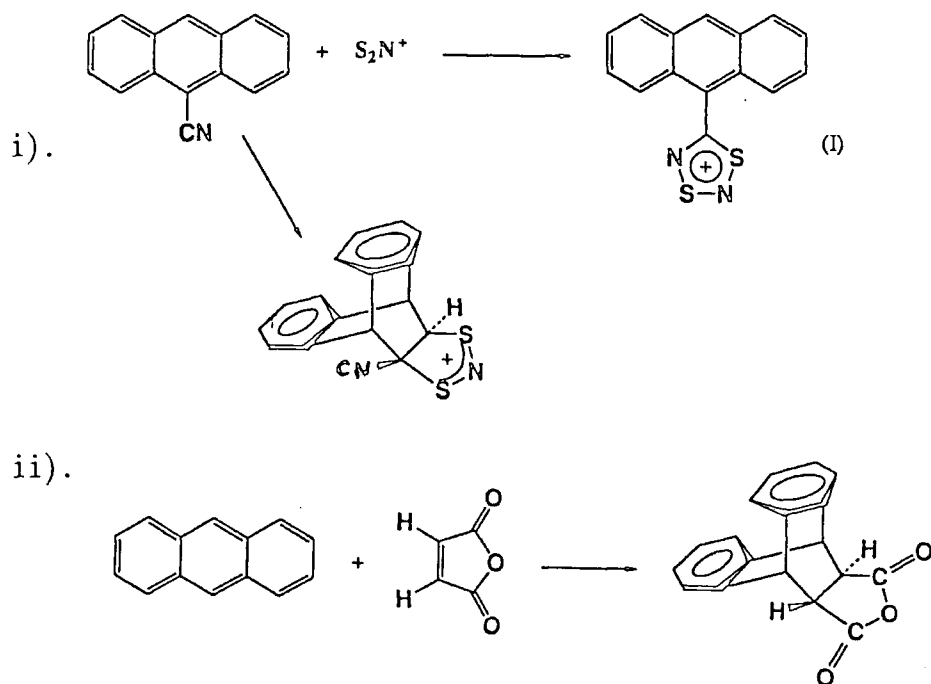
All the 1,2 compounds, however, give very strong peaks corresponding to the nitrile RCN^+ . As might be expected nitriles with increasingly electronegative groups became increasingly unreactive towards S_2N^+ . For example, most nitriles reacted almost immediately with S_2N^+ but Cl_3CCN took several 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 ΔH_{reac} with RCN to be of the order of 200 KJmol^{-1}). Generally 1,3,2,5 [RCN_2S_2] compounds are highly coloured, $\text{R}=\text{Cl}_3\text{C}$ -,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-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-isomerisation²¹ to the 1,2 isomer was envisaged. Previous attempts to obtain the 1,2 isomer direct from the reaction of $\text{C}_{14}\text{H}_9\text{CN}$ with $\text{NH}_4\text{Cl}/\text{SbCl}_2$ 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.

σ_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 substituted 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/S₂N⁺ reaction a number of 1,3 [ρ -XPhCN₂S₂]⁺ salts (X = CH₃, 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 σ_p . ^{22, 23}

Substituent	σ_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 [PhCN₂S₂]AsF₆.

Although [PhCN₂S₂]Cl was first reported in 1977², a full crystal structure determination has only just been published²⁴. 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 [Cl₃CCN₂S₂]Cl⁴. 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 salts³⁰, but also in salts of S/N cations such as S₃N₂Cl⁺Cl⁻ and S₄N₃⁺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 3.9¹⁰ it can be seen that all the S-Cl distances in [PhCN₂S₂]Cl, [PhCN₂S₂]₂Cl[S₃N₃]²⁵, [PhCN₂S₂]Cl[S₃N₂]²⁵, S₄N₃Cl, S₃N₂Cl and [Cl₃CCN₂S₂]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 salts¹¹ (anion = AsF_6^-).

Figure 3.4. The Crystal Structure of $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$.

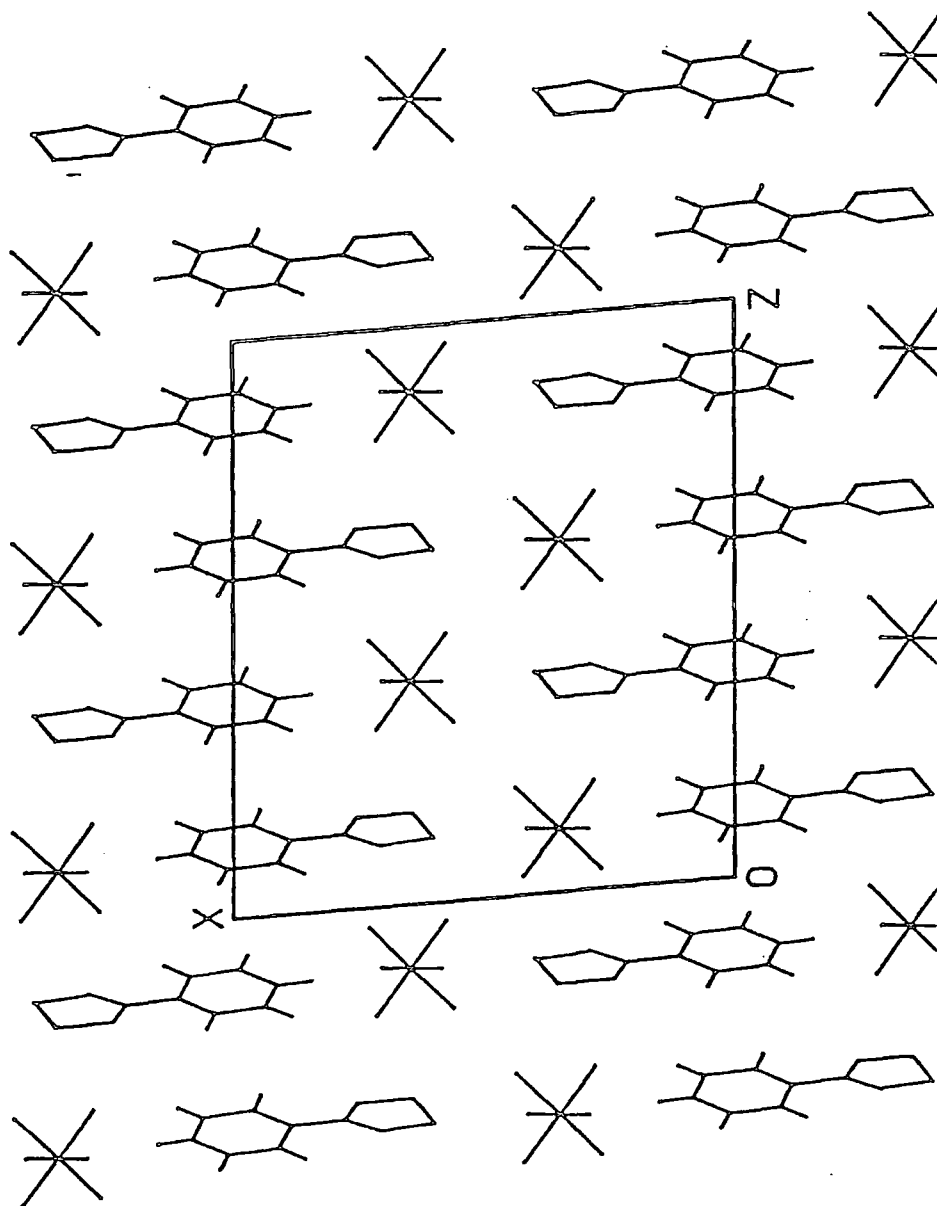
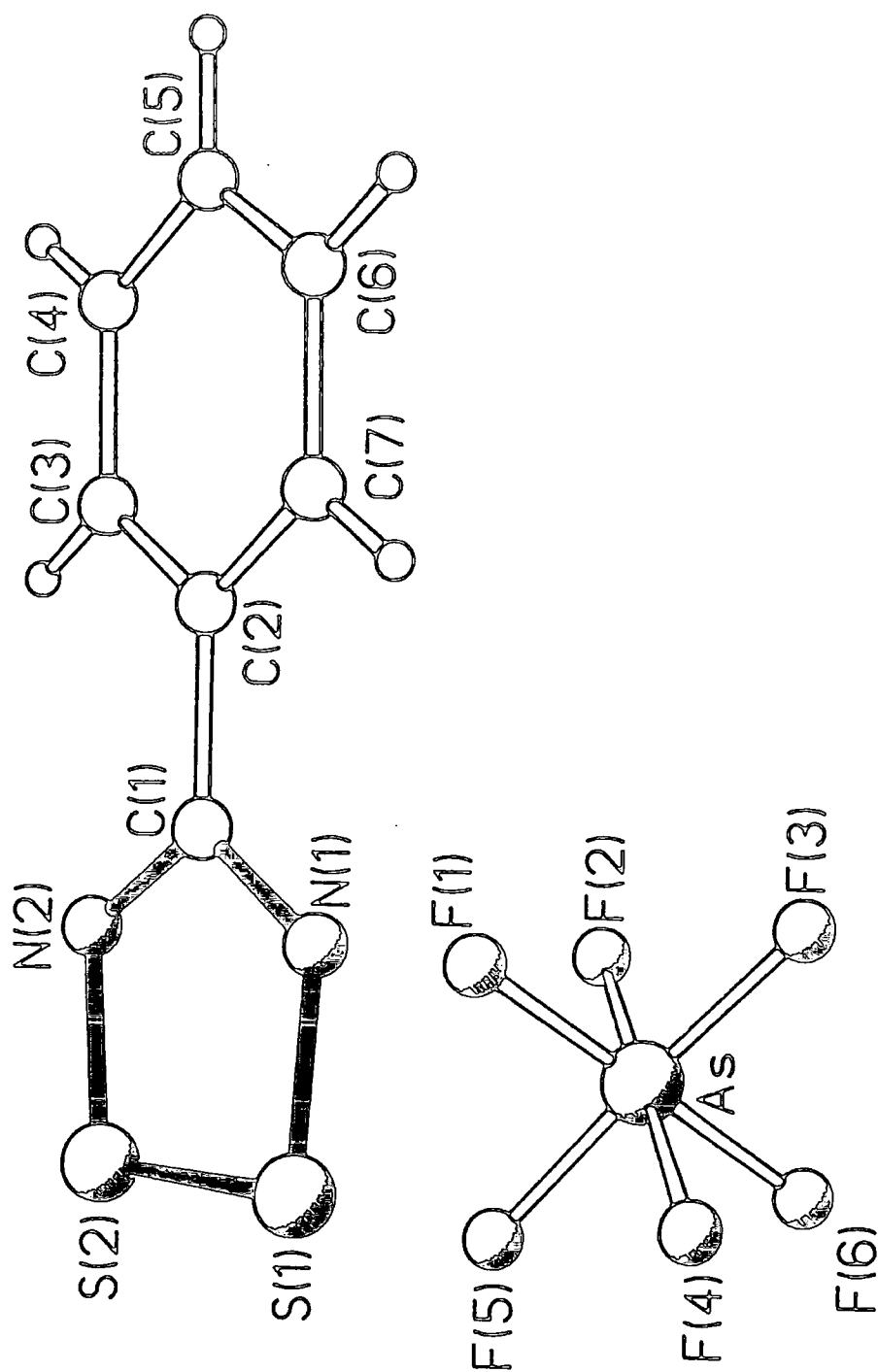


Figure 3.5. $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$



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 3.30\AA and although $[\text{CH}_3\overline{\text{CNSNS}}]\text{AsF}_6^-$ has significant interactions, there appears to be only one $\text{S}\cdots\text{F}$ contact in $[\text{PhCN}_2\text{S}_2]\text{AsF}_6^-$ (See table 3.10). This is in marked contrast to 1,3, dithidiazolium salts and to $[\text{PhCN}_2\text{S}_2]\text{Cl}$. This is probably a reflection of the hardness of the AsF_6^- anion. Figure 3.5. shows the unit cell of $[\text{PhCN}_2\text{S}_2]\text{AsF}_6^-$ 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 $[\text{PhCN}_2\text{S}_2]\text{Cl}$ structure contained disordered toluene molecules. There are only 3 ion pairs in the asymmetric unit compared to 4 in $[\text{PhCN}_2\text{S}_2]\text{AsF}_6^-$ 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. $[\text{PhCN}_2\text{S}_2]\text{Cl}$ has a shorter S-S bond (1.99\AA) than that found in the AsF_6^- salt. This strengthening of the SS bond in $[\text{PhCN}_2\text{S}_2]\text{Cl}$ is due to Cl interaction, or more specifically to Cl donation. The main SS contribution to the LUMO of the $\text{PhCN}_2\text{S}_2^+$ 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 $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$ the positive charge would be drawn to the more electronegative $\text{C}\begin{smallmatrix} \nearrow \text{N} \\ \searrow \text{N} \end{smallmatrix}$ section of the ring.

Table 3.9. Atomic coefficients of HCN_2S_2^+ for the LUMO (MO no.14) and MO no.15.

	LUMO (-9.1ev)				MO no.15 (-8.09ev)			
	S	Px	Py	Pz	S	Px	Py	Pz
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.

<u>Compound</u>	<u>C-N</u>	<u>C-S</u>	<u>S-N</u>	<u>S-S</u>	<u>S...X</u> (X=Cl)	<u>Ref.</u>
S ₃ N ₂ Cl ₂	/	/	1.543,1.617 1.580,1.615	2.136	3.04 2.93	26.
S ₄ N ₃ Cl	/	/	1.565,1.564 1.572,1.532 1.523,1.574	2.078	2.806 2.921	26.
Cl ₃ CN ₂ S ₂ Cl	1.308 1.329	/	1.587 1.579	2.009	2.884 2.864	4.
[PhCN ₂ S ₂]Cl	1.340	/	1.590	1.990	2.906 (mean)	24
D ₂ Cl [S ₃ N ₃]		/	1.611 1.597	2.034	2.904,3.082 2.964,2.897	25
DCl [S ₃ N ₃]		/	1.618 1.613	2.055	3.100,2.907 3.134,2.954	25
CH ₃ CNSNS ⁺ AsF ₆ ⁻	1.32	1.77	1.63 1.59 1.57	/	(X=F), 2.97,3.13,3.13 2.98,3.01,2.89 2.87.	11
[PhCN ₂ S ₂] ⁺ AsF ₆ ⁻	1.337 1.335	/	1.575 1.581	2.017	3.147,3.760 4.183,3.264	this work.
S ₆ N ₄ AsF ₆	/	/	1.610,1.545 1.599,1.575	2.147		26

D= 1,2 [PhCN₂S₂]

The effect of the positive charge is, however, most dramatically highlighted when $(\text{PhCN}_2\text{S}_2)_2$ is compared with $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$ with S-S bond lengths of 2.08 and 2.017Å respectively.

3.4.3. The $(\text{MeCN}_2\text{S}_2)_2$ molecule.-

The dithiadiazole $(\text{Ph}\overline{\text{CNSSN}})_2$ previously described⁵ crystallises in an eclipsed conformation with two S--S interactions between the rings. In contrast, isoelectronic $\text{S}_6\text{N}_4\text{Cl}_2$ has a trans arrangement of the two rings, thereby minimising anion/anion repulsions. The compound $[\text{CF}_3\overline{\text{CNSSN}}]_3\text{Cl}$ crystallises as a combination of $[\text{CF}_3\overline{\text{CNSSN}}]\text{Cl}$, with the chloride co-planar with the ring, and dimer $(\text{CF}_3\overline{\text{CNSSN}})_2$ with eclipsed rings (as in $(\text{PhCN}_2\text{S}_2)_2$). MNDO calculations¹⁴ 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 $(\text{PhCN}_2\text{S}_2)_2$ and $(\text{MeCN}_2\text{S}_2)_2$ would probably be similar. Table 3.11. gives a summary of the X ray crystal data for both $(\text{PhCN}_2\text{S}_2)_2$ and $(\text{MeCN}_2\text{S}_2)_2$ and an MNDO minimum energy calculation for $\text{CH}_3\overline{\text{CNSSN}}$ ¹³.

The methyl derivative, like $(\text{PhCN}_2\text{S}_2)_2$, 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 $(\text{PhCN}_2\text{S}_2)_2$ 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

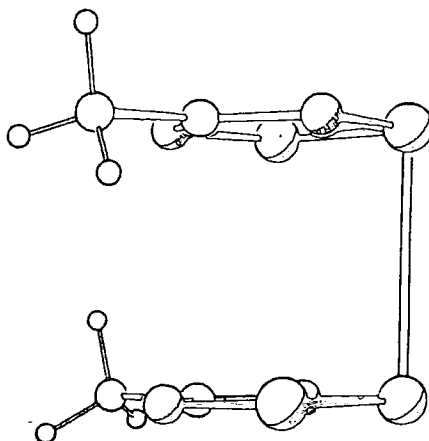
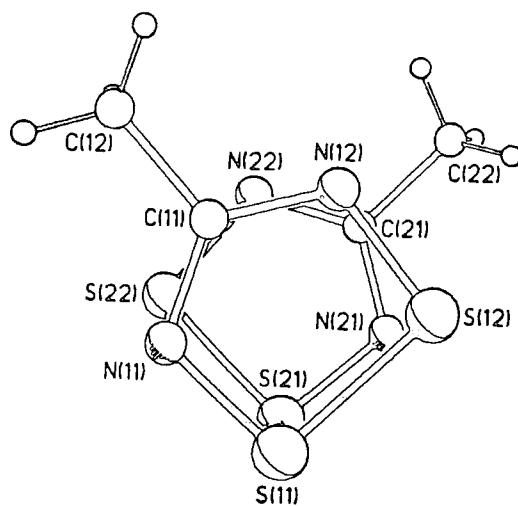


Figure 3.7. The dimeric unit of $(\text{PhCN}_2\text{S}_2)_2$.

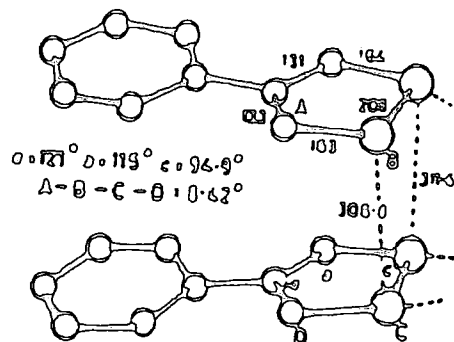
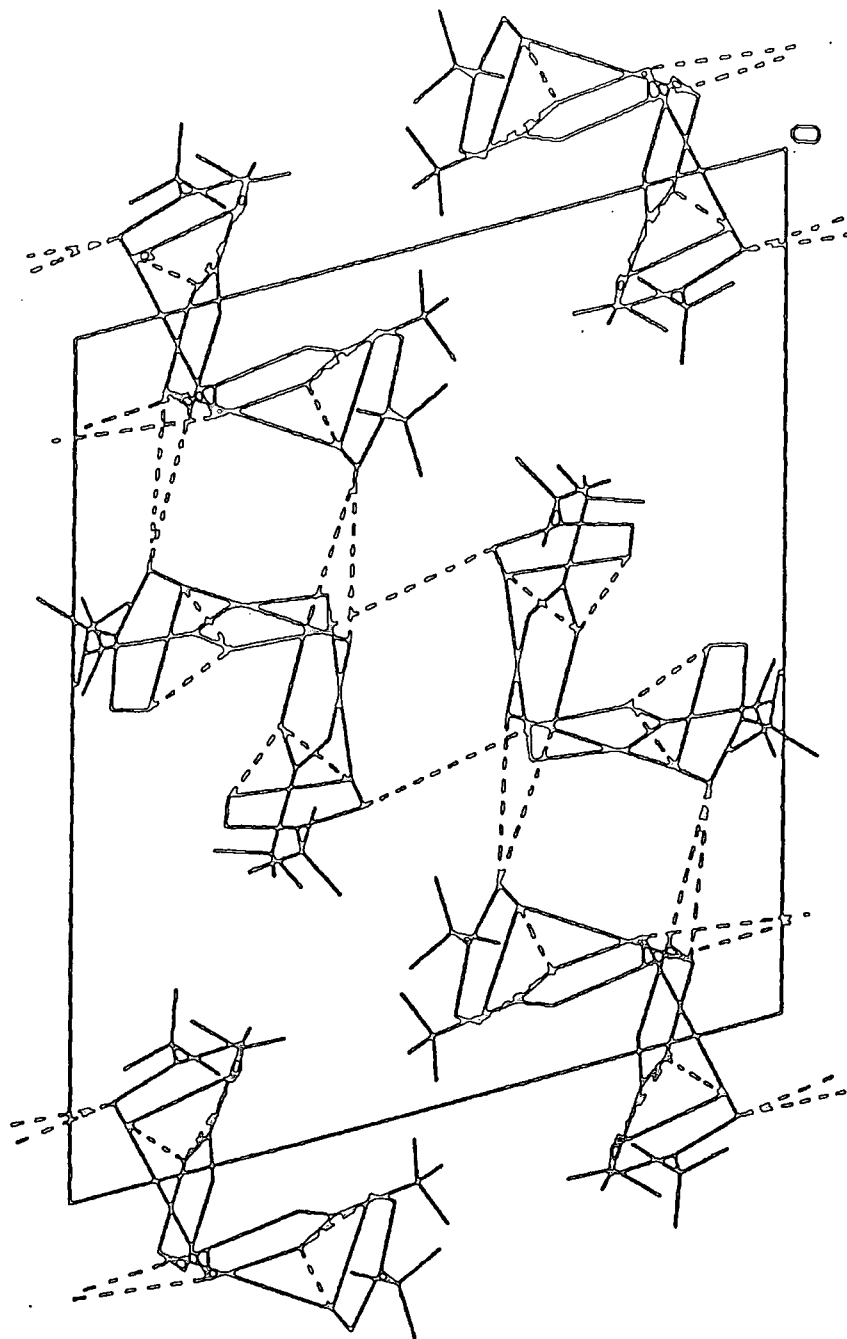


Figure 3.8. The lattice packing of $(\text{MeCN}_2\text{S}_2)_2$.



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 $(\text{CH}_3\text{CN}_2\text{S}_2)_2$ and $(\text{PhCN}_2\text{S}_2)_2$.

(Å/°)	$(\text{CH}_3\text{CN}_2\text{S}_2)_2$		$(\text{PhCN}_2\text{S}_2)_2$
	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
α .		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 calculations¹³ 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 $\text{S}_6\text{N}_4\text{Cl}_2$. However, here it appears that in $\text{S}_6\text{N}_4\text{Cl}_2$ sulphur/chloride interactions are the determining factor in the

conformation adopted; the distance from the Cl^- ion to the unique sulphur is 3.152\AA (less than the sum of the van der Waals radii, 3.7\AA). It should also be noted that these cation/anion interactions are of considerable importance for the structures of $[\text{PhCN}_2\text{S}_2]\text{Cl}$ and $[\text{PhCN}_2\text{S}_2]_2\text{Cl}^{25}$ etc.

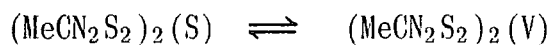
3.4.4. *Thermal studies.*

It was found that both $((\text{CH}_3)_3\text{CCN}_2\text{S}_2)$ and $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}_2\text{S}_2)$ had uncharacteristically low melting points of 22°C and 10°C respectively and it was possible therefore to measure ΔH_{fus} and ΔH_{vap} for these radicals. As shown in Table 3.11., however, the ΔH_{fus} are very similar for a whole variety of dithiadiazoles; a reflection not only of the inherent stability of the 7π 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 ΔH_{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 ΔH_{fus} , $\text{Ph} > \text{Me} > 1,2\text{-tBu.} > \text{CF}_3 > \text{propyl}$ 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 ΔH_{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 $(\text{MeCN}_2\text{S}_2)_2$ 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, $\text{R=tBu, Propyl, CF}_3$, from dimerising. The strong

electronegativity of the CF₃ group in CF₃ $\overline{\text{CNSSN}}$ 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 R $\overline{\text{CNSSN}}$ (R=tbutyl,CF₃,) 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 ΔH_{fus} would be obtained if the disorder in the solid propyl $\overline{\text{CNSSN}}$ 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 Δ_{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 ΔH_{fus} which is presumably due to the greater degree of dimerisation in Me $\overline{\text{CNSSN}}$. No direct comparison, however, can be made between the two ΔH_{vap} values obtained for the ^tBu and Me derivatives since in the determination of the methyl value the equilibrium



was assumed¹³. 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 (MeCN₂S₂)₂ is 95.5°C, the same as the melting point, it would not be valid to extrapolate the ΔH_{vap}

figure for the liquid/vapour equilibrium from this. It should also be noted that the ΔH_{fus} and hence the ΔS_{fus} for these $\overline{RCN_2S_2}$ compounds are very much higher than values for many other compounds, eg. H_2O . $\Delta S_{fus} = 22.0^{27}$, benzene $\Delta S_{fus} = 38.0 \text{ Jmol}^{-1}\text{deg}^{-1}$ again an indication of considerable structural ordering. Propyl $\overline{CN_2S_2}$ has a ΔH_{fus} comparable with many organic compounds indicating that Pr $\overline{CN_2S_2}$ lacks the structural order found in other $\overline{RCN_2S_2}$ compounds. However, the ΔH_{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. $I_2 M_r = 254$, $\Delta H_{vap} = 41.8 \text{ KJmol}^{-1}$. 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 ΔH_{fus} and ΔH_{vap} for some dithiadiazoles

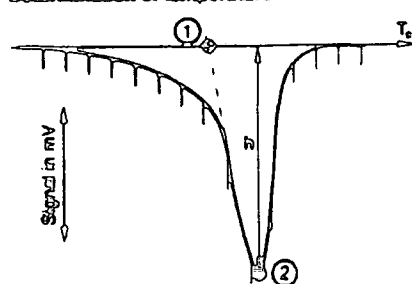
Compound	Mr	Mpt. °C	ΔH_{fus}	ΔS_{fus}	ΔH_{vap}
$(PhCN_2S_2)_2$	181	119.7	59.0	35.3	/
$(MeCN_2S_2)_2$	119	95.5	43.0	27.9	55.2
tBu $\overline{CN_2S_2}$	161	22.0	35.3	28.6	65.6
$CF_3CN_2S_2$	173	21.0	21.61	17.5	/
Pro $\overline{CN_2S_2}$	147	10.0	13.6	11.48	/
$CF_3CSNSCF_3$	240	1.8	23.1	20.1	38.1 ^b

Pro = $CH_3CH_2CH_2$.
 $\Delta H_{fus} = \text{KJmol}^{-1}$

$\Delta S_{fus} = \text{calmol}^{-1}\text{deg}^{-1}$

$\Delta H_{vap} = \text{KJmol}^{-1}$

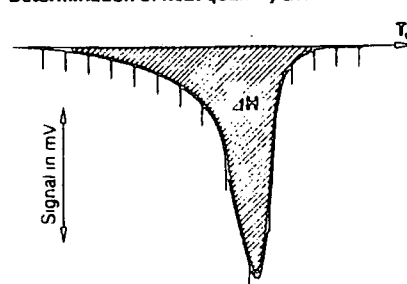
Determination of temperature



- ① Onset temperature
 $T_{onset} = T_c - \beta/3$
- ② Sample temperature
 $T_{sample} = T_c - \beta/3 - h/35$ (endo)
 $T_{sample} = T_c - \beta/3 + h/35$ (exo)

β = Heating rate (°C/min)
 h = Peak height in (mV)
 T_c = Temperature (°C)
 T_c = Cell temperature (marks and display)

Determination of heat quantity ΔH



$\Delta H = \frac{\text{Weight of cut out peak (mg)} \cdot F \cdot G}{E_{cd}}$

ΔH = 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_{cd} = Temperature dependent calorimetric sensitivity (see table)
 T_c = Cell temperature (marks and display)

Table of calorimetric sensitivity E_{cd} as a function of temperature:

T_c [°C]	E_{cd}	T_c [°C]	E_{cd}	T_c [°C]	E_{cd}
-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 $\Delta H_{f\text{ us}}$ for ${}^t\text{BuCNSSN}$ radical - Figure 3.3.

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

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

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

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

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

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 compound and in solution, although there is a photodecomposition with high energy UV light²⁸. $\overline{\text{RCNSNS}}$ radicals undergo photochemical isomerisation in which a concerted process via a head to tail $\pi^*-\pi^*$ dimeric intermediate is indicated¹⁰. 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 ($305 + 427 \text{ KJmol}^{-1}$) being stronger than the S-C and S-N bonds broken ($301 + 209 \text{ KJmol}^{-1}$). 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 studied²¹ by esr, for example $\overline{\text{MeCNSNS}}$ gives a simple three line spectrum which decreases with

time to give the five line spectrum of $\overline{\text{MeCNSSN}}$. 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 $\overline{\text{t-BuCNSSN}}$ 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 sunlight²⁸). Similar isomerisations have been reported to occur within a few seconds, when R=CF₃ 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/SCl₂/NH₄Cl route has been extended to [CH₃CH₂CH₂CN₂S₂]Cl and [PhCH₂CN₂S₂]Cl by careful control of reaction conditions to reduce the competing α H extraction reaction. 1,2,3,5 [PhCN₂S₂]AsF₆, 1,2,3,5 [tButylCN₂S₂]AsF₆ and 1,2,3,5 [MeCN₂S₂]AsF₆ were obtained by metathesis from the corresponding chloride and AgAsF₆, a useful reagent in SO₂. S₂NAsF₆ was reacted with a series of increasingly deactivated aryl nitriles, XPhCN (X=CH₃,Cl,CN) to give the 1,3,2,5 dithiadiazolium salt. The reduction products of 1,2,3,5 [CH₃CH₂CH₂CN₂S₂]Cl and 1,2,3,5 [tButylCN₂S₂]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 (tButylC₂S₂)[•] also a liquid at room temperature was also followed. A report concerning this and 1,2 (tButylCN₂S₂)[•] appeared in the literature while this work was being carried out¹⁶.

A variety of dithiadiazoles were shown to have similar ΔH_{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 (CF₃,^tButyl,propyl, all liquid radicals at room temperature) was also reflected in the ΔH_{fus} and ΔH_{vap} measurements.

The crystal structure [PhCN₂S₂]AsF₆ shows that the small anion/cation interactions leads to a longer S-S bond than that found in [PhCN₂S₂]Cl. The crystal structure of (MeCN₂S₂)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 discharges¹, the more exotic ones, eg. N_4^+ still attract attention². However, the main species is the ground state nitrogen atom (4S), from the dissociation of N_2 , which lies at 12.139eV³. See Figure 4.1.

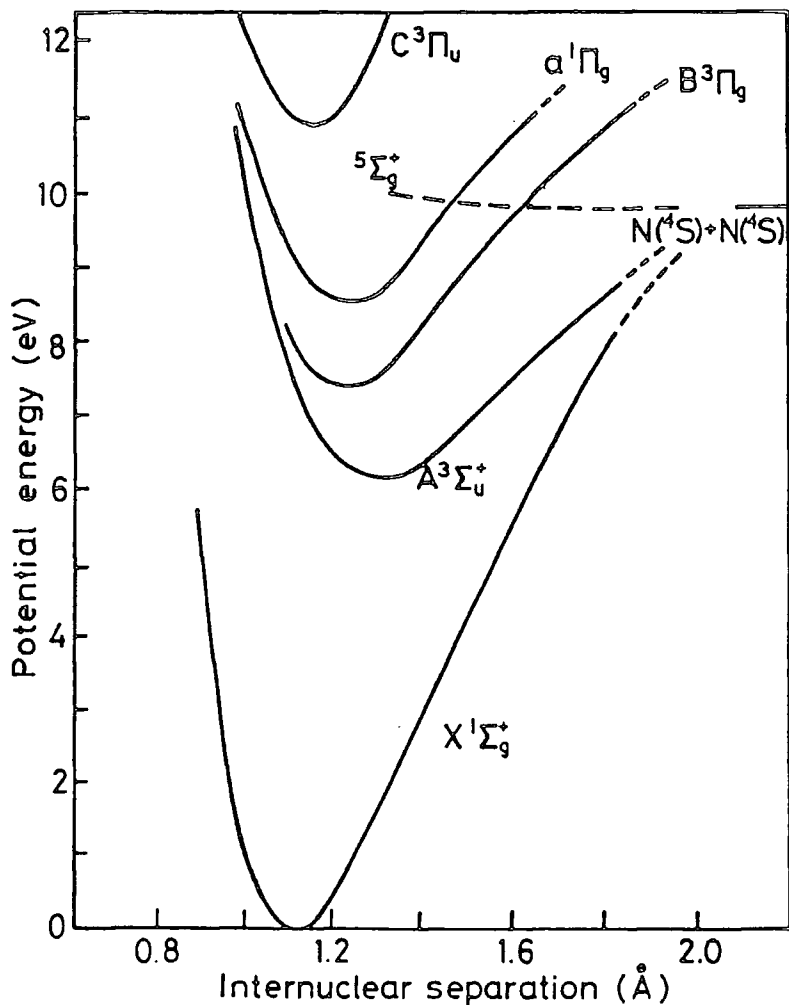


Figure 4.1. Potential Energy Diagram for the Nitrogen Molecule.

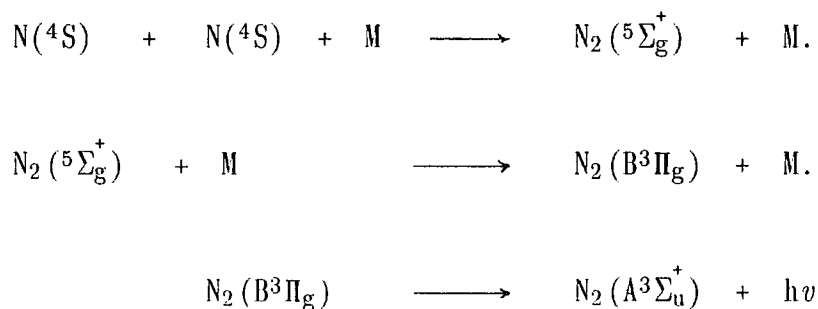
It is the 4S nitrogen atoms that are the chemically active species³ in free radical active nitrogen reactions. Electronically excited atoms and molecules and vibrationally excited molecules have a lower concentration and the longest lived excited molecular state, the $A^3\Sigma_u^+$ state, has a life 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.,



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 afterglow¹, 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;



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

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 reactions³. 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,- diene⁴ and in particular in the preparation of phosphorus nitrides⁵. Furthermore, there is increasing interest in ^{their} use in the fabrication of silicon nitride films for the micro-electronics industry and in polymer film formation⁶.

In sulphur chemistry a few gas/gas reactions between singlet atomic nitrogen generated in a microwave discharge and various divalent sulphur compounds have been investigated⁷, 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 S₂Cl₂ 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. SOCl₂, SO₂, SO₃ (which would have a formal positive charge). The plasma method has also been used to convert NH₃/H₂S and N₂/H₂S mixtures to impure amorphous (SN)_x⁸.

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 $\sigma = 1000 - 3000 \text{ S cm}^{-1}$)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.*

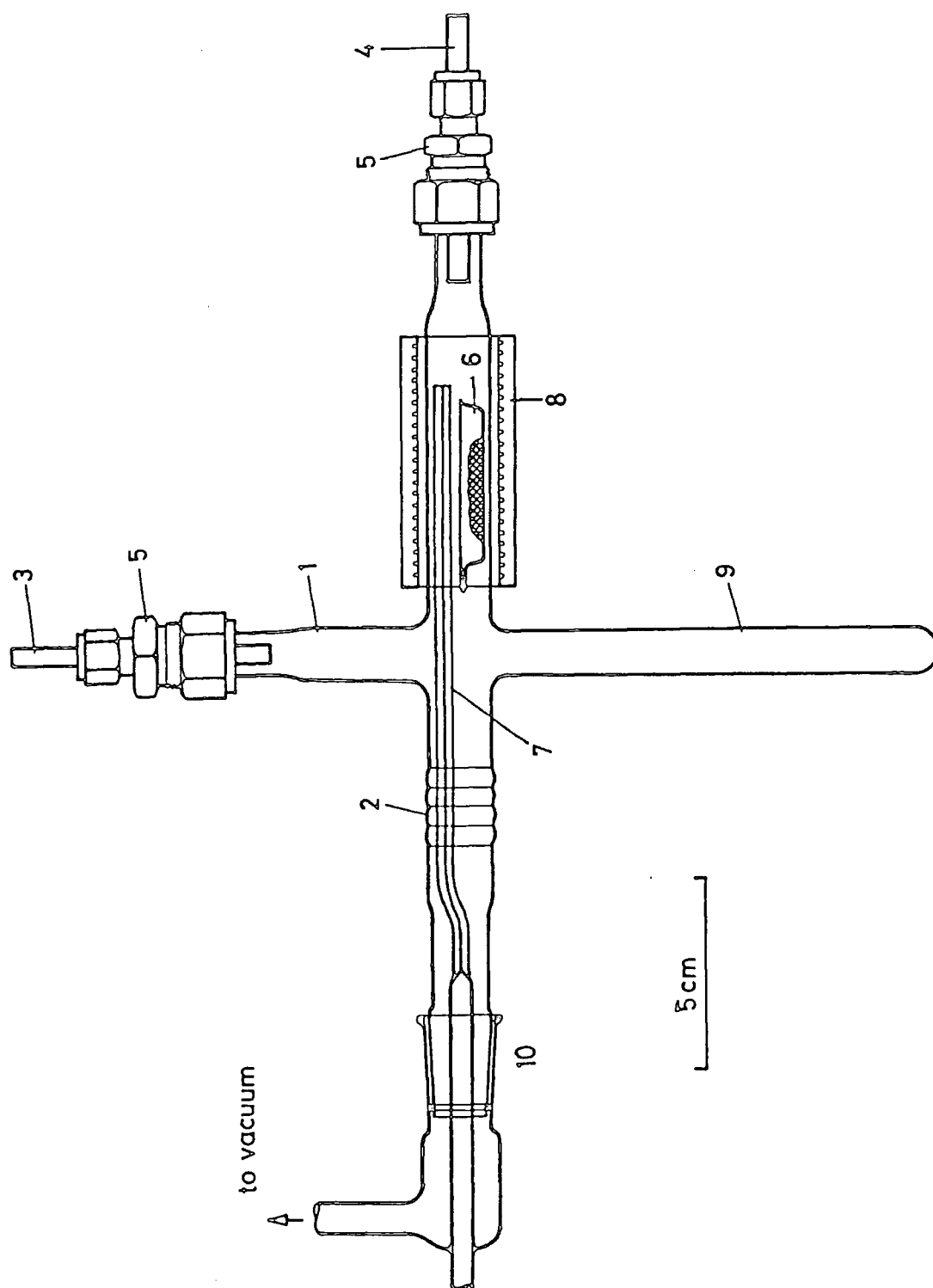
The two tubes used in the plasma experiments involving relatively low volatility solid starting materials are shown in Figures 4.2 and 4.3. (pages 86 and 87). Tube 4.2 was used generally for exploratory work and small scale synthesis whilst tube 4.3 proved useful in later work for scaling up reactions 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). N₂ 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 N₂ 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 cm³ 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.



5 cm

Figure 4.3. Large Reaction Apparatus

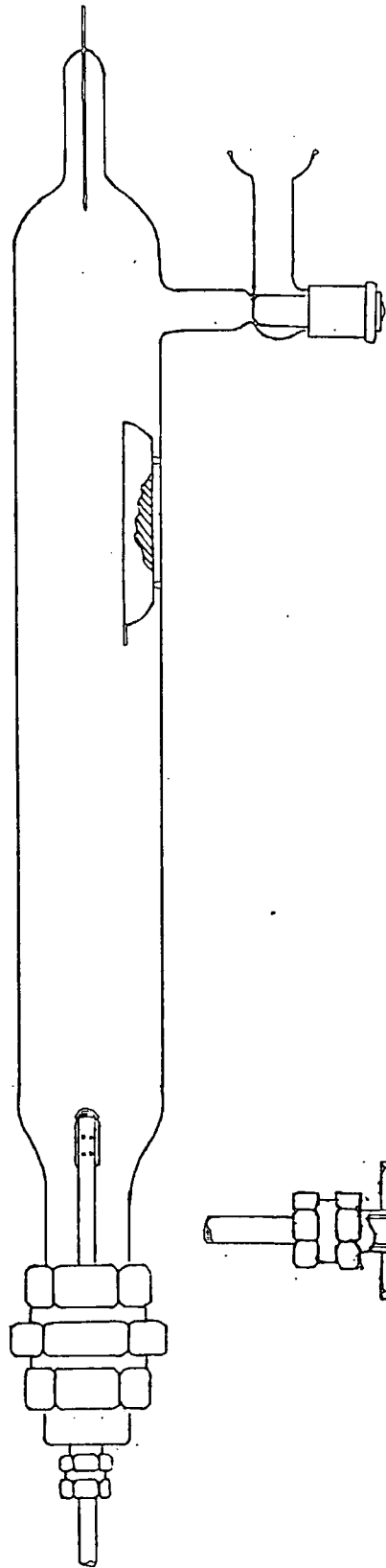
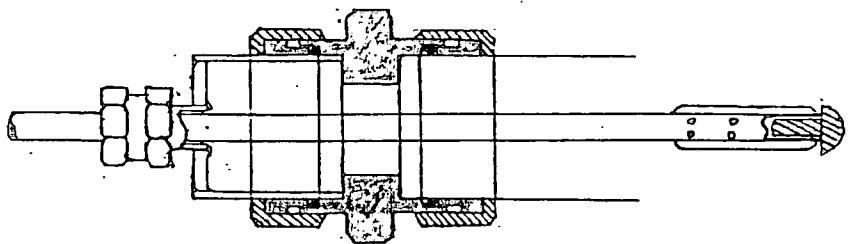


Figure 4.4.



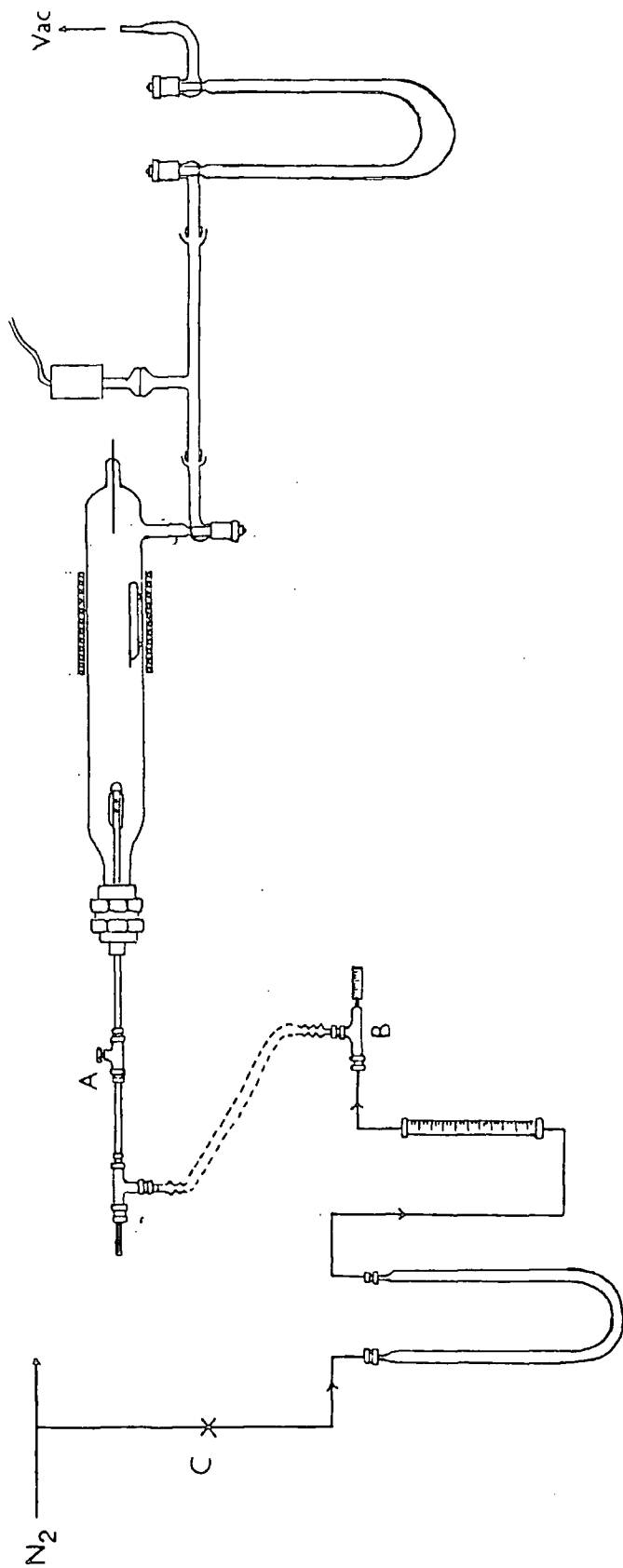
This effectively maintained a pressure of about 1 Torr (8×10^{-1} to 1.0 Mbar) in the tube as measured on an Edwards Pirani PRE 10K gauge head connected to a Pirani 502 control unit. For both tubes a current of 2 MA was used, which required about 900 to 1000 V across the electrodes. The electrodes used 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 $(\overline{\text{PhCNSNSN}})_2$.*

$(\overline{\text{PhCN}_2\text{S}_2\text{N}})_2$ (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 $(\text{PhCN}_3\text{S}_2)_2$ and a small amount of black polymer.

Figure 4.5. Nitrogen and Vacuum lines for Discharge Tubes.



A very thin continuous polymeric film also formed on the walls of the discharge tube. The pure product is largely insoluble in liquid SO_2 and so unreacted $(\text{PhCN}_2\text{S}_2)_2$ was washed from the product with liquid SO_2 using a closed extractor.¹⁰ Typical yields of $(\text{PhCN}_3\text{S}_2)_2$ were 0.22 g (80%), and thus the energy consumption was $1.3 \times 10^8 \text{ J mol}^{-1}$ (i.e. 92 kWh kg^{-1}) of the product. Found: C 42.8, H 2.1, N 21.2, S 32.9; $\text{C}_7\text{H}_5\text{N}_3\text{S}_2$ requires C 43.0, H 2.6, N 21.4, S 32.8; mass spectrum (CI), m/e 181 $(\text{PhCNS}_2)^+$, and m/e 195 $(\text{PhCN}_3\text{S}_2)^+$ relative abundance 76% and 68% respectively. Typical composition of the concomitant polymer was $\text{C}_3\text{H}_{2.5}\text{NS}$; C 41.4, H 3.0, N 18.0; S 37.5; DSC ($4^\circ\text{C}/\text{min}$), 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 $(\text{PhCN}_2\text{S}_2)_2$ before and after nitrogenation is shown in Figure 4.8.

The unit cell parameters of $(\text{PhCN}_3\text{S}_2)_2$ 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) $d_{\text{hkl}}/\text{\AA}$ (obs), $d_{\text{hkl}}/\text{\AA}$ (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 $(\text{PhCN}_2\text{S}_2)_2$.

(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. $(\text{PhCN}_2\text{S}_2)_2$ 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. $(\text{PhCN}_2\text{S}_2)_2$ was then irradiated with UV light of 190 nm and above for 36 hours. The flow rate was adjusted to $70 \text{ Torr cm}^3\text{s}^{-1}$ 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.

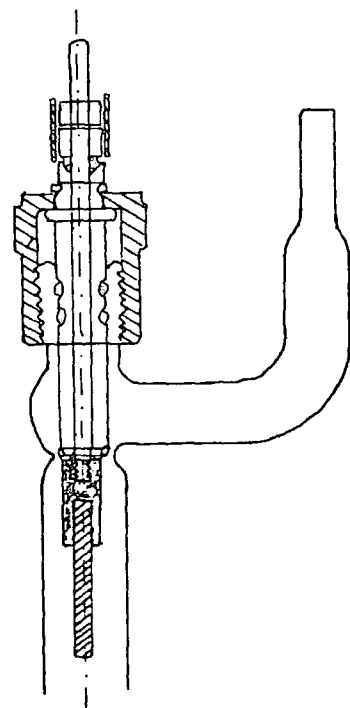
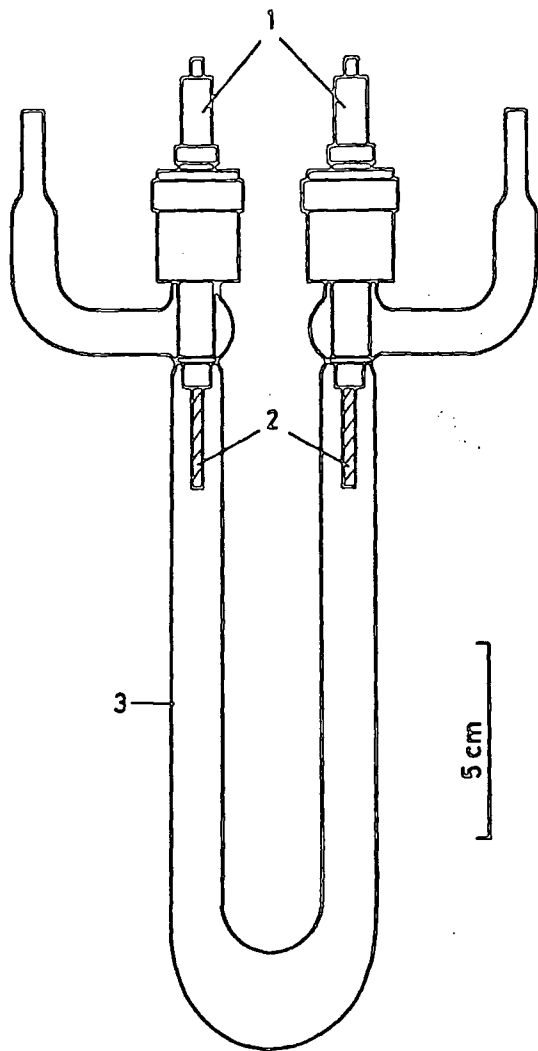


Figure 4.7

(2). *In solution.* - A solution of $(\text{PhCN}_2\text{S}_2)_2$ (0.18 g, 0.5 mmol) in 10 cm³ 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 cm³ (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 $(\text{PhCN}_2\text{S}_2)_2$.

4.2.4. Preparation of $(p\text{-ClC}_6\text{H}_4\overline{\text{CNSNSN}})_2$.

$(p\text{-ClPhCN}_2\text{S}_2)_2$ 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 ($p\text{-ClPhCN}_3\text{S}_2$) was purified as for $(\text{PhCN}_3\text{S}_2)$. Found: C 36.7, H 1.5, N 18.1, S 27.4, Cl 15.1; $\text{C}_7\text{H}_4\text{N}_3\text{S}_2\text{Cl}$ requires: C 36.6, H 1.7, N 18.3, S 27.8, Cl 15.4 ; m.s. (CI): m/e 230 [$p\text{-ClC}_6\text{H}_4\text{CN}_3\text{S}_2$]⁺, 29%; m/e 215 [$p\text{-ClC}_6\text{H}_4\text{CN}_2\text{S}_2$]⁺, 71%; DSC (4°C/min), 114.5°C (endotherm) followed by decomposition at 118.2°C. Infrared spectra of $(p\text{-ClPhCN}_2\text{S}_2)_2$ and $(p\text{-ClPhCN}_3\text{S}_2)$ are shown in Figure 4.8.

4.2.5. Preparation of $[\text{PhCN}_2\text{S}_2]\text{CN}$.

$[\text{PhCN}_2\text{S}_2]\text{Cl}$ (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.

SO₂ was condensed onto both solids (8 ml, 12.0 g. in each) and left for 1 day. Although [PhCN₂S₂]Cl is readily soluble in SO₂, AgCN is only slightly so giving a very pale solution. The orange [PhCN₂S₂]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 SO₂, a white SO₂ insoluble solid was left (largely AgCl, from analysis and infrared). On removal of the SO₂, a dark brown crystalline solid was obtained. Yield = 0.69 g, 95% based on [PhCN₂S₂]Cl. This solid (0.45g) was further purified by transferring to an extractor and washing with SO₂ for 2 hours. This left a trace amount of AgCN (0.005 g), identified with infrared, on the frit. The SO₂ was evaporated leaving again a brown crystalline product. C₇H₅N₃S₂ 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 (RCN₃S₂)₂ from [RCN₂S₂] X (R = Ph, p-ClC₆H₄ X = CN⁻, Br⁻, I⁻).*

i). For X = I⁻, Br⁻; Compounds [RCN₂S₂] 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. [PhCN₂S₂]⁺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 SO₂ leaving red/brown (PhCN₃S₂)₂ (0.049 g) on the frit, according to infrared spectroscopy. The solid obtained from the SO₂ fraction (0.018 g, 18% of original) gave infrared bands corresponding to [PhCN₂S₂]Cl, but with broad polymer bands.

4.2.7. *The effects of a nitrogen plasma on [PhCN₂S₂]Cl.*

[PhCN₂S₂]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 (RCN₂S₂)₂ with a nitrogen DC plasma (R = Pr, But).*

Both these derivatives are liquids at room temperature and are presumably largely present as free radical monomers¹³. 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 cm³s⁻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.

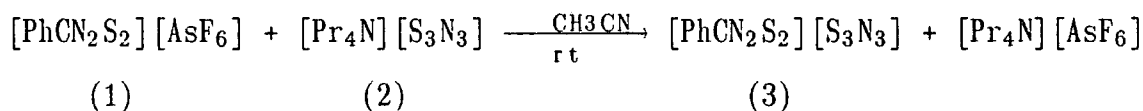
After about 8 h there was no remaining liquid in the bulb and a dense coating of a brown film had formed which infrared spectra revealed to be polymeric with broad ill-defined absorptions.

4.2.9. *Reaction of [RCN₂S₂] 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 [alkylCN₂S₂]⁺ X⁻ was placed in the bulb and cooled to -5°C. Using a flow rate of 50 Torr cm³s⁻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 (I₂ or Br₂) was identified with infrared and Raman spectra.

4.2.10. *Preparation of [PhCNSSN][S₃N₃] and its reaction with nitrogen plasma.*

It is most easily prepared by a simple metathesis;



Compound (1) was prepared by the reaction of (PhCN₂S₂)₂ with AgAsF₆ in SO₂ and (2) was prepared according to literature¹⁴.

(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 cm³ of CH₃CN 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%). C₇H₅N₅S₅ 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 (PhCN₃S₂). A thick black polymer film also quickly formed.

4.2.11. Preparation of $[\overline{\text{PhCNSSN}}]_2\text{Cl}$.

(PhCN₂S₂)₂ (0.0418 g, 0.115 mmol) and [PhCN₂S₂]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. C₁₄H₁₀N₄S₄Cl 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 (PhCN₃S₂)₂ with SO₂Cl₂.

(PhCN₃S₂)₂ (0.5 g, 1.28 mmol) was placed into one bulb of a dog and an excess of dry SO₂Cl₂ (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 PhCN₃S₂Cl₂ (identified by infrared spectroscopy and elemental analysis) grew on reduction of the volume of SO₂Cl₂. The remaining liquid was decanted into the first bulb and all the SO₂Cl₂ removed under vacuum to leave a yellow powder also shown to be PhCN₃S₂Cl₂. First yield of crystals = 0.491 g (72%). Total yield = 0.67 g, (98%). C₇H₅N₃S₂Cl₂ 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 ν_{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 $\text{PhCN}_3\text{S}_2\text{Cl}_2$ with $(\text{Me}_3\text{Si})_2\text{NCN}$.

$\text{PhCN}_3\text{S}_2\text{Cl}_2$ (0.5 g, 1.88 mmol) was dissolved in 50ml of MeCN in a Schlenk and cooled to 0° C. $(\text{Me}_3\text{Si})_2\text{NCN}$ (0.5 ml, 1.88 mmol) dissolved in 10 ml of MeCN was added dropwise to the $\text{PhCN}_3\text{S}_2\text{Cl}_2$ 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 $\text{PhC}_2\text{N}_5\text{S}_2$ by chemical analysis, m.s. and infrared spectroscopy. Yield of $\text{PhC}_2\text{N}_5\text{S}_2$ = 0.15 g, (34%). $\text{C}_8\text{H}_5\text{N}_5\text{S}_2$ 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 ν_{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 $\text{PhC}_2\text{N}_5\text{S}_2^+$ (9%), 195 $\text{PhCN}_3\text{S}_2^+$ (51%), 103 PhCN^+ (100%), 40 CN_2^+ (2%)

4.2.14. Cyclic voltammetry.

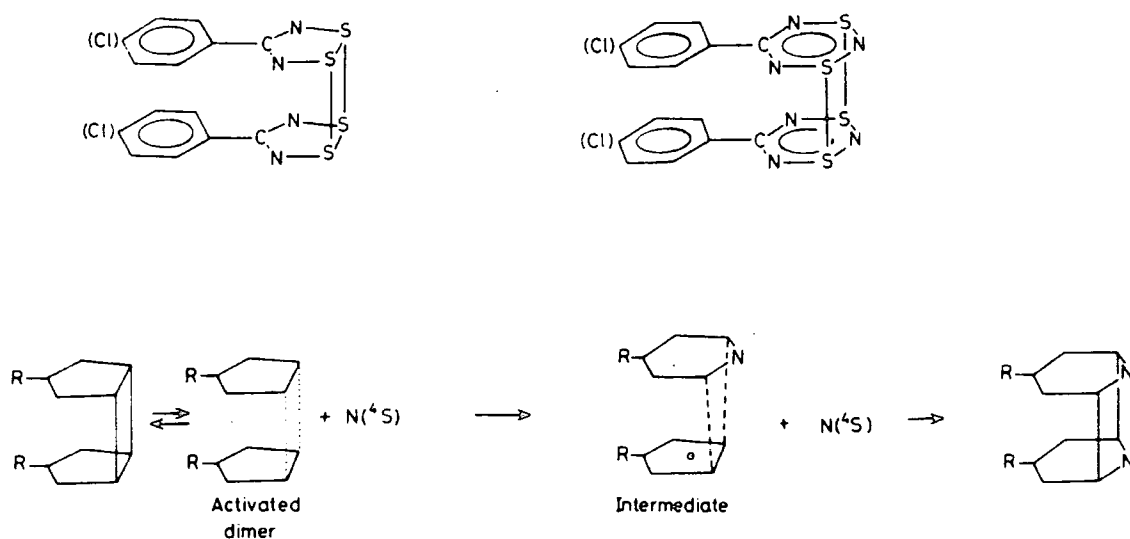
All electrochemical measurements were carried out under strict exclusion of moisture and oxygen in a specially designed airtight three limbed electrode cell described elsewhere¹⁵. Cyclic voltammograms were recorded using a Bioanalytical System Inc. CV-1B instrument and a Linseis LY17100 XY chart recorder. The working electrode was a platinum disc (0.002 cm²) 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 $\pm 0.002\text{v}$ 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 $\text{Ph}\overline{\text{CNSNSN}}$* - 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 $+5.0^\circ\text{C}$ showed an oxidation half-wave potential ($E_{p/2}^{\text{ox}}$) at +1.3V and a reduction half wave-potential ($E_{p/2}^{\text{red}}$) at -0.52V).

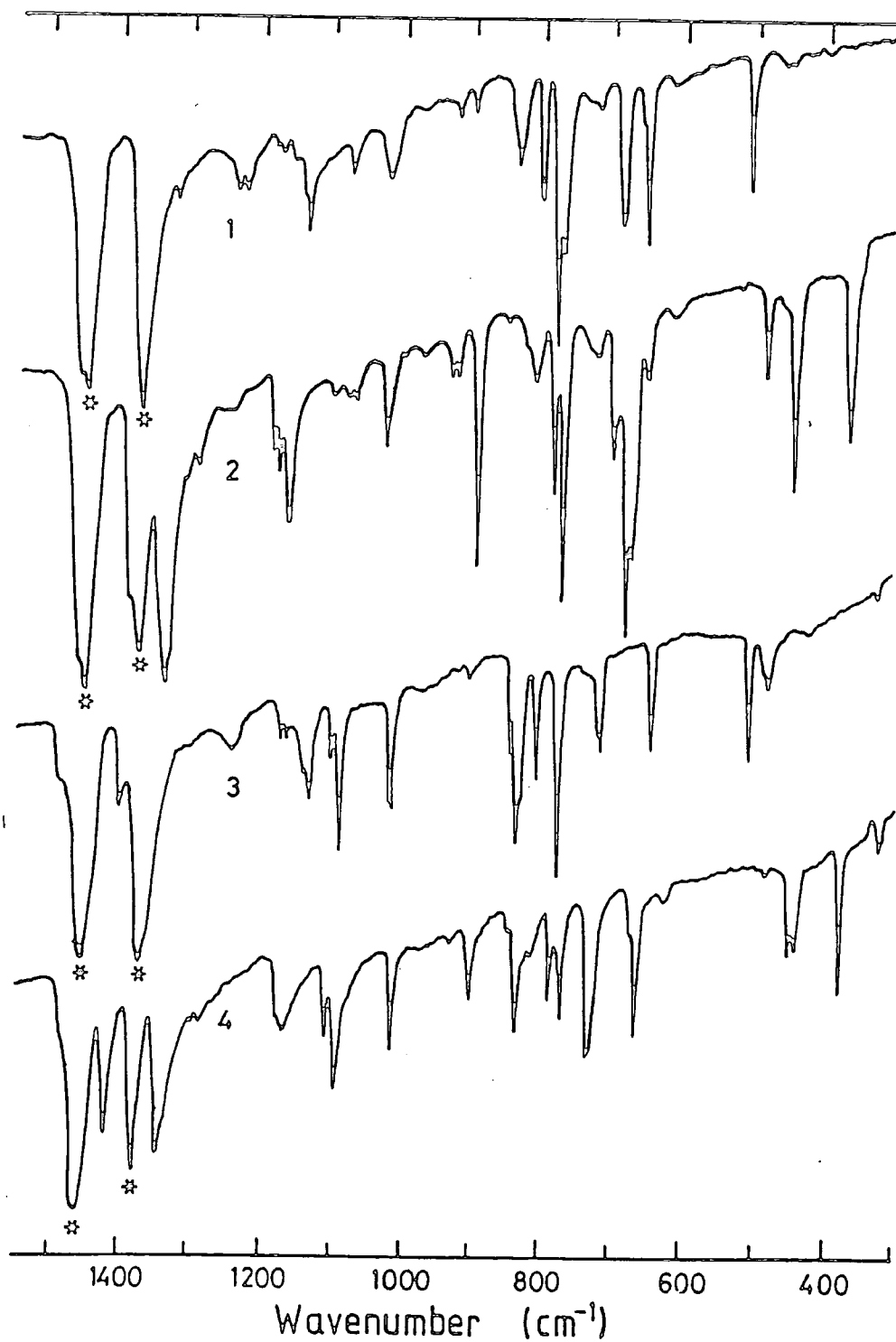
4.3. RESULTS AND DISCUSSION.

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 ($\text{R} = \text{Ph}, p\text{-ClPh}$) has been reported previously¹⁶. Scheme 4.2.



Scheme 4.2.

Figure 4.8. Comparison of infrared spectra of $(\text{PhCN}_2\text{S}_2)_2$ and $(p\text{-ClPhCN}_2\text{S}_2)_2$ 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 ($\text{R} = \text{Me}, \text{Pr}, \text{Bu}^t$) and with $\text{RCN}_2\text{S}_2^+ \text{X}^-$ ($\text{R} = \text{Ph}, \text{p-ClPh}, \text{Pr}, \text{Bu}^t, \text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$). Structural criteria which facilitate the nitrogenation reaction are discussed with particular regard for $(\text{CH}_3\text{CN}_2\text{S}_2)_2$ for which the X-ray data has been given in Chapter 3.

MNDO calculations¹⁷ 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 σ 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 $\text{R} = \text{Pr}, \text{Bu}^t$) 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 $\text{R} = \text{Pr}, \text{Bu}^t$ which are liquids at room temperature the apparatus was slightly modified and used at -30°C to $+40^\circ\text{C}$ (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. Diagrammatic representation of the SOMO and the overlap of the P_z component in the $(\text{PhCN}_2\text{S}_2)_2$ dimer unit.

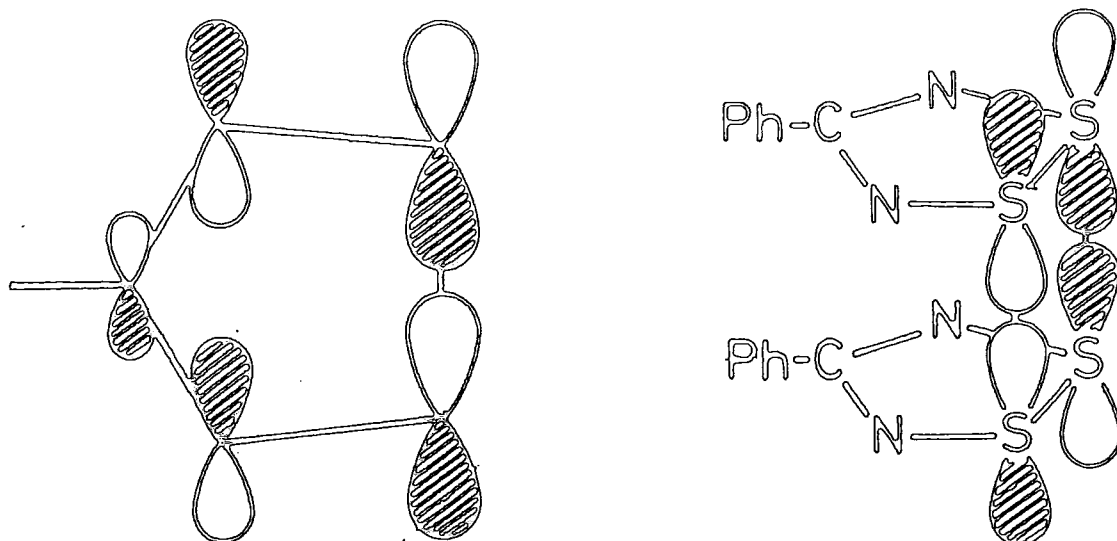


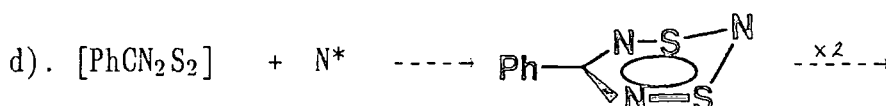
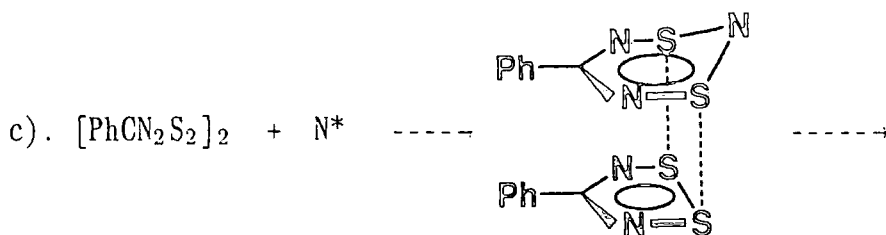
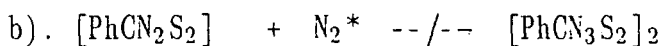
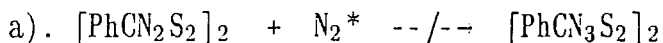
Table 4.1. HOMO/LUMO MNDO data for HCN_2S_2^+ .

HOMO (-17.62ev)					MO no.15 (-8.09ev)				
	S	Px	Py	Pz	S	Px	Py	Pz	
S_1	0	0	0	-0.52	+0.09	+0.66	+0.03	0	
S_2	0	0	0	-0.52	+0.09	+0.66	-0.03	0	
N_3	0	0	0	+0.30	-0.70	-0.16	-0.10	0	
N_4	0	0	0	+0.30	+0.70	-0.17	-0.10	0	
C	0	0	0	+0.53	0	+0.16	0	0	

LUMO (-9.1ev)				
	S	Px	Py	Pz
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



Scheme 4.



X-ray crystal structure studies²⁰ have shown that for $(\text{PhCN}_2\text{S}_2)_2$ 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 $(\text{RCN}_2\text{S}_2)_X$ increases with the atomic number of the halogen, X. Consequently the various halides ($X = \text{Cl}^-$, 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 $\text{Ar}\overline{\text{CNSNSN}}$ with release of halogen. As expected, the iodides required the lower reaction temperatures.

In the case of the alkyl derivatives, however, the corresponding

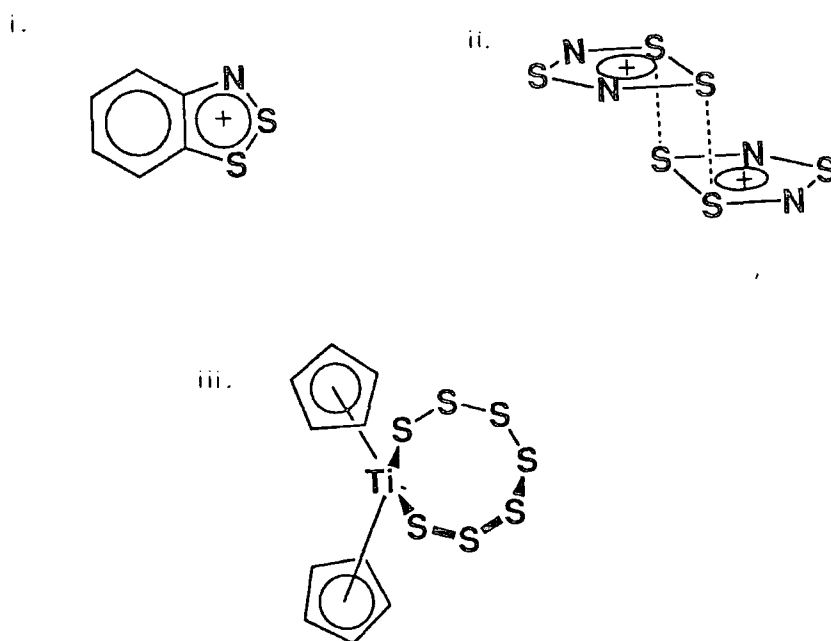
halogen was again released, but with almost complete conversion to brown polymer. Presumably because their radicals are monomeric, the alkyl derivatives are too volatile and are quickly lost into the gas phase where they are subjected to the vigorous conditions of the plasma with consequent molecular fragmentation and conversion to a non-stoichiometric polymer. Thus no compounds alkylCN₃S₂ 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 $\overline{\text{RCNSSN}}$. 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 RCN₂S₂⁺, 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 $\overline{\text{RCNSSN}}$ ⁺ 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 S₈, S₄N₄, S₃N₂Cl₂, S₄N₃Br. It was thought that, in particular, the structural similarities of S₃N₂Br or C₆H₄NS₂⁺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 $[PhCNSSN]_2Cl$ was also placed under a nitrogen plasma. No reaction was observed until externally heated to $100^\circ C$ 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 $(\text{PhCN}_2\text{S}_2)_2$; the reaction occurred readily at room temperature. There was no observed $(\text{SN})_x$ 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.

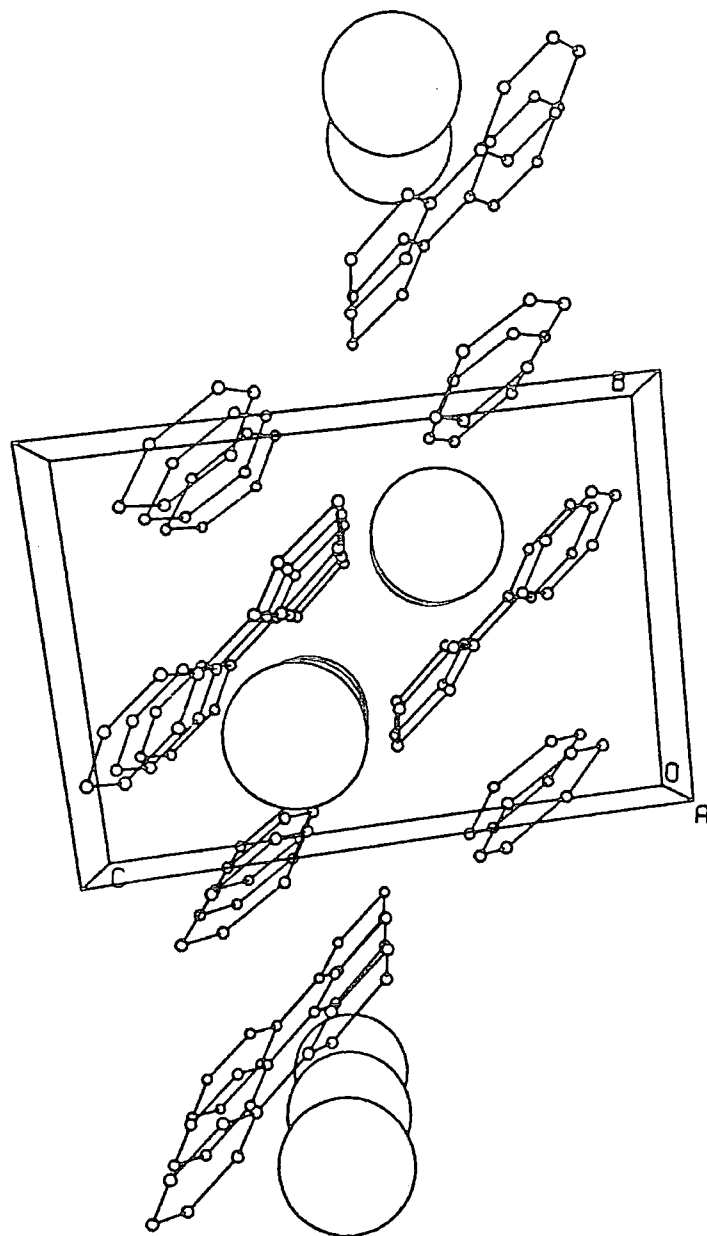
Of the 1,2,3,5 dithiadiazoles (RCN_2S_2) studied, it was only in the case of $\text{R} = \text{Ph}$ or $p\text{-ClC}_6\text{H}_4$ that the plasma nitrogenation produced the corresponding 1,3,2,4,6 dithiatriazine (RCN_3S_2). The experimental results indicated several general criteria for successful nitrogen 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, whilst 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 $\text{R} = \text{aryl}$ 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, $\text{R} = \text{alkyl}$ 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 $[\text{PhCN}_2\text{S}_2][\text{S}_3\text{N}_3]$.



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, But.), 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: $(\text{PhCN}_2\text{S}_2)_2$ and $(\text{MeCN}_2\text{S}_2)_2$.

Both these are dark green/purple bichromic crystalline dimeric solids at room temperature, both melt without decomposition, $(\text{PhCN}_2\text{S}_2)_2$ at 127°C and $(\text{MeCN}_2\text{S}_2)_2$ at 95.5°C. The vapour pressure of $(\text{MeCN}_2\text{S}_2)_2$ was measured in this laboratory²². Unfortunately there are no vapour pressure/temperature data for $(\text{PhCN}_2\text{S}_2)_2$, 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 $(\text{PhCN}_2\text{S}_2)_2$ was obtained by examining the cross section of a single crystal of $(\text{PhCN}_2\text{S}_2)_2$ 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 $(\text{PhCN}_2\text{S}_2)_2$ and the surrounding buff coloured layer of PhCN_3S_2 . While the nitrogenation of $(\text{PhCN}_2\text{S}_2)_2$ 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 $(\text{PhCN}_2\text{S}_2)_2$ there was no analogous formation of $(\text{MeCN}_3\text{S}_2)_2$ from $(\text{MeCN}_2\text{S}_2)_2$ 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 $(\text{PhCN}_2\text{S}_2)_2$ and $(\text{MeCN}_2\text{S}_2)_2$. While the structure of $(\text{PhCN}_2\text{S}_2)_2$ has been known for some time²⁰, it has not previously been possible to obtain crystals of $(\text{MeCN}_2\text{S}_2)_2$. Figure 4.11.a-d juxtaposes the molecular packing in the structures of $(\text{PhCN}_2\text{S}_2)_2$ and $(\text{MeCN}_2\text{S}_2)_2$. A perspective view down the b axis of the orthorhombic unit cell ($P2_12_12_1$) of $(\text{PhCN}_2\text{S}_2)_2$ reveals sizable van der Waals regions (channels) through which atomic nitrogen can reach the S-S links. The structure of $(\text{MeCN}_2\text{S}_2)_2$ (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 $(\text{MeCN}_2\text{S}_2)_2$ with respect to $(\text{PhCN}_2\text{S}_2)_2$.

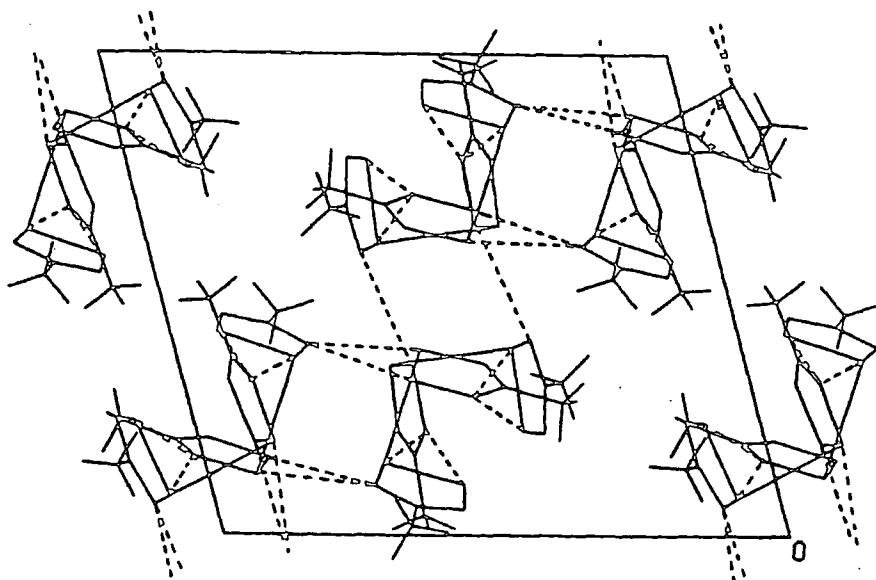
Both the geometry and the reaction temperature considerations have dealt with the kinetic aspects. It is, however, possible that an important contributory factor to the successful plasma nitrogeation of $(\text{PhCN}_2\text{S}_2)_2$ is the stabilisation energy which arises from a weak overlap of the uppermost π orbitals of the two cofacial PhCN_3S_2 rings¹¹. This is reflected in the considerably shorter distances, viz., 2.53 Å between the sulphur atoms of the two cofacial rings in $(\text{PhCN}_3\text{S}_2)_2$ as compared with an average distance 3.11 Å of the dimeric $(\text{PhCN}_2\text{S}_2)_2$.

Figure 4.11. Comparison of the $(\text{MeCN}_2\text{S}_2)_2$ and $(\text{PhCN}_2\text{S}_2)_2$ crystal structures.

a. Stick model projection of the $(\text{MeCN}_2\text{S}_2)_2$ 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 omitted for clarity).

a.



b.

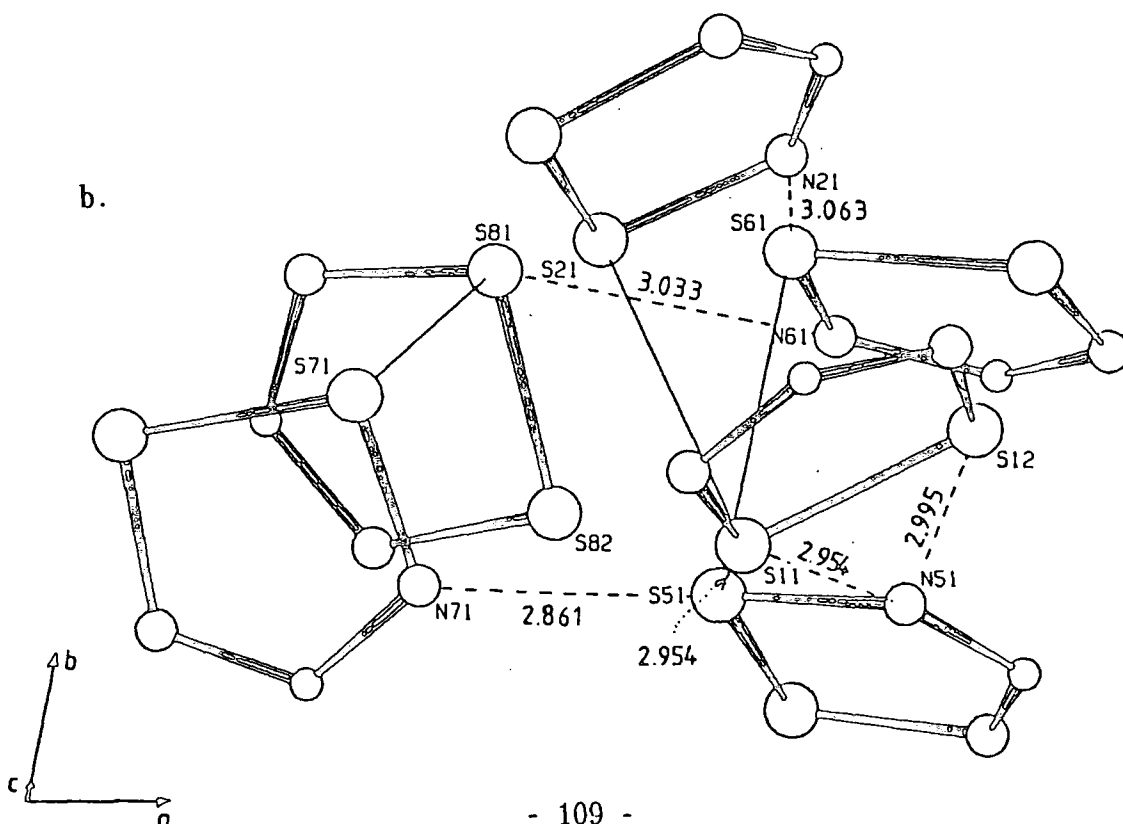
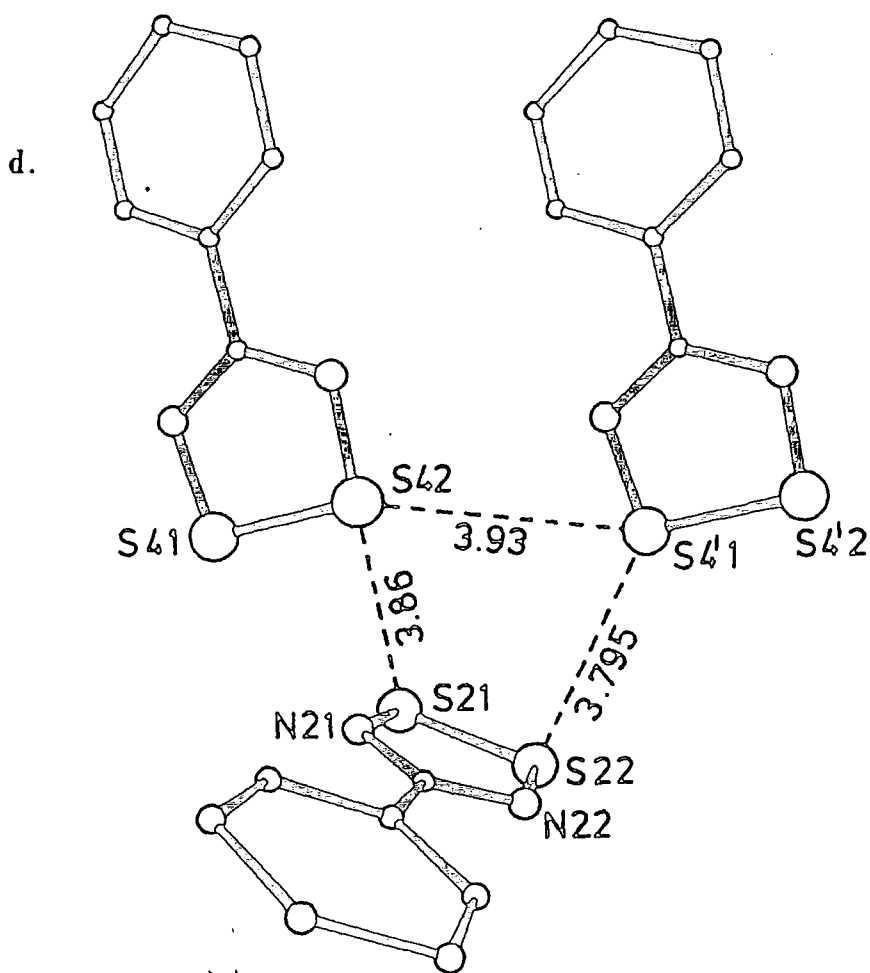
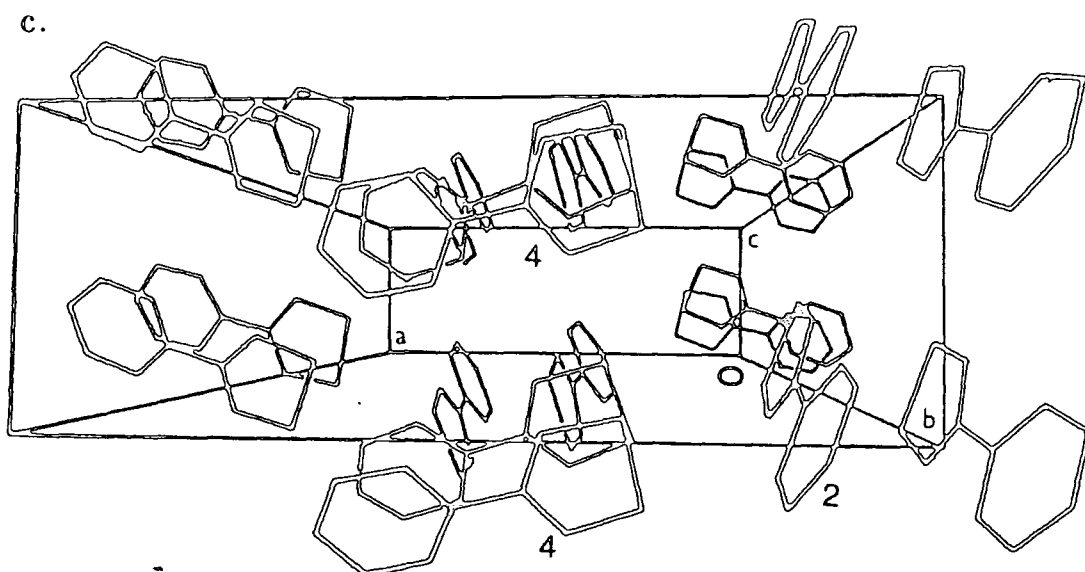


Figure 4.11. c. A perspective view down the b axis (32.98 Å) of the $(\text{PhCN}_2\text{S}_2)_2$ orthorhombic unit cell, showing the van der Waals channels (cf. d.). Only the molecules filling the upper half of the unit cell are shown.

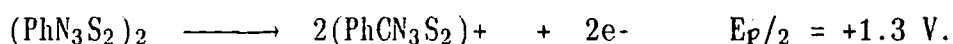
d. The 'bottle-neck' of the channels with the S-S intermolecular distances shown (corresponding to positions of three of the $(\text{PhCN}_2\text{S}_2)_2$ molecules in Figure 4.10c., numbered 2, 4 and 4').



There is yet another kinetic advantage to be considered, namely the 'least motion' principle. The relatively minor spatial reorganisation occurring during the conversion of $(\text{PhCN}_2\text{S}_2)_2$ to $(\text{PhCN}_3\text{S}_2)_2$ 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 $(\text{PhCN}_3\text{S}_2)_2$ according to Boeré¹¹ gave fewer diffused lines probably due to a high degree of subdivision. Similar differences in the resolution quality apply to the infrared spectra.

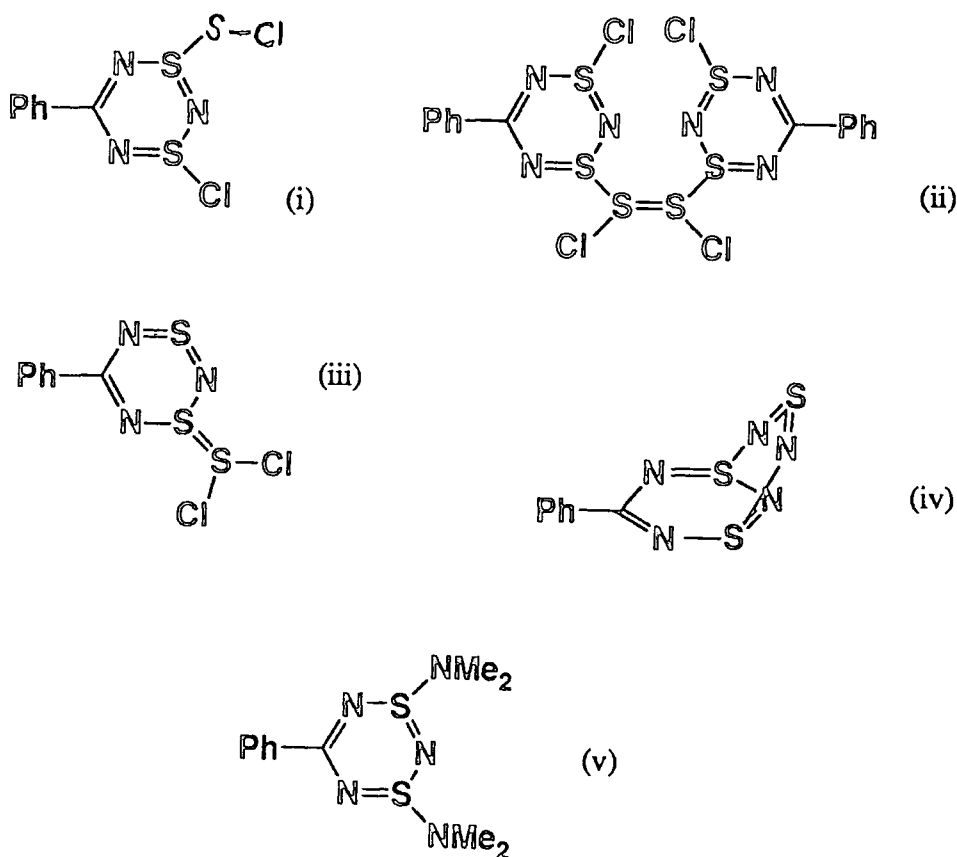
4.3.2. PhCN_3S_2 : CV and reactions.

$(\text{PhCN}_3\text{S}_2)_2$ is air stable and rather chemically unreactive: This stability is also reflected in the high oxidation potential, found experimentally (page 98);



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, $\text{PhCN}_3\text{S}_2\text{Cl}_2$ 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. $-\text{NMe}_2$. $(\text{PhCN}_3\text{S}_2)_2$ 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 $\text{PhCN}_3\text{S}_2 \cdot \text{SCl}_2$ (Scheme 4.5), however, Weissenberg diffraction photograph indicated thermal disorder which thwarted a full X-ray structure determination. By analogy with $\text{PhCN}_3\text{S}_2\text{Cl}_2$ and $\text{PhCN}_3\text{S}_2(\text{NMe}_3)_2$, $\text{PhCN}_3\text{S}_2 \cdot \text{SCl}_2$ may have structure 4.5.(i) which would account for the thermal disorder, 4.5.(ii) is less likely since SS double bonds are not strong, 4.5.(iii) is least likely since the $-\text{SCl}_2$ group, a strong chlorinating agent, will chlorinate the other sulphur. $(\text{Me}_3\text{Si})_2\text{NCN}$ reacted to form the novel bicyclic compound $\text{PhC}_2\text{N}_5\text{S}_2$ with a bridging carbon atom. This is analogous to the known compound PhCN_5S_3 with a bridging sulphur atom in the same position.



Scheme 4.5.

4.4 Conclusion

It is concluded that the uniqueness of the plasma nitrogeneration of $(\text{Ph}\overline{\text{CNSSN}})_2$ and $(\text{ClC}_6\text{H}_4\overline{\text{CNSSN}})_2$ 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 suitable 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 potential¹. 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 $[\text{tBuCNSNS}]^+\text{AsF}_6^-$

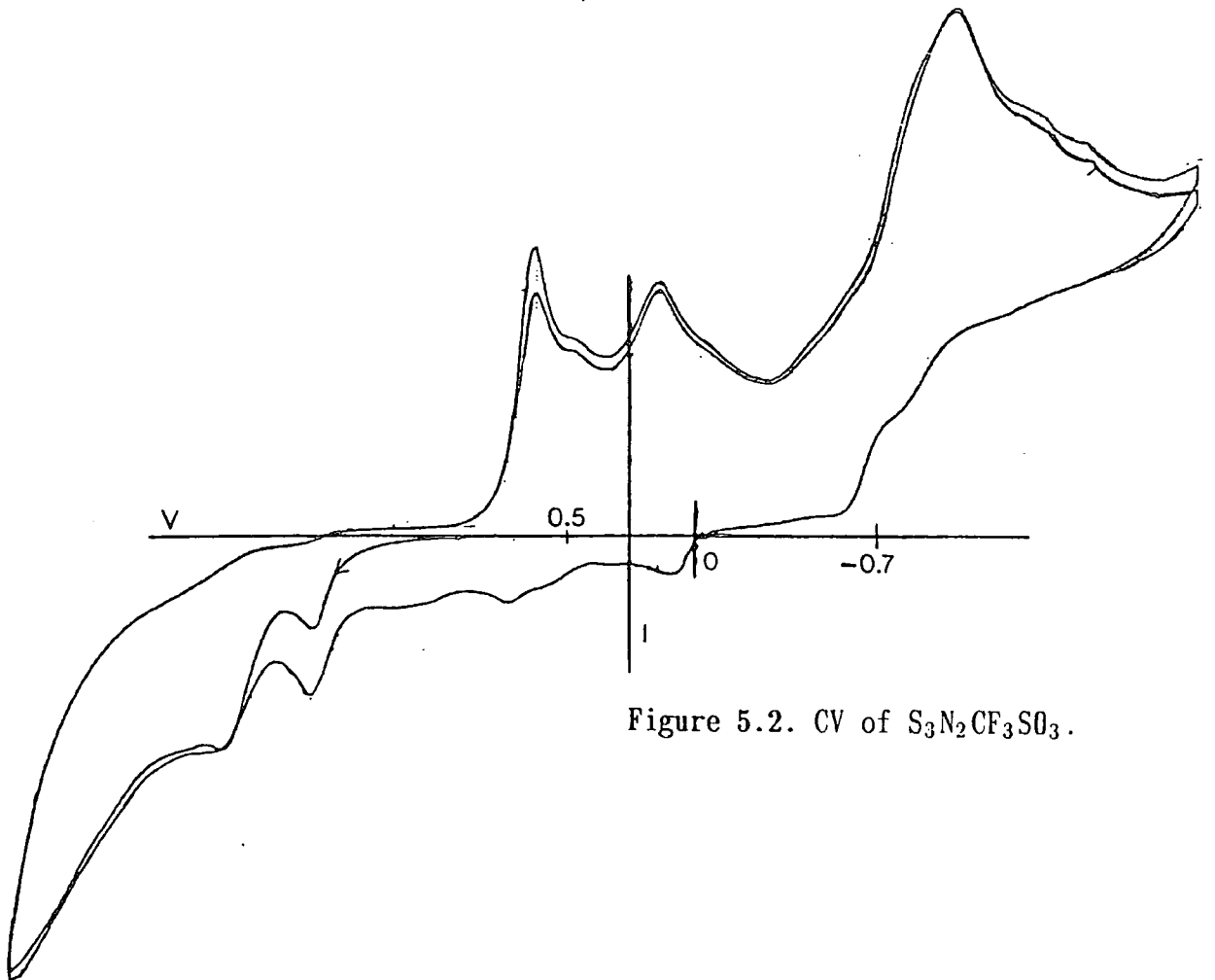
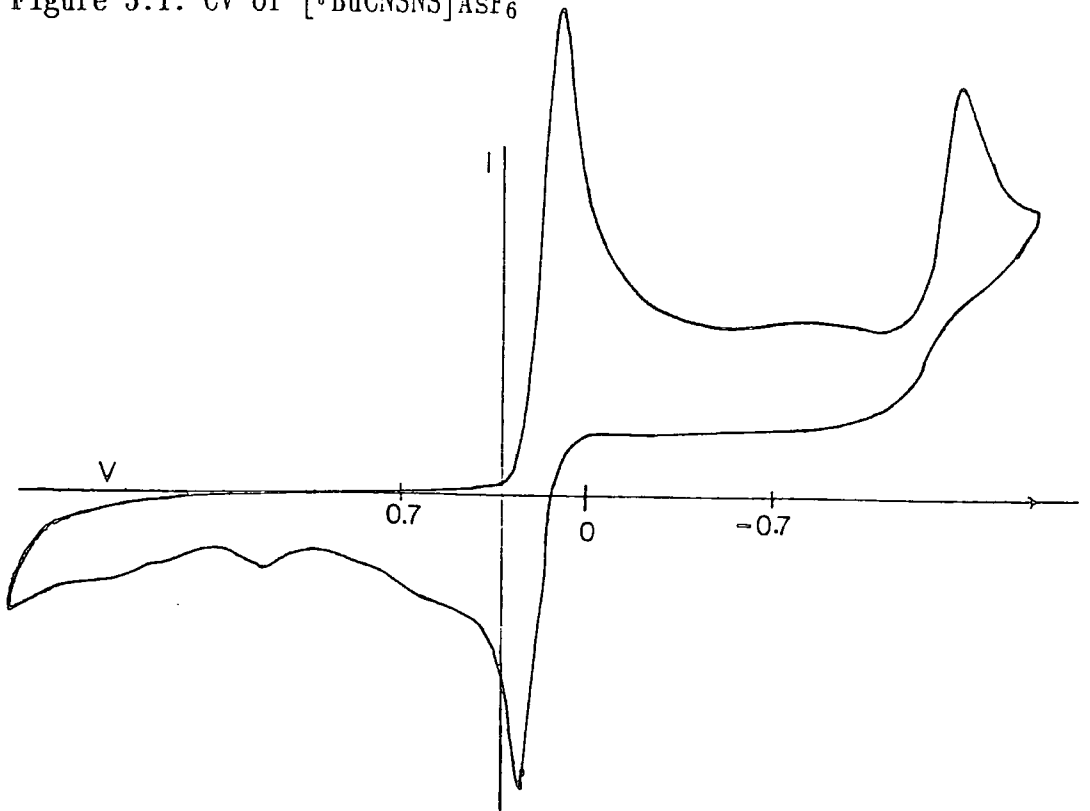


Figure 5.2. CV of $\text{S}_3\text{N}_2\text{CF}_3\text{SO}_3$.

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}:-

$$5.2.1.1 \quad I_{\text{net}} = i_0 A [e^{-\alpha nF / RT} - e^{(1-\alpha)nF / RT}]$$

i_0 = exchange current density.

α = Transfer coefficient.

A = Area, cm^2 .

η = Overpotential = $E - E_{\text{eq}}$.

which itself leads to the important Tafel Equation;

$$\ln i_{\text{net}} = \ln i_0 - \alpha n f \eta$$

In the three electrode 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:-

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

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

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

$$\Delta E = \eta_{we} + IR_{we-re}.$$

I = Current, R = Resistance of cell.

ϕ = Potential of electrode through which the current is flowing.

ϕ_e = Potential at equilibrium.

η = 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:-

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

A = electrode area, cm².

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. $i_p/v^{1/2} \cdot C = K'$.

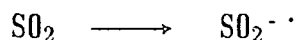
K' = all constants from 5.2.1.4.

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, $\text{SO}_2(\text{liq.})$ 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.



On the anodic side, however, the range stretches to approximately $+3.5\text{V}$. 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 chloride; 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 method⁴.

5.3.1. *Cyclic Voltammetry of S₂NAsF₆.*

(i). *CV in SO₂.*

An oven dried 3 limbed cell was placed in a glove box. S₂NAsF₆ (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. SO₂ (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

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

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

(ii). *CV in Acetonitrile.*

S₂NAsF₆ (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 CH₃CN 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 S₂NAsF₆. Two repeat experiments were carried out. In the first the cell was cooled to -196° C and the CH₃CN frozen as it was syringed in.

Figure 5.3. CV of S_2NAsF_6 in SO_2 .

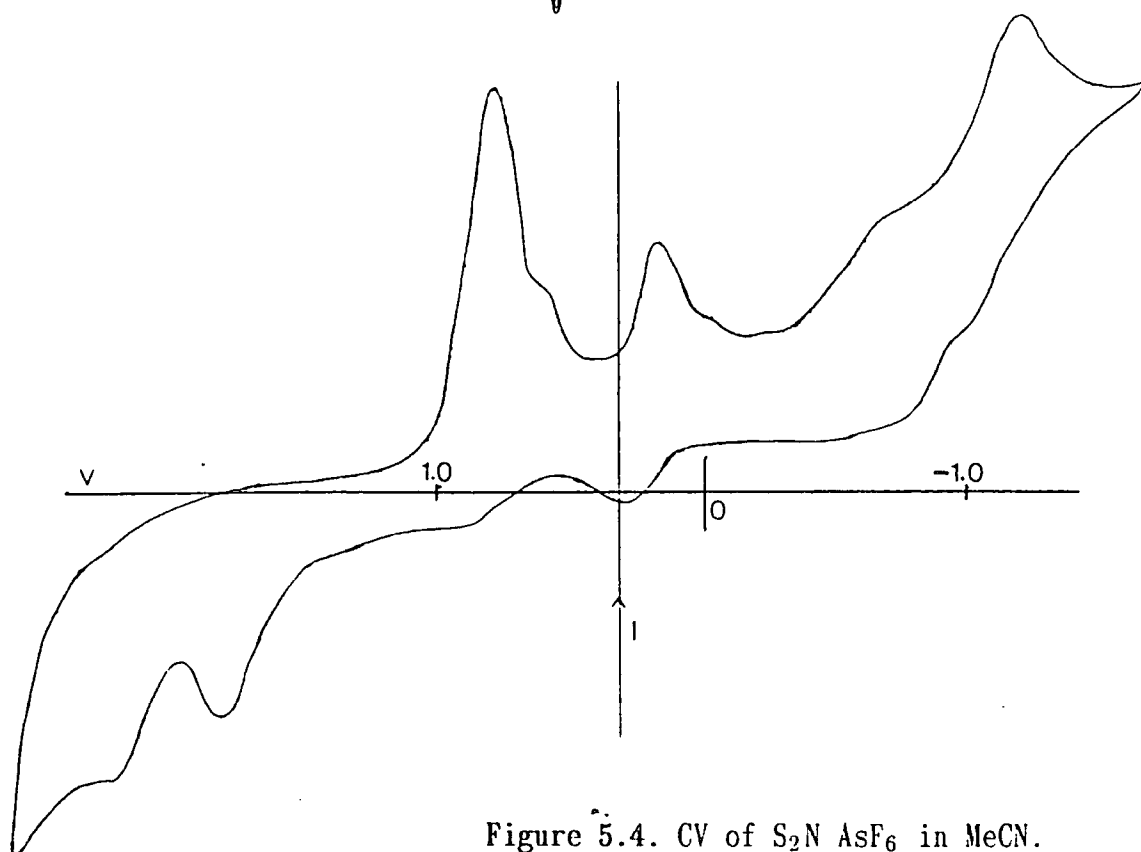
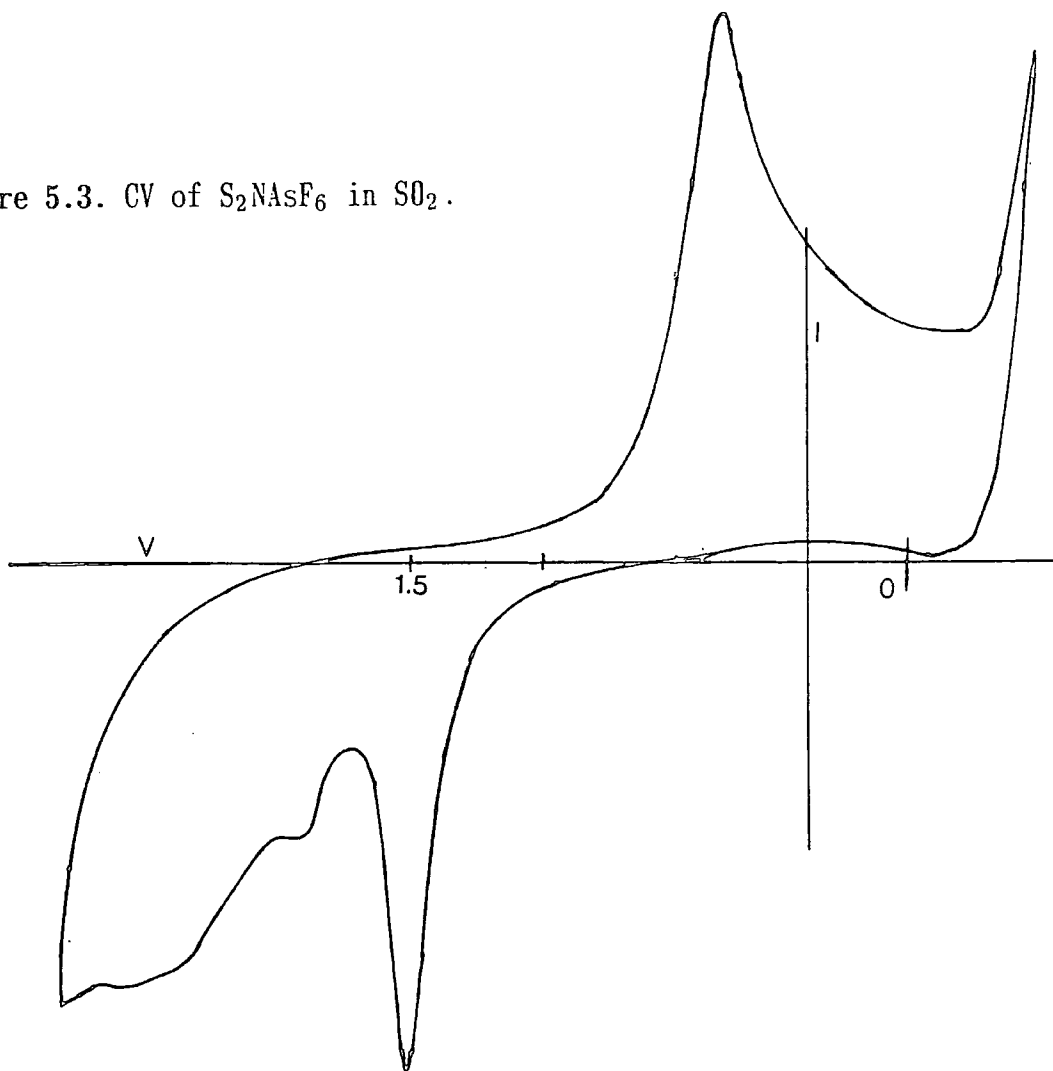


Figure 5.4. CV of S_2NAsF_6 in MeCN.

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 $\text{S}_2\text{N}^+\text{AsF}_6/\text{CH}_3\text{CN}$ were:-

$$E_p = + 0.65 \text{ V}$$

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

5.3.2. Kinetic Study of $\text{S}_2\text{NAsF}_6/\text{CH}_3\text{CN}$.

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^{+} cation.

(i). $\text{S}_3\text{N}_2\text{AsF}_6$ in MeCN. - This is a brown crystalline solid only moderately soluble in MeCN. However, a solution of $\text{S}_3\text{N}_2\text{AsF}_6$ (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.

$$\begin{array}{ll} E^1_p = + 0.58V & [\text{cf. } S_2N^+ \quad E^1_p = +0.66V \\ E^2_p = + 0.16V & E^2_p = +0.08V] \end{array}$$

(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.

$$\begin{array}{l} E^1_p = +0.7V \\ E^2_p = +0.24V \end{array}$$

(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 $E_{p/2}$.

$$\begin{array}{l} E_p = +0.68V \\ E_{p/2} = +0.85V \end{array}$$

(iv). $S_3N_2CF_3SO_3$ in MeCN. - The preparation of this black/blue crystalline solid is described 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.

$$\begin{array}{l} E^1_p = +0.62V \\ E^2_p = +0.15V \end{array}$$

Figure 5.5. CV of the reaction between S_2NAsF_6 and MeCN

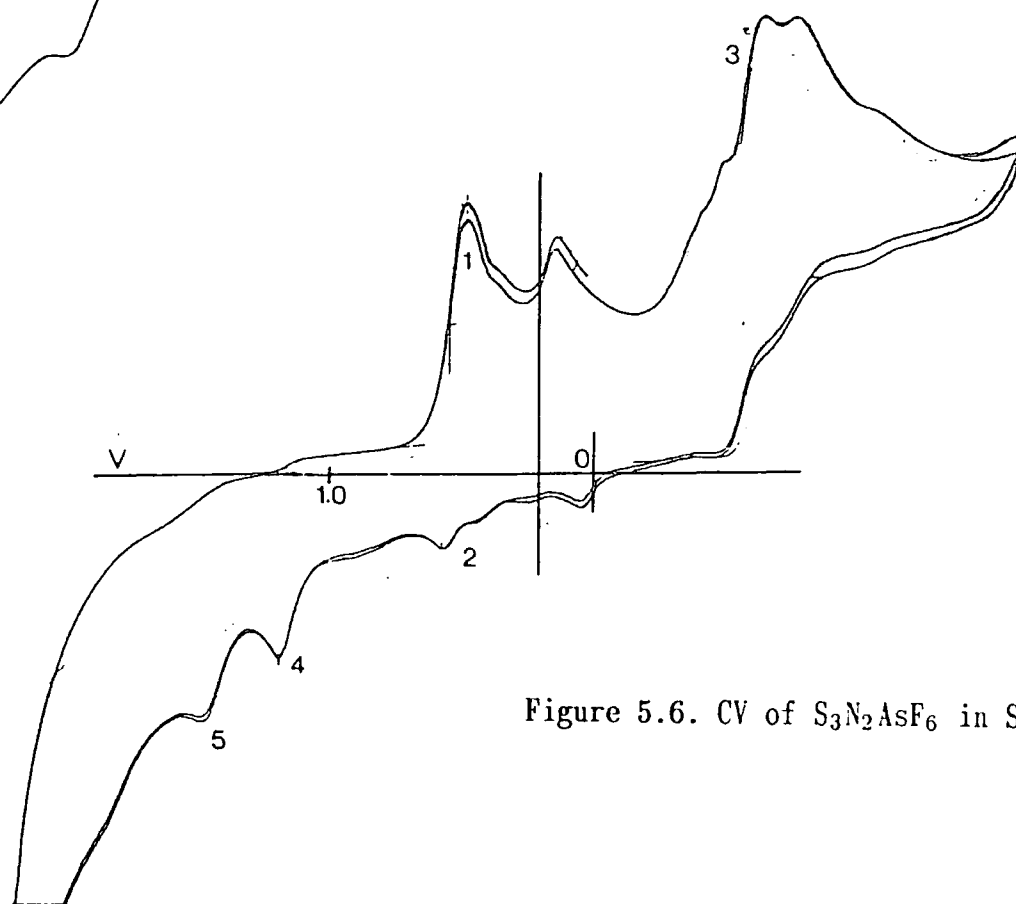
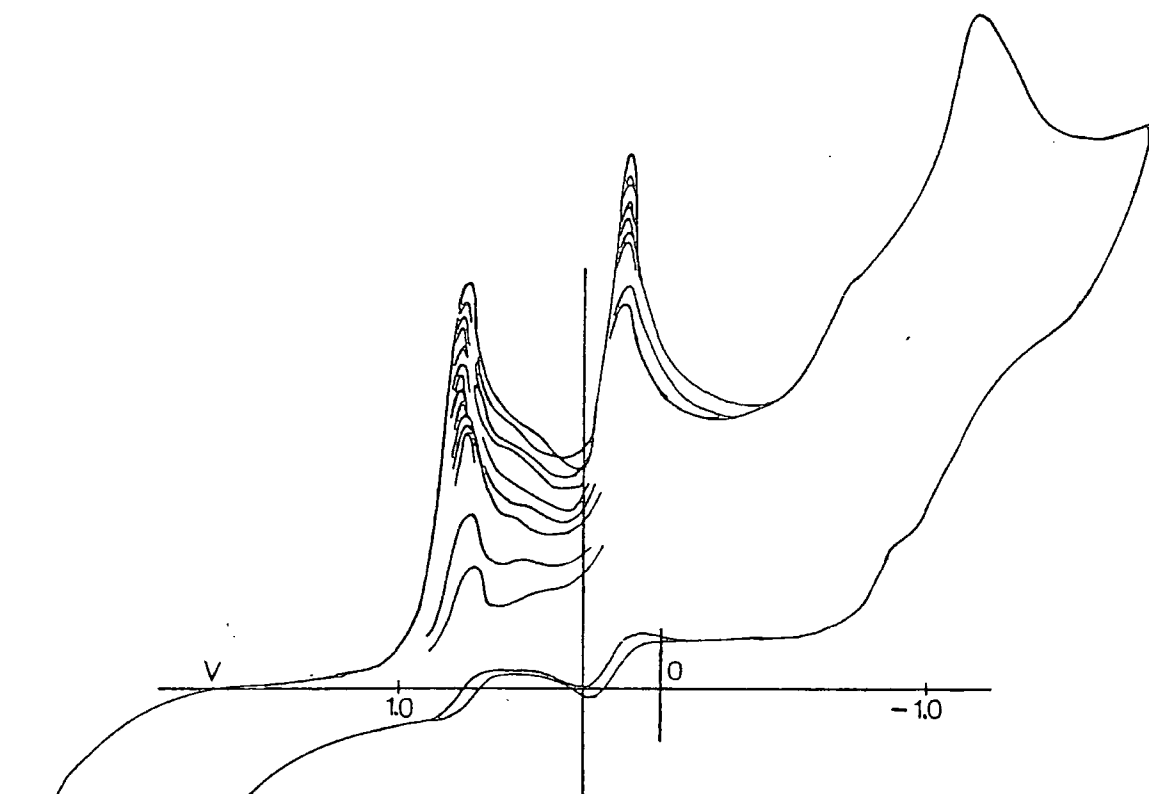


Figure 5.6. CV of $S_3N_2AsF_6$ in SO_2

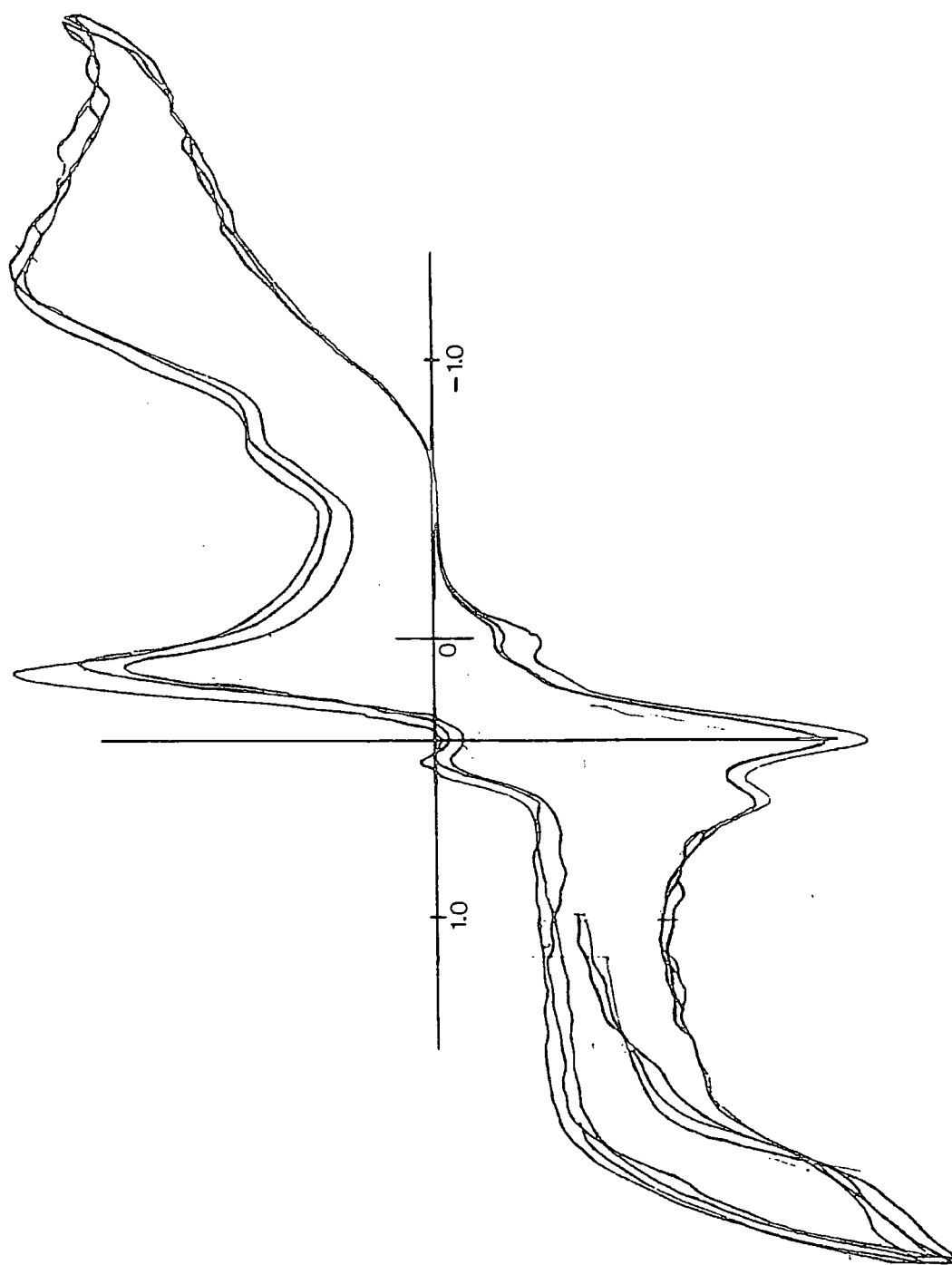
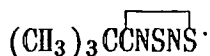


Figure 5.7. The Isomerisation of "1,3", $t\text{ButylCN}_2\text{S}_2$ to "1,2", $t\text{ButylCN}_2\text{S}_2$.

5.3.4. *Cyclic Voltammetry of 4-t-butyl 1,3,2,5 dithiadiazole,*



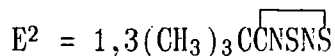
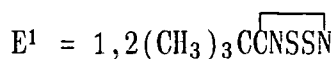
A prepared 3 limbed cell was placed in a glove box. Freshly prepared 1,3 t-butyl dithiadiazole (0.02g, 0.12mmol) was quickly transferred via a special teflon micro syringe to the cell which was wrapped in foil. To ensure complete exclusion of moisture, MeCN (15.0ml) was also added whilst in the glove 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).

$$E^1_p = +0.38\text{V}$$

$$E^2_p = +0.32\text{V}$$

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

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



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

Using the above procedure, (5.3.1. (i)) $[\text{PhCN}_2\text{S}_2]\text{Cl}$ (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) $[\text{PhCN}_2\text{S}_2]\text{Cl}$ in 15.0 ml MeCN and the same result was obtained.

$$E_p = +0.52\text{V}$$

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

Figure 5.8. CV of 1,2,3,5 [PhCN₂S₂]Cl.

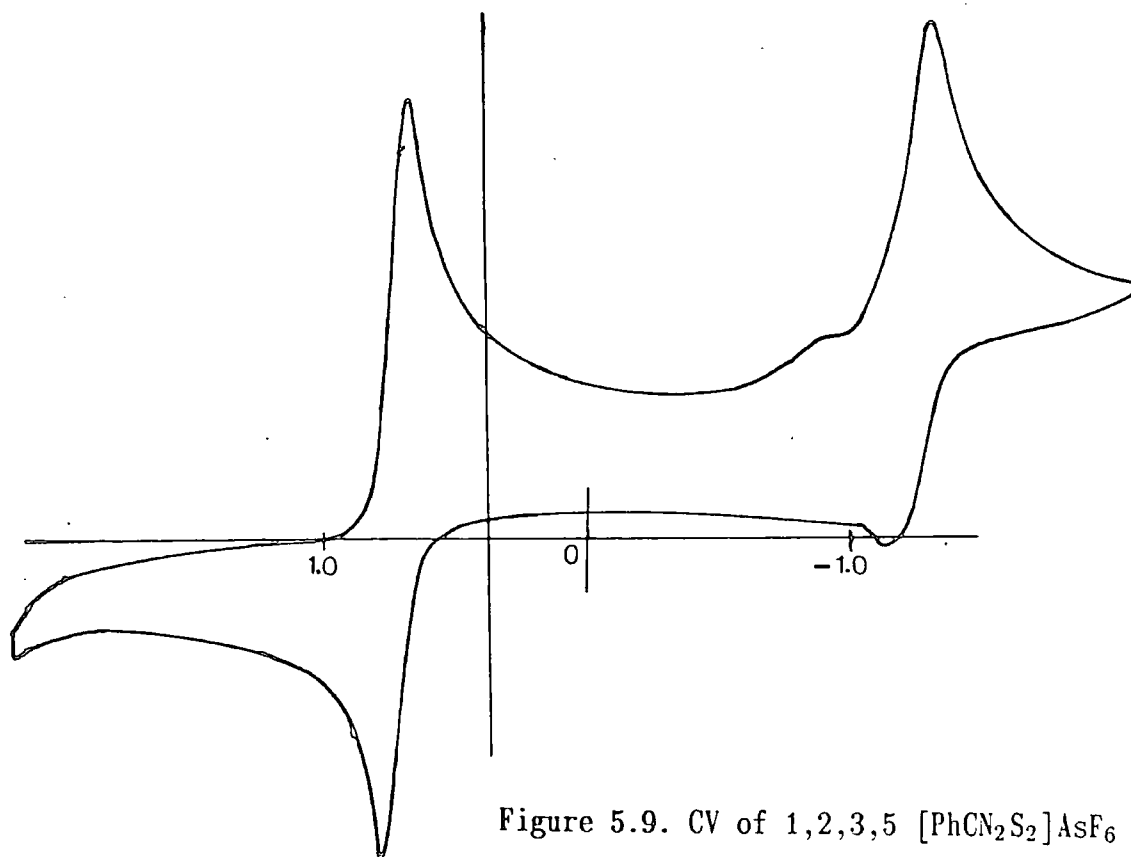
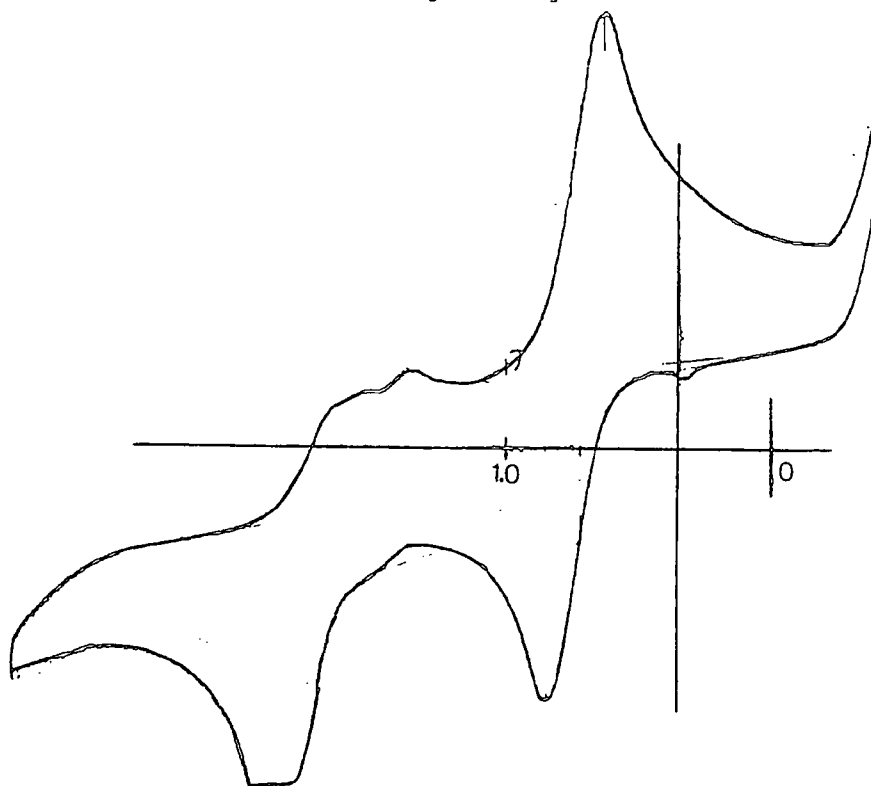
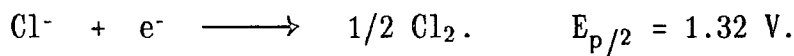


Figure 5.9. CV of 1,2,3,5 [PhCN₂S₂]AsF₆

Figure 5.8. shows a good reversible CV. Peak 2 is the oxidation peak for the chloride ion¹². 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.



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

The above procedure was repeated using bright orange $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$ (0.006g, 0.016mmol) which readily dissolved in MeCN (cf. $[\text{PhCN}_2\text{S}_2]\text{Cl}$). Furthermore the system was very clean and clearly showed a sharp quasi reversible 2nd electron process. Figure 5.9.

$$E_p = +0.46\text{V}$$

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

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) $[\text{p-ClPhCNSNS}]\text{AsF}_6$. The CV run at -10°C showed a reasonably clean system, but noticeably there is now no sharp peak corresponding to a 2nd electron process. The broad peak at -1.46V indicates chemical complications and was entirely irreversible.

$$E_p = +0.19\text{V}$$

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

5.4. RESULTS AND DISCUSSION.

5.4.1. *The Redox Potentials of the Dithionitronium and S_3N_2^+ cations.*

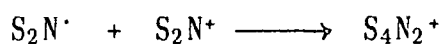
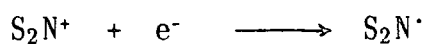
(i) S_2NAsF_6 in liquid SO_2 .

The experiments described in this chapter were made possible by use of

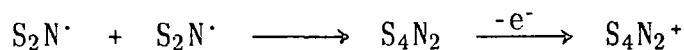
developments (by Z.V.H.) which overcame many of the serious problems, like low electrolyte solubility, encountered in earlier attempts to apply CV to SO_2 solutions. Indeed it was not until 1979 that Bard et al⁹ found that tertiary butyl ammonium salts act as suitable background electrolytes in SO_2 . 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 incompressibility 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 $E = +0.76\text{V}$ 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 consistent with recent measurements of the redox potential of SN^+ at $E_{\text{P}}^{\text{red}} \geq +0.8\text{V}^{13}$ and S_3N_2^{+} at $E_{\text{P}}^{\text{red}} = +0.66\text{V}$ (MeCN). As expected SN^+ , behaving like a pseudo-metal atom, is the most oxidising, having a value similar to that for Ag/Ag^+ , $\text{Fe}^{3+}/\text{Fe}^{2+}$, Hg^{2+}/Hg and $\text{NO}_3^-/\text{NO}_2^{14}$. 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 $E_{1/2}^{\text{ox}} = +1.52\text{V}$, but is unlikely to be the reverse of the process at $E = +0.76\text{V}$ since the half peak potential difference is 0.76V , compared to $59/n \text{ mV}$ at 25°C potential difference allowed for a reversible process¹⁵. Indeed its value is very close to that for S_4N_2^+ ($E_{P/2} = 1.43\text{V}$)¹⁶. The formation of this species can be explained in the following sequence:-
Scheme 5.1.

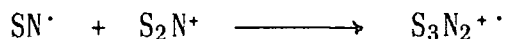
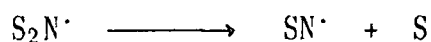


or



Neither of these processes appears to be reversible. Previous workers¹⁷ expected to see the formation of S_3N_2^+ via the mechanism in scheme 5.2. Although there is no correlation with the voltammogram of S_3N_2^+ 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 $\text{S}_3\text{N}_2^+/\text{S}_2\text{N}^+$ equilibrium.

Scheme 5.2.



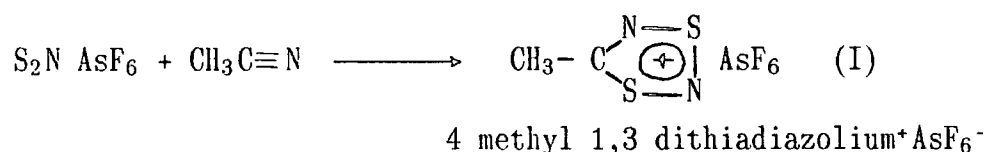
It is possible that both S_2N^\cdot and SN^\cdot are too reactive to remain in solution long enough to be detected by the returning sweep. However, on prolonged electrolysis of a $\text{S}_2\text{NAsF}_6/\text{SO}_2$ solution at $+0.70\text{V}$, a third peak at $E_p^{\text{red}} = +1.34\text{V}$ did 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 established¹⁰ that in solution $S_3N_2^{2+}$ is in equilibrium with SN^+ and 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 reaction¹⁸;



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 therefore its concentration can be considered constant. The reaction thence becomes pseudo 1st order.

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

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

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

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

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_∞ value for the product and so it was this that was plotted. See Graph 5.1.

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

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

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

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

(Intercept = 2.98).

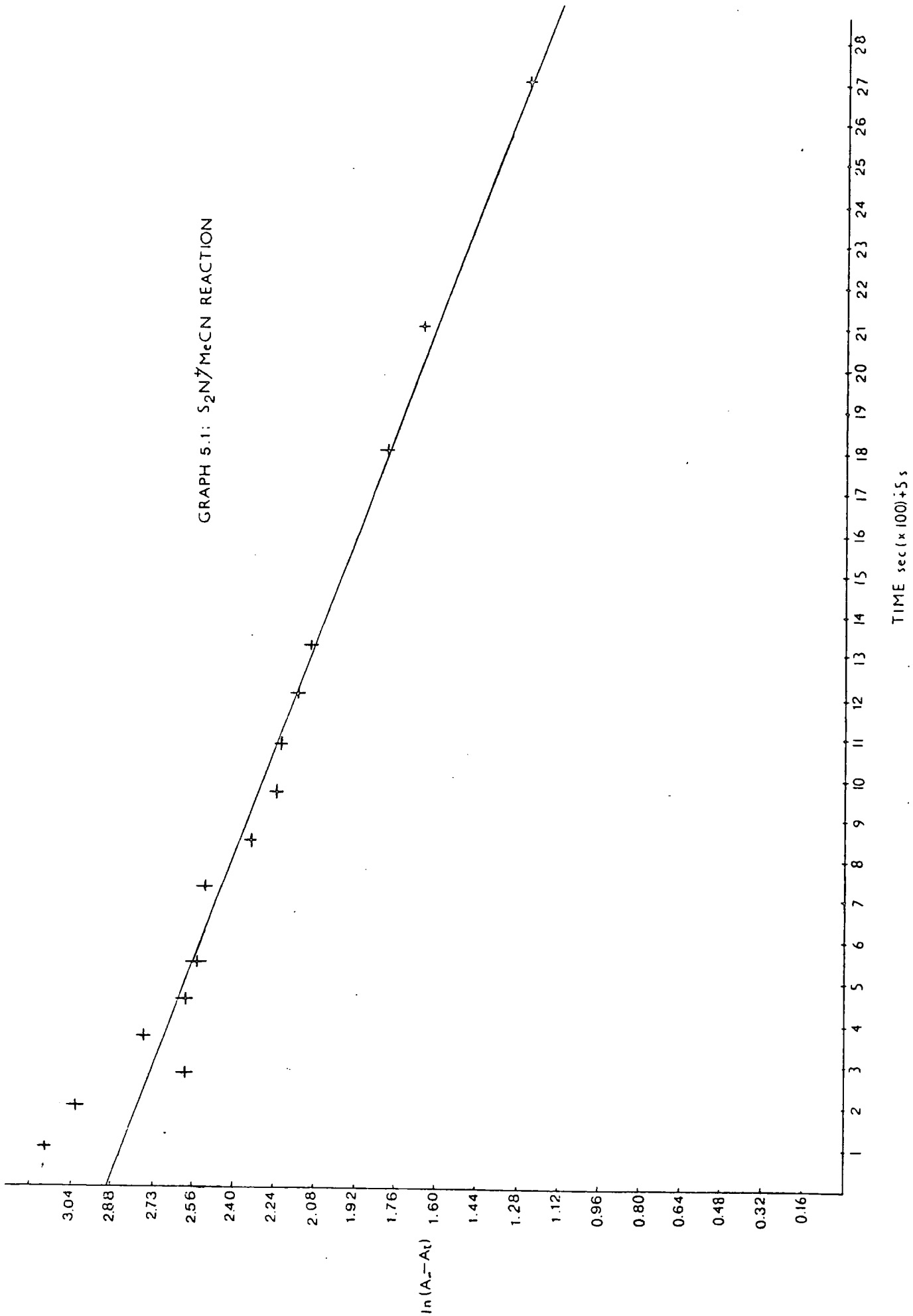
[Value obtained by missing out anomolous point.

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

(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 Arrhenius' equation.

GRAPH 5.1: S_2N^+MeCN REACTION

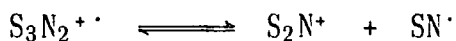


(iii) The $S_3N_2^{+\cdot}$ cation. - S_3N_2Cl is only slightly soluble in SO_2 and it proved necessary to use the $S_3N_2AsF_6$ salt which, although more soluble, is still only moderately so. The several peaks obtained in SO_2 were superficially similar to those obtained for S_2N^+ in MeCN, Figures 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)	$E^1_{red P/2} = +0.66V$
$[E^1_p = +0.74V$	(SO_2)	
$E^2_p = +0.69V$		$E^3_p = +0.18V$
$E^4_p = +1.45V$		$E^5_p = +1.78V$

The reduction product from E^1 will be $S_3N_2^{\cdot}$ which is an 8π , 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 $S_3N_2^{+\cdot}$:



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 σ_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; $\text{Log } k/k_0 = \sigma\rho$

k_0 = Rate or equilibrium constant for $X = H$. k = Constant for group X .

ρ = a constant for a given reaction under a given set of conditions.

σ = a constant characteristic of the group X .

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

$$\Delta G = - RT \ln k \quad \text{for the unsubstituted case.}$$

and;

$$\Delta G = - RT \ln k_0. \quad \text{Then the Hammett equation may be}$$

written:-

$$\ln k - \ln k_0 = \sigma\rho$$

so that,

$$\frac{-\Delta G}{2.3RT} + \frac{\Delta G_0}{2.3RT} = \sigma\rho$$

$$-\Delta G = \sigma\rho \cdot 2.3RT - \Delta G_0$$

For a given reaction, under a given set of conditions ρ, R, T , and ΔG_0 are all constants, so that σ is linear with ΔG .

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 $E_{P/2}$, σ_P and σ_{P^+} are given in Table 5.1. Generally σ_{P^+} values relate to a developing positive charge and so were plotted against $E_{P/2}$ (ox) values, whilst $E_{P/2}$ (red) values were plotted against σ_P to obtain the two graphs 5.4.2. Small deviations occur for H in σ_{P^+} vs $E_{P/2}$ (ox) and for Me in σ_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 $\overline{\text{RCNSNS}^+}$ R	$E_{P/2}$ (ox) V (± 0.005)	$E_{P/2}$ (red)	σ_P	σ_{P^+}
$\rho\text{-CH}_3\text{C}_6\text{H}_4\text{-}$	0.24	0.21	-0.14	-0.31
$\rho\text{-HC}_6\text{H}_4\text{-}$	0.25	0.22	0.0	0.0
$\rho\text{-ClC}_6\text{H}_4\text{-}$	0.28	0.25	0.24	0.11
$\rho\text{-CNC}_6\text{H}_4\text{-}$	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

X

X

σ_p vs $E_{1/2}(\text{red})$

σ_p^+

σ_p^+ vs $E_{1/2}(\text{ox})$

X

X

X

X

X

X

0.8

0.6

0.7

0.5

0.6

0.4

0.5

0.3

0.4

0.2

0.3

0.1

0.2

0

0.1

0.1

0

-0.2

-0.1

-0.3

0.2

0.3

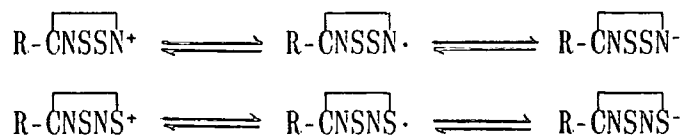
0.2

0.3

POTENTIAL, $E_{1/2}$ (VOLTS)

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:-



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 $\overline{\text{RCNSN}}^+$ Chlorides and Hexafluoroarsenates.

Compound, R.	1st e Transfer		2nd e Transfer.	
	$E_{p/2}$ (ox)	$E_{p/2}$ (red)	E_p (ox)	$E_{p/2}$ (ox)
Chloride salts				
PhCH ₂ -	0.78	0.72	-0.94	/
Ph-	0.60	0.61	-0.86	/
Cl ₃ C-	0.53	0.47	-0.72	-0.60
CH ₃ -	0.28	0.29	-1.12	-0.95
CH ₃ CH ₂ CH ₃ -	0.45	/	/	/
(CH ₃) ₃ C-	0.33	0.28	-1.06	-0.93
AsF ₆ salts.				
Ph-	0.51	0.50	-0.92	-0.77
(CH ₃) ₃ C-	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, $\overline{\text{RCNSNS}^+ \text{AsF}_6^-}$ 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
ρ -ClPh-	0.28	0.25	/	/
Ph-	0.25	0.22	-1.35	-1.23
ρ -CNPh-	0.33	0.31	/	/
CH ₃ -	0.16	0.16	/	/
(CH ₃) ₃ C-	0.18	0.18	-1.41	-1.33
ρ -CH ₃ Ph-	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
ρ -ClPh-	0.53	0.50	-0.90	-0.80
CF ₃ -	0.80	0.76	-0.68	-0.54
(CH ₃) ₃ C-	0.44	0.50	-1.18	-1.03
CH ₃ CH ₂ CH ₂ -	0.52	0.74	-1.12	/
(1,3 (CH ₃) ₃ C-)	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 ₃ CNSNCCF ₃	0.48	0.56	/	/
CF ₃ CNSNCCF ₃ AsF 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.

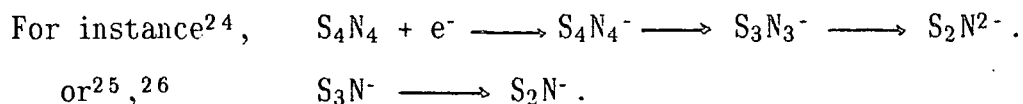
Compound	$E_{p/2}$ (ox)	$E_{p/2}$ (red)	E_p (ox)	E_p (red)	E^3_p	E^4_p	E^5_p	
S ₂ NAsF ₆	SO ₂	0.76	1.52	0.60	1.62	/	/	/
	MeCN	0.72	1.45	0.65	0.08	/	1.47	/
S ₃ N ₂ AsF ₆	SO ₂	/	/	0.74	0.86	0.28	1.56	1.88
	MeCN	0.66	/	0.58	/	0.16	1.45	1.78
S ₃ N ₂ CF ₃ SO ₃	SO ₂	/	/	/	/	/	/	/
	MeCN	0.70	/	0.62	/	0.14	1.49	/
S ₃ N ₂ Cl	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 $\overline{CN_2S_2}$ 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 6π and 7π electrons is reflected in the integrity of the ring throughout many reactions and the existence of stable paramagnetic free radical liquids²³ - 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 $t\text{-butyl}\overline{CNSSN}$. 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.



The anion $RCN_2S_2^-$ would be an 8π 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 these 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 $\text{PhCN}_2\text{S}_2^+$ 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 $E_{P/2} [0x]$ 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 $E_{P/2} [0x]$ 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

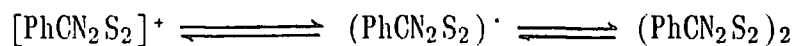
Table 5.7. Comparison of $E_{P/2}$ values according to isomer and salt type.

Salt	2,Cl ₃ C-	2,Pro-	2, ^t Bu-	3, ^t Bu-	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 [PhCN₂S₂]Cl/AsF₆ system. Not only are the values much closer together but they are also reversed. [PhCN₂S₂]Cl has a more positive $E_{P/2}$ [0x] value than [PhCN₂S₂]AsF₆ (0.60 and 0.52V respectively), although a value of 0.7V might be expected of [PhCN₂S₂]AsF₆. 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 PhCN₂S₂⁺ would be expected in the double layer than in the bulk solution.



It is well established that RCN₂S₂[·] is a particularly stable free radical, frequently observed for a range of R substituents. However, the dimeric unit (RCN₂S₂)₂ is less often seen, though still known for a range of R groups eg. CF₃²⁷, Me²⁸, Ph²⁹, *p*-ClPh. The particular structure of (PhCN₂S₂)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, $[\text{CH}_3\text{CN}_2\text{S}_2]\text{Cl}$

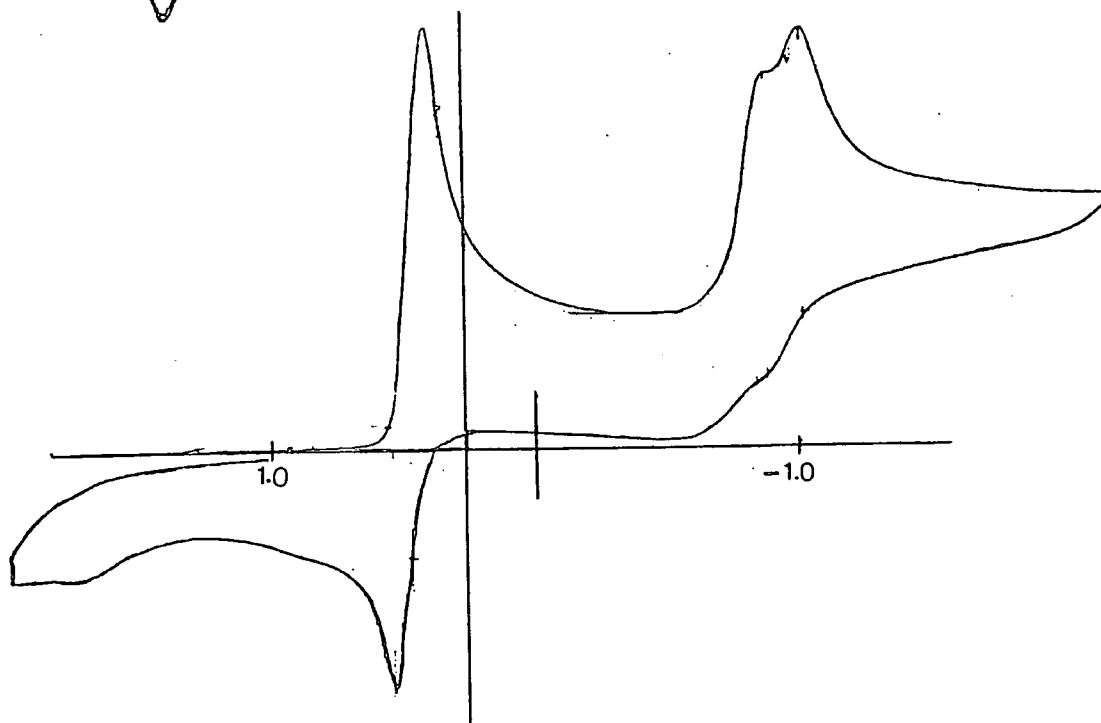
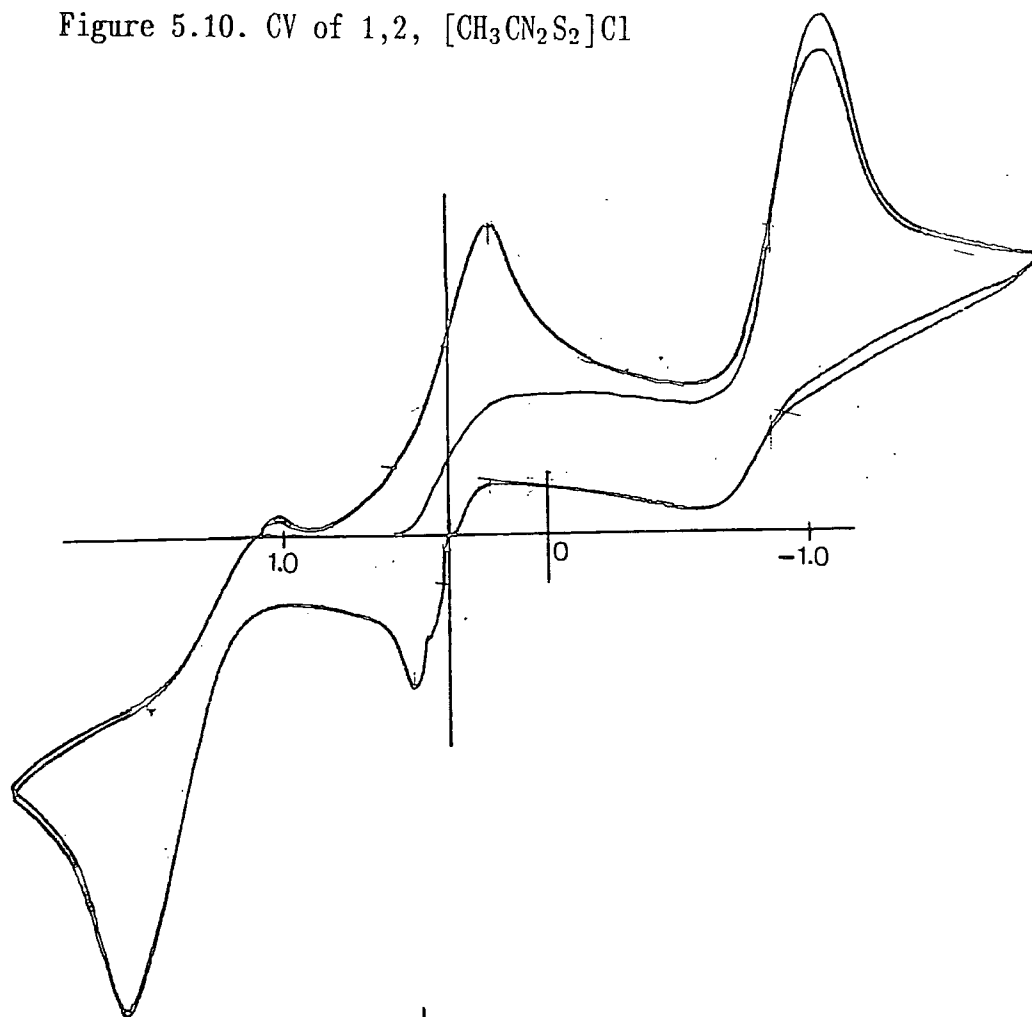


Figure 5.11. CV of 1,2, $[\text{CH}_3\text{CN}_2\text{S}_2]\text{AsF}_6$

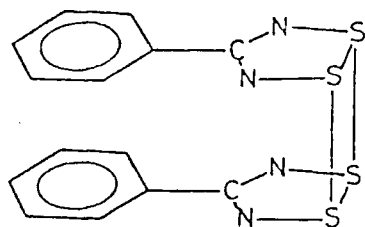


Figure 5.12. Dimer structure of PhCN_2S_2

For all three compounds $[\text{PhCN}_2\text{S}_2]\text{Cl}$, $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$ and $(\text{PhCN}_2\text{S}_2)_2$ the process $\text{PhCN}_2\text{S}_2^+ \rightleftharpoons \text{PhCN}_2\text{S}_2^\cdot$ 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 $[\text{PhCN}_2\text{S}_2]\text{AsF}_6$ 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, $^t\text{Bu}\overline{\text{CNSSN}}$, $p\text{-Cl-Ph}\overline{\text{CNSSN}}$, 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 $\overline{\text{tBuCNSSN}}$ and $\overline{\text{PhCNSSN}}$. 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 isomer³⁰, 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 days³⁰.

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 independently³¹.

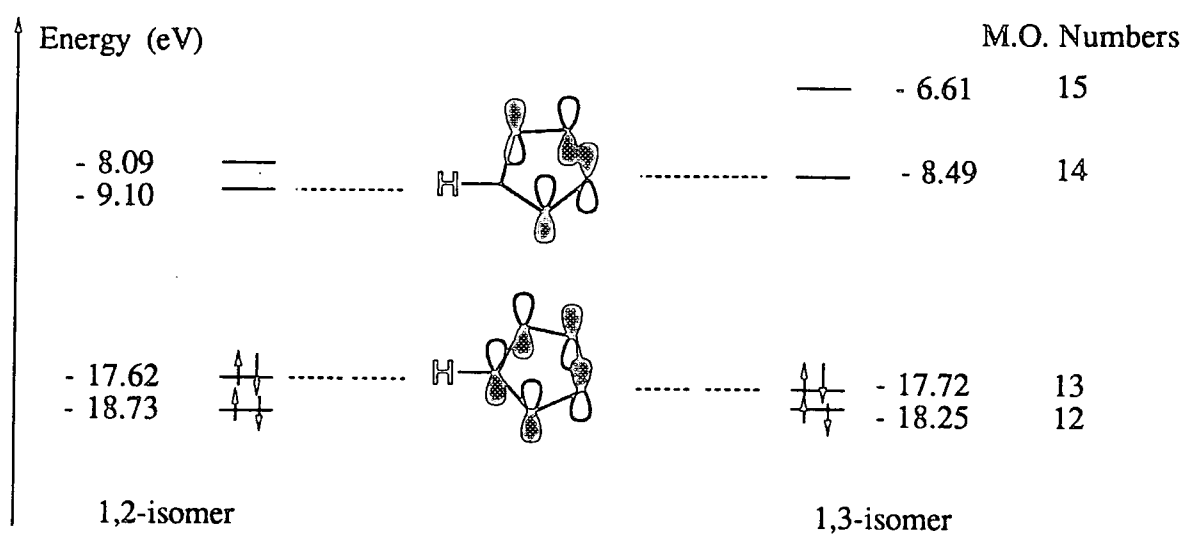


Figure 5.13. HOMO/SOMO(LUMO) energy levels of 1,2 and 1,3 dithiadiazoles..

Scheme 5.4. Redox Series.

- (i). 1,2, Radicals; $\text{CF}_3 > \text{Ph} > \rho\text{-ClPh} > \text{propyl} > \text{tbutyl} > \text{CH}_3$.
- (ii) 1,2, Chlorides; $\text{CF}_3 > \text{CH}_2\text{Ph} > \text{Ph} > \text{Cl}_3\text{C} > \text{propyl} > \text{tbutyl} > \text{CH}_3$.
- (iii). 1,2, AsF_6 salts; $\text{Cl}_3\text{C} > \text{Ph} > \text{tbutyl}, \text{CH}_3$.
- (iv). 1,3, AsF_6 salts; $\text{Cl}_3\text{C} > \text{anthr} > \rho\text{-CNPh} > \rho\text{-ClPh} > \text{Ph} > \rho\text{-CH}_3\text{Ph} > \text{tbu}, \text{Me}$
- (v). EN values³²; $\text{Cl}_3\text{C}, 2.65; \text{propyl}, -0.115; \text{tBu}, -0.3; \text{Ph}, 0.46;$

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

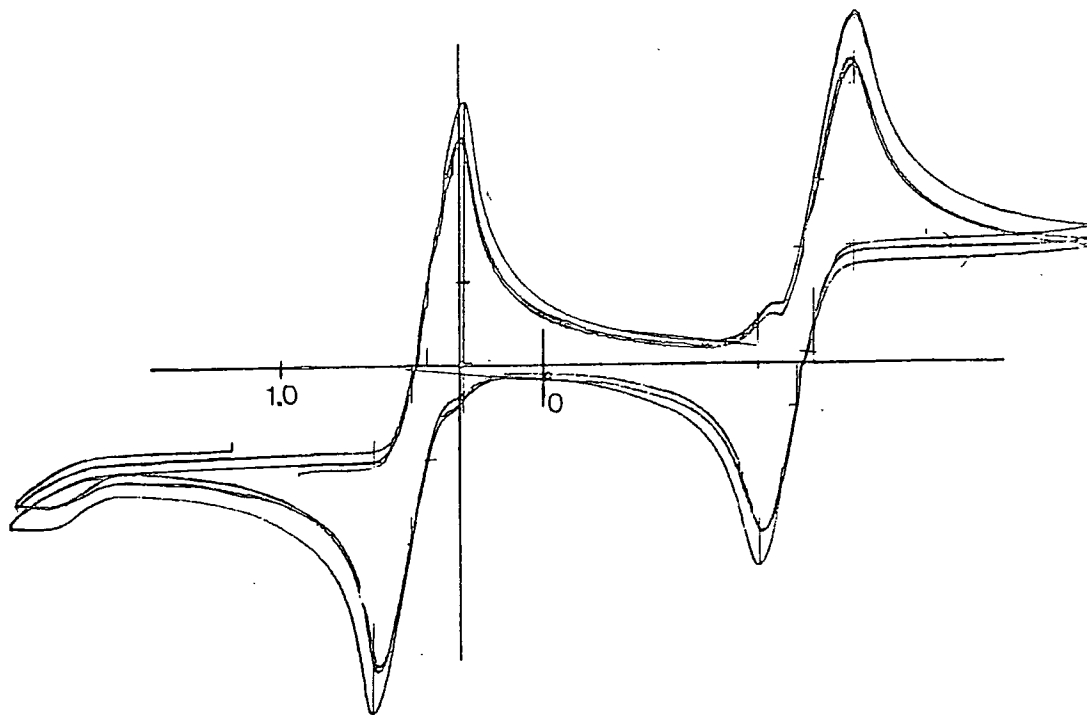
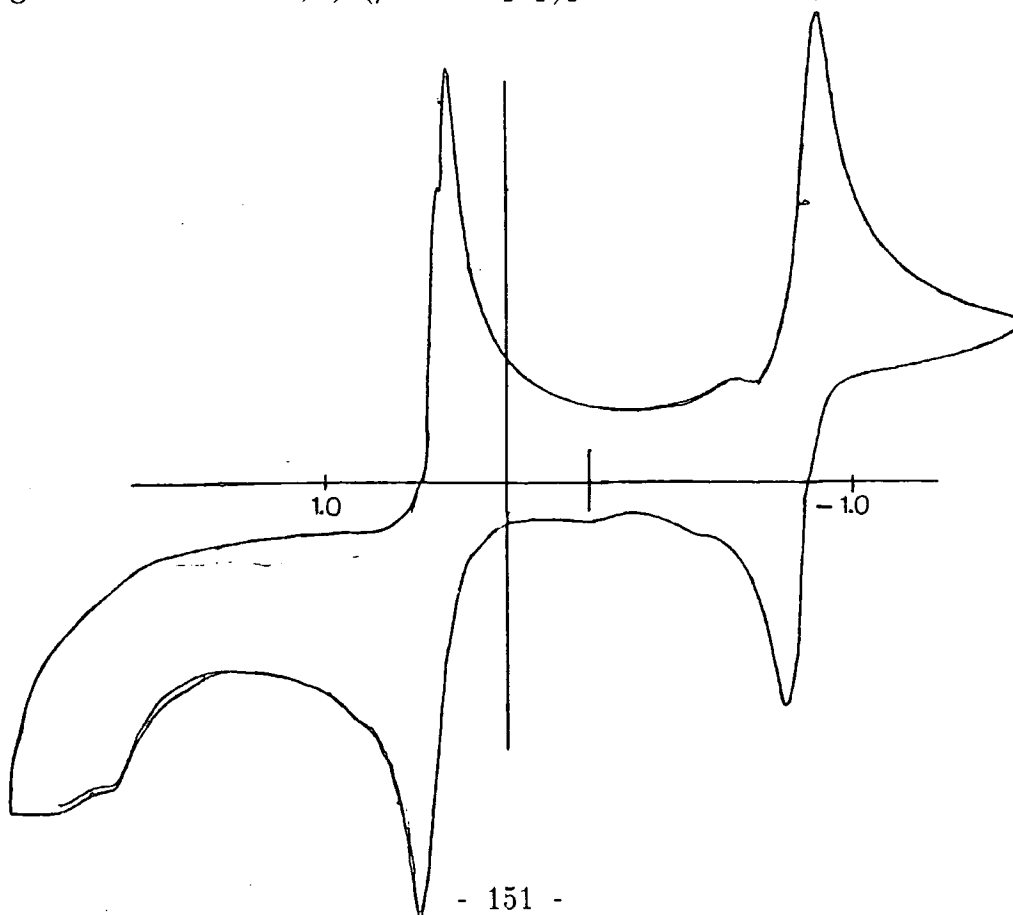


Figure 5.14. CV of 1,2, $(\rho\text{-ClPhCN}_2\text{S}_2)_2$



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 possibility 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.

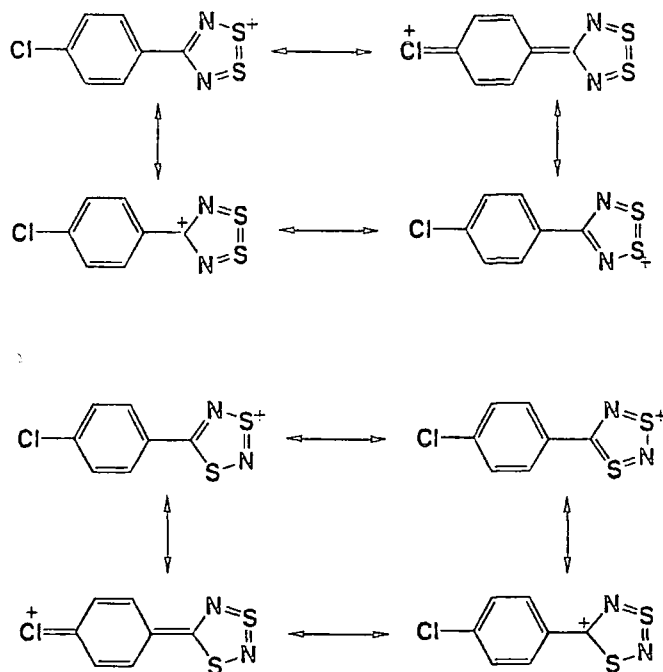


Table 5.8. Correlation of EN with $E_{P/2}$ for the alkyl derivatives.

	CH ₃	^t Bu	Pr ⁿ	Cl ₃ C
$E_{P/2}$ (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

Prⁿ=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 $\text{S}_3\text{N}_2^{++}$. 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 be 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 salt¹ 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 1980² 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 $S_2N^+/S_3N_2^{+}$ 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 1980⁵ 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 $S_2NCF_3SO_3$.

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 SO₂. This left bright yellow crystals (0.65g, 37% based in silver triflate), whilst removal of the SO₂ from the decanted liquid left a sticky red oil, (unidentified), but which contained crystals of S₂NCF₃SO₃ (0.09g) and S₃N₂CF₃SO₃ (0.04g). The crystals of S₂NCF₃SO₃ were extremely moisture and oxygen sensitive and even slowly decomposed when exposed to the atmosphere of the glove box for any length of time. S₃NCF₃SO₃ requires C 5.28%, N 6.2%, S 42.3%. Found C 5.26%, N 6.0%, S 41.5%; Infrared spectrum, ν_{\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%) S₂N⁺, 227 (8%) 149 (8%) CF₃SO₃⁻.

6.2.2. Reaction of S₂N CF₃SO₃ with CH₃CN.

S₂NCF₃SO₃ (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 SO₂ (15ml) was condensed onto the mixture and the whole solution stirred for 24h at room temperature. The remaining unreacted S₂NCF₃SO₃ 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 SO₂ and identified by infrared

spectroscopy as $[\text{CH}_3\overline{\text{CNSNS}}]\text{CF}_3\text{SO}_3$. Yield = 0.085g (30% based on $\text{S}_2\text{NCF}_3\text{SO}_3$). Infrared spectrum, ν_{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; $\text{C}_3\text{H}_3\text{S}_3\text{N}_2\text{F}_3\text{O}_3$ 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 $\text{S}_2\text{NCF}_3\text{SO}_3$ with Benzonitrile.

Yellow $\text{S}_2\text{NCF}_3\text{SO}_3$ (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 $\text{S}_2\text{NCF}_3\text{SO}_3$) identified by infrared spectroscopy as $[\text{PhCNSNS}]\text{CF}_3\text{SO}_3$. $\text{C}_8\text{H}_5\text{S}_3\text{N}_2\text{F}_3\text{O}_3$ 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 $\text{S}_3\text{N}_2\text{AsF}_6$.

Green $\text{S}_3\text{N}_2\text{Cl}$ (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 $\text{S}_3\text{N}_2\text{Cl}$ and (10g) onto the AgAsF_6 . The solutions were allowed to warm to room temperature, when the AgAsF_6 dissolved completely, whilst the $\text{S}_3\text{N}_2\text{Cl}$ gave a dark green solution over undissolved solid. On addition of the AgAsF_6 solution to the $\text{S}_3\text{N}_2\text{Cl}$ 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 $\text{S}_3\text{N}_2\text{AsF}_6$ (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 = 768.34Å³, Z = 4, D_c = 2.36 g/cm.

F(000) = 540, $\lambda(\text{Mo}, k\alpha) = 0.71069$.

$\mu = 12.17\text{cm}^{-1}$, 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)-0(1a)	2.966	S(2)-0(2e)	3.045
S(2)-0(1b)	3.173	S(4)-0(3c)	2.871
S(3)-0(2d)	2.705	S(2)-0(3e)	2.956
F(3)-0(2e)	3.313	S(4)-F(1d)	3.155
N(1)-0(2e)	3.097	S(4)-0(2e)	3.302
N(2)-0(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 ($\times 10^4$) 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,

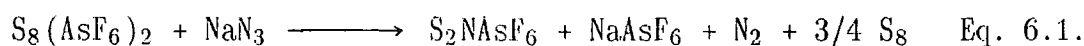
As 18.37, F 27.93; Found S 29.73, N 13.1, H 1.81, C 14.58.

6.3. RESULTS AND DISCUSSION.

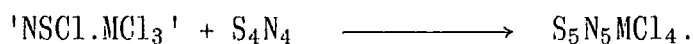
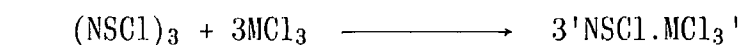
6.3.1. Preparation of $S_2NCF_3SO_3$.

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_7NI , S_7NBCl_2 or 1,4- $S_6N_2H_2$ with

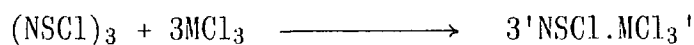
SbCl₅ in liquid SO₂¹. S₂NA1Cl₄ has also been isolated in unspecified yield from the reaction of S₄N₄ with AlCl₃ in CH₂Cl₂⁶, whilst S₂NAsF₆ may be prepared according to equations 6.1 & 6.2. in liquid SO₂². The yields were 20% and 77% respectively, though in the absence of traces of bromine, the yield for equation 6.2. was only 30%.



The reaction according to equation 6.3 has also been shown to produce S₂NAsF₆⁷ in 50% yield, but has the disadvantage of requiring the previous isolation of extremely moisture sensitive SNAsF₆. All these routes involve the use of hazardous chemicals, eg. S₄N₄, NaN₃ and AsF₅. AsF₅ cannot be bought in this country and therefore must be made by burning arsenic in fluorine, whilst AgAsF₆ is hazardous to prepare and expensive to buy. A more convenient preparation of S₂NSbCl₆⁷ made use of the reaction of a stoichiometric amount of sulphur added to an *in situ* source of SN⁺ to give S₂N⁺. This principle has been utilised before in the preparations of S₅N₅⁺⁸ and N(SCl)₂⁺⁹, see Scheme 6.1. The participation of SN⁺ in these reactions was confirmed by the isolation of S₅N₅AsF₆ and N(SCl)₂AsF₆ from the reactions of SNAsF₆ with S₄N₄ and SCl₂ respectively¹⁰. Reactions of Lewis acids with (NSCl)₃ have been extensively studied¹¹. **Scheme 6.1:-**



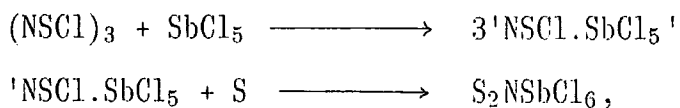
M = Fe, Al⁸.



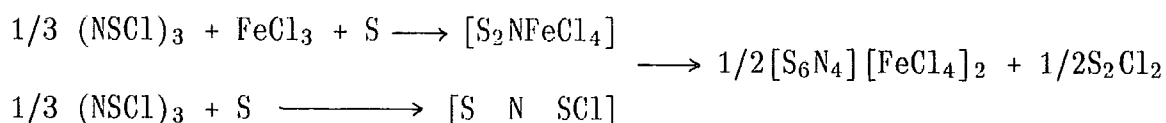
M = Fe, Al⁹.

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

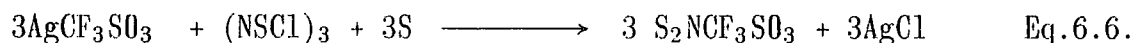
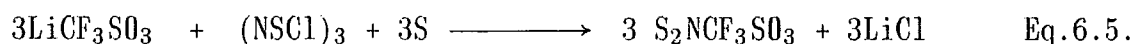
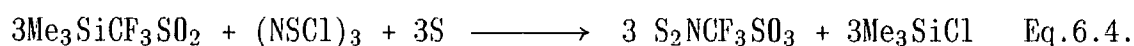
Scheme 6.2.



Besides S_2NSbCl_6 , $\text{S}_3\text{N}_2\text{Cl}^+\text{SbCl}_6^-$ 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 $[\text{S}_6\text{N}_4][\text{FeCl}_4]_2$. 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.

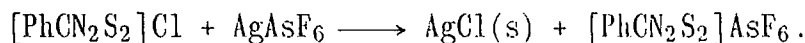


The use of a strong chloride ion acceptor suggested the mechanism of removing the chlorine as a volatile or insoluble organic or inorganic chloride. Initial experiments made use of a silyl reagent, since silyl reagents have been used to great effect elsewhere in S/N chemistry¹³⁻¹⁶.



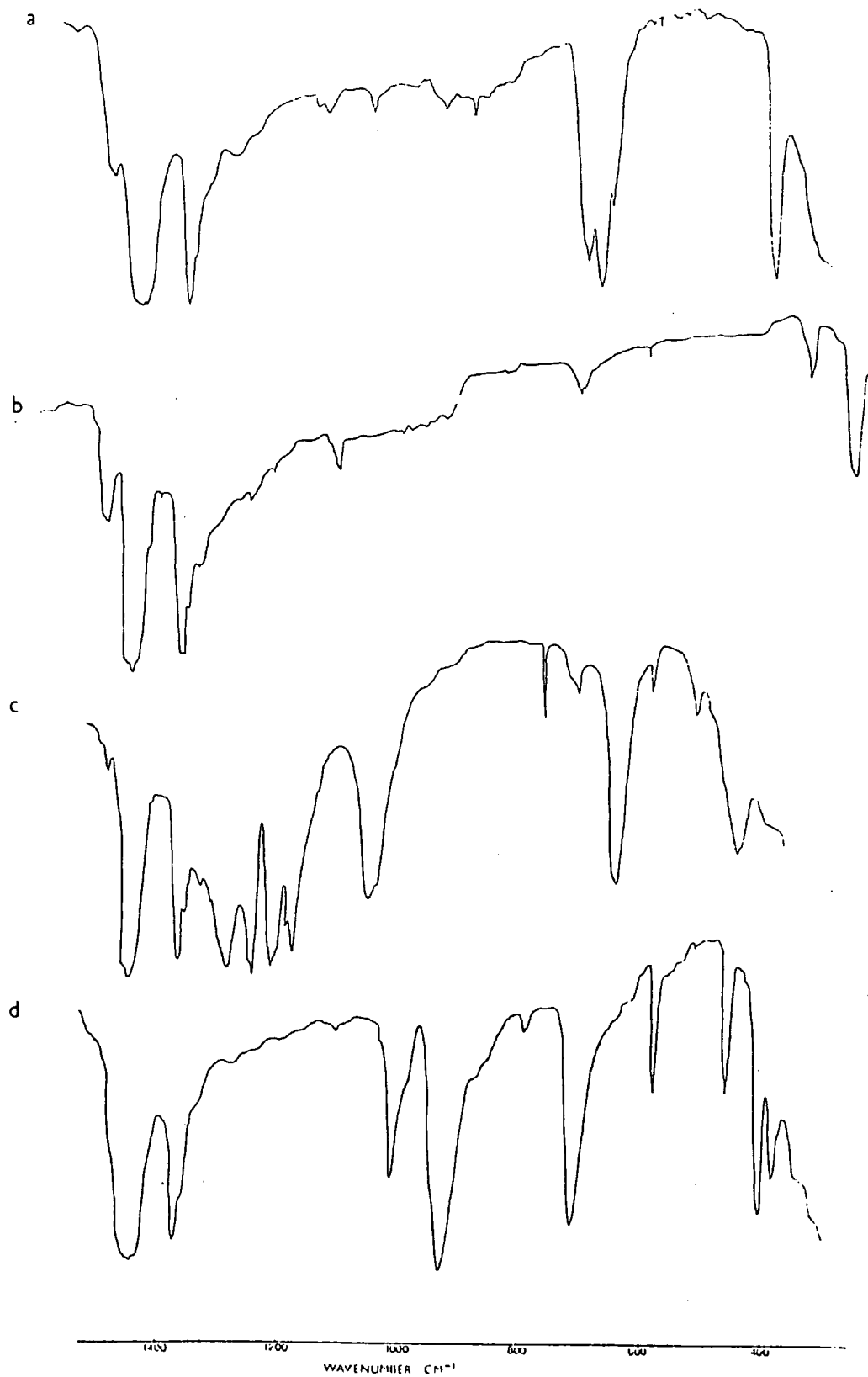
$\text{Me}_3\text{SiCF}_3\text{SO}_3$ was reacted with $(\text{NSCl})_3$ in both CH_2Cl_2 at reflux and SO_2 but in both cases a black oily tar was the only product. This was probably due to the highly reactive chlorines on the $(\text{NSCl})_3$ attacking the hydrogen atoms of the methyl groups.

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.



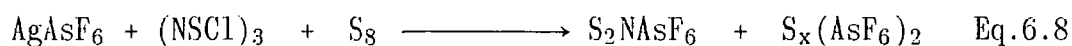
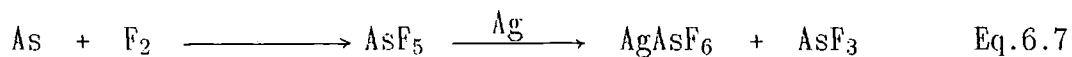
Although AgCF_3SO_3 is only sparingly soluble in SO_2 , AgCl is even less so, and the reaction $\text{AgCF}_3\text{SO}_3(\text{s}) + \text{SO}_2 \rightleftharpoons \text{AgCF}_3\text{SO}_3(\text{solv})$ proceeds to the right. On addition of AgCF_3SO_3 to $(\text{NSCl})_3$ in SO_2 a bright yellow solution 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^{+} 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 $\text{S}_3\text{N}_2\text{O}_2$ by comparison with products reported¹¹ 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 $\text{S}_2\text{NCF}_3\text{SO}_3$, 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. $\text{S}_3\text{N}_2\text{Cl}_2$.

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 literature¹, 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 $S_2NCF_3SO_3$.



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 .

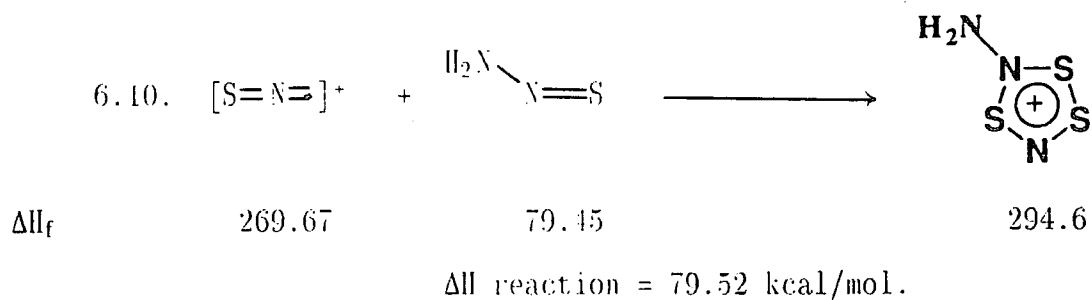
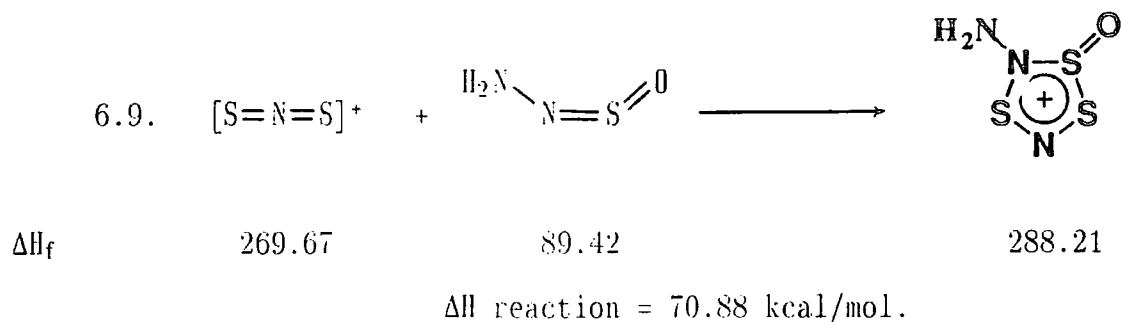
S_2N^+ salts have an extensive and diverse chemistry and are of increasing use as a building block in the synthesis of S/N and S/N/C heterocycles.

Figure 6.2.



They all appear to react in an identical manner, i.e. via a concerted symmetry allowed cycloaddition¹. This process is assisted by the large contribution of the S centres in both the HOMO and the LUMO orbitals of S₂N⁺. 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 shown¹⁷ 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 S₂N⁺ with various unsaturated S/N compounds.

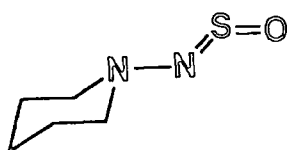
6.3.3.1. Reaction with R N S O.



ΔH_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 compounds¹⁰. 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.

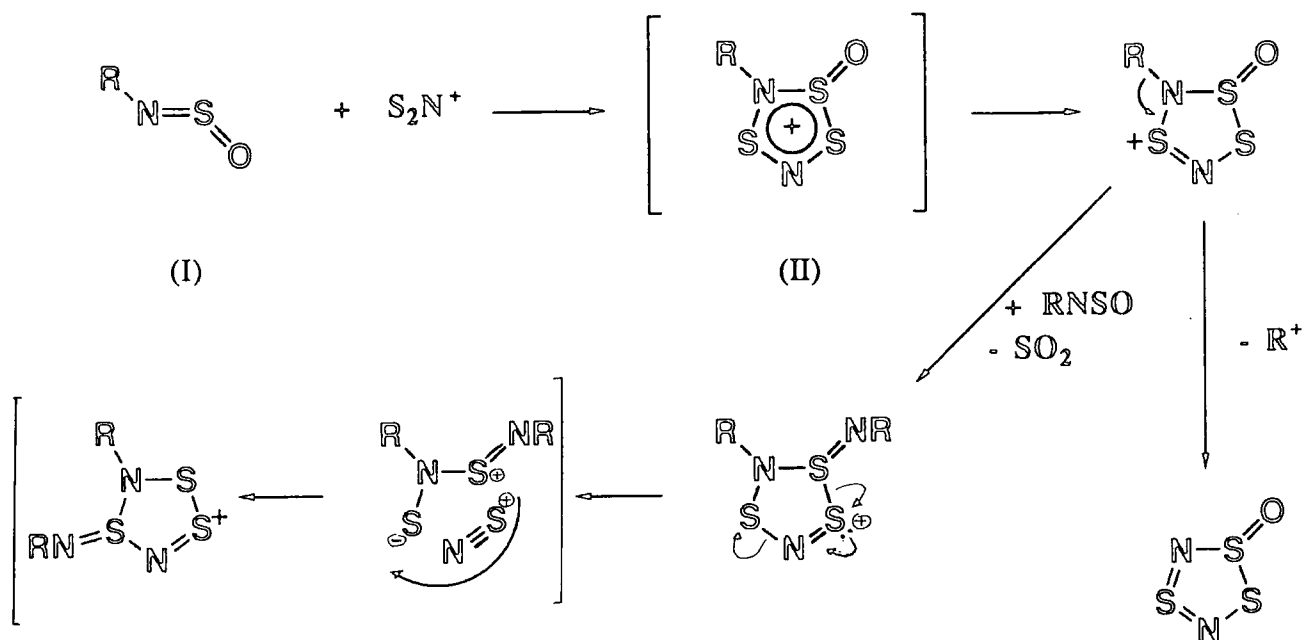


Figure 6.3.

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 results⁴.

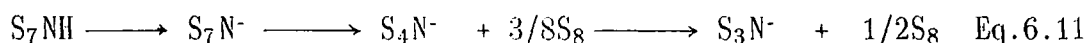
With COD a more complex reaction occurred. It was thought desirable to attempt to react just one double bond with S_2N^+ to leave one double bond free for coordination. A 1:1 mole ratio reaction, with SO_2 as solvent, was attempted in which the COD was syringed into the dog. Some of this, however, polymerised 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 spectroscopy 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 $[\text{Pt}(\text{S}_2\text{N}_2\text{H})(\text{PMe}_3)_2][\text{PF}_6]$ 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 $\text{S}_2\text{N}_2\text{H}^-$. M/S/N complexes and metallacycles also have the ability of stabilising otherwise unknown S/N anions, eg. $\text{AuCl}_2(\text{S}_3\text{N})$ and providing useful S/N intermediates. The S_3N^- ion is obtained by deprotonation of S_7NH^{20} ,



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. $\text{CpTaCl}_2\text{OCH}_2\text{CH}=\text{CH}_2(\text{I})^{21}$ has a free vinyl group, coordination being through the oxygen atom.

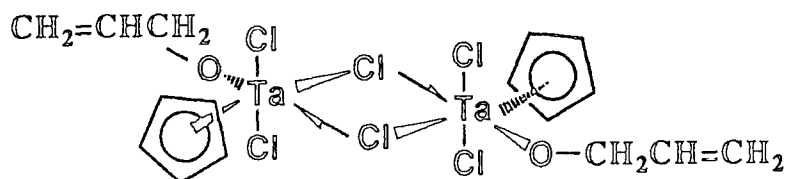
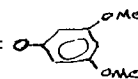


Figure 6.4. $\text{CpTaCl}_2\text{OCH}_2\text{CH}=\text{CH}_2$.

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

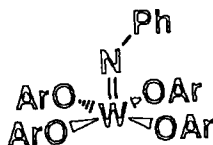


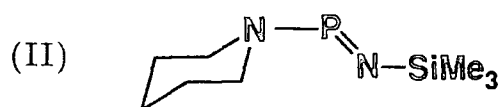
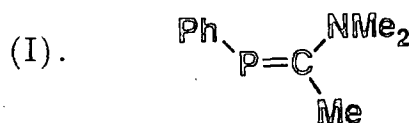
Figure 6.5. $\text{W}=\text{NPhMe}(\text{OAr})_4$.

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 $(\text{Co})_2(\text{CO})_8$, dicobalt octacarbonyl.

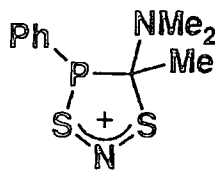
After heating to reflux and stirring for 2 days, no significant displacement of carbonyls had occurred, although a metal sheen did form on the glass walls. Although it is possible to imagine a number of complexes which might be expected to react in a similar fashion, eg cycloheptatriene chromium tricarbonyl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

6.3.3.4. Further Reactions.

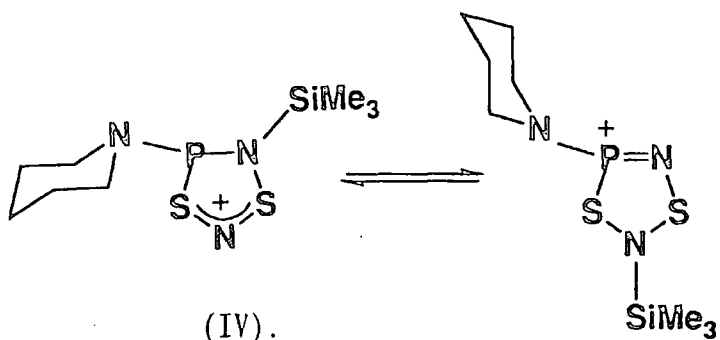
A recent development has been the synthesis of compounds of the type (I) and (II).



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



(III).



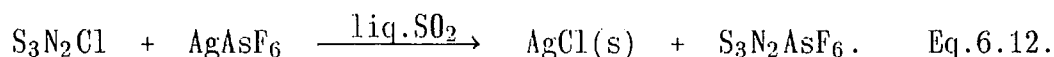
(IV).

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.

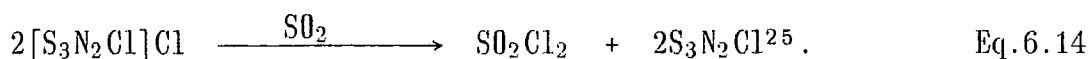
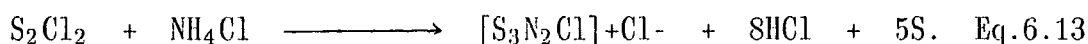
6.4. The $S_3N_2^{+\cdot}$ Cation.

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 is unknown. It would be an 8π Huckel anti-aromatic³⁰ with a triplet ground state and would therefore be unstable. The generation of the di-cation is more favoured.

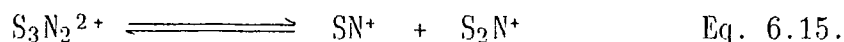
Indeed $S_3N_2^{2+}$, a 6π aromatic cation, has recently been prepared via a symmetry cycloaddition of S_2N^+ and SN^+ ⁷. The radical cation, $S_3N_2^{+\cdot}$ is a 7π species, which like many S/N compounds the exact nature of the structure and bonding remained a matter of some speculation until the 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 configuration¹³. Monomeric salts have also been reported but these are generally early publications²³⁻²⁶ and have been the subject of some dispute²³. 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:-



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;

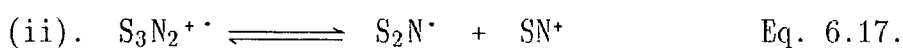
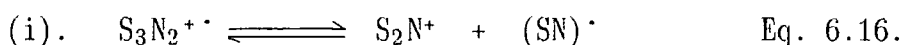


It has been proposed that $S_3N_2^{2+}$ exists in solution as an equilibrium mixture containing SN^+ and S_2N^+ and this seems to have been confirmed by the reaction with hexafluorobut - 2 - yne⁷.



Since $S_3N_2^{+}$ 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 $S_3N_2^{+}$ 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;



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 $S_3N_2^{+}$ since from 6.16 and 6.17 the presence of sulphur would favour the formation of more S_2N^+ from any $S_3N_2^{+}$ 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 $S_3N_2^{+}$ equilibrium. The presence of both S_2N^+ and $S_3N_2^{+}$ 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 1980⁵. 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 structure²⁸ 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.	$P2_1/m-C_2^n$	$P2_1/n$
Z	4	4
a	7.494	8.632
b	23.390	10.614
c	6.094	8.8387
β	110.94	90.79
D_c	1.914	2.36

Figure 6.6. $S_3N_2CF_3SO_3$

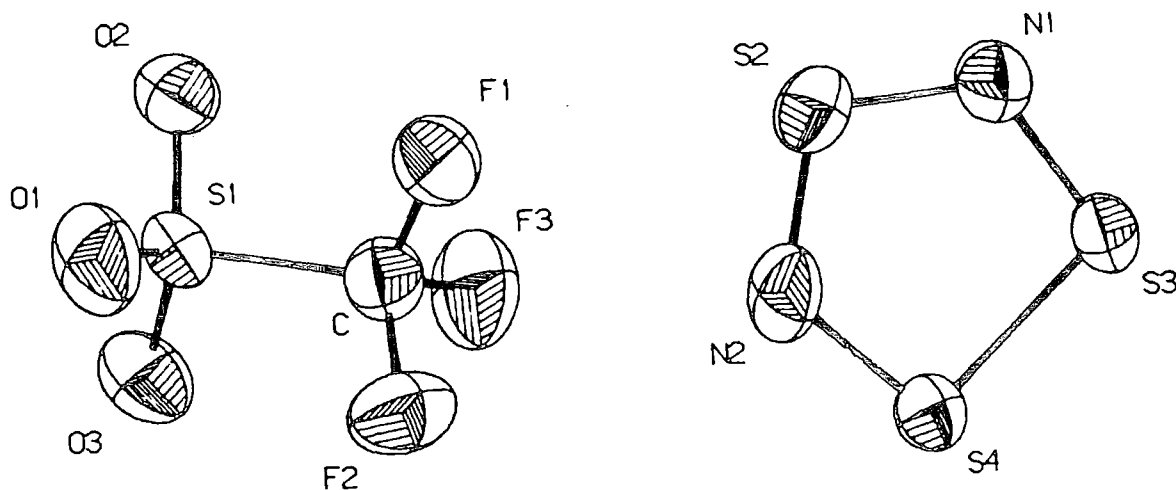


Table 6.4. compares the previous data with those from the present study in which the R value is much better. Although the previous lattice parameters are different there is good agreement between bonding distances and angles. The structure may be considered as a dimer with two S_3N_2 rings lying in a 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 2.97\AA , 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 2.65\AA as shown in Figure 6.8.

Figure 6.7. The unit cell of $S_3N_2CF_3SO_3$.

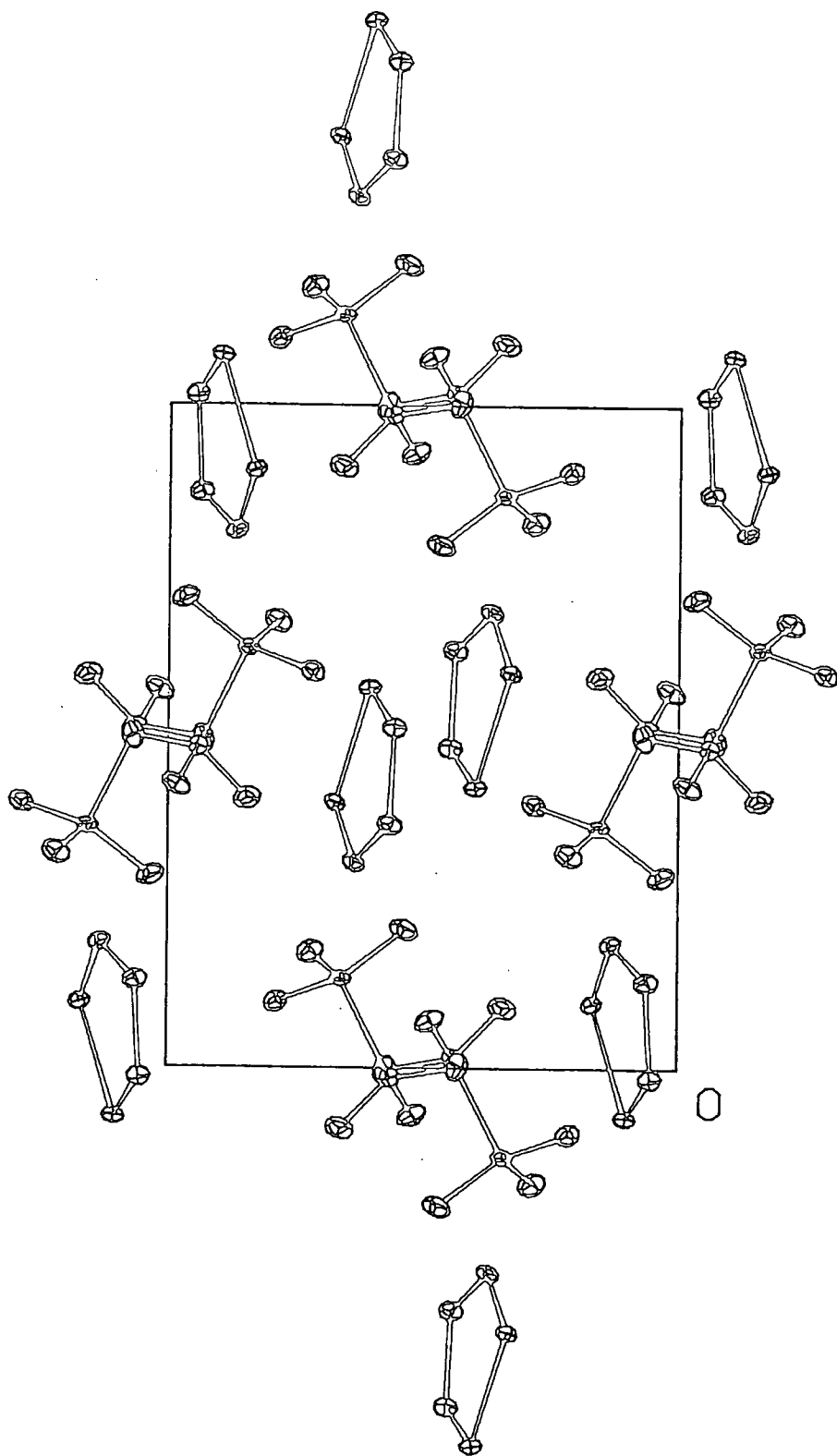
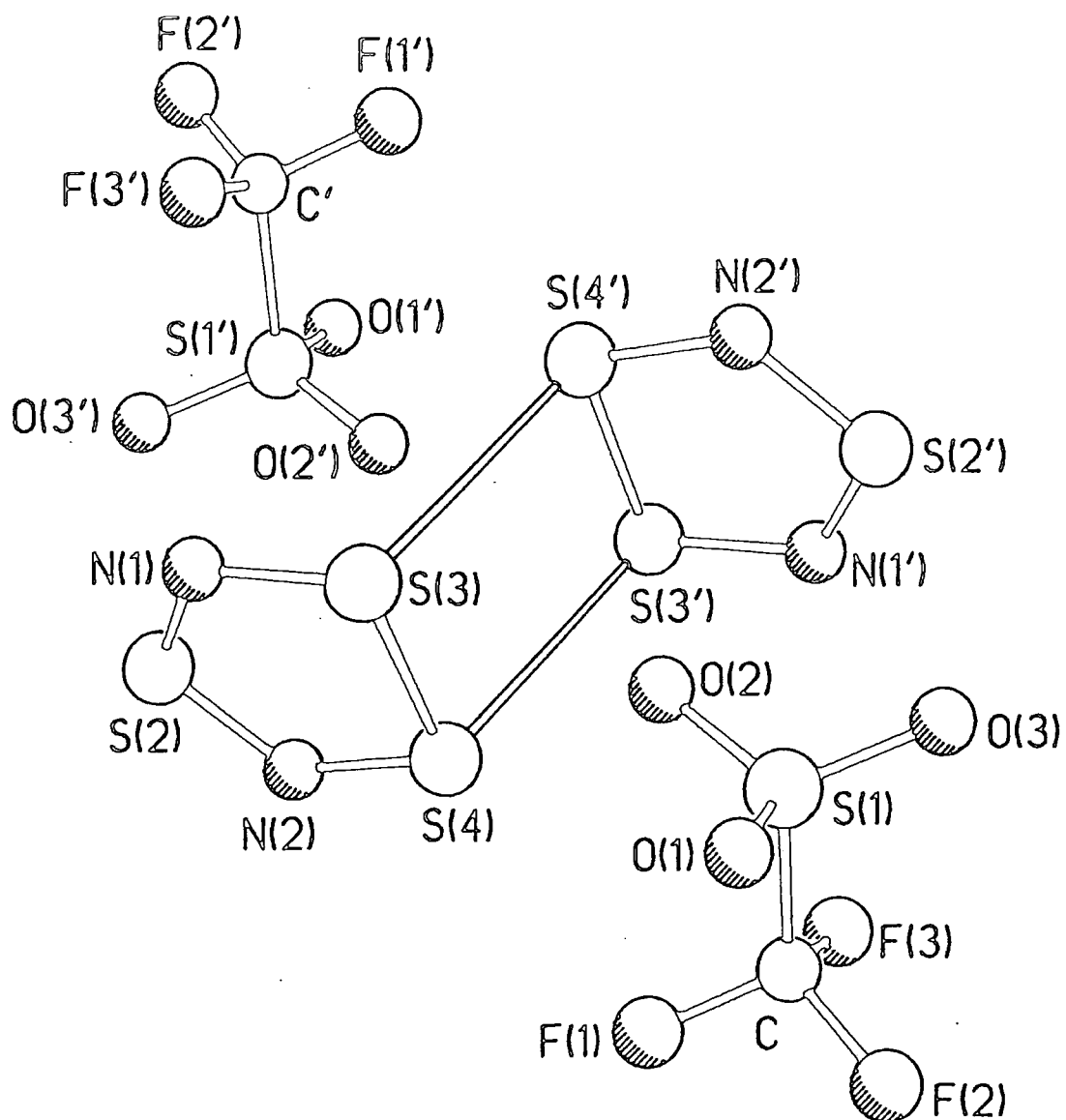


Figure 6.8. The Dimeric structure of $S_3N_2F_3SO_3$ showing close approach of the O(3) atom,



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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. Dorfmueller (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 Magneto-optics".
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.C.I. 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".

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. Pasykiewicz (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".

- 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"".

- 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.

