Some sulphur-nitrogen ring transformations using tetrasulphur tetranitride and trichlorotrithiatriazene as precursors

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SOME SULPHUR-NITROGEN RING TRANSFORMATIONS
USING TETRASULPHUR TETRANITRIDE
AND TRICHLOROTRITHIATRIAZENE AS PRECURSORS

A Thesis Submitted to
The University of Durham

by

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(Grey College)

For The Degree of
Doctor of Philosophy
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Final copy for [illegible].

To the Heys, past, present and future

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Finally my most sincere thanks go to Mrs. Marion Wilson for the many exasperating hours spent deciphering and typing this thesis.

MEMORANDUM

The work described in this thesis was carried out by me in the Chemistry Departments of the University of Durham and New Brunswick between October 1976 and September 1979. I declare that this work has not been submitted for any other degree. This thesis is my original work, except where indicated by reference to other work.

Parts of this work have been published in or submitted for publication to the following Journals:

"Producing Sulphur-Nitrogen Groups"

by A.J. Banister, A.J. Fielder, Z.V. Hauptman, R.G. Hey and N.R.M. Smith.

British Patent 7924580, July 1979.

"Some Reductions of Sulphur-Nitrogen Compounds to give Tetrasulphur Tetranitride"

by A.J. Banister, A.J. Fielder, R.G. Hey and N.R.M. Smith,

J.Chem.Soc. Dalton (in press)

"The crystal structure of 4-phenyl-1,2-dithia-3,5-diazole"

by A. Vegas, A. Perez-Salazar, A.J. Banister and R.G. Hey

J.Chem.Soc. Perkin 2 (in press)

"The preparation of thiazyl hexachloroantimonate (V) $NS^+sbCl_6^-$"

by A.J. Banister, R.G. Hey and J. Passmore

J.Chem.Soc. Dalton (submitted)

"Reactions of Chlorine Monofluoride with Tetrasulphur Tetranitride, Trichlorotrithiatriazene and Thiazyl chloride"

by A.J. Banister, R.G. Hey, J. Passmore and G. Sutherland

J.Chem.Soc. Dalton (submitted)

ABSTRACT

As part of a general study of 1,2,3,5-dithiadiazolium cations, a series of 4-phenyl-1,2,3,5-dithiadiazolium salts were produced by anion exchange reactions, both in the solid phase and in solution. The reduction of the 4-phenyl-1,2,3,5-dithiadiazolium cation gave the previously unreported, 4-phenyl-1,2-dithia-3,5-diazole, the crystal structure of which indicates that the dithiadiazole exists as an eclipsed dimer.

By analogy with the solid phase exchange reactions which occur between 4-phenyl-1,2,3,5-dithiadiazolium chloride and Group I metal halides, the metathetical reactions between S_3N_2Cl and metal halides were investigated. The product isolated from the reaction of S_3N_2Cl with CsI was identified as tetrasulphur tetranitride. The reductions of S_4N_3Cl, S_3N_2Cl, $S_3N_2Cl_2$ and $(NSCl)_3$ were studied using a variety of reducing agents. The majority of the reduction reactions gave tetrasulphur tetranitride but the reduction of trichlorotrithiatriazene by iron using sulphur dioxide as a solvent provided a convenient synthesis of the cyclopentathiapentazenium cation ($S_5N_5^+$). The reduction of chlorothiodithiazyl chloride by iron using sulphur dioxide as a solvent produced the previously unreported salt $(S_{10}N_8^{2+})(FeCl_4^-)_2$.

The synthesis of the cations S_xN^+ ($x > 1$) was approached from two angles, that of reacting sulphur polycations ($S_8^{2+}(AsF_6^-)_2$) with nitrogen containing species (MN_3 and S_4N_4) and that of reacting the thionitrosyl cation (NS^+) with sulphur.

The reactions of $S_8^{2+}(AsF_6^-)_2$ with azides and tetrasulphur tetranitride led to the formation of the S_2N^+ cation and with

excess tetrasulphur tetranitride to the production of $S_{10}N_8^{2+}(AsF_6^-)_2$. Some preliminary investigative reactions of selenium ($Se_4^{2+}(AsF_6^-)_2$ and $Se_8^{2+}(AsF_6^-)_2$) and tellurium ($Te_4^{2+}(AsF_6^-)_2$) polycations with both azides and tetrasulphur tetranitride were carried out and a selenium analogue of "$S_3N_2^+$" isolated.

In an attempt to prepare thiazyl fluoride (as a precursor to thionitrosyl salts) by a simple single stage process, chlorine monofluoride was reacted with S_4N_4 and $(NSCl)_3$. The reactions did not produce NSF in high yields, the main products being sulphur tetrafluoride (SF_4), nitrogen and chlorine. The mechanisms of the reactions of ClF with S_4N_4 and $(NSCl)_3$ are discussed.

NSF was synthesised by the metathesis reaction between thiazyl chloride and cesium fluoride.

A facile route to the thionitrosyl cation via the oxidation of $(NSCl)_3$ and S_4N_4 using Group V Lewis acids (AsF_5, SbF_5) at 100-150°C failed. However a convenient route to thionitrosyl hexachloroantimonate (V) has been found in the vapour phase reaction of thiazyl chloride with antimony pentachloride.

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NOMENCLATURE

The nomenclature used for sulphur-nitrogen heterocycles throughout this thesis is that adopted by Chemical Abstracts. A systematic nomenclature has recently been published by Banister and Heal[*] but is not, as yet, in general use.

Formula	Nomenclature
$S_5N_5^+$	Cyclopentathiapentazenium
S_4N_4	Tetrasulphur Tetranitride
$S_4N_4F_4$	Tetrafluorotetrathiatetrazocine
$S_4N_3^+$	Thiotrithiazyl
S_4N_2	Tetrasulphur dinitride
$S_3N_3X_3$	Trihalotrithiatriazene
$S_3N_2^+$	Thiodithiazyl
$S_3N_2Cl^+$	Chlorothiodithiazyl
NSX	Thiazyl halide
NS^+	Thionitrosyl

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[*] H.G. Heal and A.J. Banister
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CHAPTER ONE

EXPERIMENTAL TECHNIQUES

The work in this thesis has been carried out in two Universities;

(i) University of Durham, Durham, England.

(ii) University of New Brunswick, Fredericton, New Brunswick, Canada.

The experimental techniques adopted in each University were somewhat different and thus the University is specified when referring to specific techniques or apparatus.

1.1 Handling Techniques

The majority of compounds handled throughout this thesis were moisture sensitive. The species were, therefore, manipulated in dry-box conditions, under a top pressure of dry nitrogen or *in vacuo*.

A. Nitrogen Supply (University of Durham)

The nitrogen was obtained as boil off from the liquid nitrogen generation plant and was dried by passing it through (in series), a concentrated sulphuric acid bubbler, a liquid nitrogen cold trap, a phosphorus pentoxide column and a potassium hydroxide column. The removal of oxygen was not found necessary for the work carried out in Durham.

The nitrogen supply at the University of New Brunswick was from high pressure cylinders (equivalent to White Spot Nitrogen supplied by B.O.C. Ltd. (U.K.)).

B. Dry-Boxes

(i) Dry-box in the University of Durham

The dry-box in Durham operated with an atmosphere of dry nitrogen (dried as in 1.1.A) which was continuously recycled through a phosphorus pentoxide column. The port was purged by dry nitrogen for at least 45 min. after each opening to the external atmosphere. At least one dish of phosphorus pentoxide was kept in the box at all times to monitor the efficiency of the drying columns. All samples for infra-red, Raman and mass spectra and analyses were prepared inside the box.

(ii) Dry-box in the University of New Brunswick

A vacuum atmospheres H.E-43-2 dry-box operating with a nitrogen or argon atmosphere was employed. The nitrogen and argon were obtained from high pressure cylinders, the nitrogen being used directly, whereas the argon was dried by passage over an active metal surface.

Access to the box was via a 70 dm^3 port (60 cm in length, 40 cm dia.) which could be evacuated. The port was pumped down for 20 min. and then the atmosphere inside the box allowed into the port, the total pressure in the box being maintained by nitrogen from the high pressure cylinder. The pressure inside the box was automatically controlled to within ± 10 torr of atmospheric pressure by a Pedatrol HE-63-P. The atmosphere inside the box was continuously recycled through an HE 493 DRI-TRAIN, which is essentially a molecular sieve/ copper purifier. A water content of better than 2 ppm. was generally obtained.

C. Apparatus used for Fluorine containing compounds and High Pressure Reactions

(i) Vacuum line

For non-fluorinated compounds a glass vacuum line with high vacuum, hand ground taps and Apiezon grease was used. For fluorinated species a Monel line fitted with stainless steel Whitey valves (1KS4) using swagelock fittings with teflon ferrules was employed. The Monel line was connected via a glass muck trap to a rotary oil pump. The Monel line was passivated by flaming the line with either an atmosphere of fluorine or sulphur tetrafluoride contained within. Pressures within the line were measured in torr using a diaphram gauge (0 torr - 1500 torr).

(ii) Apparatus used for reactions involving fluorinated species or pressures greater than one atmosphere.

(a) Pyrex vessels fitted with sinters

Various types of vessels were used which fall under this heading. The simplest vessel is that shown in figure 1.1 (page 14) in which there is one teflon valve, through which the reactants and solvents may be loaded. More complex versions of the same basic design were used (figure 1.2, page 14) in which the solid reactants could be added to both bulbs and one bulb sealed off with respect to the other bulb. This allows moisture sensitive materials to be sealed in one section whilst operations are carried out in the other section under normal atmospheric conditions. Vessels with up to two sealable sections and two sinters were used in the work with Group VI polycations (Chapter Six, page 269).

(b) F.E.P. Tubes fitted with Swagelock Joints

F.E.P. tubing $\frac{1}{2}$" o.d. was purchased in 50' rolls. 20 cm lengths of this tubing were taken and one end sealed using a moderately hot glass tube. The tubing was then placed in a swagelock compression joint which was connected to a stainless steel Whitey valve (1KS4) (figure 1.3, page 15). The mode of operation using these vessels was to passivate them by pumping under reduced pressure for 2h. or by condensing in ca. 300 torr pressure of SF_4. Solid reactants were added to the tube by separating the swagelock joint. Gases and volatiles were condensed into the vessel by cryogenic pumping.

(c) High Pressure Monel Vessels

High pressure reactions($>$ 3 atmospheres) were carried out using Monel vessels (maximum working pressure ca. 20 atmospheres), (figure 1.4, page 15). The vessels were made leak tight by progressively tightening the Allen screws, with the resulting deformation of the teflon "O" ring. The vessels were passivated by heating them with a Bunsen flame whilst they contained sulphur tetrafluoride. Solids were placed in the vessels by removing the lid and volatiles by condensation via the Whitey valve.

1.1.1 Spectroscopic Data

(i) Infra-red Spectra

Infra-red spectra were recorded using nujol mulls, between KBr or AgCl plates and as discs using KBr or KCl as dispersants. Gas phase infra-red spectra of fluorine containing species were recorded using a passivated stainless steel cell with AgCl windows, whereas the spectra of non-fluorine containing compounds were recorded using a glass cell with KBr windows (figure 1.5, page 16). Perkin-Elmer 457, 577 and 467 prism grating spectrometers were used to obtain the spectra.

(ii) Raman Spectra

Raman spectra were obtained using a Cary 82 spectrometer with a Spectra Physics 125 (632.8 nm exciting line) or a Spectra Physics 164 (514.5 nm, exciting line)laser (University of Durham). Spectra were also recorded using a Raman lab.[*] machine with a Spectra Physics 125 laser (University of New Brunswick).

(iii) Mass Spectra

Mass spectra were obtained using an A.E.I. (MS9) spectrometer interfaced with a PDP8[**] mini-computer. Samples were run at 120-180°C and 70 eV with an accelerating potential of 8kV. Samples were introduced by direct insertion into the ion source.

(iv) ^{19}F-Nuclear Magnetic Resonance Spectra

^{19}F-n.m.r. were obtained using a Varian H.A 100 (94.08 mHz) or a Varian H.A.60(56.4 MHz) spectrometer. Perfluorobenzene and Freon 11 (CCl_3F) were used as reference compounds.

1.1.2 Analyses

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Nitrogen was also determined by the Kjeldhal method.

Sulphur and the halogens were determined by oxygen flask combustion followed by visual and potentiometric titration of the sulphate and halide anions respectively.

All metals were determined using a Perkin-Elmer 403 Atomic Adsorption Spectrometer.

Arsenic and tellurium were analysed by Butterworth Laboratories Ltd., Teddington, Middlesex.

[**] P.D.P. is a registered trade name.

[*] Raman lab. is a registered trade name

1.2 Preparation and Purification of Starting Materials

1.2.1 Inorganic Liquids, as both Starting Materials and Solvents

(i) Sulphur Dichloride (SCl_2)

Sulphur dichloride was purified by fractional distillation, the middle fraction (bpt.50-62°C) was retained and refractionated, the purified species being collected at 60°C.

(ii) Disulphur Dichloride (S_2Cl_2)

Disulphur dichloride was distilled from sulphur and decolourising charcoal at atmospheric pressure and the fraction collected between 130°C-140°C redistilled *in vacuo*[2].

(iii) Thionyl Chloride ($SOCl_2$)

Triphenyl phosphite (10% by weight) was added to the crude thionyl chloride. The thoroughly mixed system was then fractionated through a 12" column packed with glass helices and the middle fraction collected. Redistillation of the middle fraction gave a practically clear liquid.[3] The thionyl chloride was stored in the dark with teflon sleeves on the ground joints, as grease is attacked by thionyl chloride.

(iv) Sulphuryl Chloride (SO_2Cl_2)

Analar sulphuryl chloride was distilled under nitrogen, the fraction collected between 69-70°C being used.

(v) Sulphur Dioxide (SO_2)

Sulphur dioxide was condensed on to either calcium dihydride or phosphorus pentoxide and stored for 4 days prior to use. The solvent was always distilled off the dehydrating agent.

(vi) Arsenic Trifluoride (AsF_3)

Arsenic trifluoride was distilled on to sodium fluoride and stored for 4 days prior to use. The solvent was always vacuum distilled off the sodium fluoride.

(vii) Sulphuryl Chloride Fluoride (SO_2ClF)

Sulphuryl chloride fluoride was dried over phosphorus pentoxide for 4 days prior to use. The solvent was always distilled off the dehydrating agent.

1.2.2 Organic Liquids as both Starting Materials and Solvents

(i) Hexafluorobenzene (C_6F_6)

Hexafluorobenzene was distilled *in vacuo* on to activated molecular sieve (4.A) and stored for 24h. The solvent was then distilled (*in vacuo*) on to a second batch of activated molecular sieve (4.A) and stored for ca. 60h. prior to use. The solvent was distilled off the molecular sieve (*in vacuo*) into the required vessel.

(ii) Tetrahydrofuran (THF) and Monoglyme ($CH_3OCH_2CH_2OCH_3$)

Tetrahydrofuran and monoglyme were refluxed for 8h. with sodium-potassium alloy and then fractionally distilled.[4]

(iii) Benzonitrile (PhCN)

Benzonitrile was refluxed with magnesium sulphate for 12h. and then distilled on to and stored over activated molecular sieve (4.A).

(iv) The following solvents were dried using sodium wire

(a) 1,4-dioxan, (b) diethyl ether, (c) toluene, (d) benzene, (e) pentane, (f) hexane.

If a high degree of dryness was required for the above solvents, they were refluxed with metallic sodium for 3h. and then distilled.

(v) The following solvents were dried by refluxing with phosphorus pentoxide

(a) Nitromethane, (b) Freon 11 ($CFCl_3$), (c) carbon tetrachloride, (d) 1,2-dichloroethane, (e) dichloromethane.

1.2.3 Purification of Lewis Acids

(i) Boron trichloride (BCl_3)

Boron trichloride was distilled, *in vacuo* into the required vessel.

(ii) Aluminium Trichloride (Al_2Cl_6)

Aluminium trichloride was purified by sublimation at 130°C, *in vacuo,* on to a cold finger at -78°C.

(iii) Tin (IV) Chloride ($SnCl_4$)

Tin (IV) chloride was distilled *in vacuo* prior to use.

(iv) Iron (III) Chloride (Fe_2Cl_6)

Iron (III) chloride was purified by refluxing in thionyl chloride for 2h., filtering off the thionyl chloride and drying *in vacuo.*

(v) Antimony Pentafluoride (SbF_5)

Antimony pentafluoride was distilled four times, *in vacuo*, to remove all traces of HF, and stored *in vacuo*.

(vi) Antimony Pentachloride ($SbCl_5$)

Antimony pentachloride was purified by double distillation *in vacuo*.

(vii) Arsenic Pentafluoride (AsF_5) (Monel Apparatus)

Arsenic trifluoride was condensed into the bottom of a bomb and fluorine added in small aliquots. The vessel was allowed to warm slowly to room temperature between each addition of fluorine. A slight excess of fluorine was added to the system to ensure complete conversion. After all the fluorine had been added and the fluorination was complete the bomb was cooled to -196°C and the excess fluorine removed. The arsenic pentafluoride was used directly from the bomb.

1.2.4 Gaseous Reactants

(i) Chlorine and Bromine

Chlorine and bromine were distilled on to phosphorus pentoxide and stored for two days prior to use. The halogens were distilled, *in vacuo*, into the required vessels.

(ii) Chlorine Monofluoride (ClF) (Monel Apparatus)

The gas was condensed at -196°C and pumped on to remove nitrogen and/or fluorine. No attempt was made to remove any chlorine present.

1.2.5 Solid Reactants

All solid reactants were dried, *in vacuo*, at either room temperature or elevated temperatures as required. Salts that decompose *in vacuo* or on heating were used from a freshly opened sample.

1.2.6 Sulphur-Nitrogen Starting Materials

(i) Tetrasulphur Tetranitride (S_4N_4)

Tetrasulphur tetranitride was prepared by the method described by Jolly,[5] in which chlorine gas was passed through a carbon tetrachloride solution of disulphur dichloride until saturated, followed by ammonia gas. The solid was washed with water, then ether and extracted with 1,4-dioxan finally being recrystallised from benzene.

(ii) Trichlorotrithiatriazene ($S_3N_3Cl_3$)

(a) Excess sulphuryl chloride was added to powdered chlorothiodithiazyl chloride and stirred at room temperature for 24h. The reaction mixture was filtered and the residue recrystallised from carbon tetrachloride.[6]

(b) A higher melting and thermally more stable compound was formed when chlorine gas was passed over chlorothiodithiazyl chloride for 30 min. producing a deep red slurry. The sulphur dichloride formed was removed *in vacuo* and the process repeated until no further sulphur dichloride was produced. The crude material was then recrystallised from anhydrous carbon tetrachloride (2.5 cm^3 $gram^{-1}$).[7]

(iii) Chlorothiodithiazyl Chloride[7] ($S_3N_2Cl_2$)

Dry ammonium chloride (200g) and sulphur (40g), were mixed in a 1000 cm^3 flask fitted with an air condenser (100 cm in length, 2 cm diameter) on top of which was attached a calcium chloride drying tube. Disulphur dichloride (200 cm^3, 336g) was added to the reactants and the reaction mixture heated (using an isomantle) to reflux. The reflux point was controlled and stabilised about 2/3rds of the way up the air condenser. Over a period of 10h. the reflux level dropped and large orange crystals formed on the condenser walls. It was found essential to use a fume cupboard with a high extraction rate, in order to increase the temperature gradient up the column. The temperature gradient should not be altered throughout the course of the experiment. After ca. 10h. the reaction was cooled down, the air condenser was removed and pumped down to remove all traces of SCl_2. The condenser was then filled with dry nitrogen and the product stored in a dry-box.

(iv) Thiodithiazyl Chloride[7] (S_3N_2Cl)

Thiodithiazyl chloride was prepared from chlorothiodithiazyl chloride ($S_3N_2Cl_2$) by heating the latter at 80°C, *in vacuo*, for ca. 1h. The orange-red $S_3N_2Cl_2$ gradually turned very deep green. The system was filled with dry nitrogen and the product stored in a dry-box.

(v) Thiotrithiazyl Chloride[7] (S_4N_3Cl)

Powdered chlorothiodithiazyl chloride was added to a mixture of excess disulphur-dichloride in dry carbon tetrachloride. The system was refluxed for 6h. until all the orange $S_3N_2Cl_2$ had reacted yielding the fine yellow S_4N_3Cl product. The product was isolated and the impurities present extracted from it with refluxing pentane. The purified S_4N_3Cl was dried *in vacuo* and stored in a dry-box.

Although the above procedure is reported to give quantitative yields of S_4N_3Cl[7], yields of only 60% were normally obtained.

1.2.7 Preparation of Group VI Polycations

(i) $S_8^{2+}(AsF_6^-)_2$

$S_8^{2+}(AsF_6^-)_2$ was prepared by the action of arsenic pentafluoride on sulphur.[8]

$$S_8 + 3AsF_5 \xrightarrow[SO_2]{} S_8^{2+}(AsF_6^-)_2 + AsF_3$$

Pre-dried sulphur was placed in a vacuum tight pyrex vessel and sulphur dioxide condensed in. The correct volume of AsF_5 to satisfy the above equation was then condensed in and the reaction stirred for two days at room temperature. The deep blue product was then filtered off and dried *in vacuo*. The compound was stored in a dry-box.

(ii) $Se_8^{2+}(AsF_6^-)_2$

The same procedure was adopted as for the preparation of $S_8^{2+}(AsF_6^-)_2$.[9]

(iii) $Te_4^{2+}(AsF_6^-)_2$

The same procedure was adopted as for the preparation of $S_8^{2+}(AsF_6^-)_2$.[10]

(iv) $Se_4^{2+}(AsF_6^-)_2$.[11]

$Se_4^{2+}(AsF_6^-)_2$ was produced by essentially the same procedure as $S_8^{2+}(AsF_6^-)_2$ but the system was heated to 80°C for 4 days and the solubles removed ($Se_8^{2+}(AsF_6^-)_2$). The $Se_4^{2+}(AsF_6^-)_2$ is relatively insoluble in SO_2 and thus a slight excess of AsF_5 was used to ensure complete conversion of the elemental selenium.

Figure 1.1

Pyrex reaction vessel

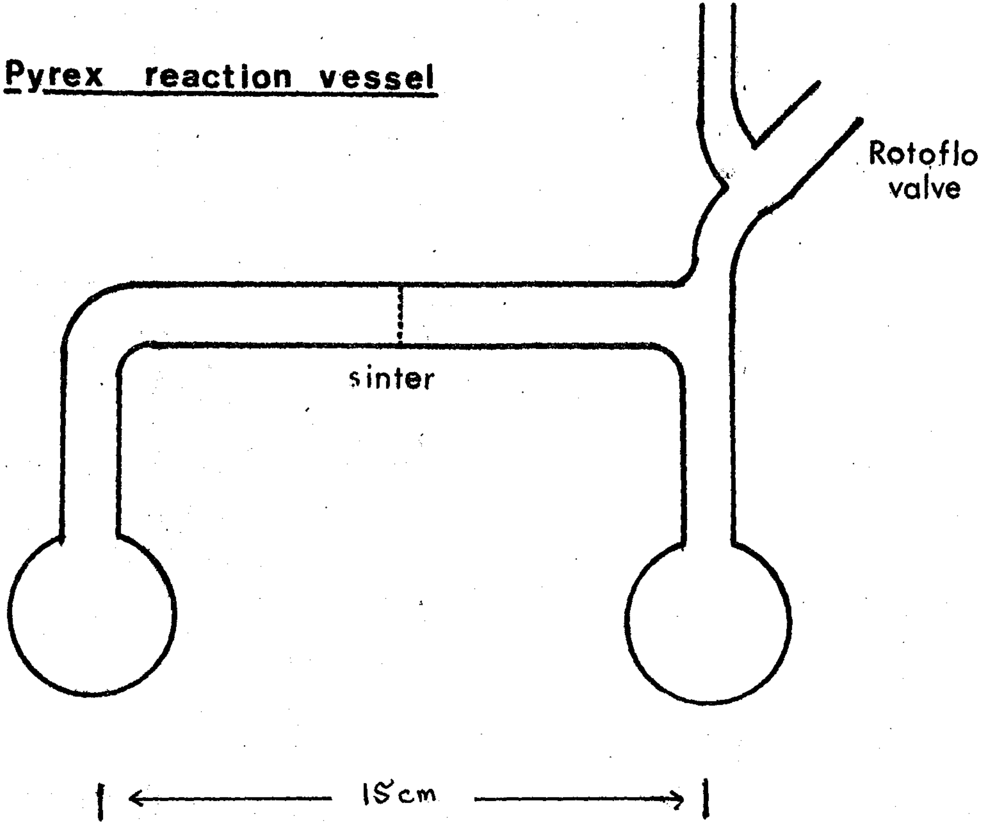


Figure 1.2

Pyrex reaction vessel

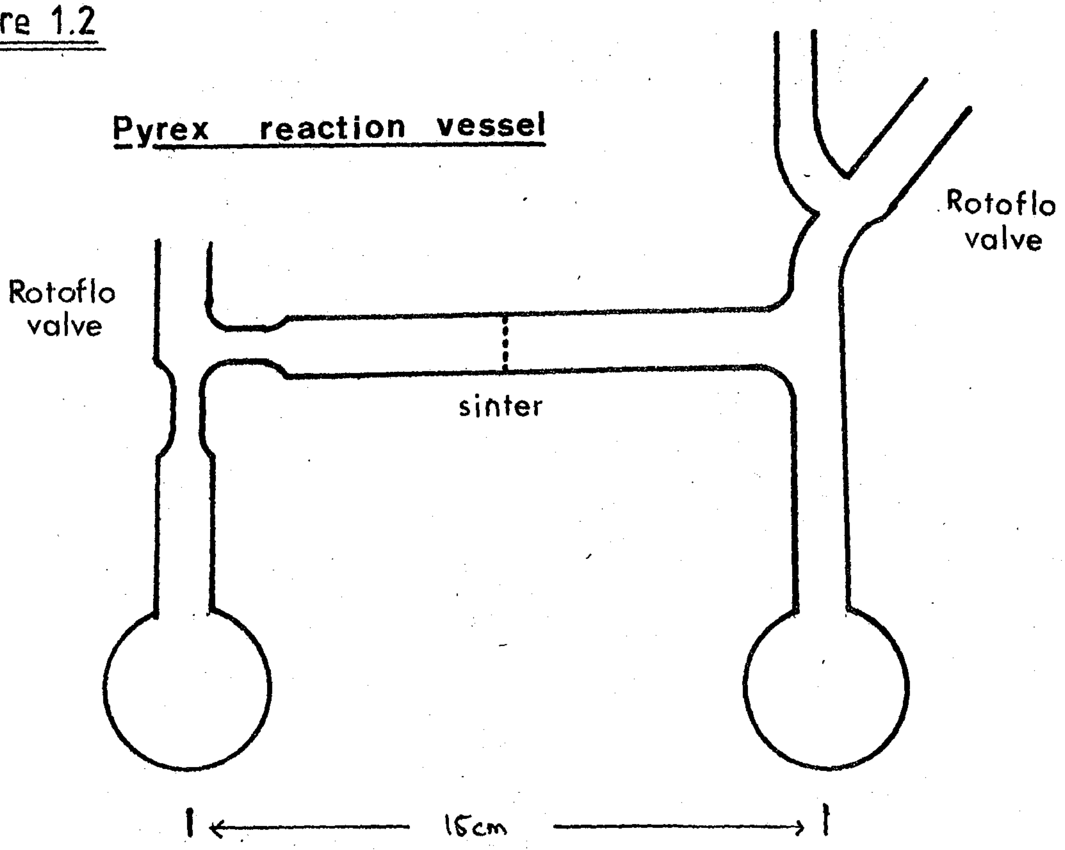


Figure 1.4.

High Pressure Monel Vessel

Figure 1.3.

F.E.P. Reaction Vessel and Assorted Valves

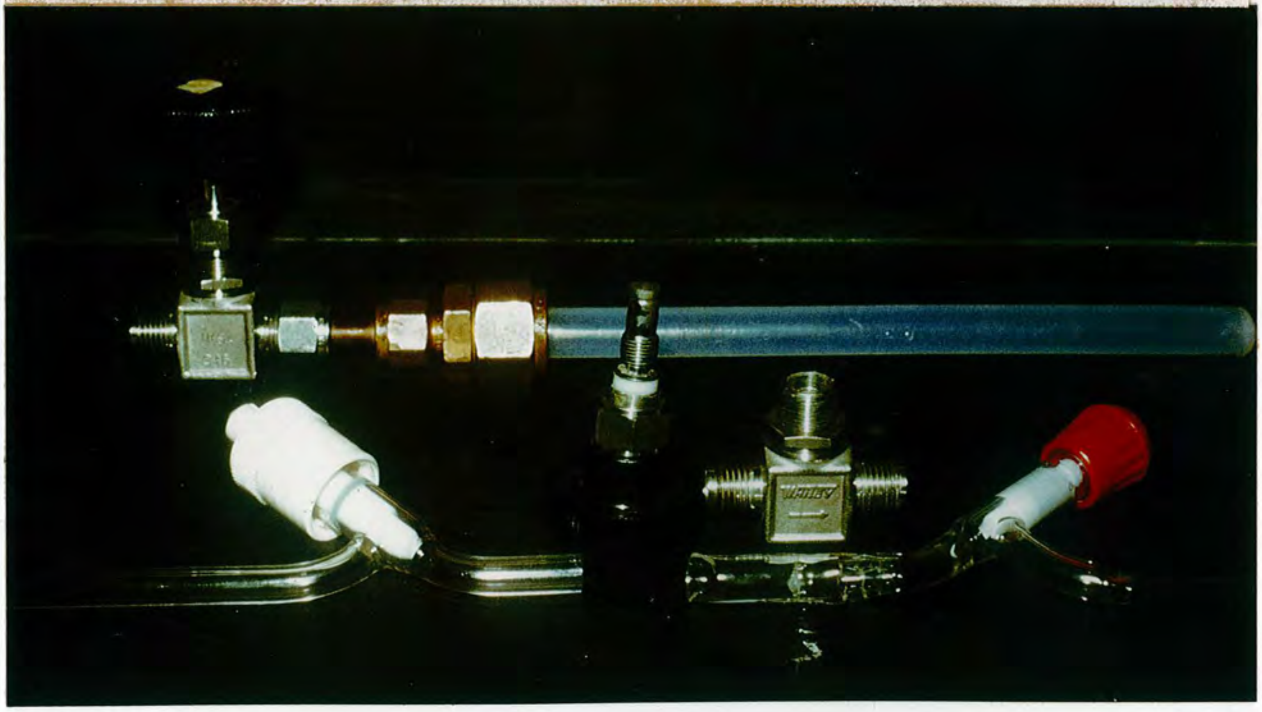


Figure 1.5.

Modified Infra-red Gas Cell

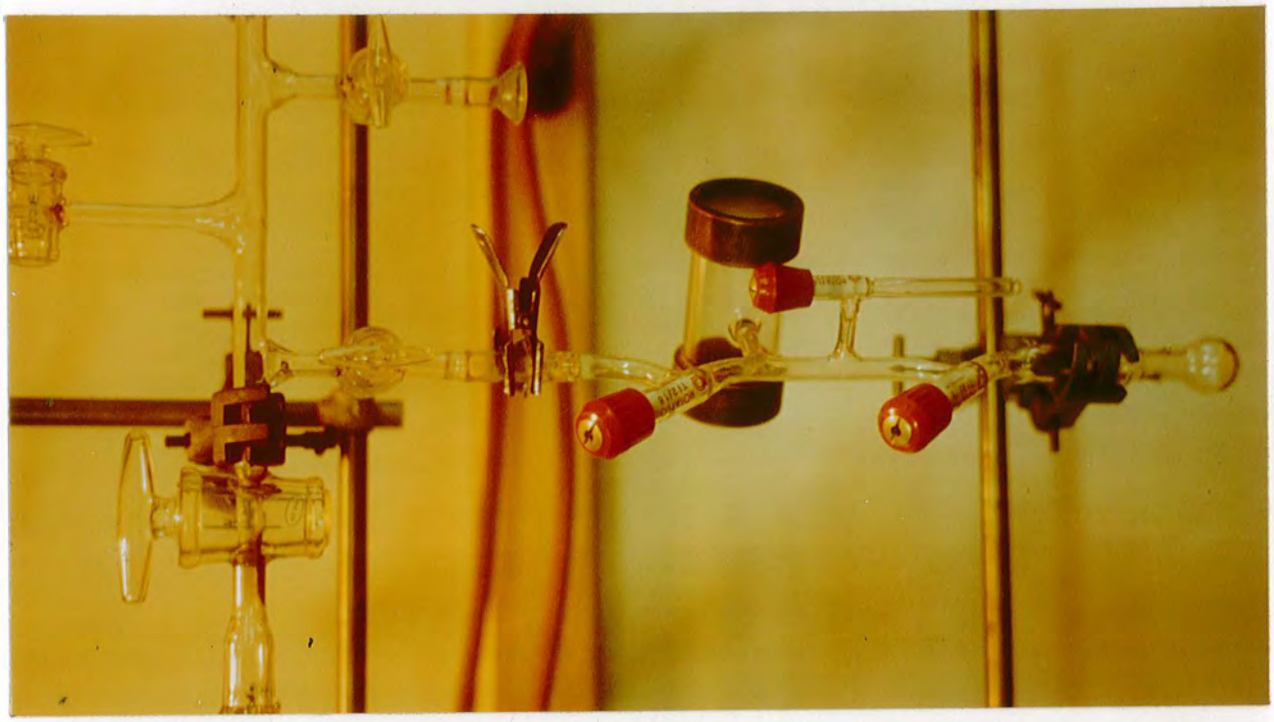
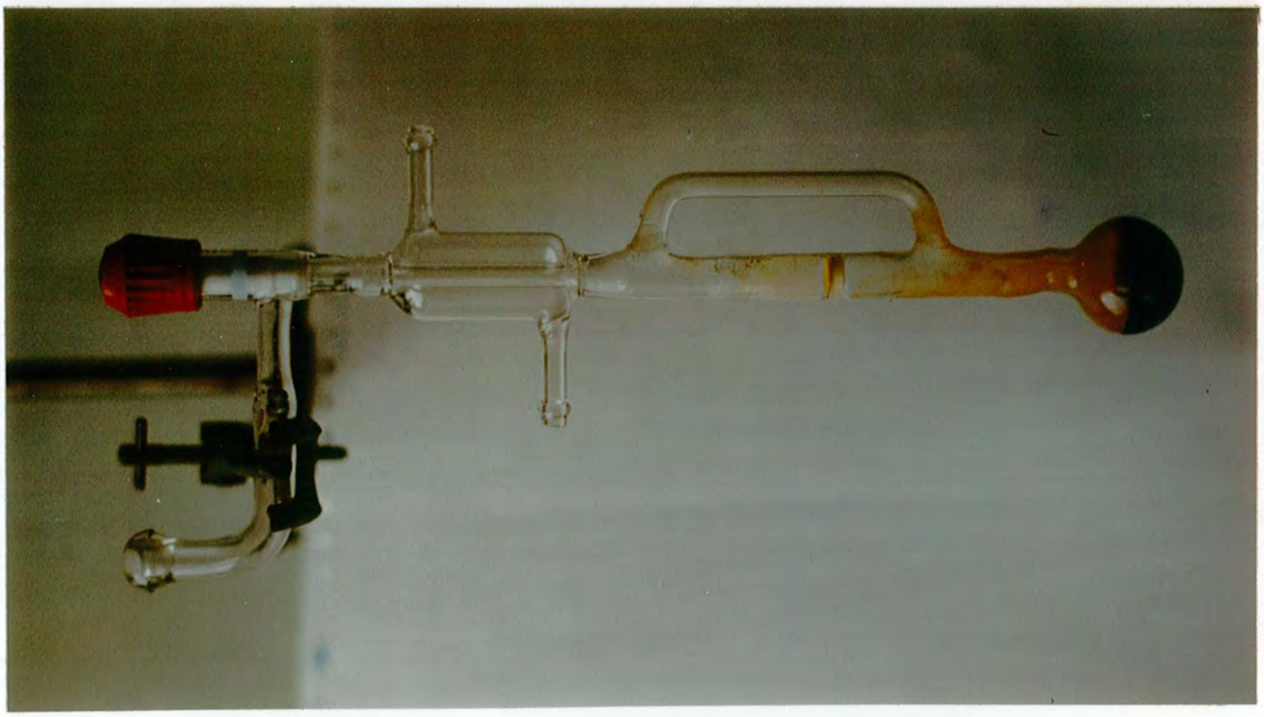


Figure 1.6.

Sealed system Soxhlet Extraction Apparatus



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CHAPTER TWO

THE PREPARATION AND REACTIONS OF THE 4-PHENYL-1,2,3,5-DITHIADIAZOLIUM CATION

2.1 Introduction

Carbon-Sulphur-Nitrogen Heterocycles containing $(4n + 2)\pi$-electrons (Hückel Aromatic Species)

There is a vast chemistry of heterocyclic five and six membered rings containing carbon, sulphur and nitrogen. There is no comprehensive review of all the permutations and combinations of cyclic C/S/N species, although Barton and Ollis in their excellent series "Comprehensive Organic Chemistry" (Volume 4, Heterocyclic Chemistry)[1] do discuss some of these species. The Specialist Periodical Reports on the organic compounds of Sulphur, Selenium and Tellurium also provide useful lead references into this area of chemistry.[2a-d; 3a,b; 4a-i; 5]

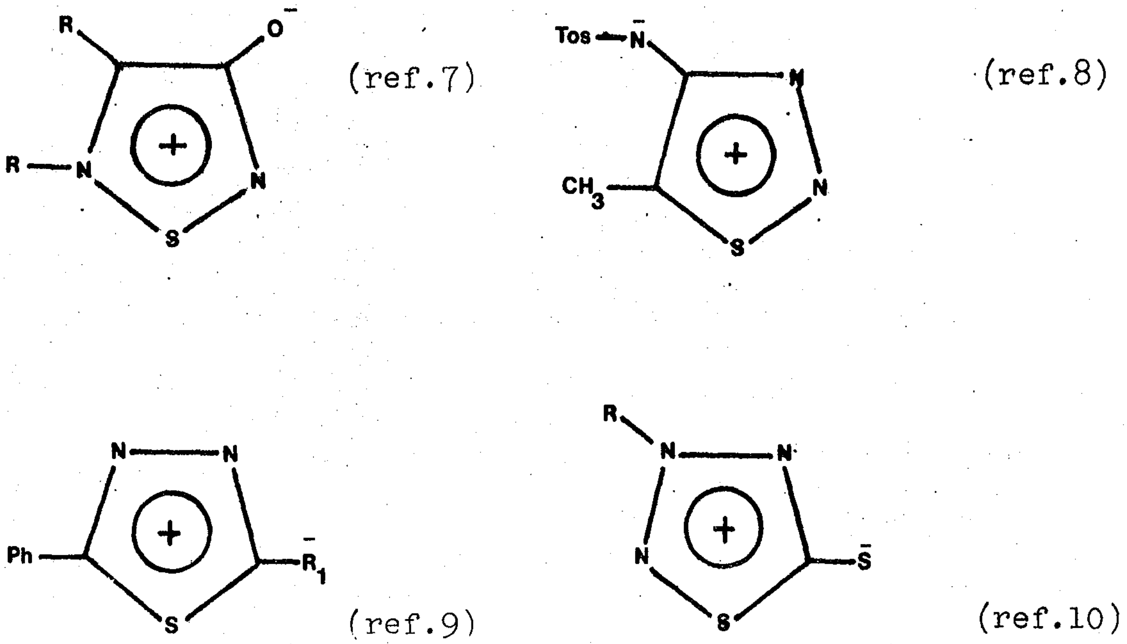
Heterocyclic C/S/N compounds can be categorised into groups depending on the number of atoms in the heterocyclic ring and by the charge on the ring. Figures 2.4-7 (pages 81 - 84) indicate the skeletal arrangements of the majority of known C/S/N heterocycles containing a $(4n + 2)\pi$ system.

2.1.1 Meso-ionic C/S/N Heterocycles

There is a class of compounds named "meso-ionic" compounds, of which a large proportion of known examples contain a five membered carbon-sulphur-nitrogen ring. Although these compounds are not discussed at length in this thesis it is worth noting their existence when discussing examples of cationic C/N/S heterocycles.[1] (figure 2.1)

"A compound may be appropriately called meso-ionic if it is a five-membered heterocycle which cannot be represented satisfactorily by any one covalent or polar structure and possesses a sextet of electrons in association with the five atoms comprising the ring".[6]

Figure 2.1 Some examples of C/S/N meso-ionic compounds



(ref.7) (ref.8) (ref.9) (ref.10)

2.1.2 Neutral C/S/N Heterocycles containing a Five Membered Ring

All the C/N/S heterocycles containing 6π-electrons are known up to and including -CN_2S_2 in either neutral or cationic forms. Rings containing more than two atoms of either sulphur or nitrogen are generally not known except for 5 substituted 1,2,3,4 thiatriazole (compound 2.13, figure 2.4 page 81).

The thiazoles ("C_3NS" compounds 2.1, 2.3 figure 2.4 page 81) and benzothiazoles (compounds 2.2, 2.4 figure 2.4 page 81) have been known for many years and are of great pharmaceutical interest as diuretics, antihistamines, mitostatics[2b] and inflammatories.[2a] Recent industrial uses have included the use as vulcanisation accelerators,[2b] antioxidants,[2b] as photochromics[2a,d], as dyestuffs [2a,c,d] and in polymeric applications.[2a,b,d]

2.1.3 Neutral C/S/N Heterocycles containing a Six Membered Ring

There are fewer C/S/N six membered Hückel aromatic ring systems than would, at first, be anticipated. All the "C_4NS" rings are known, including examples with sulphur in the $S^{(IV)}$ and $S^{(VI)}$ states due to bonding of an oxygen and a further group to the sulphur (compounds 2.14-16, figure 2.5, page 82). Of the three possible isomers of the dithiazine ring system only the 1,4,2-isomer has been isolated (compound 2.17, figure 2.5, page 82). The ring systems of the form "C_3SN_2" (thiadiazines) are well documented[12] and the chemistry of the S,S-dioxides has been widely studied.[14] Not all the isomers of the thiadiazine rings are known and those that are tend to be stabilised by coordination to a benzo or naphtho ring (compounds 2.18-23, figure 2.5, page 82). The chemistry of the heterocycles containing two sulphur-atoms and two nitrogen atoms (dithiadiazines) has not been widely studied and only the 1,3,2,4-isomer (compound 2.22, figure 2.5, page 82) has been synthesised. Heterocycles of the form "C_2SN_3" and "CS_2N_3" have been synthesised (compounds 2.23,24, figure 2.5, page 82) but as yet their uses and chemistry have not been systematically investigated.

2.1.4 Neutral C/S/N Heterocycles containing other than Five or Six Membered Rings

Although rings of other sizes than 5 or 6 do exist they do not, in general, exist without one or more bonds in the ring being fully saturated (i.e. an incomplete delocalised system). The only exceptions to this are the 1,4,5-thiadiazepine, and 1,2-thiazepine ring systems (compounds 2.25,26, figure 2.6, page 83).

2.1.5 Cationic Five Membered C/S/N Heterocycles with no substituents on Nitrogen or Sulphur

Although there are quite a few C/S/N cationic heterocycles with a five membered ring the majority are substituted at nitrogen (compounds 2.27-32, 35, 36, figure 2.7, pages 83,84).

There are however four five membered C/S/N heterocyclic cations without the nitrogen being substituted (compounds 2.33, 34, 37, 38, figure 2.7, page 84).

(i) The 1,2,4-dithiazolium cation (comp. 2.33)

(ii) The 3,5-benzo-1,2,3-dithiazolium cation (Herz compound: 2.34)

(iii) The 4-substituted-1,2,3,5-dithiadiazolium cation (compound 2.37)

(iv) The 4-substituted-1,3,2,5-dithiadiazolium cation (comp. 2.38).

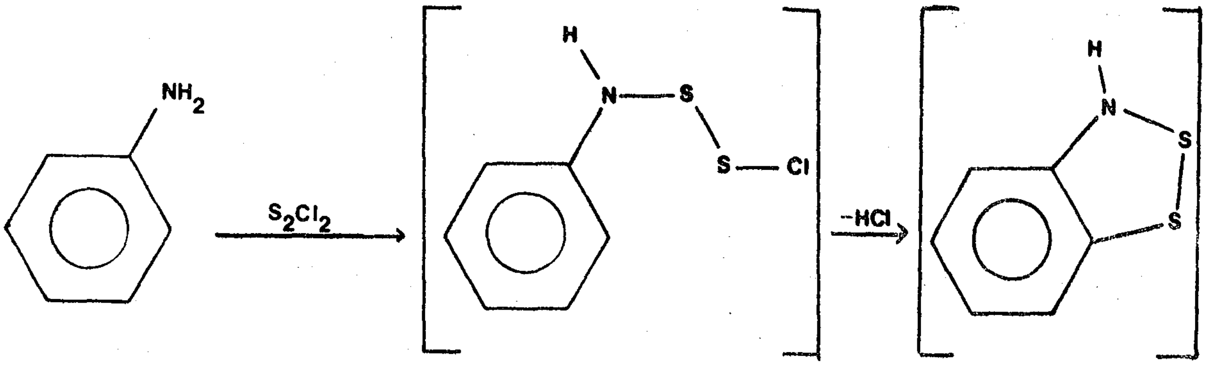
The 1,2,4-dithiazolium salts are, by far, the most investigated species of the four cations. Many salts have been synthesised with a large range of substituents at the 3 and 5 positions. The dithiazolium cations have found pharmaceutical and industrial uses as sterilizers,[14-17] male contraceptives[18,19] and photographic development accelerators.[14,20]

Although the derivatives of the 1,2,4-dithiazolium cation are of significant industrial interest they are not discussed further in this thesis as there is no sulphur-nitrogen bond in the ring.

2.1.5a The Herz Compounds (Benzo-1,2,3-dithiazolium salts) (comp. 2.34, figure 2.7, page 84)

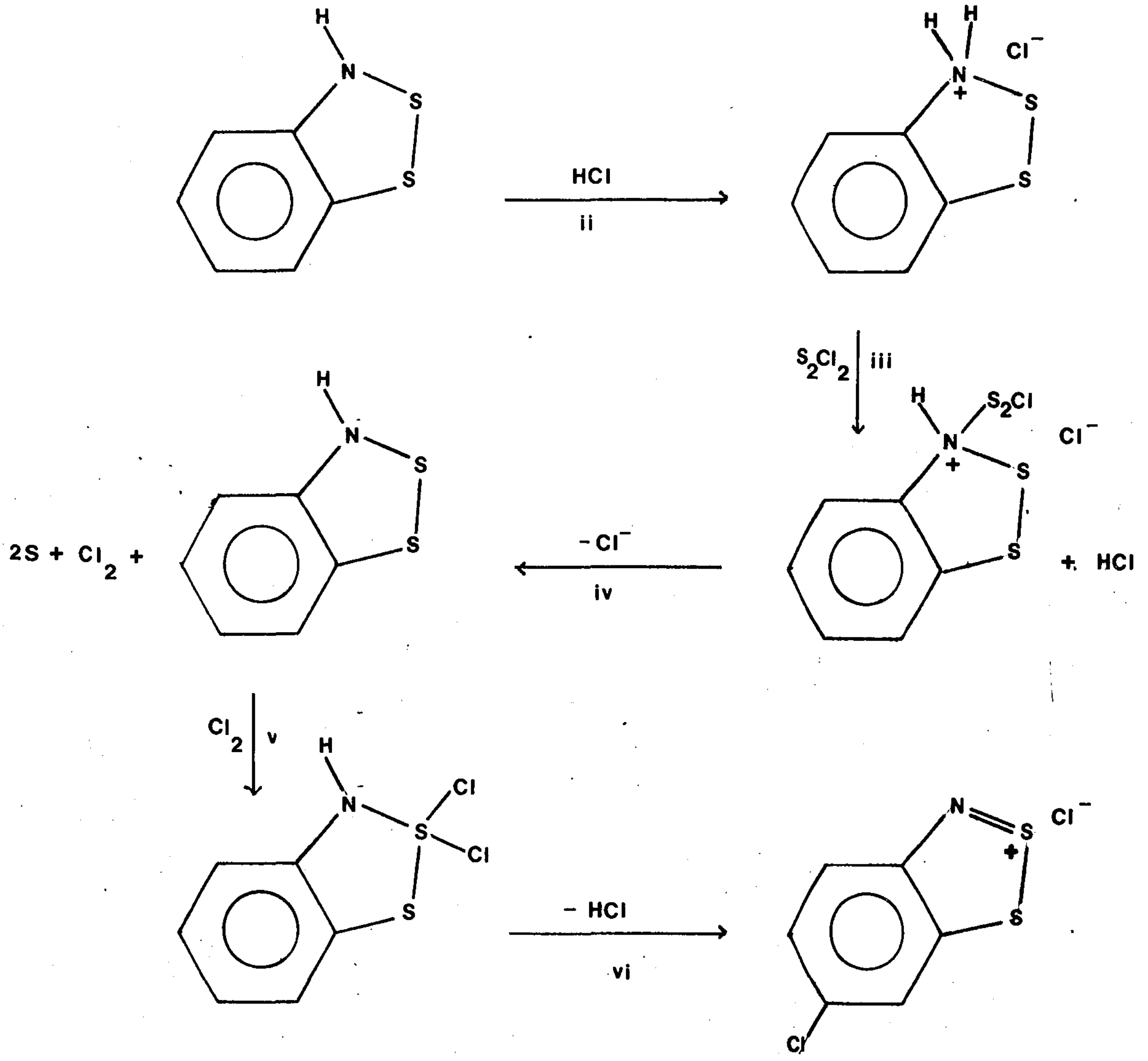
The only salts of the 1,2,3-dithiazolium cation synthesised are the 3,5-benzo derivatives, known as Herz compounds. The Herz compounds were first synthesised by Richard Herz in 1914 and a patent was published in 1922.[21] The mechanism by which aniline hydrochloride or any aromatic amine reacts with disulphur dichloride to form the benzodithiazolium ring system has been an area of much interest for many years. Bezzubets *et al* (1939,[22] 1948[23]) showed that the rate of formation of the Herz compounds was much greater in polar solvents and hence suggested a series of initial reaction sequences.[23] Gompper *et al* (1964)[24] were however the first to postulate a plausible initial reaction sequence (figure 2.2).

Figure 2.2 Initial reaction sequence in the reaction of aniline with disulphur dichloride suggested by Gompper[24]



Gompper suggested that the S_2Cl_2 subsequently chlorinated position 6. This was however disputed by Hope and Wiles (1967)[25] who, due to their observation of molecular chlorine in the reaction, postulated the mechanism presented in figure 2.3.

Figure 2.3 Subsequent mechanism (suggested by Hope and Wiles) to the initial reaction of S_2Cl_2 with amines (figure 2.2)



Steps ii-iv outlined in figure 2.3 indicate the probable route by which chlorine is produced for the subsequent chlorination of the carbon at position 6 and of the sulphur. (cf. the chlorination of sulphenyl chlorides; RSCl to $RSCl_3$[26]).

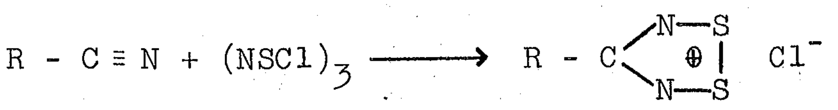
The mechanism suggested by Hope and Wiles is generally accepted to be substantially correct.

The main interest in Herz compounds was shown by the dye industry. The compounds were hydrolysed by alkali providing a valuable synthetic route to σ-aminobenzenethiols which in turn opened the way for the systematic, large scale production of a variety of dyes. During the past two decades the potential synthetic value of the cations in general heterocyclic chemistry has been realised.[27-31] Evdokimov *et al*[32] have synthesised the 1,2,3-thiaselenazolium and 1,2,3-benzodiselenazolium chloride analogues.

Although many different benzo-substituted Herz compounds have been produced relatively few salts with anions other than chloride have been synthesised. The first salt containing an anion other than chloride was 6-methoxy-8-bromo-1,2,3-benzothiadiazolium bromide[25] and subsequently salts containing the tetrafluoroborate,[33] perchlorate[34] and trichlorozincate[10] anions were prepared. The hydrolysis and substitution of the salts with primary[35] and secondary[31] amines have been areas of great interest over the past decade due to the formation of substituted 3-H-1,2,3-benzodithiazole-2-oxides, which are of considerable importance as herbicides.

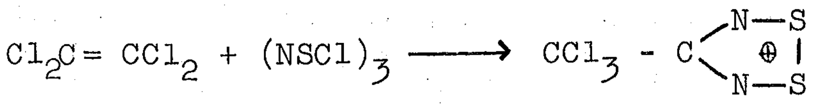
2.1.5b The Dithiadiazolium Cations ($R\text{-}CN_2S_2^+$)

Two isomers of the dithiadiazolium ring system have been synthesised, the 1,2,3,5-isomer[36-38] and the 1,3,2,5[39] isomer (equations 2.1-5).

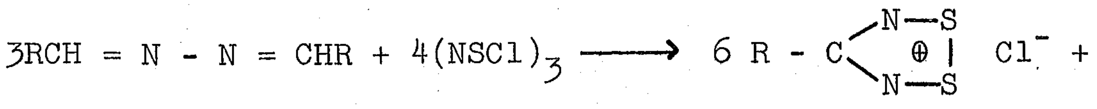


(ref.37) (2.1)

(R = CCl_3, Ph, ^tBu)



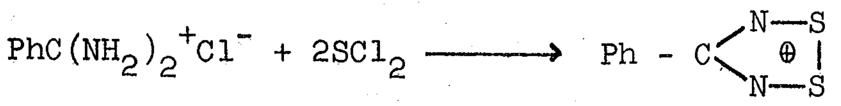
(ref.37) (2.2)

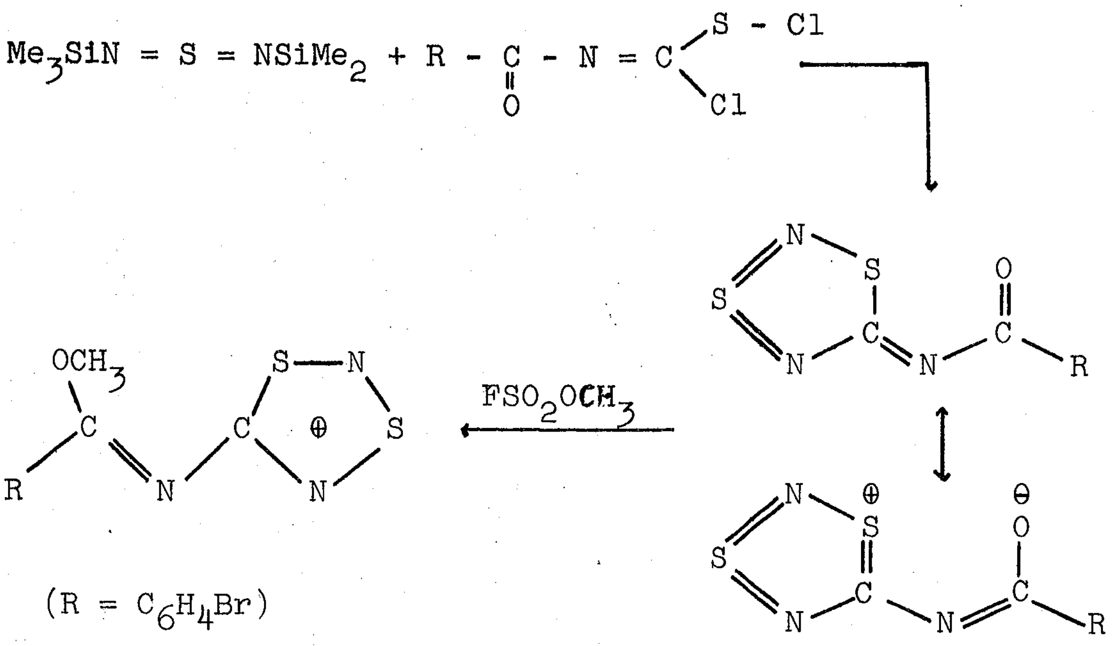


$3N_2 + 3Cl_2$

(R = Ph, ^tBu)

(ref.38) (2.3)


(ref.37) (2.4)


$(R = C_6H_4Br)$

The chemistry of these cations is still in its infancy. The preparation of the 1,3,2,4-isomer has been reported by Neidlein *et al*[39] but none of its chemistry has, as yet, been published. The only chemistry reported for the 1,2,3,5-dithiadiazolium cation is that of varying the substituent at position 4 (Ph, CCl_3, ^tBu)[37,38] and the anions ($SbCl_6^-$, $CF_3SO_6^-$, $N(SO_2F)_2$, BF_4^- and PF_6^-).[38]

2.1.6 Cationic C/S/N Heterocycles containing (4n + 2) π-electrons, with ring sizes other than five

There are only two cations that fall into this category the 1,3-thiazinium[1] and the 1,4-thiadiazinium cations.[40] (comps. 2.39, 40, figure 2.7, page 84). Both species have a six membered heterocyclic ring containing 6π-electrons. The 1,3-thiazinium cation is known to react readily with oxygen, sulphur and carbon nucleophiles cleaving the 5,6 bond to give thioacyl derivatives of vinylamines. Reduction of the salts with sodium borohydride yields 2H-, 4H-, and 6H-thiazines.[1]

Very little work has been reported on the 1,4-thiadiazinium cations,the only compounds produced being four 2,4,6-trisubstituted derivatives stabilised as either the iodide[40] or the perchlorate.[41]

2.2 Experimental

2.2.1 Preparation and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride[36]

Ammonium chloride (105g, 1.96 mole), benzonitrile (250cm^3, 2.45 mole) and sulphur dichloride (250cm^3, 3.93 mole) were stirred at 140°C for 16h. Further aliquots of sulphur dichloride (SCl_2) (each of 100cm^3, 1.57 mole) were added until no further evolution of hydrogen chloride was noted. The slurry was then cooled slowly to room temperature, filtered, washed with anhydrous ether (4 x 100cm^3) and dried *in vacuo*. The crude product was then recrystallised from a number of solvents. The most successful results were obtained by recrystallisation from a 4:1 mixture (by volume) of dichloroethane:thionyl chloride and using sulphur dioxide.

Analysis for a double dichloroethane: thionyl chloride recrystallisation;

Found: C,38.46; N, 12.57; H, 2.42; S,29.23; Cl, 16.88%.

$C_7H_5ClN_2S_2$ requires: C, 38.8; N, 12.9; H, 2.3; S, 29.6; Cl, 16.4%.

The crude material was extracted using sulphur dioxide in a sealed system (figure 1.6, page 16). The product obtained was heated at 50°C *in vacuo* for 4h. to remove any traces of trapped sulphur dioxide.

Analysis of the product recrystallised from sulphur dioxide; Found: C, 38.58; N, 12.44; H, 2.64; S, 29.82; Cl, 16.18%.

The infra-red, Raman and mass spectra for the product recrystallised from sulphur dioxide are given below:

Infra-red spectrum (nujol mull): 1600m, 1582vw, 1495w, 1444s, 1396vs, 1345w, 1295w, 1260vw, 1212w, 1172w, 1150m, 1145w(sh), 1070w, 1031m, 1000w, 935m, 895s, 845vs, 795m, 785m, 740w, 708m, 698vs, 686w(sh), 670vw, 554s, 532w, 475w cm^{-1}.

Raman Spectrum (red line): 1600m, 1500w, 1392m, 1160m, 1004m, 927w, 845vs, 664vw, 512vs, 383m, 318w, 290w, 152m, 64s, 35s, cm^{-1}.

Mass Spectrum (m/e (abundance) assignment): 181(100) $PhCN^*$; 135(12) $PhCNS^*$; 104(12) PhCNH ; 103(98) $PhCN^*$; 78(29) NS_2^*; 77(13) Ph^*; 76(29) CS_2^*; 64(4) S_2 ; 52(5) C_4H_4; 51(13) C_4H_3; 50(13) C_4H_2; 46(27) NS^*; 39(6) C_3H_3; 38(7) HCl^{37} ; 36(19) HCl^{35} :

(A diagrammatic representation of the above spectrum is shown in figure 2.8a, page 85 . * Denotes the main peaks of interest in the spectrum and those used for comparison with spectra of other dithiadiazolium salts).

Crystals suitable for X-ray crystal studies of 4-phenyl-1,2,3,5-dithiadiazolium chloride were produced by slowly cooling a saturated refluxing solution of the salt in toluene, to room temperature. Needle shaped crystals of approximately 2mm, in length and 0.5mm diameter were formed which contained one molecole of toluene of crystallisation for every six molecules of 4-phenyl-1,2,3,5-dithiadiazolium chloride.[47]

2.2.2 Preparation of the 4-Phenyl-1,2,3,5-Dithiadiazolium Halides

(i) Preparation of 4-Phenyl-1,2,3,5-Dithiadiazolium Bromide

The exchange reactions between 4-phenyl-1,2,3,5-dithiadiazolium chloride ($PhCN_2S_2Cl$) and sodium bromide or potassium bromide using toluene, nitromethane, 1,4-dioxan, monoglyme,T.H.F., acetic anhydride, dichloromethane and dichloroethane as solvents, were unsuccessful yielding only starting materials. The reaction of $PhCN_2S_2Cl$ with KBr in the solid state and with LiBr or AgBr in a variety of solvents (monoglyme, T.H.F., 1,2-dichloroethane, and sulphur dioxide) produced the desired dithiadiazolium bromide.

(a) Solid state reaction between $PhCN_2S_2Cl$ and KBr

On grinding together KBr and $PhCN_2S_2Cl$ it was noted that a deep red mixture was obtained which when pressed into an infra-red disc gave a spectrum of similar form to that recorded for a $KCl/PhCN_2S_2Cl$ disc (orange in colour).

Infra-red spectrum of the ($KBr/PhCN_2S_2Cl$ disc): 1600m, 1495w, 1455s, 1398vs, 1345w, 1295w, 1215w, 1180vw, 1165w, 1150m, 1070w, 1032m, 1005w, 924m, 892s, 842s, 795w, 782m, 760w, 708m(sh), 696vs, 680w(sh), 658vw, 610vw, 550m, 536w(sh), 330m cm^{-1}.

A preparative scale solid phase reaction was carried out by grinding together $PhCN_2S_2Cl$ (4.36g, 20.14 mmoles) with anhydrous KBr (15.23g, 0.13 moles),under dry box conditions, and subliming the deep red product on to a liquid nitrogen cold finger, the system being heated to 220°C at 2.5×10^{-2} torr. The infra-red spectrum recorded of the sublimed product was identical to that observed for the $PhCN_2S_2Cl/KBr$ disc.

Analysis of the sublimed product.

Found: S, 22.69; N, 11.08; C, 31.21; Br, 29.16%

$C_7H_5N_2S_2Br$ requires: S, 24.52; N, 10.73; C, 32.18; Br, 30.65%.

(b)Reaction of $PhCN_2S_2Cl$ with LiBr in various solvents

Using a coordinating ether as a solvent (monoglyme, T.H.F.)

In a typical reaction anhydrous LiBr (0.20g, 2.3 mmole) was added to a stirred suspension of $PhCN_2S_2Cl$ (0.5g, 2.3 mmole) in T.H.F. (30 cm^3). A deep red solution was immediately formed. The reaction mixture was allowed to stir at room temperature for 16h. to ensure complete reaction. The reaction was then brought to reflux and the deep red refluxing solution filtered off. On cooling a bright red microcrystalline product was obtained which was washed with ether (2 x 10 cm^3) and dried *in vacuo*.

The crude product was recrystallised from toluene and also from sulphur dioxide. The recrystallisation of the bromide from toluene yielded deep red needle shaped crystals which from their analyses indicated that toluene of crystallisation was present.

Analysis of the toluene recrystallised product:

Found: C, 41.93; N, 8.83; H, 3.36; S, 21.19; Br, 26.0%.

$2C_7H_5N_2S_2Br.PhCH_3$ requires: C, 41.04; N, 9.12; H, 2.93; S, 20.88; Br, 26.06%.

The product from the sulphur dioxide recrystallisation was paler in colour and after heating to 50°C *in vacuo* for 2h., gave analyses consistent with the formulation $C_7H_5N_2S_2Br$.

Analysis of the sulphur dioxide recrystallised product.

Found: C, 32.49; N, 10.36; H, 2.21; S, 24.86; Br, 29.92%.

$C_7H_5N_2S_2Br$ requires: C, 32.18; N, 10.73; H, 1.92; S, 24.52;
Br, 30.61%.

The infra-red spectra of the above products were identical to that observed for the $PhCN_2S_2Cl$/KBr disc.

(c) Reaction of KBr and $PhCN_2S_2Cl$ using SO_2 as a solvent.

$PhCN_2S_2Cl$ (0.5621g, 2.60 mmole) and KBr (0.3241g, 2.72 mmole) were placed in two separate bulbs of a pre-dried, vacuum tight, pyrex vessel (figure 1.2 , page 14) and sulphur dioxide (7.1344g) condensed in to both bulbs. The KBr solution was then filtered on to the $PhCN_2S_2Cl$ solution and an immediate reaction occurred forming a deep red solution. The sulphur dioxide was repeatedly recondensed on to the remaining KBr until all the reactant had been dissolved and then the KBr solution filtered into the bulb originally containing the $PhCN_2S_2Cl$. The reaction was agitated for 12h. and then the sulphur dioxide solubles filtered off. The solvent was slowly evaporated from the solution and bright red platelets of $PhCN_2S_2Br$ were produced. The product was heated at 60°C *in vacuo* for 2h. to remove any occluded solvent.

Analysis of the product:

Found: C, 31.98; N, 10.46; H 1.74; S, 24.93; Br, 30.12%.

$C_7H_5N_2S_2Br$ requires: C, 32.18; N, 10.73; H, 1.92; S, 24.52;
Br, 30.61%.

The infra-red spectrum of the product was identical to that observed for the $PhCN_2S_2Cl$/KBr disc.

(ii) Preparation of 4-Phenyl-1,2,3,5-Dithiadiazolium Iodide

(a) Solid phase Reactions between $PhCN_2S_2Cl$ and Iodides

An infra-red disc of $PhCN_2S_2Cl$ was made using cesium iodide as the dispersant. A very deep purple disc resulted which gave an infra-red spectrum significantly different from that of either $KCl/PhCN_2S_2Cl$ or $KBr/PhCN_2S_2Cl$ discs.

Infra-red spectrum ($CsI/PhCN_2S_2Cl$ disc): 1600w, 1498w, 1455s, 1358vs, 1212w, 1176m, 1130s, 1028m, 1005w, 930w, 904m, 860m, 848w(sh), 828m, 775vs,br, 692s, 600w, 536w, 525s, 460s cm^{-1}.

A preparative scale solid phase reaction was carried out by grinding together $PhCN_2S_2Cl$ (1.26g, 5.82 mmole) with anhydrous NaI (1.5g, 10 mmole), under dry box conditions and subliming the purple-black product on to a liquid N_2 cold finger, the system being heated to 160°C at 10^{-2} torr. The infra-red spectrum of the sublimed product was identical to that observed for the $PhCN_2S_2Cl/CsI$ disc.

Analysis of the sublimed product.

Found: S, 22.63; N, 8.79; C, 25.23; H, 1.18%.

$C_7H_5N_2S_2I$ requires: S, 20.78; N, 9.09; C, 27.27; H, 1.62%.

(b) Reaction of $PhCN_2S_2Cl$ with Iodides using Organic Solvents

The reaction of NaI with $PhCN_2S_2Cl$ was studied in a variety of organic solvents.

(i) Toluene, dichloroethane, dichloromethane, ether and 1,4-dioxan.

(ii) Nitromethane, monoglyme, T.H.F. and acetonitrile.

The solvents listed in category (i) did not facilitate halide transport, whilst virtually immediate reaction occurred in those solvents in category (ii).

In a typical reaction $PhCN_2S_2Cl$ (1.06g, 4.90 mmole) and sodium iodide (0.75g, 5.00 mmoles) were stirred in T.H.F. (25 cm^3) for 60h. An immediate reaction occurred yielding a deep purple solution which did not change in appearance over the 60h. The reaction mixture was filtered at room temperature and the filtrate pumped to dryness. The deep purple residue was washed with ether and the product dried *in vacuo*.

Analysis of the deep purple product.

Found: N, 9.29; S, 22.58; I, 30.67; C, 29.41; H, 2.33%.

$C_7H_5N_2S_2I$ requires N, 9.09; S, 20.78; I, 41.23; C, 27.27, H, 1.62%.

The infra-red spectrum of the product was identical to that observed for the CsI/$PhCN_2S_2Cl$ disc.

(c) Reaction of $PhCN_2S_2Cl$ with KI using SO_2 as a solvent

$PhCN_2S_2Cl$ (0.6057g, 2.798 mmole) and KI (0.4763g, 2.869 mmole) were placed in separate bulbs of a pre-dried vacuum tight pyrex vessel (figure 1.2 , page 14) and sulphur dioxide (7.1321g) condensed into both bulbs. The potassium iodide was completely dissolved and to this yellow-orange solution was added the solution of $PhCN_2S_2Cl$. An immediate reaction occurred yielding a brown-green precipitate which was only sparingly soluble. The $PhCN_2S_2Cl$ was completely washed on to the KI solution and then the SO_2 was removed and the crude product isolated. The crude product was then extracted from the potassium chloride by-product using SO_2 (figure 1. 6, page 16).

Analysis of the extracted product.

Found: C, 21.48; H, 1.25; N, 6.9; S, 16.9; I, 32.6%.

The recrystallised product was then sublimed in a sealed system (120°C, 10^{-3} torr) yielding a deep purple-black sublimate and a white residue. No iodine vapour was noted.

Analysis of the sublimed product.

Found: C, 27.19; H, 1.47; N, 9.30; S, 21.21%.

$C_7H_5N_2S_2I$ requires: C, 27.27; H, 1.62; N, 9.09; S, 20.78%

The infra-red spectrum of the sublimed and the recrystallised product was identical to that recorded for the $PhCN_2S_2Cl$/CsI disc.

Mass spectrum (m/e, (abundance), assignment): 181(24) $PhCN_2S_2$; 135(9) PhCNS ; 104(9) PhCNH ; 103(100) PhCN ; 78(24) NS_2 ; 77(9) Ph ; 76(26) CS_2 ; 51(8) C_4H_3 ; 50(11) C_4H_2 ; 46(2) NS .

(A diagrammatic representation of the above spectrum is given in figure 2.8b(page 86)).

2.2.3 Formation of the Pseudo-Halides and Organic Acid salts of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation

(i) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Thiocyanate

(a) Metathesis reactions using Organic Solvents

It is believed that the $PhCN_2S_2^+$ NCS^- salt is produced as an intermediate in the metathesis reaction between $PhCN_2S_2^+Cl^-$ and sodium thiocyanate. However a subsequent reaction occurs (see Section 2.2.5, page 40) and the thiocyanate salt was not isolated.

(b) Metathesis reactions using liquid Sulphur Dioxide as a Solvent

$PhCN_2S_2Cl$ (0.26g, 1.20 mmole) and $NH_4^+NCS^-$ (0.097g, 1.28 mmole) were placed in two separate bulbs of a pre-dried vacuum tight pyrex vessel, and sulphur dioxide (6.13g condensed in). The $PhCN_2S_2Cl$ solution was then added to the NH_4NCS solution. An immediate reaction occurred forming an intense purple-red solution. The SO_2 was recondensed on to the $PhCN_2S_2Cl$ until all the reactant had been filtered on to the NH_4NCS. The product was highly soluble in the solvent and this solution was filtered off leaving a white residue (0.07g) behind. The solvent was slowly removed from the filtrate yielding a black, deep purple crystalline product.

Infra-red spectrum of the crystalline product (nujol mull):

2200vs, 1592m, 1585w(sh), 1577w(sh), 1495w, 1449vs, 1395vs, 1335w, 1312w, 1289w, 1235w, 1208m, 1178m, 1158w, 1148m, 1090vw, 1064vw, 1023m, 1000w, 972w, 923m, 900s, 843s, 780s, 763w, 690vs, 688s(sh), 679m, 662w, 614w, 552s, 509w cm^{-1}.

Analysis of the crystalline product.

Found: C, 40.64; N, 17.3; S, 41.2; H, 1.89%.

$C_8H_5N_3S_3$ requires: C, 40.17; N, 17.57; S, 40.17; H, 2.09%

Mass Spectrum (m/e, (abundance), assignment). 181,(38) $PhCN_2S_2$; 135(14) PhCNS ; 104(12) PhCNH ; 103(100) PhCN ; 78(45) NS_2 ; 77(13) Ph ; 76(39)CS_2 ; 50(12) C_4H_2; 48(17) SO.

(A diagrammatic representation of the above spectrum is given in figure 2.8c, (page 87)).

(ii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Benzoate

Ammonium benzoate (0.89g , 6.40 mmoles) and $PhCN_2S_2Cl$ (0.64g, 2.96 mmole) were placed in two separate bulbs of a pre-dried vacuum tight pyrex vessel (figure 1.2 , page 14) and SO_2 (12.33g) condensed on to both reactants. The solvent was warmed to room temperature and the solution of ammonium benzoate filtered on to the solution of $PhCN_2S_2Cl$. No reaction occurred. Suspecting that the solubility of $PhCOO^-NH_4^+$ was low on SO_2 the solution of $PhCN_2S_2Cl$ was filtered on to the $PhCOO^-NH_4^+$. Immediate reaction occurred forming a deep purple slurry. The reaction was agitated for 2h. and then a second aliquot of $PhCN_2S_2Cl$ was filtered in to the reaction bulb. The process was repeated until no further $PhCN_2S_2Cl$ remained. The system was then agitated overnight (16h.) and the soluble product filtered off. The solvent was slowly evaporated off, with the resulting deposition of black-purple needle shaped crystals.

Infra-red spectrum of the crystalline product (nujol mull):

1690s,br, 1605 w(sh), 1598m, 1584m, 1575w(sh), 1495w, 1450vs, 1398s, 1372vs, 1124s, 1290s,br, 1182m, 1178m(sh), 1144m, 1135m, 1128m(sh), 1100w, 1070m, 1032w(sh), 1028m, 1015w(sh), 1000w, 933w, 922w, 895w, 842m, 800s, 790s, 788s(sh), 780s, 772w, 768m, 709s, 706s(sh), 700s(sh), 690m(sh), 685s, 682s(sh), 668m, 660m, 652m, 614w, 550m, 530w, 520w, 508m cm^{-1}.

Analysis of the crystals.

Found: C, 54.84; N, 8.88; S, 22.4; H, 3.54%.

$C_{14}H_{10}S_2N_2O_2$ requires C, 55.63; N, 9.27; S, 21.19; H, 3.31%.

Mass spectrum of the crystals run at 200°C and 70eV(m/e (abundance) assignment): 181(10) $PhCN_2S_2$, 135(6) PhCNS , 104(12) PhCNH , 103(100) PhCN , 78(20) NS_2; 77(64) Ph ; 76(28) CS_2; 64(22) S_2, SO_2; 52(7) C_4H_4; 51(14) C_4H_3; 50(15) C_4H_2; 46(15) NS ; 44(73) CO_2, CS .

(iii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Acetate

$PhCN_2S_2Cl$ (0.44g, 2.03 mmole) and ammonium acetate (0.16g, 2.08 mmole) were placed in a pre-dried vacuum tight pyrex vessel (figure 1.1 , page 14) and sulphur dioxide

(8.41g.) condensed on to the reactants. A rapid reaction occurred on warming the system to room temperature yielding a deep purple-red solution. The reaction was agitated for 5h. at room temperature and then the solubles were filtered off. The insolubles were washed with recondensed sulphur dioxide to remove all traces of the solubles. The solvent was then slowly removed from the filtrate resulting in the deposition of a black-purple microcrystalline material.

Infra-red spectrum of the product (nujol mull): 1698s, 1595m, 1580w, 1495w, 1455vs, 1400vs, 1375vs, 1315m, 1290m, 1210w, 1165w, 1150s, 1064w, 1045w(sh), 1025m, 1000w, 920s, 892s, 840vs, 834m, 800w, 782s, 762w, 698vs, 680s, 660w, 650w, 548s, 520m, 508w. cm^{-1}

The product was dissolved in T.H.F. but the product isolated after removing the T.H.F. was not the acetate but a species with an infra-red spectrum considerably different from that of the dithiadiazolium cation (section 2.2.5(v), page 42).

2.2.4 Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Lewis Acids

(i) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Tetrachloroborate (III)

$PhCN_2S_2Cl$ (0.4373g, 2.020 mmole) was placed in a pre-dried, vacuum tight, pyrex vessel (figure 1. 1 , page 14). Sulphur dioxide (3.4819g,) and BCl_3 (0.2775g, 2.366 mmole) were condensed on to the dithiadiazolium salt and the reaction warmed to room temperature. The reaction occurred readily forming a slightly deeper orange compound than the parent chloride. The volatiles at room temperature were completely removed and the product weighed (0.5524g). From the weight of product it was deduced that incomplete reaction had occurred (48% conversion). Therefore SO_2 (0.5118g) and BCl_3 (0.2513g, 2.142 mmole) were condensed on to the reaction mixture and the system stirred at room temperature for 4h. The volatiles present at room temperature were then removed and the product (0.6655g corresponds to 97% conversion) isolated.

Infra-red spectrum of the product (nujol mull): 1595m, 1498m, 1451s, 1392vs, 1345w, 1325vw, 1295w, 1195w, 1182m, 1165w(sh), 1160m, 1156w(sh), 1070vw, 1026m, 1000w, 935w, 922s(sh), 919s, 841s, 779s, 725m(sh), 770s(sh), 695vs, 675m(sh), 662s, 632m, 558s cm^{-1}.

Mass spectrum (m/e, (abundance), assignment): 181(28) $PhCN_2S_2$; 135(14) PhCNS ; 103(100) PhCN ; 83(18) $B^{11}Cl^{35}Cl^{37}$; 81(26) $B^{11}Cl_2{}^{35}$; 80(9) $B^{10}Cl_2{}^{35}$; 78(84) NS ; 77(55) Ph ; 76(50) CS_2; 47(10) $B^{11}Cl^{37}$; 46(77) NS, $B^{11}Cl^{35}$; 45(7) $B^{10}Cl^{35}$; 38(24) HCl^{37} ; 36(70) HCl^{35} ; 32(15) S_2.

Analysis of the BCl_4^- salt.

Found: C, 24.23; N, 7.64; S, 19.40; Cl, 40.65; H, 1.40%.

$C_7H_5N_2S_2BCl_4$ requires C, 25.16; N, 8.39; S, 19.17; Cl, 42.54; H, 1.50%.

(ii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Hexachloroantimonate(V).

(a) Using Thionyl Chloride as the Solvent

$SbCl_5$ (2.8g, 9.4 mmole) was added to a stirred solution of $PhCN_2S_2Cl$ (1.8g, 8.3 mmole) in refluxing $SOCl_2$ (25 cm^3). An immediate reaction occurred forming a bright red precipitate. After refluxing for 10 min. the reaction mixture was cooled to room temperature and the product filtered off. The salt was recrystallised from dry nitromethane (50 cm^3) and dried *in vacuo*.

Infra-red spectrum of the product (KCl disc): 1600m, 1505m, 1459m, 1400s, 1268w, 1190m, 1168m, 1035w, 939w, 928s, 845s, 784m, 698s, 675s, 629m, 566s, 355s(sh) 348s cm^{-1}.

Major mass spectral peaks (m/e, (abundance), assignment).

191(78) $SbCl_2$; 181(28) $PhCN_2S_2$, 156(10) SbCl ; 135(8) PhCNS ; 121(4) Sb ; 104(13) PhCNH ; 103(100) PhCN ; 78(52) NS_2 ; 77(34) Ph ; 76(51) CS_2; 46(28) NS .

Analysis of the product.

Found: C, 16.18; N, 5.38; S, 12.80; Cl, 40.61; Sb, 22.69; H, 1.10%.

$C_7H_5N_2S_2SbCl_6$ requires: C, 16.29; N, 5.43; S, 12.41; Cl, 41.30; Sb, 23.61; H, 0.97%.

(b) Using Sulphur Dioxide as a Solvent

$PhCN_2S_2Cl$ (0.7557g, 3.491 mmole) was loaded into a pre-dried, vacuum tight, pyrex vessel (figure 1.1 , page 14). $SbCl_5$ (6.9875g, 23.35 mmole) and SO_2 (8.4519g) were condensed on to the salt and the reaction warmed to room temperature. An immediate reaction occurred forming a bright red precipitate that was virtually insoluble in the solvent. The excess antimony pentachloride was removed from the product by washing the salt with recondensed SO_2. The product was then isolated and dried *in vacuo*.

Infra-red spectrum of the product (nujol mull): 1600m, 1505m, 1395vs, 1345w, 1295w, 1194m, 1189m, 1172w(sh), 1164m, 1030w, 972vw, 935m, 924s, 840w, 780s, 692vs, 680s, 562s, 340vs,br, cm^{-1}.

Analysis of the product.

Found: C, 15.94; N, 5.05; S, 13.1; Cl, 42.1; H, 1.23%.

$C_7H_5N_2S_2SbCl_6$ requires: C, 16.29; N, 5.43; S, 12.41; Cl, 41.30; H, 0.97%.

The $PhCN_2S_2^+SbCl_6^-$ was found to be very soluble in arsenic trifluoride (AsF_3). However it was found that the hexachloroantimonate(V) salt crystallises from the solvent with AsF_3 of crystallisation.

Infra-red spectrum of $PhCN_2S_2^+SbCl_6^-.xAsF_3$ (nujol mull):

1595m, 1500m, 1395vs, 1295w, 1185m(sh), 1162m, 1030w, 932m(sh), 920s, 842m, 775s, 720m*, 699vs, 662w(sh)*, 645s(sh)*, 630vs,* 620s,* 585s, 560s, 370m, 340vs cm^{-1}.

(* Denotes peaks assignable to AsF_3).

(iii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Hexachlorostannate(IV).

$SnCl_4$ (0.4 cm^3, 3.4 mmole) was added to a stirred suspension of $PhCN_2S_2Cl$ (1.32g, 6.1 mmole) in $SOCl_2$ (60 cm^3), at room temperature. An immediate reaction occurred yielding a bright yellow precipitate. The precipitate was filtered off, washed with pentane (3 x 20 cm^3) and dried *in vacuo*.

Infra-red spectrum of product (KCl disc): 1602w, 1595m, 1502m, 1469s, 1400vw, 1340vw, 1320vw, 1298vw, 1209m, 1184w(sh), 1175m, 1160m, 1072vw, 1026m, 1000w, 935m, 920s, 958vw(sh), 946s, 790s, 700vs, 670w, 617vw, 560s, 322vs, 315s(sh), 290m(sh) cm^{-1}.

Analysis of the product.

Found: C, 23.51; N, 7.93; H, 1.32; S, 18.93; Cl, 30.14%.

$C_{14}H_{10}N_4S_4SnCl_6$ requires: C, 24.22; N, 8.07; H, 1.44; S, 18.45, Cl, 30.70%.

2.2.5 Reactions in which the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation is Reduced forming 4-Phenyl-1,2-Dithia-3,5-Diazole

(i) Reaction 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Sodium Thiocyanate using Organic Solvents

Anhydrous NaNCS (1.42g, 17.5 mmole) was added to a stirred suspension of $PhCN_2S_2Cl$ (3.8g, 17.6 mmole) in dry monoglyme (50 cm^3). An immediate reaction occurred forming a deep purple solution, which after refluxing for 10 min. (stirring for 6h. at room temperature has the same effect), yielded a dense orange precipitate. The reaction was refluxed for 6h. and the reaction mixture filtered hot. The deep purple filtrate was cooled slowly to -20°C and the resulting deep purple-black needle shaped crystals isolated. The crystals were then recrystallised from dry 1,2-dichloroethane (15 cm^3) and reprecipitated by slowly cooling the solution in a -78°C slush bath. The combined filtrates were pumped to dryness and the residue recrystallised from dry dichloroethane (20 cm^3), crystals being obtained as above.

Analysis of the purple-black crystals:

Found: C, 46.60; N, 15.64; S, 34.92; H, 2.84%.

$\left[C_7H_5N_2S_2\right]_x$ requires; C, 46.41; N, 15.47; S, 35.36; H, 2.76%.

Infra-red spectrum of the crystals (nujol mull): 1600w, 1496w, 1450s, 1322w, 1240w, 1228w, 1186vw, 1181vw, 1178vw, 1161vw, 1159vw, 1145w, 1139m, 1077w, 1025w, 982w, 932vw, 923vw, 901vw, 858vw, 842w, 838m, 830w, 776s, 770m, 690s, 688m, 685m, 660w, 653s, 618vw, 512s cm^{-1}.

Major mass spectral peaks (m/e (abundance), assignment); 181(86) $PhCN_2S_2$, 135(65) PhCNS , 103(90) PhCN ; 78(100) NS_2 ; 77(56) Ph ; 76(72) CS_2; 46(20) NS .

The mass and infra-red spectra listed above were used for identification of the 4-phenyl-1,2-dithia-3,5-diazole produced in all the reactions presented in this section.

(ii) The Thermal Decomposition of 4-Phenyl-1,2,3,5-Dithiadiazolium Thiocyanate.

$PhCN_2S_2^+NCS^-$ (1.23g, 5.15 mmole, see experiment 2.2.3(i,b), page 33) was placed in a pre-dried pyrex sublimation tube and sealed off, (vacuum: 1×10^{-3} torr). The lower portion of the tube was then heated to 80°C and a black sublimate was noted to form above the oil bath level. After ca. 3h. it was noted that the residue was deep orange and no further sublimation was occurring. The system was cooled to room temperature and the sealed system separated in an atmosphere of dry nitrogen. The infra-red and mass spectra of the sublimate (0.91g) were recorded and found to be identical to those recorded in experiment 2.2.5(i) (page 40).

(iii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Azides

In a typical reaction lithium azide (1.1g, 22.5 mmole) was added to a slurry of $PhCN_2S_2Cl$ (3.52g, 16.26 mmole) at room temperature, An immediate, highly exothermic reaction occurred with evolution of nitrogen and the formation of a deep purple solution with a pale coloured precipitate. The reaction was stirred for 6h. at room temperature. No nitrogen was evolved after ca. 10 min. The reaction mixture was filtered and cooled (using a dry-ice acetone slush bath) a white precipitate (lithium chloride) precipitating out of the solution. The solution was filtered at ca. -78°C and pumped to dryness. The residue was recrystallised from dry 1,2-dichloroethane (30 cm^3) and the crystals formed, on cooling this solution, were isolated. The crystals were identified by their infra-red and mass spectra and found to be identical to the product obtained in experiment 2.2.5(i), (page 40).

Sodium azide does not react readily with phenyl dithiadiazolium chloride in organic solvents but does so in sulphur dioxide.

(iv) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Potassium Cyanide

$PhCN_2S_2Cl$ (0.9612g, 4.44 mmole) and KCN (0.3461g, 5.32 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel (figure 1. 1 , page 14) and AsF_3 (8.1246g) condensed on to the reactants. On warming to room temperature a rapid reaction occurred yielding an intensely coloured solution and a brown precipitate. The product was recrystallised using arsenic trifluoride. However it was noted that either KCN or KCl was also soluble in the AsF_3 and thus the solvent was removed and SO_2 (6.3148g) was condensed into the vessel as the recrystallisation solvent. The product was recrystallised from sulphur dioxide yielding a purple-brown microcrystalline material which was identified as 4-phenyl-1,2-dithia-3,5-diazole by the analysis and infra-red and mass spectra (experiment 2.2.5(i), page 40).

Analysis of the microcrystalline product:

Found: C, 45.92; N, 14.83; H, 2.96%.

$C_7H_5N_2S_2$ requires: C, 46.41; N, 15.47; H, 2.76%.

(v) Decomposition of 4-Phenyl-1,2,3,5-Dithiadiazolium Acetate

$PhCN_2S_2^+ \; CH_3COO^-$ (0.41g, 1.7 mmole, experiment 2.2.3(iii), page 35) was stirred for 12h. at room temperature in dry T.H.F. (4.32g). The resulting purple solution was filtered off from the residue and pumped to dryness. The infra-red and mass spectra of the species were recorded and found to be consistent with 4-phenyl-1,2-dithia-3,5-diazole (experiment 2.2.5(i), page 40).

(vi) Decomposition of 4-Phenyl-1,2,3,5-Dithiadiazolium Benzoate

$PhCN_2S_2^+PhCOO^-$ (0.59g, 1.95 mmole, experiment 2.2.3(ii)) was stirred in dry monoglyme (5 cm^3), at room temperature for 12h. The solvent was then removed and the residue identified by its infra-red spectrum as 4-phenyl-1,2,3,5-dithiadiazolium benzoate. Monoglyme (10 cm^3) was added to the residue and the solution was refluxed for 8h. The solvent was then removed by pumping at reduced pressure and the resulting residue was identified as being a mixture, in which 4-phenyl-1,2-dithia-3,5-diazole was present (experiment 2.2.5(i), page 40). Purification of the product was not attempted.

(vii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Phenyl Magnesium Bromide

A solution of PhMgBr in ether (23.10 mmoles of PhMgBr in 14.26 cm^3 of solution) was added to a stirred suspension of $PhCN_2S_2Cl$ (5.06g, 23.37 mmole) in toluene (60 cm^3). A slow reaction occurred at room temperature which, over a period of 6h., produced a deep purple solution. The solution was filtered off from the pale coloured precipitate and pumped to dryness. The residue was sublimed at a pressure of 1×10^{-2} torr and a temperature of 120°C, yielding a black sublimate. The sublimate was identified by its infra-red spectrum as 4-phenyl-1,2-dithia-3,5-diazole (experiment 2.2.5(i), page 40).

(viii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with n-Butyl Lithium

In a typical reaction n-butyl lithium (2.4 cm^3, 3.96 mmole) was syringed into a suspension of $PhCN_2S_2Cl$ (0.85, 3.93 mmole) in toluene (60 cm^3), cooled to -196°C. The reaction was warmed slowly to room temperature via -95°C and

-78°C slush baths. No reaction was noted at temperatures below room temperature and even at room temperature the reaction was relatively slow. The reaction was stirred at room temperature for 16h. during which time a deep purple solution and a white precipitate were formed. The reaction mixture was then filtered and the filtrate pumped to dryness. The resulting residue was identified as 4-phenyl-1,2-dithia-3,5-diazole from its infra-red and mass spectra (experiment 2.2.5(i), page 40).

(ix) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Methyl Lithium

Methyl lithium (7.2 cm^3, 12.56 mmole) was syringed into a pre-cooled (-196°C) suspension of $PhCN_2S_2Cl$ (2.7g, 12.47 mmole) in monoglyme (30 cm^3) contained in a pre-dried vacuum tight, pyrex vessel (figure 1.2 , page 14). The reaction was warmed slowly to room temperature. Reaction occurred at ca. -50°C forming a deep purple solution and a pale precipitate. The reaction was agitated at room temperature for 4h.

The volatiles present at room temperature were then removed and the residue obtained was identified as 4-phenyl-1,2-dithia-3,5-diazole from its infra-red spectrum (experiment 2.2.5(i), page 40).

(x) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Tin (II) Chloride

Anhydrous tin (II) chloride (0.71g, 3.7 mmole) was added to a stirred suspension of $PhCN_2S_2Cl$ (0.52g, 2.4 mmole) in monoglyme (20 cm^3) at room temperature. An immediate reaction occurred forming a deep purple solution. The reaction was refluxed for 15 min. and the reaction mixture filtered hot. The filtrate was then pumped to dryness and the resulting residue extracted with refluxing pentane (50 cm^3). The pentane solution was pumped to dryness and the product thus obtained identified, by its infra-red spectrum (experiment 2.2.5(i), page 40) as 4-phenyl-1,2-dithia-3,5-diazole.

(xi) Reduction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride by Metals

No reduction of the phenyl dithiadiazolium cation occurred on refluxing $PhCN_2S_2Cl$ with sodium, sodium -mercury amalgam, or potassium using toluene as the solvent.

Reaction of $PhCN_2S_2Cl$ with Transition Metals in Polar or Coordinating Aprotic Solvents

In a typical reaction iron powder (1.12g, 20.00 mmole) was added to a stirred solution of $PhCN_2S_2Cl$ (0.48g, 2.22 mmole) in T.H.F. (10 cm^3). An immediate reaction took place producing a deep purple-red solution. The reaction was stirred at room temperature for 2h. and then the solubles filtered off. The filtrate was pumped to dryness and the infra-red spectrum of the residue recorded. From the infra-red spectrum of the residue it was deduced that 4-phenyl-1,2-dithia-3,5-diazole had been produced. (experiment 2.2.5(i), page 40).

A series of reactions with various metals using ethers as solvents were investigated and found to yield 4-phenyl-1,2-dithia-3,5-diazole (table 2.1).

TABLE 2.1 Reduction reactions of $PhCN_2S_2Cl$ by Metals

$PhCN_2S_2Cl$ (weight, mmole)	Metal (excess)	Solvent (cm^3)	Conditions
1.8g, 8.31 mmole	Zn/Cu	T.H.F. (30cm^3)	R.T.
0.93g, 4.30 mmole	K	Monoglyme (30cm^3)	Reflux
0.91g, 4.20 mmole	Hg	T.H.F. (40cm^3)	R.T.

(xii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Hydrogen

$PhCN_2S_2Cl$ (0.41g, 1.89 mmole) was partially dissolved in T.H.F. (10 cm^3) and pre-dried hydrogen bubbled through the system at room temperature. The reaction was terminated after ca. 1h. as no apparent reaction had occurred. The infra-red spectrum of the residue indicated only the presence of 4-phenyl-1,2,3,5-dithiadiazolium chloride (experiment 2.2.1, page 26).

2.2.6 Reactions of 4-Phenyl-1,2-Dithia-3,5-Diazole

(i) Reactions with the Halogens and Halogenated Species

(a) Reaction with Sulphuryl Chloride and Thionyl Chloride

4-Phenyl-1,2-dithia-diazole $(PhCN_2S_2)_x$ (0.33g, 1.82 mmole) was added to SO_2Cl_2 (4 cm^3, 49.4 mmole). An immediate reaction occurred yielding a very bright yellow-orange precipicate. The precipitate was isolated, washed with pentane (3 x 10 cm^3) and dried *in vacuo*.

Infra-red spectrum of the bright yellow product (nujol mull):

1602m, 1586w, 1455s, 1395s, 1300w, 1225w, 1180w, 1158m, 1075w, 1035m, 1008w, 930m, 900s, 850s, 800w, 790m, 715m(sh), 702vs, 670w, 555s cm^{-1}. (cf. $PhCN_2S_2Cl$, experiment 2.2.1, page 26).

Analysis of the product.

Found: C, 38.34; N, 12.86; H, 1.64; S, 29.18; Cl, 17.54%.

$C_7H_5N_2S_2Cl$ requires: C, 38.80; N, 12.93; H, 2.31; S, 29.56; Cl, 16.40%.

An analogous reaction occurred on adding 4-phenyl-1,2-dithia-3,5-diazole to thionyl chloride, 4-phenyl-1,2,3,5-dithiadiazolium chloride being produced.

(b) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Trichlorotrithiatriazene.

Trichlorotrithiatriazene ($(NSCl)_3$)(0.15g, 0.61 mmole) was added to a stirred solution of $(PhCN_2S_2)_x$ (0.28g, 1.55 mmole) in benzene (30 cm^3). An immediate reaction occurred yielding a flocculent orange precipitate in an orange solution. The precipitate was isolated and dried *in vacuo*.

Infra-red spectrum of the precipitate (nujol mull): 1600w, 1582w(sh), 1455vs, 1400vs, 1318w, 1295w, 1220w, 1175w, 1155m, 1150m, 1069w, 1029m, 1002w, 925m, 892s, 844s, 780s, 702s(sh), 698vs, 551s cm^{-1} (cf. $PhCN_2S_2Cl$, experiment 2.2.1, page 26).

A thin layer chromatogram of the toluene solution using an S_4N_4 standard for comparison was run.

T.L.C. (benzene elutant): R_f = 0.84, S_4N_4 standard R_f = 0.84. The toluene solution was slowly evaporated to dryness and the infra-red spectrum of the residue recorded. Infra-red spectrum of the residue (nujol mull): 928s, 730m, 700s, 555s, 355s cm^{-1}. (cf. S_4N_4[42]).

(c) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Bromine

Bromine (0.5 cm^3, 9.76 mmole) was added to a stirred solution of $(PhCN_2S_2)_x$ (0.8g, 4.42 mmole) in carbon tetrachloride (10 cm^3). An immediate reaction occurred forming a bright red insoluble compound. The product was filtered off, washed with carbon tetrachloride (2 x 10 cm^3) and pentane (2 x 10 cm^3) and dried *in vacua*.

Infra-red spectrum of the product (nujol mull): 1595m, 1495w, 1455s, 1395s, 1150m, 1022w, 918m, 895s, 837s, 779m, 692vs, 658w, 610w, 545s cm^{-1}. (experiment 2.2.2(i)(a), page 28).

Analysis of the bright red product:

Found: C, 32.64; N, 10.44; H, 2.06%.

$C_7H_5N_2S_2Br$ requires: C, 32.18; N, 10.73; H, 1.92%

Yield of $PhCN_2S_2Br$ = 1.13g. 98% based on $(PhCN_2S_2)_x$

(d) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Iodine

Iodine (0.48g, 1.89 mmole) was dissolved in toluene (15 cm^3). To this solution was added $(PhCN_2S_2)_x$ (0.68, 3.76 mmole). An immediate reaction occurred yielding a green-brown precipitate. The reaction was stirred overnight without further observed change. The product was filtered off, washed with toluene (2 x 10 cm^3), (to remove excess iodine) and by pentane (3 x 10 cm^3) and dried *in vacuo*. The infra-red spectrum and analysis of the product was recorded.

Analysis of the product.

Found: C, 27.60; N, 9.01; H, 1.21; S, 20.4%.

$C_7H_5N_2S_2I$ requires: C, 27.27; N, 9.09; H, 1.62; S, 20.78%.

Infra-red spectrum (nujol mull): 1598m, 1494w, 1450vs, 1375vs, 1255w, 1220w, 1172w, 1162m(sh), 1135s, 1070w, 1025m, 1000w, 938w, 922 , 904m, 868m, 852m, 840m, 826m, 792vs, 776s, 765s, 686s, 680m, 675w, 550w, 536w, 520m, 462m cm^{-1}

(cf. $PhCN_2S_2I$ experiment 2.2.2(ii)(a), page 31).

(ii) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Lewis acids

(a) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Tin (IV) Chloride

$SnCl_4$ (0.22 cm^3, 1.88 mmole) was added to a stirred solution of $(PhCN_2S_2)_x$ (0.34g, 1.88 mmole) in toluene (20 cm^3). An immediate reaction occurred forming a yellow-orange precipitate. The precipitate was isolated and washed with pentane (2 x 10 cm^3) and dried *in vacuo*

Infra-red spectrum (nujol mull): 1600w, 1495w, 1398s, 1340m(sh), 1295w, 1265w, 1208w, 1182w(sh), 1172m, 1160m, 1071w, 1024m, 1000w, 932m, 918s, 844s, 789s, 752s, 738m(sh), 698vs, 660w, 558m, 320s cm^{-1}. (cf. $(PhCN_2S_2)_2$ $SnCl_6$, experiment 2.2.4(iii), page 39).

(b) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Antimony(V)Chloride

A solution of $SbCl_5$ (2.5 cm^3, 19.52 mmoles in 3.14g of SO_2) was filtered on to a slurry of $(PhCN_2S_2)_x$ (0.72g, 3.98 mmole in 4.36g of SO_2). An immediate reaction occurred forming a bright salmon pink precipitate which was virtually insoluble in the solvent. The excess $SbCl_5$ was filtered off and the precipitate washed several times to remove all traces of $SbCl_5$. The solvent was then removed and the product isolated.

Infra-red spectrum of the product: 1600w, 1495w, 1395vs, 1182w, 1160m(sh), 1155m, 1025w, 1000w, 929m, 911s, 841s, 785m, 770m(sh), 700vs, 696s(sh), 555m, 340s cm^{-1}.

Analysis of the product:

Found: C, 15.84; N, 5.02; H, 1.62%.

$C_7H_5N_2S_2SbCl_6$ requires: C, 16.29; N, 5.43; H, 0.97%.

(iii) Reactions of 4-Phenyl-1,2-Dithia-3,5-Diazole with Group VI Polycations

(a) Reaction of $(PhCN_2S_2)_x$ with S_8^{2+} $(AsF_6^-)_2$

S_8^{2+} $(AsF_6^-)_2$(0.72g, 1.136 mmoles) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1.2 , page 14) and $(PhCN_2S_2)_x$ (0.41g, 2.27 mmole) in the second bulb. Sulphur dioxide (12.38g) was then condensed into the vessel (some into each bulb) and the deep blue S_8^{2+} $(AsF_6^-)_2$ solution slowly filtered on to the $(PhCN_2S_2)_x$

slurry. An immediate reaction occurred forming an orange-red solution and a pale yellow precipitate. After all the polycation had been added the reaction was agitated for 4h. The soluble product was then filtered off leaving the pale yellow residue behind (0.28g). The solvent was removed from the system and the infra-red spectrum of the solubles and Raman spectrum of the insolubles recorded.

Infra-red spectrum of the solubles (nujol mull): 1595m. 1560w, 1500m, 1445s, 1395vs, 1320w, 1296w, 1275w, 1195m, 1185m, 1170w(sh), 1168m(sh), 1162m, 1105vw, 1075vw, 1029m, 1004m, 990vw, 978vw, 965vw, 942vw, 928s, 858m, 854m(sh), 845s, 784s, 720-680vs,br, (AsF_6^-)[63], 615vw, 609vw, 580vw, 560s, 464w, 395vs, 368m cm^{-1}. (c.f. $PhCN_2S_2Cl$, experiment 2.2.1, page 26).

Raman spectrum of the insolubles (red line) 472, 434, 243, 220m 152 cm^{-1}. (c.f. S_8 475, 471, 437, 248, 243, 218, 191, 152, 86 cm^{-1}).[43]

(Theoretical weight of sulphur if oxidation of $PhCN_2S_2$ to $PhCN_2S_2^+AsF_6^-$ and deposition of S_8 occurs = 0.29g).

(b) Reaction of $(PhCN_2S_2)_x$ with $(Se_4^{2+})(AsF_6^-)_2$

In a similar reaction to that in experiment 2.2.6 iii(a), (page 49) Se_4^{2+} $(AsF_6^-)_2$ (1.41g, 2.03 mmole) was reacted with $(PhCN_2S_2)_x$ (0.74g, 4.09 mmole) in SO_2. (Due to the low solubility of Se_4^{2+} $(AsF_6^-)_2$ in SO_2 both reactants were placed in the same bulb). A green-brown solution was quickly formed, with deposition of a black precipitate. The solubles were extracted from the residue, the solvent removed from the system and the infra-red spectra of both solubles and insolubles (0.56g) recorded.

The infra-red spectrum of the solubles is identical to that recorded for the solubles in experiment 2.2.6, iii(a).

No infra-red spectrum was obtained for the insolubles, the only peaks present being those of the mulling agent.

The theoretical weight of selenium deposited if the reaction was

$$(PhCN_2S_2)_2 + Se_4(AsF_6)_2 \longrightarrow 2PhCN_2S_2^+AsF_6^- + 4Se$$

would be 0.64g therefore 87% of the selenium is present as elemental selenium in the insolubles.

(iv) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Unsaturated Systems

(a) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Diphenyl Acetylene

Diphenyl acetylene (0.38g, 2.13 mmole) was added to a stirred suspension of $(PhCN_2S_2)_x$ (0.39g, 2.15 mmole) in toluene (30 cm^3) at room temperature. No immediate reaction occurred. The reaction was brought to reflux and refluxed for 16h. The presence of diphenyl acetylene in the reaction was monitored using T.L.C., with hexane as the elutant and a standard diphenyl acetylene solution as a reference. The chromatogram indicated that diphenyl acetylene was still remaining in high concentration after refluxing for 16h. The reaction was cooled to room temperature and the solvent removed by pumping at reduced pressure. The infra-red spectrum of the residue indicated that only 4-phenyl-1,2-dithia-3,5-diazole and diphenyl acetylene were present.

(b) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Tetrasulphur Tetranitride (S_4N_4)

S_4N_4 (0.27g, 1.47 mmole) was added to a stirred solution of $(PhCN_2S_2)_x$ (1.06g, 5.86 mmole) in T.H.F. (30 cm^3) at room temperature. The reaction was stirred for 4h. at room temperature but no change was noted. (The S_4N_4 concentration was monitored using T.L.C.). The reaction was then refluxed for 16h. but no reaction appeared to occur. (S_4N_4 was still present in high concentration in the solution and no other species were detected on the T.L.C. plate). The reaction was pumped to dryness and the infra-red spectrum of the residue recorded. From the infra-red spectrum it was deduced that the only species present were S_4N_4 and $(PhCN_2S_2)_x$.

2.2.7 Reaction to produce Benzene-1,4-(di-1,2,3,5-Dithiadiazolium) Dichloride ($C_6H_4(CN_2S_2Cl)_2$)

(i) The Reaction of 1,4-Dicyanobenzene ($C_6H_4(CN)_2$), with Sulphur Dichloride (SCl_2) and Ammonium Chloride (NH_4Cl)

NH_4Cl (20g,374.0 mmole), C_6H_4 $(CN)_2$(5.12g, 40.00 mmole), SCl_2 (50 cm^3, 786.9 mmole) and toluene (150 cm^3) were placed in a 500 cm^3 flask and the temperature slowly raised to reflux. The reaction evolved a gas which was identified as HCl. The evolution of HCl was used to monitor the reaction. After 24h. of refluxing no further gas was evolved. SCl_2 (30 cm^3) was added to the reaction and the system allowed to reflux until no further HCl was evolved. Aliquots of SCl_2 (20 cm^3) were added to the system until no further evolution of HCl was noted when SCl_2 was added to the reaction mixture (4 aliquots). The reaction was then cooled to room temperature. The orange precipitate formed on cooling was filtered off, washed with ether (4 x 25 cm^3) and recrystallised from benzene (50 cm^3). The product was then recrystallised from SO_2 (5.62g) (figure 1.2 , page 14) and the bright orange product (1.14g) dried *in vacuo*.

Infra-red spectrum of the orange product (nujol mull): 2230w, 1598m, 1580w(sh), 1495w, 1455s, 1398vs, 1320s, 1310m(sh), 1295w(sh), 1210w, 1170w, 1150m, 1138m, 1028m, 1018m(sh), 921m, 895s, 845s, 785s, 700vs, 564w, 550m, 520w cm^{-1}.

The product was heated to 200°C at a pressure of 1×10^{-2} torr and the infra-red and analysis of the non-sublimed residue recorded.

Infra-red spectrum of the residue (KCl disc): 3090w, 3040w, 2235s, 1415m, 1395vs, 1380s, 1302vw, 1289w, 1156m, 1020w, 925m, 896m, 862s, 855s, 845m(sh), 745s, 694s, 564m(sh), 558s, 532w cm^{-1}.

Analysis of the product after subliming out the impurities.
Found: C, 38.37; H, 2.22; N, 17.0; S, 25.46; Cl, 14.4%.
$C_8H_4N_3S_2Cl$ requires: C, 39.75; H, 1.66; N, 17.39; S, 26.50; Cl, 14.70%.

(ii) Reaction of $C_6H_4(CN)_2$ with $(NSCl)_3$.

$C_6H_4(CN)_2$(1.28g, 10 mmole) was added to an apple green, refluxing solution of $(NSCl)_3$ (6.55g, 26.79 mmole) in benzene (30 cm^3). After refluxing for 24h. a bright yellow precipitate formed in a deep orange solution. The reaction mixture was filtered, the precipitate washed with pentane (4 x 20 cm^3) and dried *in vacuo*.

Infra-red spectrum of the precipitate (nujol mull): 1164s, 1000vs, 680s, 568s, 472vs, 466s(sh), 332s (cf.S_4N_3Cl[44]).

The benzene solution was pumped to dryness and the resulting pale yellow residue dissolved in T.H.F. (10 cm^3). A T.L.C. plate (benzene elutant) was run of the T.H.F. solution and standard samples of S_4N_4 and $C_6H_4(CN)_2$. S_4N_4 and $C_6H_4(CN)_2$ were identified as being present. A third compound giving a red spot that faded with time was also observed which is believed to be S_4N_2.

THE CHEMISTRY OF THE DITHIADIAZOLIUM CATION

2.3 Discussion

Although the dithiadiazolium system was first synthesised by Banister *et al* in ca. 1970, little or no subsequent work had been reported at the commencement of the investigations described in this chapter (October 1976). In an attempt to find a salt (or salts) of the phenyl dithiadiazolium cation that was relatively moisture insensitive, and thus of potential industrial use, phenyl dithiadiazolium chloride was reacted with various ionic salts. A wide range of dithiadiazolium salts was produced and the previously unreported 4-phenyl-1,2-dithia-3,5-diazole. All the species produced were found to be moisture sensitive.

2.3.1 Preparation and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride ($PhCN_2S_2Cl$)

Banister *et al* reported the synthesis of $PhCN_2S_2Cl$ from NH_4Cl, PhCN and SCl_2 using $PhNO_2$ as a solvent.[37] The salt was then recrystallised from $PhNO_2$ (50 cm^3 $gram^{-1}$). Due to the very high toxicity of $PhNO_2$ (TLV-TWA: 1 ppm)[45] a synthetic route and purification procedure ~~were~~ sought not involving the solvent. It was found that the synthetic route described by Banister *et al* still gave good yields if the nitrobenzene was omitted and 25% excess benzonitrile was added. The yields recorded were improved by the addition of aliquots of sulphur dichloride to the reaction mixture until no further hydrogen chloride gas was evolved.

Many methods of purifying the crude phenyl dithiadiazolium chloride were investigated. It was found that recrystallisation of the salt from thionyl chloride gave a product of reasonable purity but the analytical results were invariably high in chlorine. The purification procedure was adapted by using a mixture (4:1 by volume) of 1,2-dichloroethane (CH_2ClCH_2Cl) and thionyl chloride as the recrystallisation solvent and washing the purified material with refluxing hexane to remove any residual thionyl chloride. Double purification by the above method yielded a compound with good analytical results and this procedure was the one generally used throughout the work in this thesis. However, recently it was found that sulphur dioxide provides a facile single stage purification solvent as sulphur, ammonium chloride and ammonium sulphate are virtually insoluble in the solvent,[46] whereas 4-phenyl-1,2,3,5-dithiadiazolium chloride is highly soluble.

Crystals of 4-phenyl-1,2,3,5- dithiadiazolium chloride were produced by slowly cooling a refluxing toluene solution of the salt to room temperature. The crystals are bright orange and needle shaped, containing toluene of crystallisation. The X-ray crystal structure of the salt was determined using these crystals by Hazell(1979).[47]

2.3.2 The Reactions of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

The reactions of 4-Phenyl-1,2,3,5-dithiadiazolium chloride reported by Bell,[48] Durrant[49] and Roesky[38] are presented in table 2.2.

From table 2.2 it can be seen that with the exception of the results published by Roesky[38] little progress had been made in the field of dithiadiazolium chemistry since 1970. (The anion exchange reactions reported by Roesky were published after the majority of the work in this chapter had been completed).

TABLE 2.2 Reported Reactions of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

Reactant	Solvent	Product	Ref.
Water	-	$PhCN_2S_2O_6H_3$	49
Nitric acid	-	$PhCN_2S_2O_6H_3$	49
Acetic Anhydride	-	$PhCN_2S_2Cl$	49
Iron (III) Chloride	$SOCl_2$	$PhCN_2S_2^+FeCl_4^-$	49
Sodium Iodide	SO_2	Hydrolysis Products	49
Sodium Iodide	CH_2Cl_2	Postulated to be $PhCN_2S_2^+I^-$	49
Epichlorohydrin	C_6H_{14}	Hydrolysis Products	48
Cyclohexene oxide	-	$PhCN_2S_2Cl$	48
Acetonitrile	-	$PhCN_2S_2Cl$	48
Antimony (V) Chloride	CCl_4	Postulated to be $PhCN_2S_2^+SbCl_6^-$	48
Phenyl Lithium	$C_2H_5OC_2H_5$	$PhCN_2S_2Cl$	48
Diphenyl Mercury	C_6H_6	Postulated as $Ph_2CN_2S_2$	48
Antimony (V) Chloride	CH_2Cl_2	$PhCN_2S_2^+SbCl_6^-$	38
Trifluoromethyl sulphonic acid	CH_2Cl_2	$PhCN_2S_2^+CF_3SO_3^-$	38
Bis(fluorosulphonyl)imide	CH_2Cl_2	$PhCN_2S_2^+N(SO_2F)_2^-$	38
Triethyl oxonium tetrafluoroborate	CH_2Cl_2	$PhCN_2S_2^+BF_4^-$	38
Nitrosyl Hexafluorophosphate	CH_2Cl_2	$PhCN_2S_2^+PF_6^-$	38

From the work reported by Durrant and Bell in their theses, four new phenyl-dithiadiazolium salts and derivatives have been formulated. Of these four species, three of the formulations ($PhCN_2S_2I$,[49] $PhCN_2S_2SbCl_6$[48] and $Ph_2CN_2S_2$[48]) have been brought into question by subsequent work in this chapter, the other $PhCN_2S_2^+FeCl_4^-$[49] was not reinvestigated.

2.3.2(i) The Preparation and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Halides

The formation of the bromide and iodide salts of the 4-phenyl-1,2,3,5-dithiadiazolium cation was first noted by the colour of the infra-red discs of $PhCN_2S_2Cl$ using KBr and CsI dispersants (experiments 2.2.2(ia)(iia), pages 28,31). The infra-red spectra of the discs was recorded and although the spectrum of the $PhCN_2S_2Cl$/KBr was very similar to that of $PhCN_2S_2Cl$, that of the $PhCN_2S_2Cl$/CsI disc was significantly different (table 2.3).

TABLE 2.3 Infra-red Spectrum of $PhCN_2S_2{}^+Cl^-$ using a series of Dispersion Salts

KCl Dispersant	KBr Dispersant	CsI Dispersant	$PhCN_2S_2I$[49]
1604m	1604m	1600m	1600w
1585w	1588w	1494m	
1498w	1500w	1480m	
1450s	1458s	1455s	1460vs
1395vs,br	1402vs,br	1380s	1378s
		1365vs	1358m
1305w	1295w	1255w	
1222w	1220w	1220w	
	1190w	1210w(sh)	
1182w	1180w	1173m	1181w
1158s	1164s	1135s	
		1080vw	
1078w	1074w	1068w	
1036m	1036m	1024s	1028m
1009w	1009w	1005w	972m
930m	930m	928w	
900s	899s	905m	
		868m	860m
850vs	850vs	852m	
		830w	832vs
802m	802m	826m	
792m	790m	795vs	
		778s	782vs
	750w	766s	
705vs	702vs	690s	694s
		682s	
		676m	676s
670w	670w	670m(sh)	
610vw.		610vw	
558s	556s	538w	
520w		522s	520m
470w	470w	472m(sh)	
		462s	
410w	420w	408w	
318m	328m	325w	
	286w	285w	

(A photographic comparison of the chloride and iodide salts of the 4-phenyl-1,2,3,5-dithiadiazolium cation is given in figure 2.9).

From the infra-red data presented in table 2.3, page 57, it appears as though the deep red $PhCN_2S_2Br$ and $PhCN_2S_2Cl$ adopt the same configuration with possibly slightly more anion-cation interaction in the case of the bromide than the chloride. However the infra-red spectrum of the presumed iodide is significantly different and will be discussed later (page 76). It can be seen from table 2.3 that the infra-red spectrum reported by Durrant[49] for $PhCN_2S_2I$ is significantly different from that of the $PhCN_2S_2Cl/CsI$ disc. Hence doubt is thrown on the identity of the species postulated as $PhCN_2S_2I$ by Durrant.

Initially the bromide and iodide salts were isolated in a reasonable pure state by subliming the product out of the ground mixture of either $PhCN_2S_2Cl$ and KBr or $PhCN_2S_2Cl$ and NaI (experiments 2.2.2(ia),(iia), page 28,31). However as yields achieved by this method were low, the synthesis of the salts by solution reactions were investigated.

(a) Synthesis of 4-Phenyl-1,2,3,5-Dithiadiazolium Bromide

The reactions of sodium and potassium bromides with phenyl-dithiadiazolium chloride using toluene, benzene, 1,4-dioxan, dichloromethane and nitromethane were unsuccessful almost certainly due to the relatively low solubility of the alkali metal bromides in the aforementioned solvents. The exchange reaction did however occur with $Et_4N^+Br^-$, $NH_4^+Br^-$ and LiBr using the solvents nitromethane, dichloroethane, monoglyme, tetrahydrofuran and sulphur dioxide. The reaction probably proceeds in the above examples due to the bromides having a reasonable solubility in the solvents listed.

Of all the reactions that yield 4-phenyl-1,2,3,5-dithiadiazolium bromide the best route is probably that in which phenyl dithiadiazolium chloride is reacted with lithium bromide using tetrahydrofuran as a solvent, the crude product thus produced, being recrystallised from sulphur dioxide (experiment 2.2.2(i,b), page 29).

(b) Synthesis and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Iodide

Reaction of phenyl dithiadiazolium chloride with sodium iodide was found to occur in numerous solvents (CH_3NO_2, CH_2ClCH_2Cl, $C_6H_5CH_3$, T.H.F., $CH_3OCH_2CH_2OCH_3$, 1,4-dioxan and sulphur dioxide) producing a deep purple solution from which a green-brown precipitate was isolated. The infra-red spectrum of this precipitate was identical to that recorded for the $PhCN_2S_2Cl$/CsI disc (table 2.3, page 57). Great difficulty was however experienced in purifying the product to give consistent, good analytical results. Recrystallisation from a variety of solvents was investigated but invariably poor analytical results were obtained. Initially this was thought to be due to hydrolysis products but after the reaction using sulphur dioxide as the synthetic and recrystallisation solvent, it was deduced that the basic impurity was the alkali metal chloride by-product (experiment 2.2.2(ii,c), page 32). The metal chloride, although virtually insoluble in all the recrystallisation solvents used, therefore appears to pass through the sinters (grade 4) thus affecting the recorded analysis of the product. The reason for the metal chloride passing through the sinter must be due to the fact that the particle size of the metal chloride is smaller than the pore size of the sinter used. Hence it seems likely that the metal chloride produced in the reaction is so insoluble in the synthetic solvent, that precipitation of the salt occurs in a very fine form. Consequently virtually no recrystallisation process except that using a very fine sinter (very small pore size) will purify the product. Purification of the salt was however achieved by the use of vacuum sublimation, consistent analytical results being recorded.

2.3.2(ii) The Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Lewis Acids

As would be anticipated for an ionic chloride containing a large cation, reactions of 4-phenyl-1,2,3,5-dithiadiazolium chloride with the Lewis acids boron trichloride, tin tetrachloride and antimony pentachloride readily occur (section 2.2.4, page 36). All the products are brightly coloured, ($SnCl_6^{2-}$ yellow; BCl_4^- orange and $SbCl_6^-$ bright red). Hence the $SbCl_6^-$ salt of the phenyl dithiadiazolium cation synthesised by Bell[48] which is reported to be white must be regarded with some suspicion, especially as Roesky[38] also reports that the $PhCN_2S_2^+SbCl_6^-$ is red. All the salts give infra-red and mass spectra consistent with the species containing the $PhCN_2S_2^+$ cation (cf. $PhCN_2S_2^+FeCl_4^-$[49]).

2.3.2(iii) Formation of other salts of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation

(a) Salts containing Fluoro-anions

Both the tetrafluoroborate and hexafluorophosphate salts were prepared but not isolated in purified forms, such that consistent analytical data could be obtained. (These reactions are not reported in the experimental section).

The tetrafluoroborate salt was obtained from the reaction of silver tetrafluoroborate with phenyl dithiadiazolium chloride using nitromethane as a solvent. The salt obtained was deep red and gave infra-red and mass spectra consistent with the formulation $PhCN_2S_2^+BF_4^-$.

The hexafluorophosphate salt was synthesised by the reaction of ammonium hexafluorophosphate with phenyl dithiadiazolium chloride using sulphur dioxide as a solvent. The infra-red spectrum of the soluble product indicated that the hexafluorophosphate salt of the phenyl dithiadiazolium cation had been produced ($NH_4^+PF_6^-$ only very slightly soluble in SO_2).

No further investigations into the synthesis and purification of the above salts were made due to the isolation and characterisation of the compounds by Roesky.[38]

(b) Formation of the Acetate and Benzoate Salts of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation (experiments 2.2.3(ii,iii), pages 34, 35).

Attempts to produce the benzoate and acetate salts of the 4-phenyl-1,2,3,5-dithiadiazolium cation from the reaction of sodium benzoate and acetate with phenyl dithiadiazolium chloride using organic solvents, failed. However both salts were produced on reacting excess ammonium benzoate or acetate with $PhCN_2S_2Cl$ using sulphur dioxide as a solvent. The resulting products were very deeply coloured (black/purple). The acetate was found to be unstable decomposing in tetrahydrofuran solution at room temperature yielding another carbon-sulphur-nitrogen heterocycle (see section 2.3.3, page 62).

The infra-red spectra of the isolated benzoate and acetate salts were consistent with them containing the phenyl dithiadiazolium cation and the acetate or benzoate anion. Although the colour is very deep, probably implying a relatively high degree of anion-cation interaction, little or no shifting of the basic infra-red bands associated with the dithiadiazolium cation (reference $PhCN_2S_2Cl$, table 2.3, page 57) is observed. Hence the degree of interaction required to modify the observed colour of the salts must be much less than that required to effect the vibrational spectrum.

(c) The Formation of the Thiocyanate salt of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation (experiment 2.2.3(i,a,b), page 33, 34).

The reaction of sodium thiocyanate with phenyl dithiadiazolium chloride using monoglyme, tetrahydrofuran, or dichloroethane as solvents produced a deep purple solution virtually immediately. However after refluxing for ca. 20 min. or stirring at room temperature for 6h. an orange precipitate was formed which was identified as $(NCS)_x$. Hence a reaction subsequent to the metathesis reaction occurs.

The intermediate 4-phenyl-1,2,3,5-dithiadiazolium thiocyanate was however isolated from the reaction of sodium thiocyanate with 4-phenyl-1,2,3,5-dithiadiazolium chloride using sulphur dioxide as a solvent. The salt is very deeply coloured (cf. acetate and benzoate salts) and gives an infra-red and mass spectrum (figure 2.8c) consistent with the formulation $PhCN_2S_2^+NCS^-$.

2.3.3 The Formation and Reactions of 4-Phenyl-1,2,-Dithia-3,5-Diazole $(PhCN_2S_2)_2$

(i) 4-Phenyl-1,2,-dithia-3,5-diazole was first synthesised by the reaction of sodium thiocyanate with phenyl dithiadiazolium chloride using monoglyme as a solvent (experiment 2.2.5(i), page 40). The compound was isolated in a high state of purity as deep purple, needle shaped crystals. The crystals gave excellent analyses and mass and infra-red spectra which enabled the species to be identified, with ease, in the products of other reactions. (The infra-red spectrum is shown in figure 2.9, page 88). The crystals obtained from the NaNCS/$PhCN_2S_2Cl$ reaction were sent for X-ray structural determination studies to Vegas (Instituto de Quimica Inorganica "Elhuyar" Madrid), the results of which are discussed in section 2.3.4, page 72.

It was found that 4-phenyl-1,2,-dithia-3,5-diazole is formed in many reactions of the phenyl dithiadiazolium cation with organo-metallic species, metals, and reducing anions.

Equations 2.6-13

$$2PhCN_2S_2Cl + 2LiN_3 \xrightarrow[(CH_3OCH_2)_2]{} (PhCN_2S_2)_2 + 2LiCl + 3N_2 \qquad (2.6)$$

$$2PhCN_2S_2Cl + 2KCN \xrightarrow[SO_2]{} (PhCN_2S_2)_2 + 2KCl + (CN)_2 \qquad (2.7)$$

$$\begin{aligned} 2PhCN_2S_2Cl + 2CH_3COONa \xrightarrow[SO_2]{} {} & 2PhCN_2S_2{}^{+}CH_3COO^{-} + 2NaCl \\ & \qquad \Big\downarrow \text{THF} \qquad\qquad\qquad\qquad (2.8) \\ & (PhCN_2S_2)_2 + C_2H_6 + 2CO_2 \end{aligned}$$

$$\begin{aligned} 2PhCN_2S_2Cl + 2PhMgBr \xrightarrow[(C_2H_5)_2O/C_6H_5CH_3]{} {} & (PhCN_2S_2)_2 + MgBr_2 \\ & + MgCl_2 + C_{12}H_{10} \qquad (2.9) \end{aligned}$$

$$\begin{aligned} 2PhCN_2S_2Cl + 2CH_3Li \xrightarrow[C_6H_{14}/(CH_3OCH_2)_2]{} {} & (PhCN_2S_2)_2 \\ & + 2LiCl + C_2H_6 \qquad (2.10) \end{aligned}$$

$$\begin{aligned} 2PhCN_2S_2Cl + 2C_4H_9Li \xrightarrow[C_6H_{14}/C_6H_5CH_3]{} {} & (PhCN_2S_2)_2 \\ & + 2LiCl + C_8H_{18} \qquad (2.11) \end{aligned}$$

$$2PhCN_2S_2Cl + SnCl_2 \xrightarrow[(CH_3OCH_2)_2]{} (PhCN_2S_2)_2 + SnCl_4 \qquad (2.12)$$

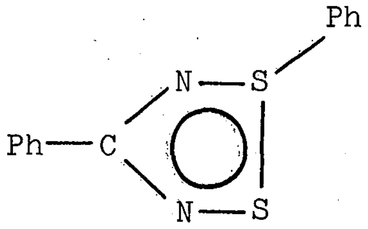
$$xPhCN_2S_2Cl + M \xrightarrow[T.H.F.\ or\ (CH_3OCH_2)_2]{} {}^x/_2\ (PhCN_2S_2)_2 + MCl_x \qquad (2.13)$$

(M = Zn, Hg : table 2.1, page 45)

Therefore, as can be seen from the above equations 4-phenyl-1,2,-dithia-3,5-diazole is a thermodynamically stable species.

Particular note is made of the reactions of phenyl dithiadiazolium chloride with Grignard and organo-lithium species. Bell[48] reported the reactions of diphenyl mercury and phenyl lithium with 4-phenyl-1,2,3,5-dithiadiazolium chloride and from the diphenyl mercury reaction isolated PhHgCl and a compound postulated to be $Ph_2CN_2S_2$ (figure 2.10).

Figure 2.10 Postulated structure of $Ph_2CN_2S_2$.[46]

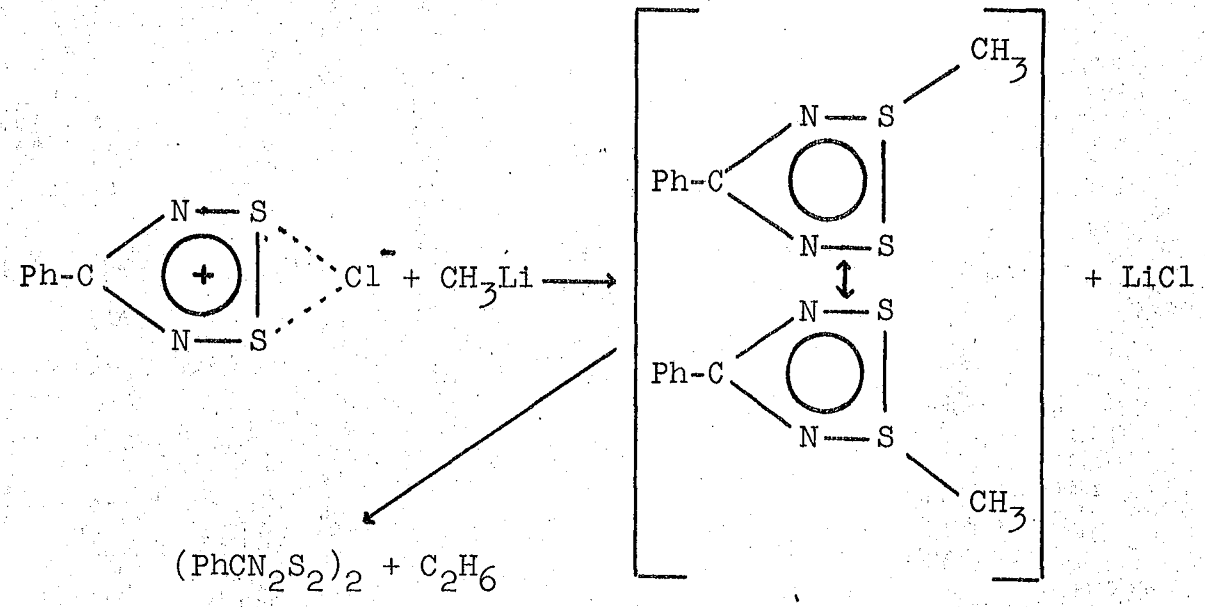


The product obtained by Bell from both the reactions of $PhCN_2S_2Cl$ with Ph_2Hg and PhLi was black and by analogy with the reactions of $PhCN_2S_2Cl$ with PhMgBr, C_4H_9Li and CH_3Li (experiments 2.2.5(vii-ix), pages 43 , 44) it is believed that Bell isolated partially hydrolysed 4-phenyl-1,2-dithia-3,5-diazole,with a biphenyl impurity.

The mechanism by which 4-phenyl-1,2-dithia-3,5-diazole is formed in the reactions of phenyl dithiadiazolium chloride with Grignard and organolithium species is believed to proceed via an intermediate in which the organo grouping is bonded to one or both of the sulphurs in the "CN_2S_2" ring.

The intermediate then dissociates yielding phenyl dithiadiazole (figure 2.11).

Figure 2.11 Suggested mechanism by which CH_3Li reacts with $PhCN_2S_2Cl$.



The colours of all the known phenyl dithiadiazolium salts fall into two categories, those that are brightly coloured, (red, orange and yellow), and those that are purple-black (table 2.4). With the exception of phenyl dithiadiazolium iodide (which is discussed separately in section 2.3.4(iv), page 75) all purple-black salts decompose on heating to yield phenyl dithiadiazole, whereas the brightly coloured salts do not. It is suggested that the degree of anion-cation interaction is greatest in the purple-black salts and thus they are more prone to decomposition than the brightly coloured salts in which the degree of anion-cation interaction is much less. The anions of the black-purple salts are those anions which are generally regarded as being "soft", i.e. relatively highly polarisable. Thus with a large cyclic cation the degree of interaction is expected to be significant. There are various salts (e.g.

TABLE 2.4 Colours of the 4-Phenyl-1,2,3,5-Dithiadiazolium Salts

Salt	Colour
$PhCN_2S_2Cl$	Orange
$PhCN_2S_2Br$	Red
$PhCN_2S_2I$	Black-Purple
$PhCN_2S_2BF_4$	Red
$PhCN_2S_2BCl_4$	Orange
$PhCN_2S_2SbCl_6$	Red
$PhCN_2S_2PF_6$	Orange
$(PhCN_2S_2)_2(SnCl_6)$	Yellow
$PhCN_2S_2FeCl_4$[45]	Orange
$PhCN_2S_2CF_3SO_3$[38]	Yellow
$PhCN_2S_2NCS$*	Black-Purple
$PhCN_2S_2CH_3COO$*	Black-Purple
$PhCN_2S_2PhCOO$*	Black-Purple

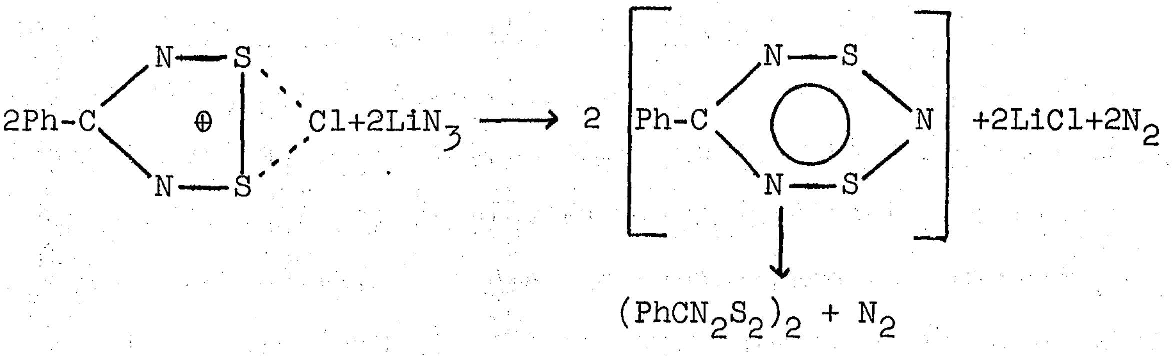
(* Denotes the salts that decompose yielding phenyl dithiadiazole).

$SbCl_6^-$ and Br^-) in which a lesser degree of anion-cation-interaction is noted. The $SbCl_6^-$ and Br^- ions are spherically symmetrical and thus the degree of cation-anion interaction is not as great as in the cases of NCS^-, CH_3COO^- and $PhCOO^-$, consequently the $SbCl_6^-$ and Br^- salts are red not black-purple.

Both the acetate and thiocyanate salts decompose in T.H.F. or monoglyme at room temperature. However the benzoate does not decompose in the above solvents at room temperature but requires refluxing for 8h. in monoglyme to achieve the decomposition. It is thought likely that the relative stability of the benzoate salt is derived from the fluidity of the π-electrons associated with the phenyl ring, which maintain a relatively strong carbon-carbon bond between the "CO_2" and "C_6H_5" fragments, even when there is significant anion-cation interaction draining electron density away from the anion.

In the reactions of the phenyl dithiadiazolium cation with thiocyanates, cyanides and azides it is believed that the mechanism proceeds via an intermediate in which the anion interacts strongly with the sulphur-sulphur bond in the dithiadiazolium ring. Complete one electron transfer from the anion to the cation then occurs with the formation of two radical species which dimerise with their own kind forming 4-phenyl-1,2,-dithia-3,5-diazole and the by-product (e.g. $(CN)_2$ and $(NCS)_2$). Due to the highly exothermic nature of the reaction of the dithiadiazolium cation with azides it is not thought likely that an intermediate cage species of the form $PhCN_3S_2$ (figure 2.12) will be isolated.

Figure 2.12 Postulated Mechanism by which $PhCN_2S_2Cl$ reacts with LiN_3



2.3.3(ii) Purification of 4-Phenyl-1,2-dithia-3,5-diazole

Phenyl dithiadiazole is highly soluble in most organic solvents and is soluble to a limited extent in hexane and pentane. Two main procedures for the purification of the compound have been found. The first is by the extraction of the material using refluxing pentane and the second is by sublimation *in vacuo*.[50] The purified product obtained by the above methods, although in a high state of purity, is recommended to be recrystallised from a solvent such as refluxing monoglyme, dichloroethane or T.H.F., the solvent being cooled slowly to room temperature, so as to form reasonably large crystals. The reason for the above recommendation is that the phenyl dithiadiazole, obtained by extraction with pentane or by sublimation, has a very high surface area and as the salt is highly mdsture sensitive the degree of hydrolysis on exposure to the atmosphere for only a few seconds is very significant. In the case of crystals the surface area is much less, per unit mass, and consequently so is the percentage hydrolysis if exposed to moisture.

2.3.3(iii) Reactions of 4-Phenyl-1,2-Dithia-3,5-Diazole

(a) The Reactions of Phenyl-Dithiadiazole with the Halogens and Lewis acids

4-Phenyl-1,2-dithia-3,5-diazole reacts readily with chlorine, bromine and iodine (experiments 2.2.6(i)(a,c,d), pages 46 - 48) yielding compounds which are the same colour and give the same analyses, mass and infra-red spectra as the 4-phenyl-1,2,3,5-dithiadiazolium chloride, bromide and iodide salts (table 2.3, page 57). Hence it appears as though phenyl dithiadiazole is oxidised back to the phenyl dithiadiazolium cation by chlorine, bromine and iodine.

A similar style of reaction was found in the reactions of excess tin(IV)chloride and antimony(V)chloride with phenyldithiadiazole (experiments 2.2.6(ii),(a,b), pages 48,49). The dithiadiazole appears to abstract a halogen from the Lewis acid, forming phenyl dithiadiazolium chloride which then reacts with the excess Lewis acid to produce either $(PhCN_2S_2)_2SnCl_6$ or $PhCN_2S_2SbCl_6$. It is thought likely that the reduced species $SnCl_2$ and $SbCl_3$ are formed which are not able to reduce the respective $SnCl_6^{2-}$ and $SbCl_6^-$ salts back to the dithiadiazole.

2.3.3(iv) Reactions designed to substitute atoms, or groups of atoms, into the basic five membered "CN_2S_2" ring

(a) The Reactions of Phenyl Dithiadiazole with Group VI Polycations

Phenyl dithiadiazole was reacted with $S_8^{2+}(AsF_6^-)_2$ and $Se_4^{2+}(AsF_6^-)_2$ (experiments 2.2.6(iii),(a,b), page 50) in an attempt to synthesise $PhCN_2S_4^+AsF_6^-$ and $PhCN_2S_2Se_2^+AsF_6^-$, respectively. The reactions occurred virtually immediately on mixing the two components. From the infra-red spectrum of the soluble product and the weight of insolubles it was readily deduced that oxidation of the dithiadiazole to the hexafluoroarsenate(V) salt of the dithiadiazolium cation occurs, with deposition of elemental sulphur and selenium (equations 2.14,15).

$$(PhCN_2S_2)_2 + S_8^{2+}(AsF_6^-)_2 \xrightarrow[SO_2]{} 2PhCN_2S_2^+AsF_6^- + S_8 \qquad (2.14)$$

$$(PhCN_2S_2)_2 + Se_4^{2+}(AsF_6^-)_2 \xrightarrow[SO_2]{} 2PhCN_2S_2^+AsF_6^- + 4Se \qquad (2.15)$$

(b) Reactions of Phenyl Dithiadiazole with Unsaturated Species

No reaction was noted to occur in the reactions of phenyl dithiadiazole with diphenyl acteylene or tetrasulphur tetranitride in refluxing solutions. Fielder[50] also investigated the photolytic reaction of tetrasulphur tetranitride with phenyl dithiadiazole but no reaction was found to occur.

A reaction did occur between phenyl dithiadiazole and trichlorotrithiatriazene but by analogy with the reactions of the dithiadiazole with the halogens and Lewis acids ($SnCl_4$, $SbCl_5$), the main product isolated was that of phenyl dithiadiazolium chloride with tetrasulphur tetranitride as the by-product (cf. Chapter Three, page 101).

It is therefore concluded that the basic five membered CN_2S_2 ring, in the conformation found in 1,2,3,5-dithiadiazoles and 1,2,3,5-dithiadiazolium species, is highly stable with respect to ring expansion. It is, therefore, thought somewhat unlikely, that cations containing larger ring sizes are formed in the reaction of ammonium chloride with sulphur dichloride and benzonitrile, (experiment 2.2.1, page 26; synthetic route to $PhCN_2S_2Cl$).

2.3.4 The X-ray Crystal Structures of 4-Trichloromethyl and 4-Phenyl-1,2,3,5-Dithiadiazolium Chlorides compared with that of 4-Phenyl-1,2-Dithia-3,5-Diazole

(i) 4-Trichloromethyl-1,2,3,5-Dithiadiazolium Chloride

The crystal structure of 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride has been determined by Andreasen et al[51] (1977) (figure 2.15, page 93). The cation is a five membered planar ring with the trichloromethyl group co-planar with it. From the relatively short bond lengths within the ring, it is concluded that there is extensive delocalisation of the π-system. The cation is probably best regarded as an aromatic 6π-system[52]. A notable feature of the structure is the strong interaction between the chloride ion and the cation. The anion is almost symmetrically situated across the disulphide linkage, the contact distance being some 75pm. shorter than that using Pauling's formula, assuming a $^{+1}/_{2}$ charge on each sulphur and a -1 charge on the chlorine.[53]

(ii) 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

The X-ray crystal structure of 4-phenyl-1,2,3,5-dithiadiazolium chloride has been determined by Hazell[47] (figure 2.16 and tables 2.7-2.9, pages 94,89-90).

It would be anticipated that the "CN_2S_2" ring in both $CCl_3CN_2S_2Cl$ and $PhCN_2S_2Cl$ has the same basic configuration, possibly with slightly modified bond lengths due to the different inductive effects of the CCl_3 and Ph groups. From the crystal structures of $CCl_3CN_2S_2Cl$ and $PhCN_2S_2Cl$ it is noted that the rings are virtually identical, the main differences being that the angle at the carbon closes slightly in $PhCN_2S_2Cl$ relative to $CCl_3CN_2S_2Cl$ ($N \widehat{- C -} N$: $CCl_3CN_2S_2Cl$ = 122.2°; $PhCN_2S_2Cl$ = 119.0°) whereas the angle at nitrogen opens out marginally ($C \widehat{- N -} S$: $CCl_3CN_2S_2Cl$: 113.5°; $PhCN_2S_2Cl$: 1145°).

There are three marginally different $PhCN_2S_2$ units in the crystal structure, the main difference being the position of the chlorine relative to the S-S linkage. In all cases the chlorine is virtually symmetrically placed across the disulphide linkage (on average, 291.8pm from one sulphur and 289.4pm from the other). The degree of interaction between anion and cation, as quantified by the S ······ Cl contact distances, is slightly less in $PhCN_2S_2Cl$ than in $CCl_3CN_2S_2Cl$ (average S ······ Cl distance $PhCN_2S_2Cl$ = 290.6pm; $CCl_3SN_2S_2Cl$ = 285.6pm). Hence the most significant effects on the "CN_2S_2" ring of changing the substituent at position 4 from CCl_3 to Ph is the closure of the $N \widehat{- C -} N$ angle and the slight drop in anion cation interaction. The decrease in the $N \widehat{- C -} N$ angle is probably due to the minimisation of the interaction of the hydrogens at positions 2 and 6 with the nitrogens in the heterocyclic ring.

The bond lengths and angles in benzene have been accurately determined from rotational Raman[54] and neutron diffraction[55] spectra and also by crystallographic methods.[56] It can be seen that the C-C bond lengths in the phenyl group of $PhCN_2S_2Cl$ are some 1.8pm shorter than those in benzene (C_6H_6 : 139.7pm; $PhCN_2S_2Cl$: 137.9pm). Hence it would appear as though there is some delocalisation of the positive charge into the phenyl ring.

(iii) 4-Phenyl-1,2-Dithia-3,5-Diazole

The X-ray crystal structure of 4-phenyl-1,2-dithia-3,5-diazole was determined by Vegas[57] (figures 2.17-19, tables 2.10-13, pages 95,93,90,92)

Using the π-electron counting rules set out by Banister[52], the species $PhCN_2S_2$ would be postulated to be an odd electron 7π-aromatic and would, therefore, be expected to dimerise (cf. $S_3N_2^+$ figure 3.2 page 107[58]). The structure of $(PhCN_2S_2)_2$ was therefore postulated to be basically the same as in $S_6N_4^{2+}$, with two 6π-rings being held together by a two electron four centre bridge in an opposited geometry (related through a centre of symmetry). However from the crystal structure it is seen that the units are in fact eclipsed. The difference in conformation between the $S_6N_4^{2+}$ dimer unit and that of $(PhCN_2S_2)_2$ is almost certainly a function of the inherent positive charge on the $S_3N_2^+$ rings which therefore arrange themselves, so as to minimise the electrostatic repulsions. However in the case of the $(PhCN_2S_2)_2$ dimer the eclipsed arrangement is preferred due to the increased interaction of the singly occupied H.O.M.Os of the monomeric units.

The unit cell of phenyl dithiadiazole contains 16 "$PhCN_2S_2$" units, all of which are grouped into pairs, the asymmetric unit being four "$PhCN_2S_2$" units or two pairs. Each dimer has an average S ...... S inter-ring contact distance of 310.9pm as compared with 302.7pm in $S_6N_4^{2+}$[58] (sum of the van der Waals' radii = 360pm). Hence the strength of the four centre interaction in the $(PhCN_2S_2)_2$ and $(S_6N_4^{2+})$ dimers is similar but slightly less in the case of $(PhCN_2S_2)_2$.

All the phenyl groups, as well as the S_{31}-N_{31}-C_{31}-N_{32}-S_{32} and S_{41}-N_{41}-C_{41}-N_{42}-S_{42} rings are completely coplanar. The atom groups C_1-C_2-C_3-C_7 for all four $PhCN_2S_2$ units in the asymmetric unit are also coplanar. However the rings S_{11}-N_{11}-C_{11}-N_{12}-S_{12} and S_{21}-N_{21}-C_{21}-N_{22}-S_{22} are not coplanar due to the significant deviations of N_{12} and N_{21} (81pm and 54pm, respectively), from the plane described by the other four atoms in the ring.

The two $PhCN_2S_2$ units which form the dimer unit are almost parallel but are slightly twisted with respect to each other. The dihedral angles formed by the least squares planes through the two molecules are 6.56° and 7.04° for the dimers 1-4 and 2-3 respectively. The twist of one $PhCN_2S_2$ unit relative to the other (figure 2.19, page 93) can be quantified by the values of the torsion angles at the intermolecular S-S bonds (table 2.11, page 91).

The bond lengths and angles within the phenyl group are similar to those observed in benzene. A comparison of the C-N, S-N and S-S bond distances in the $PhCN_2S_2$ unit with various related systems is given in table 2.5.

TABLE 2.5 Comparison of C-N, S-N and S-S distances of phenyl-dithiadiazole with related species

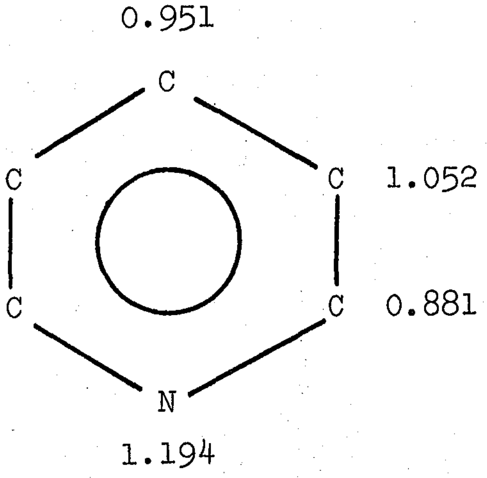
	$(PhCN_2S_2)_2$	$PhCN_2S_2Cl$	$CCl_3CN_2S_2Cl$	C_5H_5N[59]	NH_2SO_3H[60]
C-N(pm)	133.4(av)	134.0(av)	131.8(av)	134.0	-
S-N(pm)	162.5(av)	159.0(av)	158.4(av)	-	177.1
S-S(pm)	208.9(av)	199.1(av)	200.9(av)	-	-

(av = average)

It can be seen from table 2.5 that all the C-N bond lengths compared are similar, as are the S-N bonds, except for that in NH_2SO_3H which is a formal single bond and is noted for comparison, to show the evident multiple bond character of the S-N bonds within the ring. The main area of difference noted in table 2.5 is the S-S bond distances which increase by some 8pm in $(PhCN_2S_2)_2$ relative to $PhCN_2S_2Cl$ and $CCl_3CN_2S_2Cl$. It would therefore appear as though the molecular orbital into which the extra electron is placed, on reducing a dithiadiazolium salt, is of such a symmetry as to be antibonding across the S-S linkage. Hence on reducing the dithiadiazolium salt to the dithiadiazole an increase in S-S bond distance is observed.

Due to the "CN_2S_2" ring being heteronuclear the π-electron density will not be evenly distributed around the ring (cf. pyridine[61] (figure 2.13)).

Figure 2.13 π-electron densities in pyridine[61]



The greatest π-electron densities are, therefore, found at the hetero-atoms of greatest electronegativity. Hence in the case of $(PhCN_2S_2)_2$ the π-electron density will be greatest at the 3,5 nitrogens and least at the 1,2 sulphurs. It may therefore be suggested that the sulphurs of one monomer unit interact the π-system of the other thus leading to the observed sulphur-sulphur inter-ring interactions. The relatively high π-electron density at nitrogen and the relatively low density at sulphur could also be the reason for the long range inter-dimer interactions, e.g. (N_{12}′······ S_{32} and S_{12} ······ S_{21}). Both the N_{12}′···· S_{32} and S_{12} ····· S_{21} contact distances (315pm and 340.2pm respectively) are only slightly less than the sum of the van der Waals′ radii (N ····· S assuming sp^2 hybridisation of the nitrogen = 315pm, S ····· S = 360pm). It is likely that the deviations of N_{12} and N_{21} from the plane of the rings towards S_{32} and S_{42} respectively, as well as the twist in the rings forming the dimers (figure 2.19, page 93) are related to these long range interactions.

(iv) The Postulated Structures of 4-Phenyl-1,2,3,5-Dithiadiazolium Salts deduced from their Infra-red, Mass and E.S.C.A. Spectra

From the pattern and position of bands in the infra-red and mass spectra it was deduced that the following salts contain a dithiadiazolium cation with the same configuration as observed in $PhCN_2S_2Cl$.

(a) Bromide; (b) Thiocyanate; (c) Hexachloroantimonate (V); (d) Hexachlorostannate (IV); (e) Tetrachloroborate (III); (g) Tetrafluoroborate (III); (g) Hexafluorophosphate (V); (h) Benzoate; (i) Acetate.

There is insufficient anion-cation interaction in the above salts to perturb the observed vibrational spectrum of the cation.

The iodide salt does however have a significantly different infra-red spectrum to those observed for the aforementioned salts. The iodide is black but does not decompose on heating to yield phenyl dithiadiazole. It is soluble in non-polar and non-coordinating solvents and sublimes readily at 120°C.[50] The "salt," therefore, has the apparent physical properties of a non-ionic species. In order to determine whether the iodine was covalently bound, the E.S.C.A. spectrum was recorded; (A. Harrison and P.J. Stephenson, University of Durham). The binding energy of the I_{3d} orbital in $PhCN_2S_2I$ was compared with the binding energies of the I_{3d} orbitals in iodobenzene and with the I^- anion of $Ph_2I^+I^-$; (table 2.6)

TABLE 2.6 Comparison of the I_{3d} binding energies in $PhCN_2S_2I$ with those in known structures

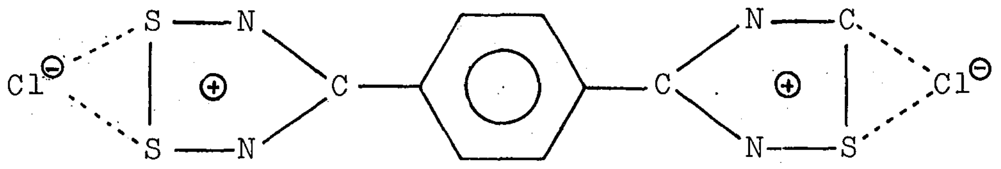
	$PhCN_2S_2\underline{\underline{I}}$	$C_6H_4\underline{\underline{I}}$	$(C_6H_5)_2I^+\underline{\underline{I}}^-$
I_{3d} binding energy (eV)	620.7	622.1	619.7

Hence from table 2.6 it would appear as though the iodine in $PhCN_2S_2I$ is essentially anionic but with significant interaction with the cation, thus raising the observed binding energy relative to that of a non-interacting iodide.

Comparison of the infra-red spectra of $PhCN_2S_2Cl$, $PhCN_2S_2I$ and $(PhCN_2S_2)_2$ indicates that there are similarities between that of $(PhCN_2S_2)_2$ and $PhCN_2S_2I$ (figure 2.9, page 88). It is thought likely that the basic difference in the infra-red spectra of $(PhCN_2S_2)_2$ and $PhCN_2S_2{}^+X^-$ is due to the neutralisation of the positive charge on the ring and not the interactions caused by the $[PhCN_2S_2^{\bullet}]$ dimerising. Thus $PhCN_2S_2I$ could be regarded as the mid point between $PhCN_2S_2^+$ and $[PhCN_2S_2^{\bullet}]$, the degree of anion-cation interaction being high. It is suggested that the[62] "soft", highly polarizable iodide anion (ionic radius ca. 212pm) is of the correct size to interact strongly with the relatively electropositive disulphide linkage in the "$CN_2S_2^+$" ring ($PhCN_2S_2^+Cl^-$;S-S : 199.1 pm). The strong cation-anion interaction will almost certainly decrease the effective positive charge on the CN_2S_2 ring and hence cause an increase in the S-S bond distance ($(PhCN_2S_2)_2$: $S\text{-}S_{(average)}$ = 208.9pm).

It is therefore concluded that although the infra-red spectrum of $PhCN_2S_2I$ is distinctly different from that of either $PhCN_2S_2Cl$ or $(PhCN_2S_2)_2$ and may therefore be regarded, at first sight, to be consistent with that of a completely different ring system, the compound does exist as $PhCN_2S_2^+I^-$ but with a high degree of cation-anion interaction thus significantly changing the basic $PhCN_2S_2^+$ spectrum.

2.3.5 Attempts to produce 1,4-di-1,2,3,5-Dithiadiazolium Benzene Dichloride

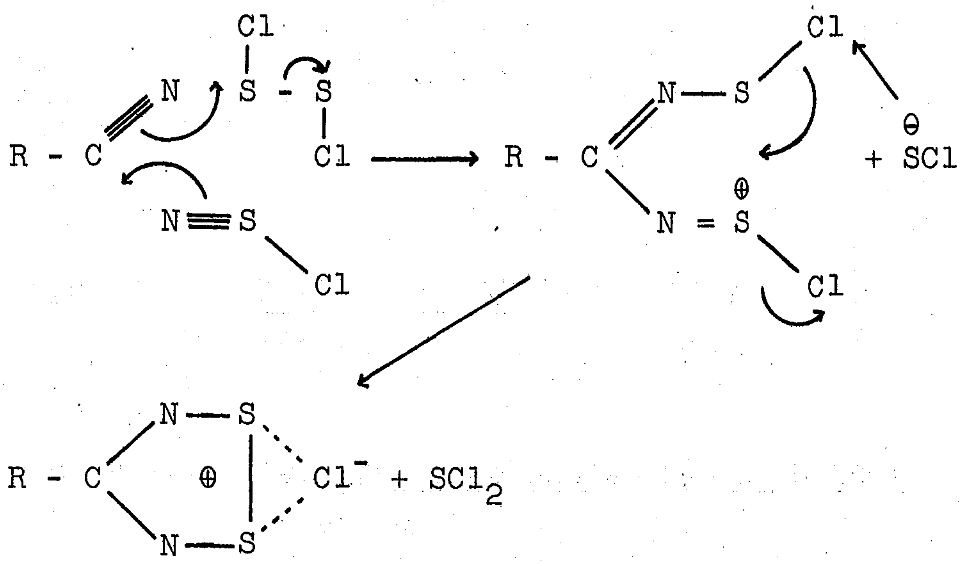


$(C_8H_4N_4S_4Cl_2)$

The mechanism by which 4-phenyl-1,2,3,5-dithiadiazolium chloride is postulated[49] to be formed in the reaction of $(NSCl)_3$ with PhCN is via the nucleophilic attack of NSCl on the carbon of the nitrile group (figure 2.14).

Figure 2.14 Postulated Mechanism by which NSCl reacts with PhCN to form $PhCN_2S_2Cl$.[49]

$$(NSCl)_3 \rightleftharpoons 3NSCl \longrightarrow {}^3/_2N_2 + {}^3/_2S_2Cl_2$$



It was, therefore, thought likely that in the reaction of 1,4-dicyanobenzene with NSCl, one cyano group would activate the other, to attack by the NSCl unit. Hence the first intermediate in the reaction sequence would be expected to be $NCC_6H_4CN_2S_2{}^+Cl^-$. The dithiadiazolium ring para to the second cyano group would then activate the cyano group to attack by the thiazyl chloride entity. However the cyano group in $NCC_6H_4CN_2S_2{}^+Cl^-$ destabilizes the dithiadiazolium ring relative to that in $PhCN_2S_2{}^+Cl^-$ and if $(S_2N_2CC_6H_4CN_2S_2{}^{2+})(Cl^-)_2$ is formed as an intermediate, the effect of one dithiadiazolium ring on the other, is such that the species decomposes yielding $NCC_6H_4CN_2S_2{}^+Cl^-$. The destabilization of the $NCC_6H_4CN_2S_2{}^+Cl^-$ salt relative to $PhCN_2S_2{}^+Cl^-$ is seen in the ease with which the $PhCN_2S_2{}^+Cl^-$ salt is produced as compared with the cyano derivative. $PhCN_2S_2{}^+Cl^-$ can be produced by the reaction of benzonitrile with trichlorotrithiatriazene in carbon tetrachloride at 60°C,[49] whereas on reacting 1,4-

dicyanobenzene with trichlorotrithiatriazene in benzene at 80°C, no dithiadiazolium product was isolated (experiment 2.2.7(ii), page 53).

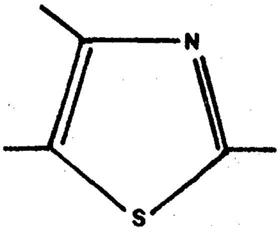
Hence it is concluded that $(C_8H_4N_2S_2{}^{2+})(Cl^-)_2$ cannot be readily synthesised due to the mutual destabilization of the two dithiadiazolium rings.

2.3.6 Comparison of the Known Chemistry of the 4-Trichloromethyl and 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

Quite an extensive chemistry of the 4-phenyl-1,2,3,5-dithiadiazolium cation has been developed in this thesis and by Roesky.[38] There is however little or no analogous chemistry of the trichloromethyl derivative. In investigations, carried out concurrently with work reported in this thesis, Fielder[50] failed to produce the reduced form of the trichloromethyl derivative or any salts by analogous reactions to those reported in this thesis for the phenyl derivative. It is suggested that the reduced form of the trichloromethyl derivative is not formed due to the repulsive interactions of the freely rotating CCl_3 groups. In the anion exchange reactions of $CCl_3CN_2S_2{}^+Cl^-$ the chlorines of the CCl_3 group may also participate to some extent, thus leading to the mixtures of products reported by Fielder.

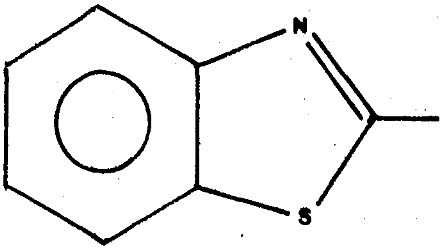
Hence it is concluded that the most extensive chemistry of any of the possible derivaties of the 1,2,3,5-dithiadiazolium cation will be for the case where, the substituent at position 4 is phenyl or some other planar delocalised system (e.g. naphtho). No interference with anion exchange reactions will be observed for such a derivative and the eclipsed dimer system can be produced without destructive interaction from freely rotating substituents at position 4.

Figure 2.4



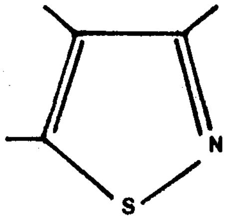
2·1

1,3-Thiazole



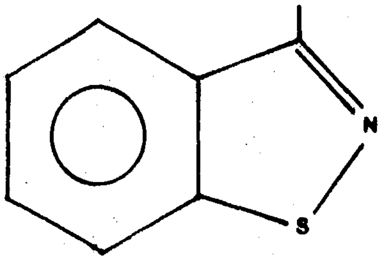
2·2

1,3 - Benzothiazole



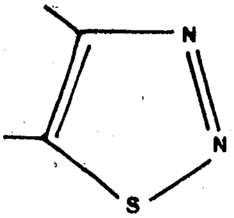
2·3

1,2-Thiazole



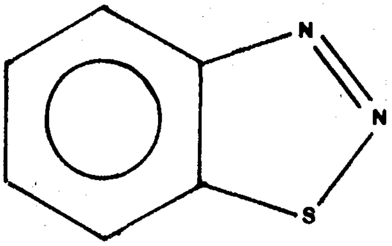
2·4

1,2 - Benzothiazole



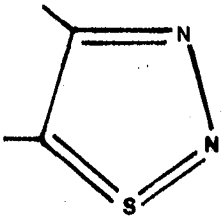
·5

1,2,3-Thiadiazole



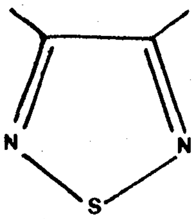
2·6

1,2,3- Benzothiadiazole



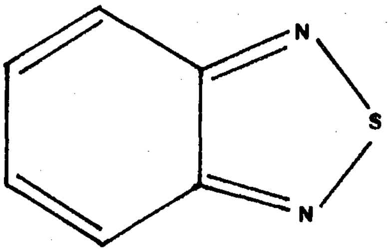
2·7

1,2,3-Thia-S^{iv}-diazole



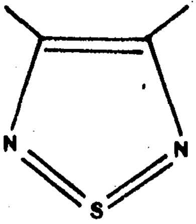
·8

1,2,5-Thiadiazole



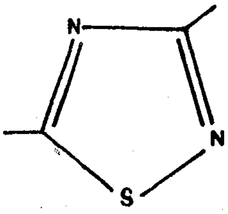
2·9

1,2,5-Benzothiadiazole



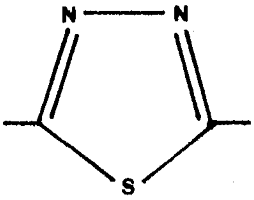
2·10

1,2,5-Thia-S^{iv}-diazole



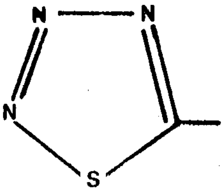
·11

1,2,4-Thiadiazole



2·12

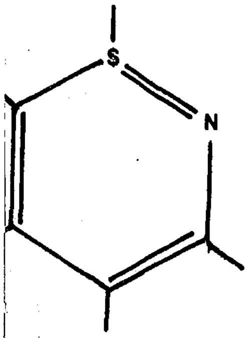
1,3,4-Thiadiazole



2·13

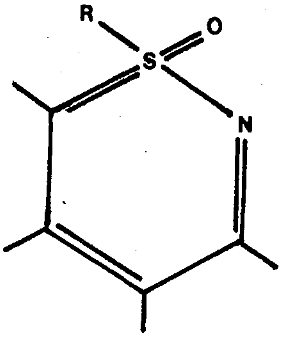
1,3,4,5-Thiatriazole

Figure 2.5



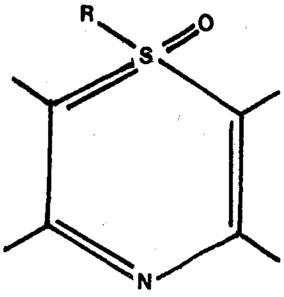
14

1,2-Thiazine



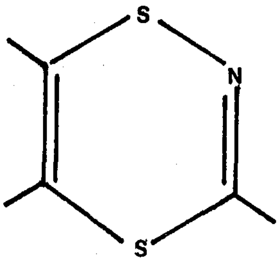
2·15

1,2-Thiazine-1-oxide



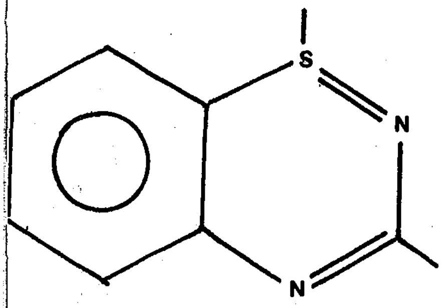
2·16

1,4-Thiazine-1-oxide



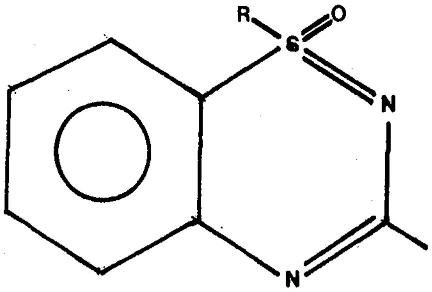
2·17

1,4,2-Dithiazine



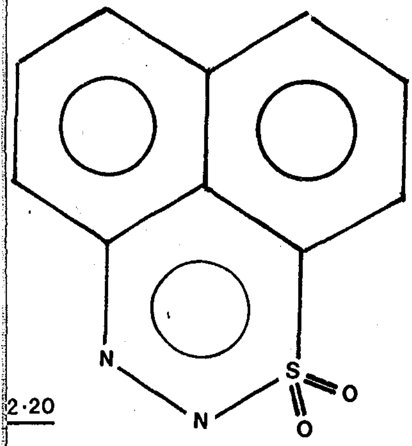
2·18

1,2,4-Benzothiadiazine



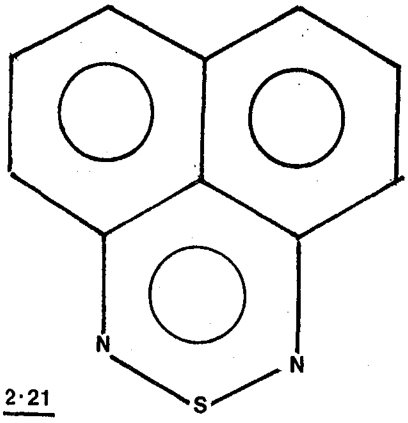
2·19

1,2,4-Benzothiadiazine-1-oxide



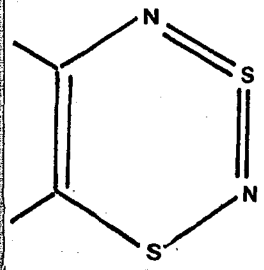
2·20

Naptho-[1,8-d,e]-1,2,3-Thiadiazine-1,1-Dioxide



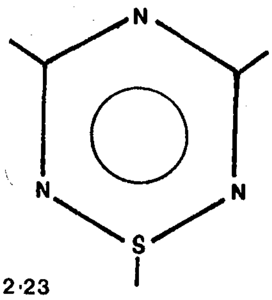
2·21

Naptho-[1,8-c,d]-1,2,6-Thiadiazine



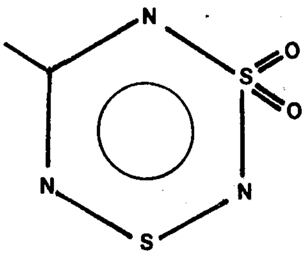
2·22

1,3,2,4-Dithiadiazine



2·23

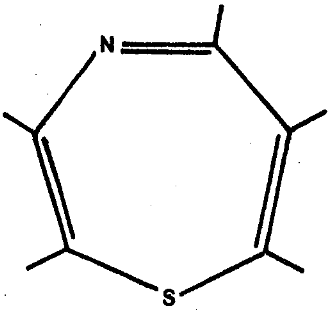
1,2,4,6-Thiatriazine



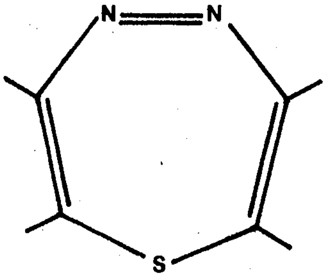
2·24

1,3,2,4,6-Dithiatriazine-3,3-Dioxide

Figure 2.6

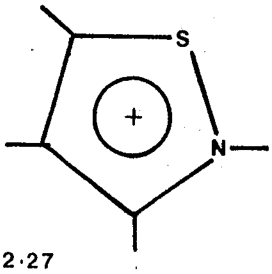

2·25

1,4-Thiazepine

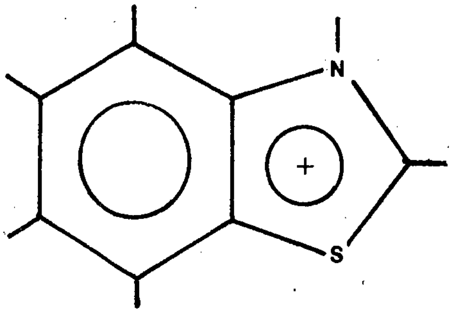

2·26

1,4,5-Thiadiazepine

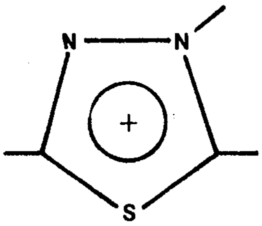
Figure 2.7


2·27

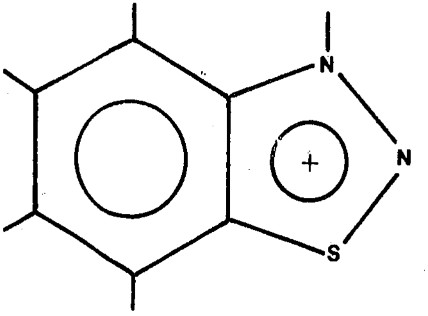
1,2- Thiazolium Cation


2·28

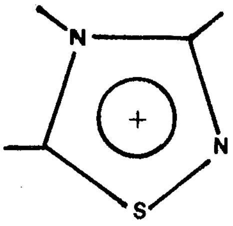
1,3-Benzothiazolium Cation


2·29

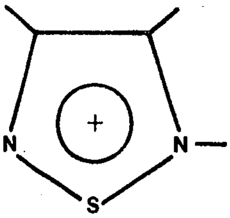
1,3,4-Thiadiazolium Cation


2·30

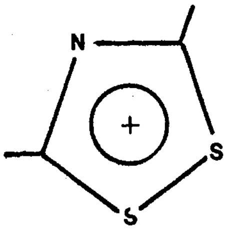
1,2,3-Benzothiadiazolium Cation


2·31

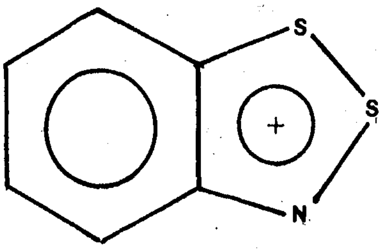
1,2,4-Thiadiazolium Cation


2·32

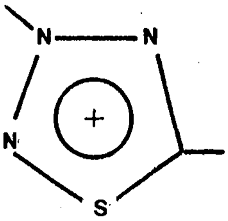
1,2,5-Thiadiazolium Cation



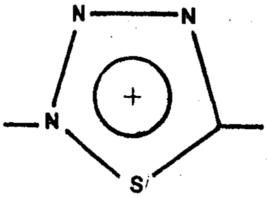
2·33
1,2,4-Dithiazolium Cation



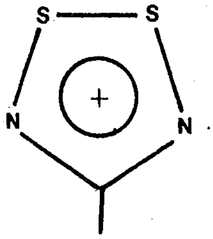
2·34
1,2,4-Benzodiazolium Cation
[Herz Compound]



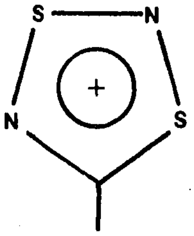
2·35
3-sub-1,2,3,4-Thiatriazolium Cation



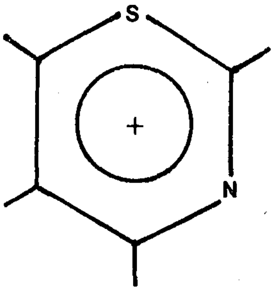
2·36
2-sub-1,2,3,4-Thiatriazolium Cation



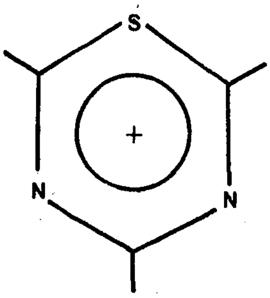
2·37
1,2,3,5-Dithiadiazolium Cation



2·38
1,3,2,5-Dithiadiazolium Cation



2·39
1,3-Thiazinium Cation



2·40
1,3,5-Thiadiazinium Cation

RHPHCl/5 Figure 2.8.a $PhCN_2S_2^+Cl^-$

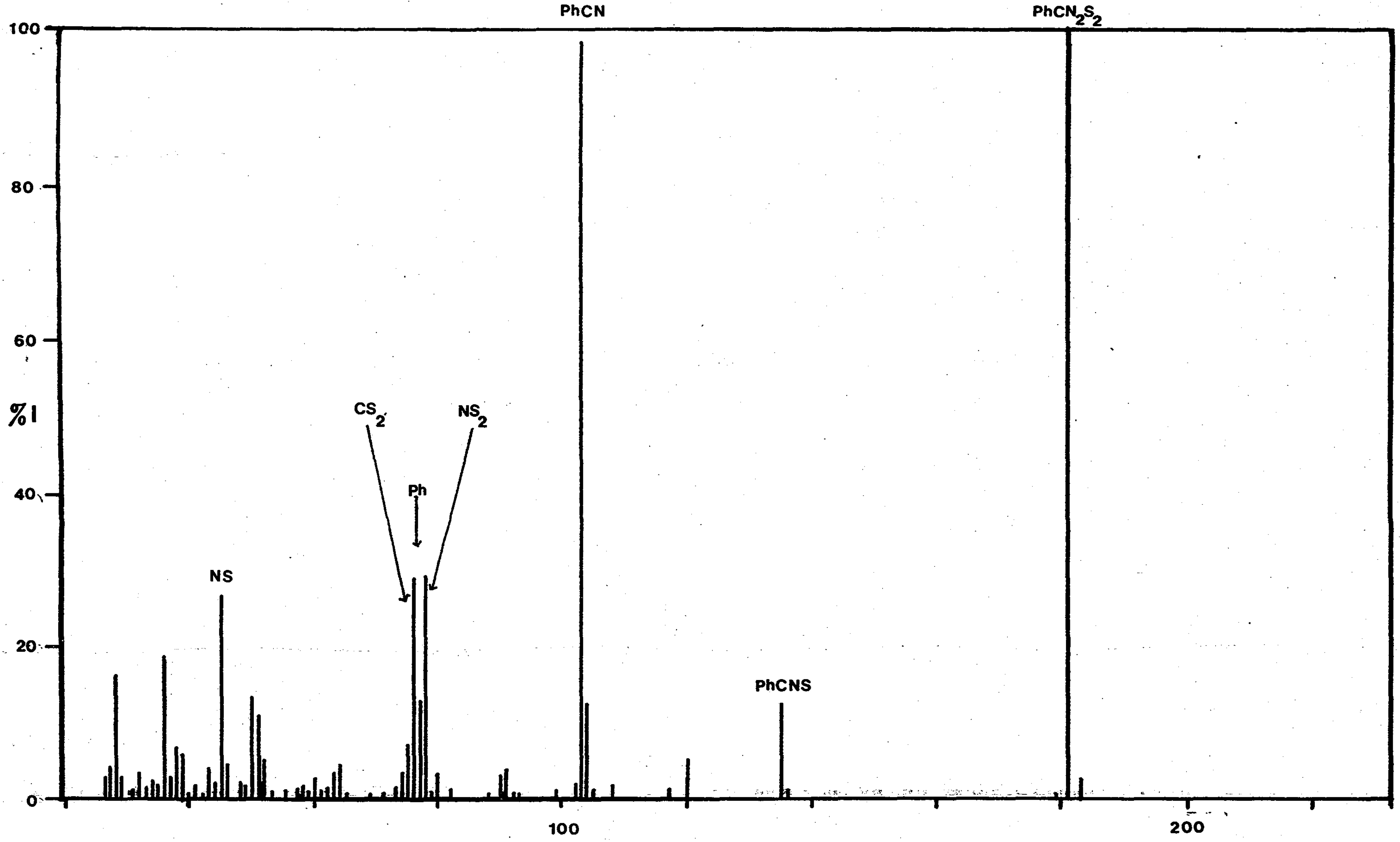


Figure 2.8.b $PhCN_2S_2^+ I^-$

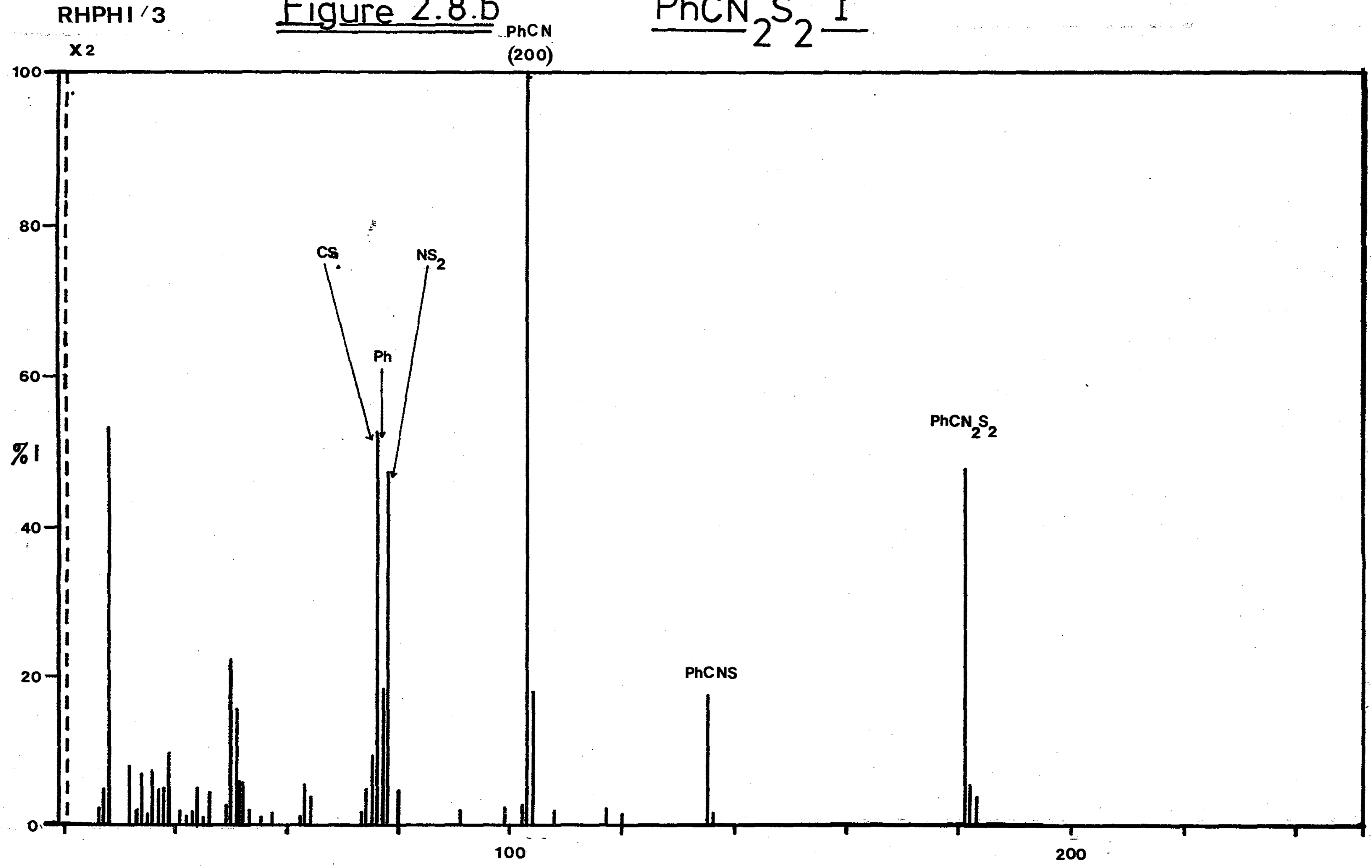


Figure 2.8.c: $PhCN_2S_2^+NCS^-$

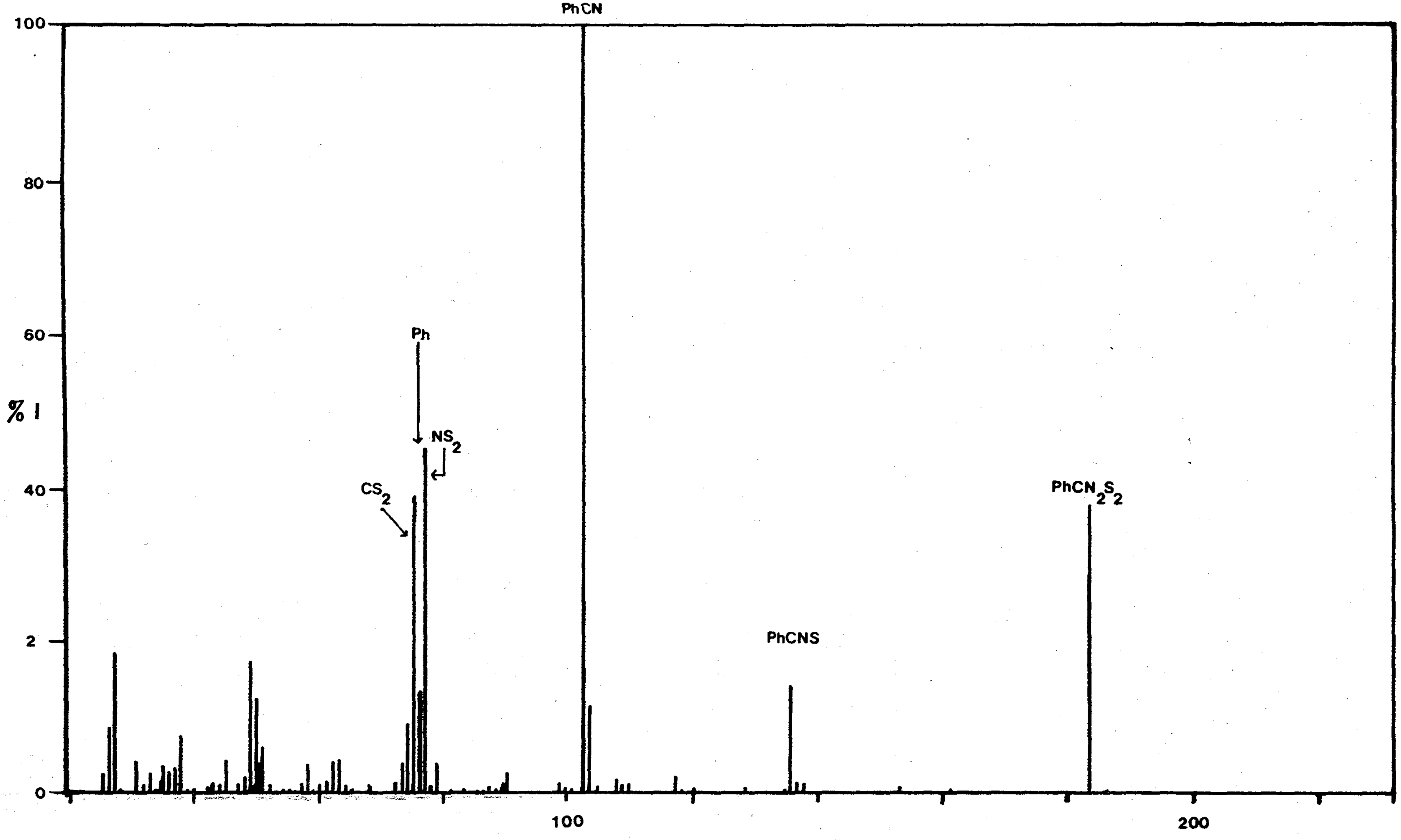


FIGURE 2,9

Infra-red Spectra of 4-Phenyl-1,2,3,5-Dithiadiazolium salts and 4-Phenyl-1,2-Dithia-3,5-Diazole.

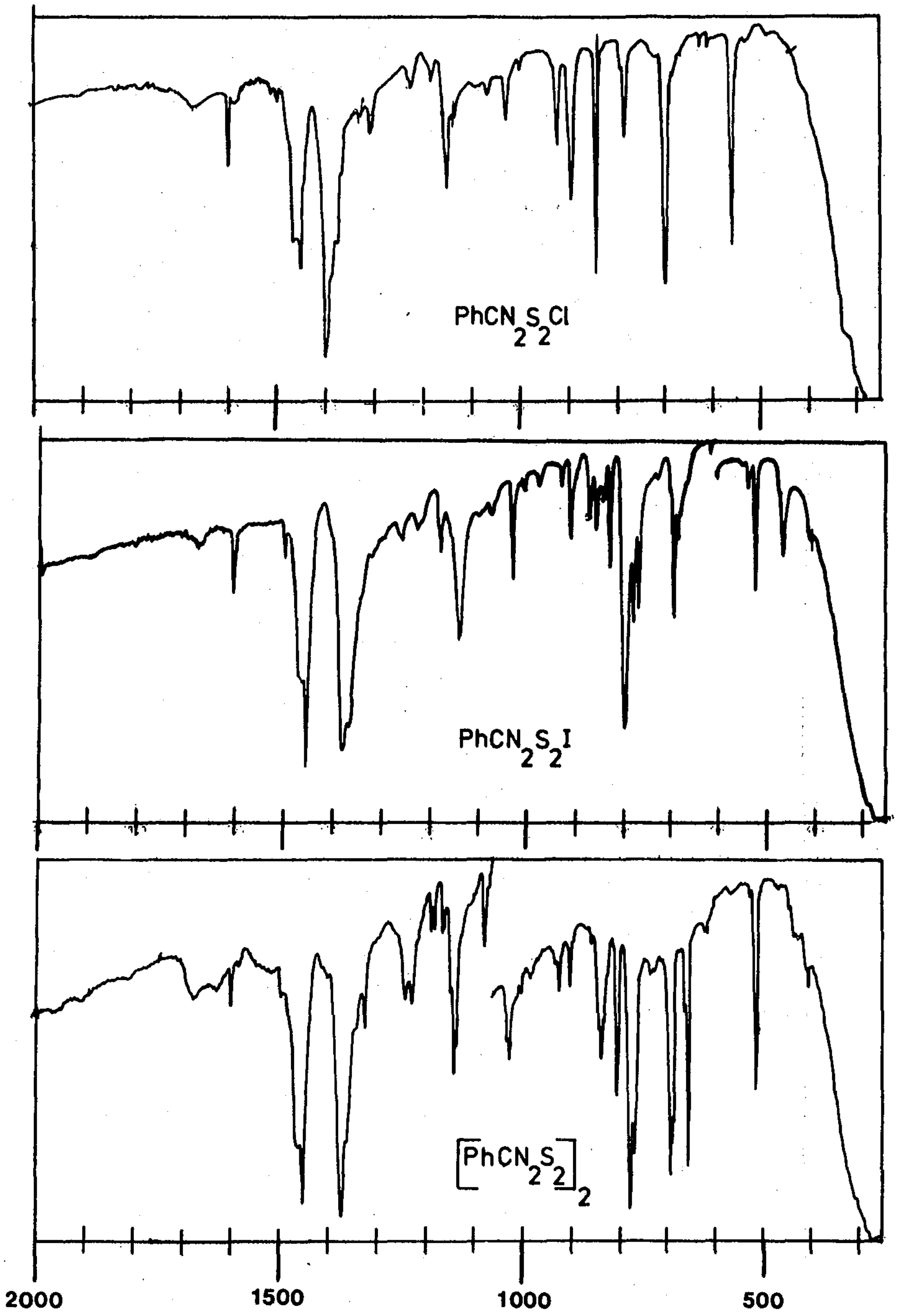


TABLE 2.7 Crystal Data for $PhCN_2S_2Cl$

$6C_6H_5CN_2S_2Cl : C_6H_5CH_3$

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

a = 1577.0(13)pm

b = 756.5(6)pm

c = 1379.1(11)pm

α = $100.25^{\circ}(4)$

β = $109.81^{\circ}(5)$

δ = $95.25^{\circ}(5)$

R = 0.056

1535 reflections 172 parameters

TABLE 2.8 Mean Standard Deviations in the Crystal Structure of $PhCN_2S_2Cl$

Lengths	Angles
σ(S-S) = 0.5pm	σ(S - Cl - S) = 0.10°
σ(S-Cl) = 0.5pm	σ(Cl - S - S) = 0.15°
σ(N-C) = 1pm	σ(S - S - N) = 0.40°
σ(C-C) = 1pm	σ(S - N - C) = 0.70°
σ(C-H) = 5pm	σ(C - C - C) = 0.70°
σ(S-N) = 1pm	σ(N - C - C) = 0.70°
	σ(N - C - N) = 0.8°
	σ(C - C - H) = 3°

TABLE 2.9 S-Cl contact distances between Molecules in the Crystal Structure of $PhCN_2S_2Cl$

$Cl_{(1)}$ ...... $S_{(1)}$ = 318.8pm

$Cl_{(1)}$ ...... $S_{(5)}$ = 320.9pm

$Cl_{(1)}$ ...... $S_{(2)}$ = 326.3pm

$Cl_{(1)}$ ...... $S_{(3)}$ = 341.1pm

$Cl_{(2)}$ ...... $S_{(2)}$ = 318.1pm

$Cl_{(2)}$ ...... $S_{(5)}$ = 319.8pm

$Cl_{(2)}$ ...... $S_{(6)}$ = 333.4pm

$Cl_{(3)}$ ...... $S_{(3)}$ = 310.2pm

$Cl_{(3)}$ ...... $S_{(4)}$ = 332.5pm

(Numbering system the same as used in figure 2.16)

TABLE 2.10 Crystal Data for 4-Phenyl-1,2-Dithia-3,5-Diazole

$C_7H_5N_2S_2$ · MW : 181.25

Orthorhombic, Space Group $P2_1 2_1 2_1$ (No.19)

a = 1606.1(1)pm

b = 3298.4(5)pm

c = 5774.0(4)pm

V = 3.0429(5) x 10^9 pm^3

Z = 16

R = 0.082

Dx = 1.58g cm^3

$F_{(000)}$ = 1488

X = 71.07pm

μ_{Mo} = 5.99 cm^{-1}

2513 reflections

132 positional parameters 264 thermal parameters

TABLE 2.11 Torsion angles in $(PhCN_2S_2)_x$ (figure 2.19)

Atoms	Angles(°)
$N_{11} - S_{11} - S_{42} - N_{42}$	8.43
$N_{12} - S_{12} - S_{41} - N_{41}$	6.91
$N_{21} - S_{21} - S_{31} - N_{31}$	3.61
$N_{22} - S_{22} - S_{32} - N_{32}$	2.81

(Numbering system same as used in figure 2.18)

TABLE 2.12 Mean Standard Deviations in the Crystal Structure of $(PhCN_2S_2)_2$

Standard deviations		lengths(pm)	Angles(°)
involving	S	0.5	0.2
	N	1.0	0.4
	C	-	0.4

TABLE 2.13 Geometry of the Intermolecular Contacts in $(PhCN_2S_2)_2$

(a) Symmetry code

$' = x - {}^1/_2, {}^3/_2 - y, -z$

$'' = x + {}^1/_2, {}^3/_2 - y, -z$

Lengths(pm)

$S_{12} \cdots\cdots S_{21} = 340.2$

$S_{32} \cdots\cdots N_{12} = 315.0$

$S_{31} \cdots\cdots N_{12}' = 338.0$

$S_{41} \cdots\cdots N_{21} = 309.0$

$S_{42} \cdots\cdots N_{21} = 317.0$

(b) Angles(°)

$S_{12} - S_{21} - S_{22}$	137.9	$S_{11} - S_{12} - S_{21}$	78.1
$S_{12} - S_{21} - S_{31}$	128.6	$S_{21} - S_{12} - S_{41}$	73.3
$S_{12} - S_{21} - N_{21}$	101.9	$S_{21} - S_{12} - N_{12}$	164.3
$S_{32}'' - N_{12} - S_{12}$	100.1	$S_{42} - N_{21} - S_{21}$	105.6
$S_{32}'' - N_{12} - C_{11}$	109.7	$S_{42} - N_{21} - C_{21}$	97.8
$S_{31}'' - N_{12} - S_{12}$	95.0	$S_{41} - N_{21} - S_{21}$	104.3
$S_{31}'' - N_{12} - C_{11}$	78.8	$S_{41} - N_{21} - C_{21}$	97.8
$S_{31} - S_{32} - N_{12}'$	77.3	$S_{41} - S_{42} - N_{21}$	72.6
$S_{22} - S_{32} - N_{12}'$	102.0	$S_{11} - S_{42} - N_{21}$	85.5
$N_{32} - S_{32} - N_{12}'$	163.9	$N_{42} - S_{42} - N_{21}$	166.8
$S_{32} - S_{31} - N_{12}'$	65.5	$S_{42} - S_{41} - N_{21}$	68.5
$S_{21} - S_{31} - N_{12}'$	97.7	$S_{12} - S_{41} - N_{21}$	80.3
$N_{31} - S_{31} - N_{12}'$	156.2	$N_{41} - S_{41} - N_{21}$	162.5

(Numbering system same as used in figure 2.17).

Figure 2.15

X-ray crystal structure of 4-Trichloromethyl-1,2,3,5-Dithiadiazolium Chloride

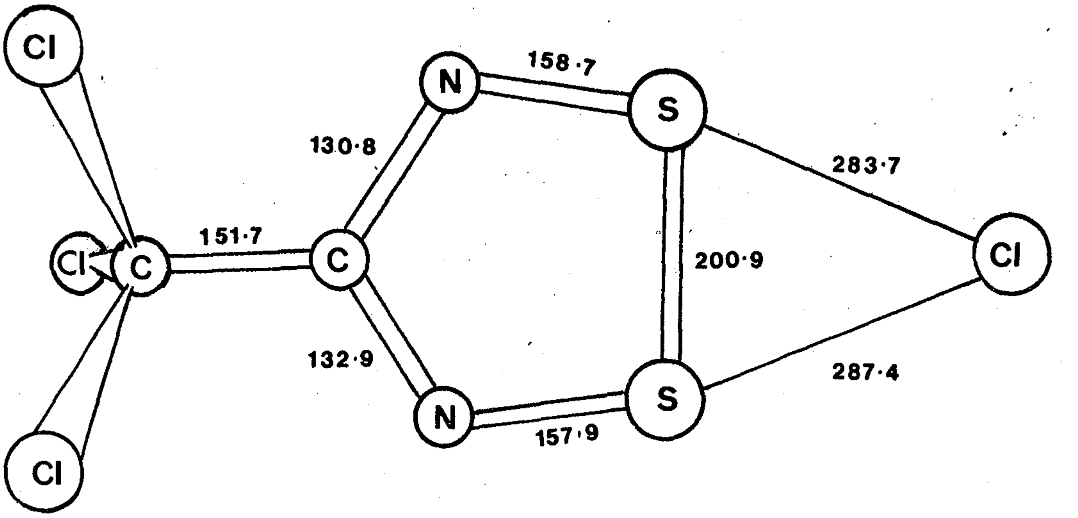


Figure 2.19

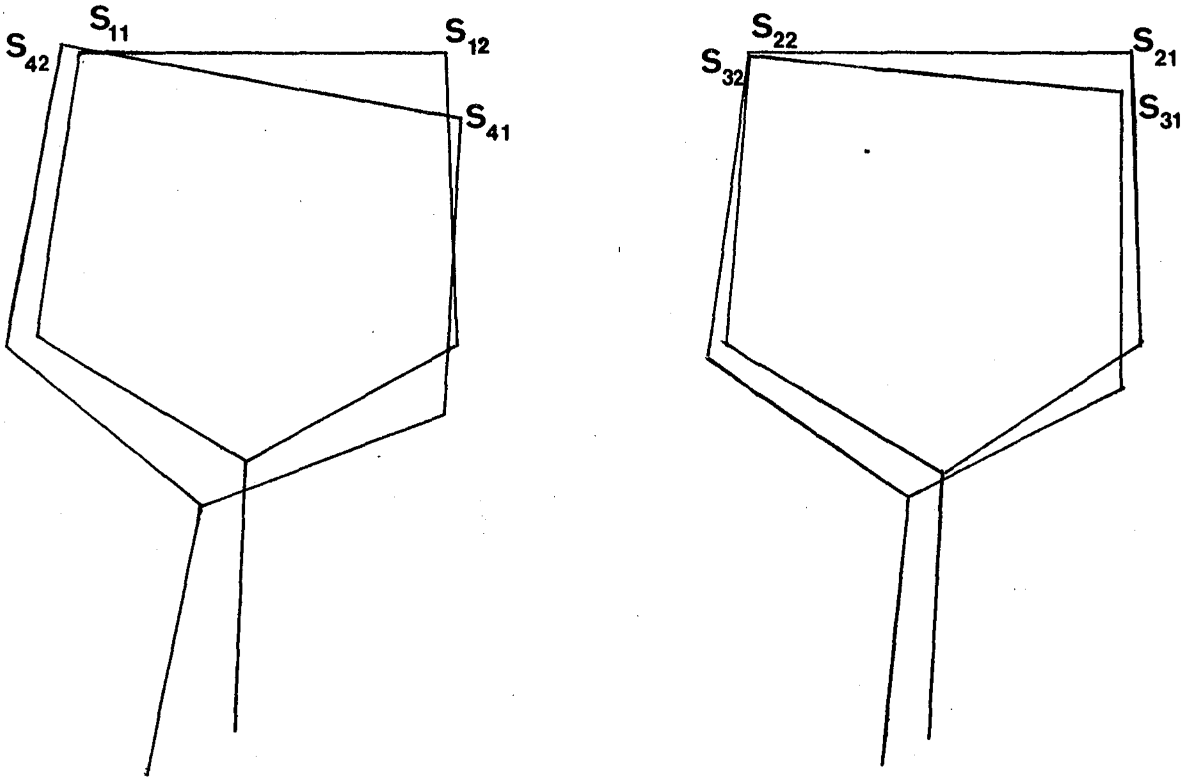


Figure 2.16

X-ray crystal structure of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

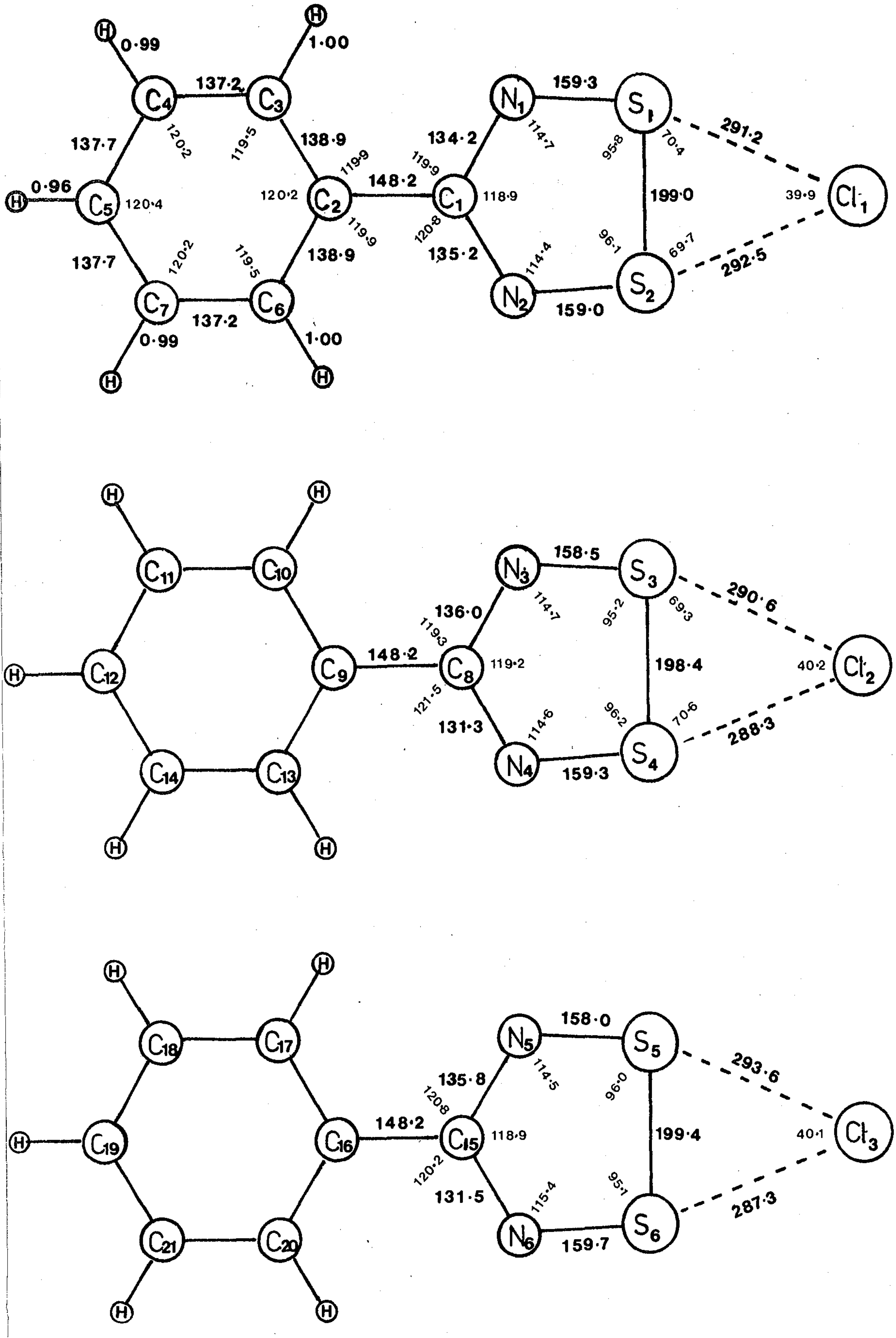


Figure 2.17

Stereogram of 4-Phenyl-1,2-Dithia-3,5-Diazole

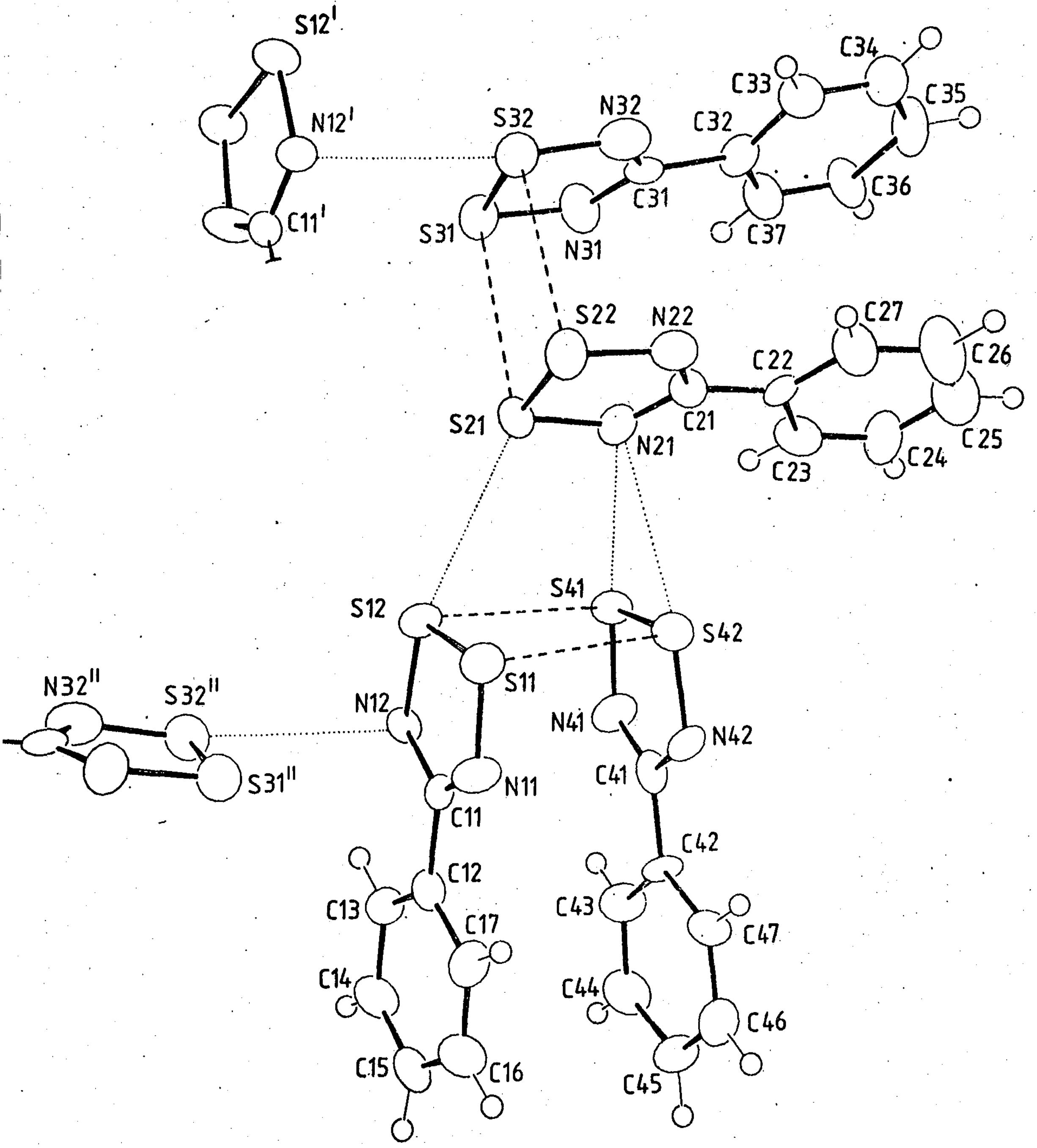
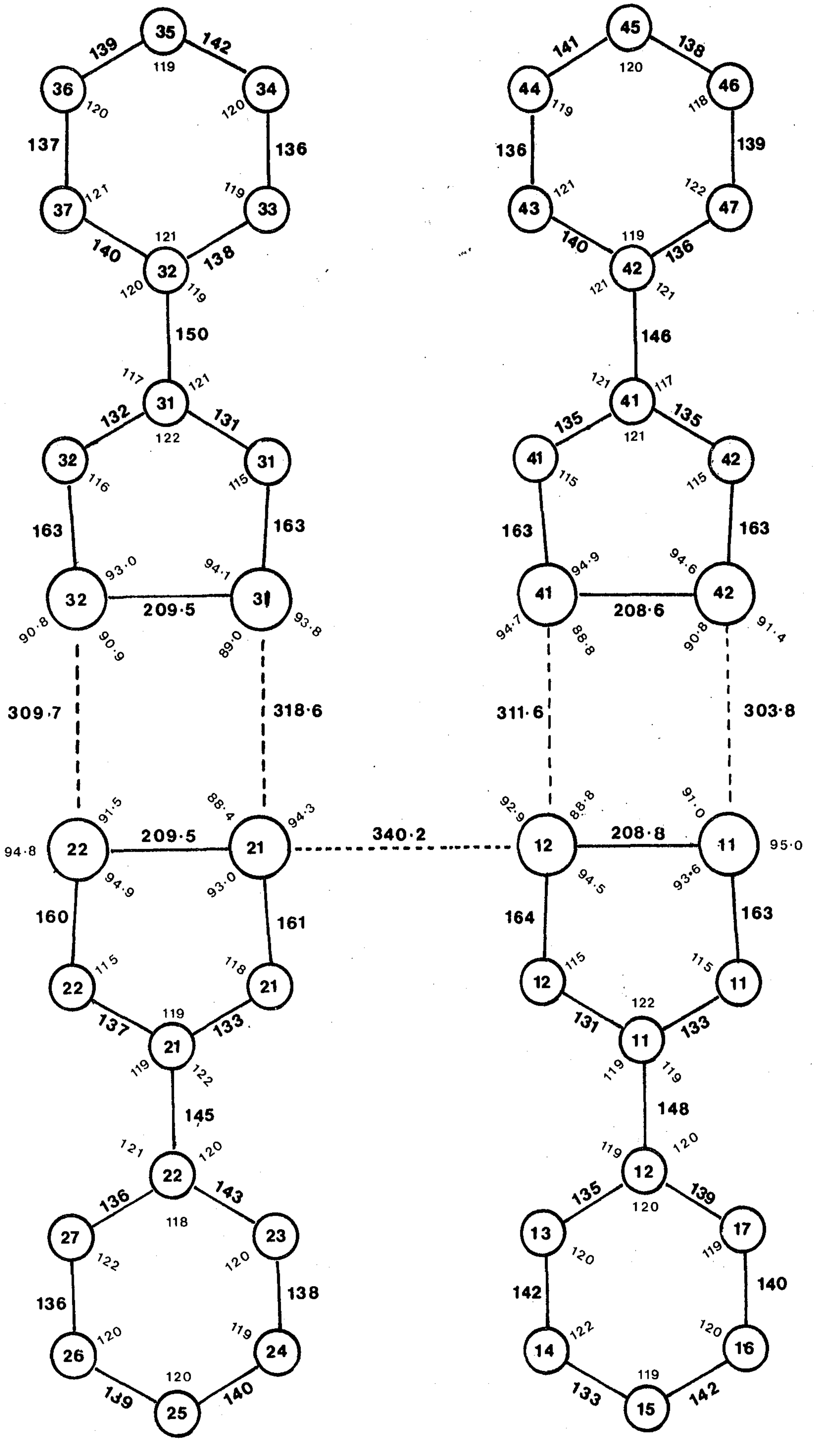


Figure 2.18

X-ray crystal structure of 4-Phenyl-1,2-Dithia-3,5-Diazole.



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CHAPTER THREE

THE REDUCTION OF SULPHUR-NITROGEN SPECIES

3.1 Introduction

There are four main sulphur-nitrogen species with which chlorine is associated in the form of the chloride anion or as covalently bound chlorine.

1. Thiotrithiazyl chloride ($S_4N_3^+Cl^-$)
2. Thiodithiazyl chloride ($S_3N_2^+Cl^-$)
3. Chlorothiodithiazyl chloride ($S_3N_2Cl^+Cl^-$)
4. Trichlorotrithiatriazene ($(NSCl)_3$).

The four compounds form a series, in which the first two species ($S_4N_3^+Cl^-$ and $S_3N_2^+Cl^-$) contain cyclic sulphur-nitrogen cations with no covalent sulphur-chlorine linkages. The species $S_3N_2Cl^+Cl^-$ represents the sole example of a cationic compound containing a covalently bound chlorine and an anionic chlorine. This compound may therefore be regarded as the mid-point of the series listed above, as $(NSCl)_3$ contains three covalently bound chlorine atoms and is therefore not ionic.

The chemistry of the aforementioned sulphur-nitrogen cations and trichlorotrithiatriazene, although investigated by a number of research groups throughout the world, over a period of two decades, is still largely unexplored. Few potential industrial uses of the species have been found and their application to organic synthetic chemistry has been, in the main, undeveloped.

3.1.1 Thiotrithiazyl Chloride (S_4N_3Cl)

The thiotrithiazyl cation is probably the least moisture sensitive of all the cationic sulphur-nitrogen species and is far more stable to moisture than any sulphur-nitrogen species containing a covalently bound chlorine (e.g. $S_3N_2Cl_2$ and $(NSCl)_3$). The cation is often formed by the thermal decomposition and rearrangement of other sulphur-nitrogen species both in the vapour phase[1] and in solution.

(a) Preparation of Thiotrithiazyl Chloride

$$3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl \qquad \text{Yield; 90\% (ref.2.4)} \qquad (3.1)$$

$$3S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2S_4N_3Cl + 3SCl_2 \qquad \text{Yield; Quantitative (ref.5)} \qquad (3.2)$$

The above two routes are those normally used to synthesise S_4N_3Cl. Various other routes via trichlorotrithiatriazene[4] and by the use of other chlorinating agents e.g. $SOCl_2$[6] and $CH_3C(O)Cl$, are known.[4,7,8] Direct synthesis by the reaction of sulphur-chlorides with ammonia[9-11] or lithium azide[12] does not provide a high yield of product.

(b) Physical Properties

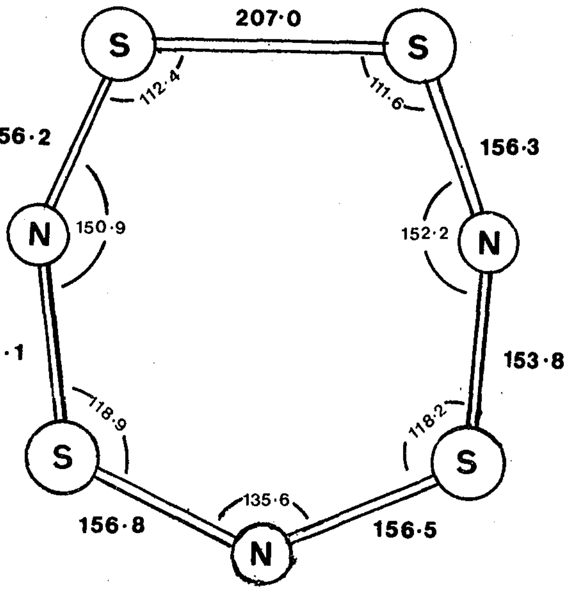
Due to the insolubility of S_4N_3Cl in non-polar solvents, the compound is normally isolated as a fine yellow powder.[5] The finely divided form of the compound can cause irritation of the nasal system and mild dermatitis. The salt is soluble in highly polar or coordinating solvents, e.g. acetonitrile, nitromethane, thionyl chloride, tetrahydrofuran, monoglyme and to a lesser extent in sulphur dioxide.

(c) The Structure of the Thiotrithiazyl cation

S_4N_3Cl was first prepared in 1880 and was shown to be ionic by salt formation, cryoscopy and conductivity measurements. The crystal structure of the ring was first determined by Weiss (1962)[13,14] and later by Cordes (1964)[15], Kruss (1972)[16,17], Row (1978)[18] and Street (1979)[19].

The structure of the $S_4N_3^+$ cation in $S_4N_3^+NO_3^-$ (1978)[18] is shown in figure 3.1.

Figure 3.1 Structure of the $S_4N_3^+$ cation.[18]



The bonding in the $S_4N_3^+$ cation has been the subject of much debate over the past decade. However Friedman[20] concluded from the U.V spectrum that the bonding was "a 10π-system, conjugated throughout the entire ring, though limited in extent across the S-S bond". This view was confirmed by Adams *et al*[21] who concluded from S.C.F.M.O. and E.S.C.A. calculations that the cation contained a 10π-delocalised ring.

(d) The Reactions of Thiotrithiazyl chloride

(i) Salt Formation Reactions

Due to its ionic nature, the majority of the reported chemistry of the thiotrithiazyl ring system is that of salt formation reactions. The salts are almost invariably synthesised from thiotrithiazyl chloride by one of three routes:

(a) Metathesis in polar solvents, e.g. Br^{-}[22,25] SCN^{-},[22,25] BPh_4^{-}[22] and I^{-}[25].

(b) Reactions with liquid or concentrated acids with the evolution of hydrogen chloride, e.g. NO_3^{-}[13,14,18,23], ClO_4^{-}[24], F^{-}[26] and salts of the oxy-acids of sulphur[24,27-30].

(c) Reactions with Lewis acids, e.g. $SbCl_6^{-}$[11], $FeCl_4^{-}$[31], $AlCl_4^{-}$[31], $HgCl_3^{-}$[32] and the bromo analogues.[33-36]

(ii) Ring expansion

Thiotrithiazyl chloride is reported to react with both lithium and aluminium azide forming tetrasulphur tetranitride.[12]

(iii) Reactions with Triphenyl Phosphine

Thiotrithiazyl chloride reacts readily with triphenyl phosphine forming a series of compounds containing both phosphorous-nitrogen and sulphur-nitrogen bonds, e.g. $\left[Ph_3P = N - PPh_3\right]Cl$, $\left[Ph_3P - NH_2\right]Cl$ and $\left[(Ph_3P = N)_3S\right]Cl_3$[37].

(iv) Reactions with Amines

Thiotrithiazyl chloride reacts with trace amounts of amines to form very highly coloured species which decompose within short periods of time. The reaction has been suggested as a possible method of observing amines in low concentrations.[38]

(v) The potential applications of S_4N_3Cl to Organic Heterocyclic Chemistry

The potential application of S_4N_3Cl to organic heterocyclic chemistry was investigated by Barton and Bubb[39], who discovered that the salt reacted readily with benzophenone hydrazone to give benzophenone azine and with benzophenone phenylhydrazone to give N-(phenylthio) diphenyl methylenamine ($Ph_2C=N-S-Ph$). No further work in this area has been reported by Barton, who concluded from his investigations that, "thiotrithiazyl chloride leads to a variety of interesting products in reactions with electron rich organic substrates. However the crude product is usually a complex mixture and yields of pure substances are generally low. The multiplicity of pathways by which these reagents can react, although mechanistically fascinating, imposes limitations on their synthetic utility."

3.1.2 Thiodithiazyl Monochloride (S_3N_2Cl)

The chemistry of the thiodithiazyl cation is by far the least studied of all the sulphur-nitrogen ring systems.

(a) Preparation of the Thiodithiazyl Cation

The thiodithiazyl cation has been prepared by five routes:

(i) $3S_3N_2Cl_2 \longrightarrow 2S_3N_2Cl + 2NSCl + SCl_2$ (ref.5) (3.3)

(ii) $2S_3N_2Cl_2 + HCOOH \longrightarrow 2S_3N_2Cl + 2HCl + CO_2$ (ref.40)(3.4)

(iii) $S_4N_4 + S_2Cl_2 \longrightarrow 2S_3N_2Cl$ (ref.41)(3.5)

(iva) $S_4N_4 + 2NOCl \longrightarrow S_3N_2Cl + \frac{1}{2}S_2Cl_2 + NO + N_2$ (ref.42)(3.6a)

(ivb) $8(NSCl)_3 + 24NO \longrightarrow 6S_3N_2Cl + 12NOCl + 3S_2Cl_2 + 12N_2O$ (ref.42)(3.6b)

(v) $4S_4N_4 + 7.5AsF_5 \longrightarrow 4S_3N_2AsF_6 + 4N_2 + \frac{1}{2}S_8^{2+}(AsF_6^-)_2 + 2.5AsF_3$

(ref.43) (3.7)

(b) Physical properties

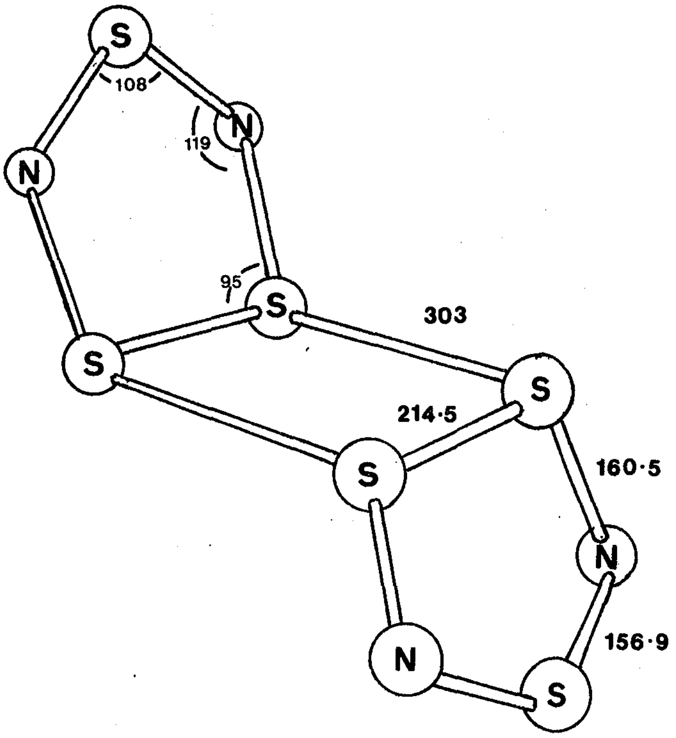
Thiodithiazyl chloride is normally obtained as a deep green powder which is mildly moisture sensitive. It is insoluble in the majority of solvents but can be dissolved to a small extent in sulphur dioxide although decomposition to thiotrithiazyl chloride does occur if the solution is warmed above ca. 35°C for prolonged periods.[44]

(c) Structure of thiodithiazyl chloride

N.Q.R. measurements on thiodithiazyl chloride indicate that the chlorine exists as a chloride ion.[45] Thus the $S_3N_2^+$ cation is postulated to be a 7π-electron cation in either a monomeric or polymeric form. The crystal structures of both the hexafluoroarsenate(V)[43] and chloro-disulphate[46] salts have been determined and a S_3N_2 ring of similar dimensions deduced. The existence of the species as a monomer or dimer was however in dispute for a period of time. Banister *et al* determined the chloro-disulphate salt to be dimeric whereas Gillespie *et al* believed that the hexafluoroarsenate(V) salt was a monomer having a five line E.S.R. spectrum. Recent work by Gillespie has however concluded that the system is dimeric with a low concentration (approx. 1 in 10^6) of monomer units, which cause the observed E.S.R. spectrum.

The crystal structure of the chloro-disulphate salt is presented in figure 3.2.

Figure 3.2 X-ray Crystal Structure of the $(S_3N_2^+)_2$ cation in $(S_3N_2^+)_2$ $(ClS_2O_6^-)_2$ [46]



(d) The Reactions of Thiodithiazyl Chloride

To date there are only two types of reactions that have been studied.

(i) The thermal decomposition of thiodithiazyl chloride:

$$S_3N_2Cl_2 \xrightarrow[80^\circ C \text{ } \textit{in vacuo}]{\Delta} S_3N_2Cl \xrightarrow[120\text{-}140^\circ C \text{ } \textit{in vacuo}]{\Delta} S_4N_3Cl \quad \text{(ref.5)} \qquad (3.8)$$

(ii) The formation of salts:

$$2S_3N_2Cl + 2HSO_3Cl \longrightarrow (S_3N_2^+)_2\ (S_2O_6Cl^-)_2 + 2HCl \quad \text{(ref.46)} \qquad (3.9)$$

$$S_3N_2Cl + 3H_2S_2O_7 \longrightarrow S_3N_2^+HS_3O_{10}^- + HSO_3Cl + 2H_2SO_4 \quad \text{(ref.47)} \qquad (3.10)$$

$$S_3N_2Cl + MCl_3 \xrightarrow[SOCl_2]{} S_3N_2Cl^+\ MCl_4^- \quad \text{(ref.46)} \qquad (3.11)$$

(M = Fe, Al)

(e) Formation of Related Species

Recent work by Street *et al*[48] has produced two closely related compounds, $SSe_2N_2^+Cl^-$ and $SSe_2N_2^+Br^-$ (equation 3.12). Both these compounds are postulated to be dimeric with a 4 centre (seleniums), 2 electron bridge (c.f. figure 3.2, page 107).

$$2SeX_4+Se_2X_2+2\left[(SiMe_3)_2N\right]_2 S \longrightarrow (SSe_2N_2X)_2+8Me_3SiX \quad \text{(Equ.3.12)}$$

3.1.3 Chlorothiodithiazyl Chloride ($S_3N_2Cl_2$)

Chlorothiodithiazyl chloride can be regarded as the pivot point in the series of sulphur-nitrogen compounds with associated chlorine atoms. It is the only cyclic sulphur-nitrogen species known that possesses both covalently bound and ionic chlorine.

(a) Preparation of Chlorothiodithiazyl Chloride

$$4S_2Cl_2+2NH_4Cl \longrightarrow S_3N_2Cl_2+8HCl+5S \qquad \text{(refs.1,5)} \quad (3.13)$$

$$S_3N_2Cl+MCl_3 \longrightarrow S_3N_2Cl^+MCl_4^- \qquad \text{(ref.46)} \quad (3.14)$$

$$(M = Al, Fe)$$

The primary synthetic route to $S_3N_2Cl_2$ is via disulphur dichloride and ammonium chloride, the product crystallising out on the walls of the air condenser. Jolly[1] quotes a yield of 12g of product from 100g NH_4Cl and 100cm^3 S_2Cl_2.

Yields of > 25g per 100g NH_4Cl and 100cm^3 S_2Cl_2 have been obtained in this thesis (ca. 40-50% yield based on S_2Cl_2).

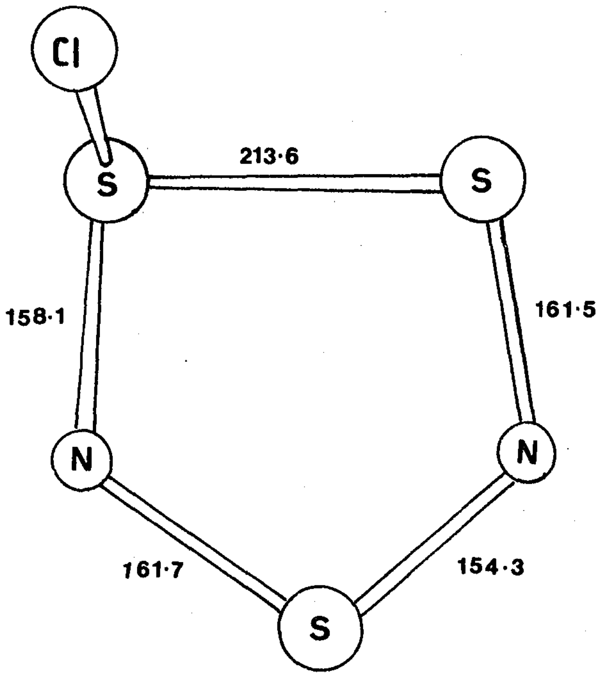
(b) Physical properties

Chlorothiodithiazyl chloride is normally obtained as large orange-red crystals which conglomerate forming a solid mass. It is highly moisture sensitive, rapidly darkening to give a black surface coating on exposure to moisture. Chlorothiodithiazyl chloride is only slightly soluble in the majority of polar and coordinating solvents and is insoluble in non polar oganic solvents.

(c) Structure of the Chlorothiodithiazyl Cation

The X-ray crystal structure of the chlorothiodithiazyl cation was determined by Zalkin *et al* (1966).[49] The structure showed that $S_3N_2Cl_2$ was an ionic species with one chlorine covalently bound to a sulphur and the other anionic. The sulphur atom to which the chlorine is covalently bonded is out of plane with the remaining "S_2N_2" fragment which, is itself virtually planar. The structure of the chlorothiodithiazyl cation is shown in figure 3.3.

Figure 3.3 Structure of the Chlorothiodithiazyl Cation[49]



(d) Reactions of Chlorothiodithiazyl Chloride

The chemistry of the chlorothiodithiazyl cation is not highly developed, even though it is probably the most readily synthesised sulphur-nitrogen compound. It is however a key material in the production of the other cyclic sulphur-nitrogen cations and trichlorotrithiatriazene.

(i) Formation of other Sulphur-Nitrogen Ring Systems:

$3S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2S_4N_3Cl + 3SCl_2$ (ref.5) (3.15)

$3S_3N_2Cl_2 \xrightarrow{\Delta} 2S_3N_2Cl + 2NSCl + SCl_2$ (ref.5) (3.16)

$3S_3N_2Cl_2 + 3Cl_2 \longrightarrow 2(NSCl)_3 + 3SCl_2$ (ref.5) (3.17)

(ii) Salt Formation:

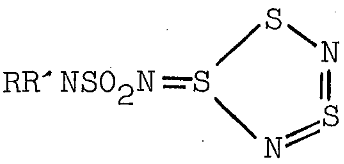
$S_3N_2Cl_2 + MCl_3 \xrightarrow[SOCl_2]{} S_3N_2Cl^+MCl_4^-$ (ref.50) (3.18)

(M = Al, Fe)

$S_3N_2Cl_2 + HSO_3F \longrightarrow S_3N_2Cl^+SO_3F^- + HCl$ (ref.50) (3.18)

(iii) Reactions with Organometallic compounds:

$S_3N_2Cl_2 + 2PhMgCl \longrightarrow S_3N_2Ph_2 + 2MgCl_2$ (ref.51) (3.19)

$RR'NSO_2N(SiMe_3)_2 + S_3N_2Cl_2 \longrightarrow$  $+ 2Me_3SiCl$

(ref.52) (3.20)

$P_3N_3F_5N(SnMe_3)_2 + S_3N_2Cl_2 \longrightarrow P_3N_3F_5S_3N_3 + 2Me_3SnCl$ (ref.53)(3.21)

3.1.4 Trichlorotrithiatriazene $(NSCl)_3$

Trichlorotrithiatriazene is the trimeric form of thiazyl chloride (NSCl) and is a neutral species, all the chlorines being covalently bound to sulphurs.

(a) Preparation of Trichlorotrithiatriazene

(i) From other Sulphur-Nitrogen Heterocycles:

$3S_4N_4 + 6Cl_2 \longrightarrow 4(NSCl)_3$ (ref.54) (3.22)

$3S_3N_2Cl_2 + 3Cl_2 \longrightarrow 2(NSCl)_3 + 3SCl_2$ (ref.4) (3.23)

$3S_4N_4 + 6SO_2Cl_2 \longrightarrow 4(NSCl)_3 + 6SO_2$ (ref.55) (3.24)

$3S_3N_2Cl_2 + 3SO_2Cl_2 \longrightarrow 2(NSCl)_3 + 3SO_2 + 3SCl_2$

(ref.55) (3.25)

(ii) From Ammonium Chloride and Disulphur Dichloride:

$6S_2Cl_2 + 3NH_4Cl \longrightarrow (NSCl)_3 + \frac{9}{8}S_8 + 12HCl$ (ref.1)(3.26)

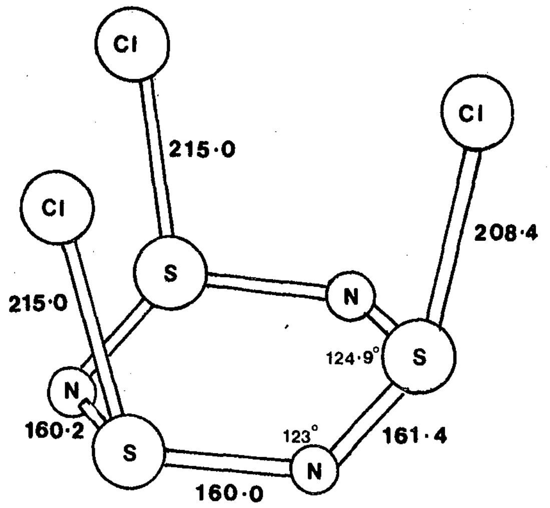
(b) Physical Properties

$(NSCl)_3$ forms yellow platelets of density 2.09g cm^{-3}. It is highly moisture sensitive, decomposing with the evolution of sulphur dioxide and the formation of ammonium chloride. The trimer is highly soluble in carbon tetrachloride and benzene, forming a mint green solution above ca.60°C. If however chlorine is bubbled through a refluxing solution of $(NSCl)_3$ in carbon tetrachloride, the green colouration is not observed. It is recommended by Jolly[56] that chlorine be passed through the recrystallisation solvent if a very high purity product is required.

(c) Structure of Trichlorotrithiatriazene

The crystal structure of $(NSCl)_3$ was first determined by Wiegers *et al* (1962)[57] who later refined the structure (1966).[58] The structure of trichlorotrithiatriazene is presented in figure 3.4.

Figure 3.4 Structure of Trichlorotrithiatriazene[58]



It is concluded from the relatively short, equi-distant, S-N bond lengths that a delocalised π-system is present in trichlorotrithiatriazene.[58]

(d) The reactions of Trichlorotrithiatriazene

(i) The reactions of trichlorotrithiatriazene with alkenes and nitriles have been discussed in Chapter Two (page 24).

(ii) The fluorination of trichlorotrithiatriazene is discussed in Chapter Four (page 158).

(iii) The reactions of trichlorotrithiatriazene with Lewis acids are discussed in Chapter Five (page 225).

(iv) The formation and reactions of thiazyl chloride are discussed in Chapter Five (page 228).

(v) The reaction of trichlorotrithiatriazene with transition metal complexes:

$Mo(CO)_6 + (NSCl)_3 \longrightarrow MoS_3N_3Cl_3 + 6CO$ (ref.59) (3.27)

$Na\left[(\eta^5C_5H_5)Cr(CO)_3\right] + (NSCl)_3 \longrightarrow (\eta^5C_5H_5)Cr(CO)_2NS$ (ref.60) (3.28)

(vi) The reaction of trichlorotrithiatriazene with N-H groups:

(a) <u>With Sulphur Imides:</u>

$4(NSCl)_3 + 3S_4N_4H_4 \longrightarrow 6S_4N_4 + 12HCl$ (ref.61) (3.29)

$(NSCl)_3 + 3S_7NH \longrightarrow 3S_4N_2 + 3HCl + {}^{12}/_8\ S_8$(ref.62)(3.30)

$2(NSCl)_3 + 6S_7NH \longrightarrow 3S_4N_4 + 6HCl + {}^{9}/_2\ S_8$(ref.3) (3.31)

(b) <u>With Organic Imides:</u>

$C_6F_5SN(H)SC_6F_5 + (NSCl)_3 \longrightarrow C_6F_5SN{:}S{:}NSC_6F_5$ (ref.62) (3.32)

$(Me_3Si)_2NH + (NSCl)_3 \longrightarrow Me_3SiN{:}S{:}NSiMe_3$ (ref.63) (3.33)

(c) <u>Reaction with Ammonia</u>:

$(NSCl)_3 + NH_3 \xrightarrow{-78^\circ C} NH_4^+\ (S_4N_5^-)$ (ref.64) (3.34)

(vii) Reaction of trichlorotrithiatriazene with trimethyl silane derivatives:

$(NSCl)_3 + Me_3SiNSNSiMe_3 \longrightarrow S_4N_5^+Cl^- + 2Me_3SiCl$ (ref.65) (3.35)

3.2 Experimental

3.2.1 Reductions of Sulphur-Nitrogen Species by Iodide

(i) The solid phase halide transport reaction between S_3N_2Cl and KI

Approximately 0.1g (0.63 mmole) of S_3N_2Cl was ground with dry potassium iodide (0.2g, 1.2 mmole) under dry box conditions. The mixture was then pressed into a disc (3000 lb. in^{-2}) and the infra-red spectrum recorded. A control disc was also made from potassium chloride and thiodithiazyl chloride. No shifting in peaks was noted for the KCl/S_3N_2Cl disc relative to the infra-red spectrum of S_3N_2Cl recorded using a nujol mull. Distinct and substantial shifts were however noted in the S_3N_2Cl/KI disc relative to the S_3N_2Cl/KCl disc.

Infra-red spectrum of the S_3N_2Cl/KI disc: 1400 w.br, 928s, 728m, 700s, 552s, 348s cm^{-1}.

(cf. S_4N_4 (main peaks) 925s, 719s, 696s, 557s, 552s, 347s cm^{-1}).[66]

(ii) Solid phase reaction between S_3N_2Cl and NaI

S_3N_2Cl (4.83g, 30.28 mmole) was ground with dry NaI (10.29g, 68.60 mmole) at room temperature, under dry box conditions. The mixture was then loaded into a soxhlet extraction thimble and extracted with 1,4-dioxan (100 cm^3). A deep brown solution was obtained which, after cooling and evaporating down to 20 cm^3, yielded a brown precipitate.

Infra-red spectrum of the brown precipitate (nujol mull): 928s, 728m, 700s, 555s, 345s cm^{-1}. (cf. S_4N_4)[66]

(iii) Reaction of S_3N_2Cl with NaI in nitromethane (CH_3NO_2)

To a slurry of S_3N_2Cl (2.13g, 13.4 mmole) in refluxing CH_3NO_2 (40 cm^3) was added dry, powdered NaI (4.00g, 26.7 mmole). The reaction was refluxed for 6h. and the resulting deeply coloured solution filtered hot and allowed to cool slowly to room temperature. The solvent was then removed, by the passage of dry nitrogen across the surface of the solution, and a red-brown residue obtained (1.51g). The crude material was recrystallised from benzene (15 cm^3) and the orange crystals formed on cooling were isolated and their infra-red spectrum recorded.

Infra-red spectrum of the crystalline material (nujol mull):

930s, 726m, 700s, 550s, 350s cm^{-1} (cf. S_4N_4)[66]

(yield of S_4N_4 : 0.62g, 50% based on S_3N_2Cl)

(iv) Reaction of S_4N_3Cl with NaI in CH_3NO_2

To a slurry of S_4N_3Cl (1.46g, 7.1 mmole) in refluxing CH_3NO_2 (30 cm^3) was added pre-dried, powdered, NaI (1.52, 10.1 mmole). The solution rapidly deepened in colour forming a very deep red-purple solution. A purple haze was noted in the flask. After refluxing for 40 min. the system was filtered hot and the filtrate evaporated to dryness using a stream of dry nitrogen across the surface of the solution. The crude product (1.24g) was recrystallised from benzene (20 cm^3) and the resulting orange needles isolated. The infra-red spectrum of the crystals was recorded.

Infra-red spectrum of the crystals (nujol mull):

930s, 728m, 700s, 555s, 350s cm^{-1}(cf. S_4N_4)[66]

(v) Reduction of S_3N_2Cl by saturated aqueous solution of NaI

NaI (1.93g, 12.87 mmole) was dissolved in ice cold distilled water (10 cm^3) and the resulting solution poured on to carbon tetrachloride (30 cm^3). To the vigorously stirred two phase system was added S_3N_2Cl (0.81g, 5.08 mmole). A rapid reaction occurred forming a deeply coloured solution. After stirring for 10 min. the two phases were allowed to separate and it was noted that the CCl_4 phase was deep purple-red in colour. The carbon tetrachloride phase was isolated and the solvent removed. The resulting residue was washed with methanol (2 x 10 cm^3) and dried *in vacuo*.

Infra-red of the product (nujol mull): 3200 m.br, 1415m, 1240m, 1200m, 1020m, 930s, 730s, 700s, 660w, 602m, 560s, 350s cm^{-1}. (cf. S_4N_4)[66]

(vi) Reaction of S_4N_3Cl with NaI in Sulphur Dioxide (SO_2)

S_4N_3Cl (1.24g, 6.03 mmole) and NaI (1.86g, 12.40 mmole) were placed in a 100 cm^3 flask and SO_2 (15 cm^3) condensed in. The reaction was stirred at -12°C for 4h. The initial yellow colouration deepened slowly to an intense orange-red over the 4h. The SO_2 was then removed and part of the residue (ca. 0.1g) shaken with CCl_4 (2 cm^3). No purple colouration in the CCl_4 was seen.

Infra-red spectrum of the red product (nujol mull): 1165s, 1000vs, 675s, 562m, 470vs cm^{-1} (cf. S_4N_3Cl[6])

3.2.2 Reduction of Sulphur-Nitrogen Species by the Sodium salts of the Oxy-acids of Sulphur

(i) Reduction of S_3N_2Cl by Sodium Metabisulphite ($Na_2S_2O_5$)

To a stirred, refluxing, slurry of S_3N_2Cl (10.58g, 66.33 mmole) in nitromethane (100 cm^3) was added $Na_2S_2O_5$ (14.23g, 74.9 mmole). An immediate reaction occurred evolving a gas (identified as SO_2). The system was refluxed for 4h. until no further evolution of gas was noted and filtered hot. On cooling the filtrate orange crystals were deposited. These crystals were isolated and the filtrate pumped to dryness. The resulting residue was then washed with ice cold water (3 x 10 cm^3), ethanol (2 x 5 cm^3) and ether (2 x 5 cm^3) and dried *in vacuo*. The crude product was then recrystallised from benzene (45 cm^3) yielding orange crystals.

Infra-red spectrum of the product (nujol mull): 1170vw, 930s, 732m, 704vs, 555s, 350s cm^{-1} (cf. S_4N_4)[66]

(yield of S_4N_4 : 3.24g, 53% based on S_3N_2Cl)

(ii) Reduction of $S_3N_2Cl_2$ by $Na_2S_2O_5$ in CH_3NO_2

To a stirred, refluxing, slurry of $S_3N_2Cl_2$ (6.13g, 31.44 mmole) in CH_3NO_2 (50 cm^3) was added $Na_2S_2O_5$(10.14g, 53.37 mmole). A deep red solution was rapidly formed as was a green-black residue. The reaction was refluxed for 16h, filtered hot and cooled slowly to room temperature. The large orange crystals formed on cooling the filtrate were filtered off and the filtrate evaporated to dryness using a stream of dry nitrogen. The residue was washed and dried as in experiment 3.2.2(i) and the product recrystallised from 1,4-dioxan, the product being deposited as orange needle shaped crystals.

Infra-red spectrum of the product (nujol mull): 932s, 733m, 706s, 560s, 355s cm^{-1} (cf. S_4N_4)[66]

Analysis found; N, 28.13%, S_4N_4 requires; N, 30.43%

(yield of S_4N_4 1.06g, 37% based on $S_3N_2Cl_2$)

(iii) Reduction of S_4N_3Cl by $Na_2S_2O_5$ in CH_3NO_2

To a refluxing solution of S_4N_3Cl (2.33g, 11.34 mmole) in CH_3NO_2 (25 cm^3) was added $Na_2S_2O_5$ (2.41g, 12.68 mmole). A rapid reaction occurred producing a deep red solution and gradually over a period of 20 min. all traces of S_4N_3Cl disappeared. The reaction was refluxed for 2h., filtered hot and allowed to cool slowly to room temperature. Orange crystals were deposited on cooling and these were filtered off. The filtrate was evaporated to dryness and the residue washed as in experiment 3.2.2(i). The resulting product was soxhlet extracted using benzene (25 cm^3) and an orange crystalline material obtained.

Infra-red spectrum of the product (nujol mull): 930s, 731m, 705s, 555s, 348s cm^{-1} (cf. S_4N_4)[66]

Analysis found; N, 26.84%, S_4N_4 requires 30.43%.

(yield of S_4N_4, 0.83g, based on S_4N_4Cl, 40%)

(iv) Reduction of S_4N_3Cl by a Saturated Aqueous solution of $Na_2S_2O_5$

$Na_2S_2O_5$ (4.23g, 22.26 mmole) was dissolved in ice cold water (20 cm^3) and S_4N_3Cl (1.94g 9.44 mmole) added to the vigorously stirred solution. A rapid reaction occurred forming a deep green suspension. The reaction was stirred for 15 min., filtered and the residue washed with ice cold water (4 x 10 cm^3), ethanol (2 x 5 cm^3) and ether (2 x 10 cm^3) and dried *in vacuo*.

Infra-red spectrum of the product (nujol mull): 3150m.br, 1415s, 1235s, 1205s, 1050m, 1015s, 930s, 730s, 702s, 662w, 605m, 560s, 528s, 350s cm^{-1}.(cf. S_4N_4)[66]

(v) Reaction of S_3N_2Cl with Sodium Dithionite ($Na_2S_2O_4$) in CH_3NO_2

To a refluxing suspension of S_3N_2Cl (4.32g, 27.08 mmole) in CH_3NO_2 (100 cm^3) was added sodium dithionite (6.16g, 35.4 mmole). A rapid reaction occurred yielding a deep orange-red solution and a finely divided yellow precipitate. The system was refluxed for 4h., filtered hot and cooled to room temperature. The precipitate was washed with ice cold water to remove any $Na_2S_2O_4$ and then by ethanol (2 x 10 cm^3) and ether (2 x 10 cm^3). The yellow product was then dried *in vacuo* and its infra-red spectrum recorded.

Infra-red spectrum of the product (nujol mull): 1165m, 1000s, 685m, 570m, 475m cm^{-1}. (cf. S_4N_3Cl[6])

3.2.3 Reduction of Sulphur-Nitrogen Systems by Metals

(a) The Reduction of S/N compounds by Metals using Organic Solvents

The reductions of S/N compounds by metals using organic solvents involved essentially the same experimental technique in each case, the results of which are presented in table 3.1.

Experimental technique

To a stirred slurry/solution of the S/N species was added excess metal powder. The reaction was monitored by T.L.C., using a standard S_4N_4 sample for comparison. If the rate of reaction was low at room temperature the system was refluxed until complete reaction had occurred. The reaction mixture was then filtered and the precipitate and excess metal washed with 1,4-dioxan. The filtrate was evaporated to dryness and the residue obtained extracted with benzene. The product was isolated and the infra-red spectrum, yield and analyses obtained where applicable.

TABLE 3.1 The reduction of S/N compounds by metals using organic solvents

S/N compound	Metal	Solvent (cm^3)	Conditions	Product	Yield (S_4N_4)
S_3N_2Cl	Fe	CH_3NO_2	R.T.	S_4N_4, S_4N_2	28%
		$C_2H_4Cl_2$	Reflux	S_4N_4, S_4N_2	
S_3N_2Cl	Zn	T.H.F.	R.T.	S_4N_4, S_4N_2	
S_3N_2Cl	Hg	CH_3NO_2	R.T.	S_4N_4	
S_3N_2Cl	Al	CH_3NO_2	R.T.	Not identified	
S_3N_2Cl	Mg	CH_3NO_2	R.T.	S_4N_4, S_4N_2	
S_3N_2Cl	Cu	CH_3NO_2	R.T.	Not identified	
S_4N_3Cl	Zn	THF	Reflux	S_4N_4, S_4N_2	60%
		Monoglyme	Reflux	S_4N_4, S_4N_2	
S_4N_3Cl	Fe	CH_3NO_2	Reflux	S_4N_4, $S_4N_3FeCl_4$	
		T.H.F.	Reflux	S_4N_4	60%
		Monoglyme	Reflux	S_4N_4	
S_4N_3Cl	Mg(*)	T.H.F.	Reflux	S_4N_4	
S_4N_3Cl	Ag	T.H.F.	Reflux	No reaction	
S_3N_2Cl	Fe	T.H.F.	Reflux	S_4N_4	35%
		CH_3NO_2	Reflux	S_4N_4	
$S_3N_2Cl_2$	Zn	Toluene	Reflux	Deep red low melting product possibly S_4N_2	
$(NSCl)_3$	Fe	Monoglyme	R.T.	S_4N_4	67%

(* Activated magnesium isolated from a Grignard reaction).

(b) Reaction of Potassium with S_3N_2Cl using 1,4-Dioxan as a solvent

To a refluxing slurry of S_3N_2Cl (1.84g, 11.54 mmole) in 1,4-dioxan (50 cm^3) was added small freshly cut pieces of potassium. A rapid reaction occurred yielding a deep red solution. The thin layer chromatogram was run of this solution using a standard S_4N_4 sample for comparison (eluting solvent benzene; R_f values of the spots = 0.93 (S_4N_2) and 0.84 (S_4N_4)). Addition of excess potassium to the system caused the solution colour to change to deep blue-purple and then with more potassium to a very deep purple. The thin layer chromatogram indicated that no S_4N_4 remained in solution. The reaction was terminated at this point.

(c) The Reduction of S/N compounds by Metals using Sulphur Dioxide as a Solvent

(i) Reduction of S_4N_3Cl by Iron powder

S_4N_3Cl (1.06g, 5.16 mmole) and Fe powder (1.28g, 22.86 mmole) were placed in a pre-dried, vacuum tight pyrex vessel, (figure 1. 1, page 14) and sulphur dioxide (12.43g) condensed in. An orange-red solution was formed which did not alter over 22h. of agitation. The sulphur dioxide solubles were filtered off and the insolubles washed ca. 20 times to remove all the soluble fraction. The solvent was then slowly evaporated off leaving an orange-red residue (0.98g).

Infra-red spectrum of the residue (nujol mull): 1165w, 1000m, 930s, 730m, 700s, 675w, 550s, 470w, 370s, 355s cm^{-1}.
(cf. S_4N_4,[66] S_4N_3Cl[6])

(ii) Reaction of $(NSCl)_3$ with Fe powder

$(NSCl)_3$ (0.69g, 2.82 mmole) and Fe (1.57g, 28.04 mmole) were loaded in to a pre-dried, vacuum tight, pyrex vessel (figure 1.1 , page 14), and sulphur dioxide (7.19g) condensed in. Initially a pale green solution was formed but after agitating at room temperature for 30 min. a deep orange-red solution was produced. The reaction was agitated at room temperature for a further 5h. to ensure complete reaction and then the solubles filtered off. The residue was washed with SO_2 until no further evidence of any solubles was noted and then the solvent slowly removed, resulting in the formation of a deep orange-red microcrystalline product (0.52g).

Infra-red spectrum of the product (nujol mull): 1130s,br, 1050w,br, 730m(sh), 720m, 529s, 515m(sh), 370vs, cm^{-1}.

Raman spectrum of the product (red line) 736w, 675m, 650m(sh), 610s, 385s, 330s, 268m, 335vs, 186vs, 133m cm^{-1}.

(cf. Infra-red spectrum $S_5N_5^+FeCl_4^-$: 1143s, 1047w, 1017vw, 731m, 721m(sh), 685m, 608m, 528s, 370s, 327s cm^{-1}).[31]

(iii) Reaction of $S_3N_2Cl_2$ with Fe powder

$S_3N_2Cl_2$ (0.65g, 3.33 mmole) and Fe powder (1.16g, 20.7 mmole) were placed in a pre-dried, vacuum tight pyrex vessel (figure 1.1 , page 14) and SO_2 (8.43g) condensed in. A deep orange solution was immediately formed which did not change in appearance over the period of 6h. of agitation. The solubles were completely filtered off from the excess iron and the sulphur dioxide slowly removed,yielding a bright orange-red microcrystalline species (0.63g).

Infra-red of the orange product (nujol mull): 1165w, 1028m, 990m, 925m(sh), 914m, 864vs,br, 750m(sh), 730s, 710m, 685s, 680m(sh), 675m(sh), 668w(sh), 580m, 570w, 555w, 490m, 470m, 430m, 370vs cm^{-1}.

Analysis: found: S,38.9; N, 14.15; Fe,13.67; Cl,33.6%.
$S_5N_4FeCl_4$ requires: S,38.65; N,13.53; Fe,13.53; Cl,34.30%

(iv) Reaction of $(NSCl)_3$ with Zn/Cu couple

$(NSCl)_3$ (0.53g, 2.17 mmole) and Zn/Cu powder (1.56g, 23.86 mmole) were placed in a pre-dried vacuum tight pyrex vessel (figure 1. 1, page 14), and SO_2 (9.13g) condensed in. A very deep red solution was formed on warming to room temperature and this was agitated for 4h. The solubles were then removed and the residue washed with recondensed SO_2. During one washing of the insolubles an exothermic reaction occurred, in which the zinc was seen to burn in the atmosphere of sulphur dioxide producing a white compound (ZnO/ZnS). The reaction was terminated at this point.

(v) Reaction of $(NSCl)_3$ with Ag wool

$(NSCl)_3$ (0.59g, 2.41 mmole) and Ag wool (0.47g, 4.35 mmole) were placed in a pre-dried, vacuum tight pyrex vessel (figure 1. 1, page 14). The vessel was then evacuated. On evacuation it was noted that the silver became black in colour and a blue film was formed around the top of the containing bulb. The bulb was cooled to liquid nitrogen temperatures and the blue coloration took on a bronze metallic appearance. Sulphur dioxide (5.32g) was then added to the system and the film dissolved yielding a very deep green solution. The vessel was agitated at room temperature for 28h., during which time the colour of the solution changed to pale orange. The solution was filtered and the residue washed with recondensed solvent to remove all the solubles. The solvent was then slowly evaporated leaving an intractable tar from which it proved impossible to remove all the sulphur dioxide. The experiment was thus abandoned.

The reaction of thiazyl chloride (NSCl) with silver metal was investigated and is reported in Chapter Five (page 238).

(vi) Reaction of $(NSCl)_3$ with Hg.

$(NSCl)_3$ (0.64g, 2.62 mmole) and Hg (28.42g, 141.7 mmole) were placed in a pre-dried, vacuum tight pyrex vessel (figure 1. 1 , page 14) and SO_2 (9.13g) condensed in. The reaction was agitated for 16h. at room temperature and the resulting orange-red solution filtered off. The residue was washed with recondensed solvent to remove all the solubles. The solvent was then slowly evaporated from the filtrate leaving an orange residue.

Infra-red spectrum of the residue (nujol mull): 928s, 728m, 700s, 550s, 350s cm^{-1}. (cf. S_4N_4)^{66}

T.L.C. (benzene elutant) R_f. of product = 0.84 (cf. S_4N_4:R_f=0.84)

(vii) Reaction of $S_3N_2Cl_2$ with Hg

$S_3N_2Cl_2$ (1.72g, 8.82 mmole) and Hg (4.16g, 20.75 mmole) were placed in a pre-dried vacuum tight pyrex vessel (figure 1.1 , page 14) and SO_2 (12.63g) condensed in. The system was warmed to room temperature and the resulting orange-red solution agitated with the metal for 4h. The solubles were then completely removed into the second bulb and the solvent slowly removed from the system yielding an orange product. The SO_2 insoluble species was essentially excess mercury but had a pinkish tinge to it. The infra-red spectra and thin layer chromatograms of both SO_2 soluble and insoluble components were recorded.

Infra-red spectrum of the soluble product (nujol mull): 1165w, 920s, 725m, 695s, 545s, 340s cm^{-1} (cf. S_4N_4)^{66}

T.L.C. of soluble product (eluting solvent benzene) R_f=0.84 (cf. S_4N_4 R_f = 0.84).

Infra-red spectrum of the SO_2 insoluble product (nujol mull):
1015m, 970s, 959s, 945s, 715vs, 585m, 570m, 480m,br, 446m, 435m, 370s cm^{-1}.

The solubility of the pinkish SO_2 insolubles was tested in benzene, hexane and ether, in which it was found to be essentially insoluble. However with D.M.S.O., nitromethane and T.H.F. a red solution was formed. The compound was therefore extracted from the excess mercury using refluxing T.H.F. (20 cm^3) and the resulting deep red solution pumped to dryness. The infra-red spectrum and thin layer chromatogram of the product were recorded.

Infra-red spectrum (nujol mull): 1165w, 1022s, 928s, 726m, 700s, 650w, 629s, 550s, 373s, 345s cm^{-1} (cf. S_4N_4[66] and S_4N_2[67]). T.L.C. (eluting solvent benzene) R_f = 0.93 and 0.84. (cf.S_4N_4 R_f = 0.84; S_4N_2 R_f = 0.92).

3.2.4 Reduction of Sulphur-Nitrogen Compounds by Molten Salts

S_4N_3Cl (1.86g, 9.05 mmole) and pre-dried KCNS (2.13g, 21.96 mmole) were ground together in dry box conditions and the resulting mixture placed in a sublimation tube fitted with a liquid nitrogen cold finger. The tube was then evacuated and the temperature slowly raised to the melting point of the KCNS (oil bath temperature of 165°C). The volatile species produced at this temperature were sublimed on to the cold finger over a period of 4h. A deeply coloured sublimate was obtained which did not change in appearance on warming to room temperature. The vessel was left under vacuum for four months to allow any polymerisation to occur. The vessel was then opened under dry box conditions and the infra-red spectrum of the sublimate recorded.

Infra-red spectrum (nujol mull): 1165w, 1000w, 928s, 728m, 705vs, 675w, 552s, 348vs cm^{-1} (cf. S_4N_4[66] and S_4N_3Cl[6])

3.3 Discussion

It has been noted in this thesis (Chapter Two, page 28) that solid phase halide transport reactions occur on grinding potassium bromide or cesium iodide with 4-phenyl-1,2,3,5-dithiadiazolium chloride. Hence due to the similarities in the heterocyclic ring between the dithiadiazolium cation and the thiodithiazyl cation (both have a 5-membered ring, the $-CN_2S_2^+$ ring having 6π-electrons and the $S_3N_2^+$ cation having 7π-electrons), the solid phase halide transport reactions of S_3N_2Cl were investigated.

KCl, KBr and CsI discs of S_3N_2Cl were made and their infra-red spectra compared, using the KCl/S_3N_2Cl disc as a control. Little or no shifting of the peaks in the KBr/S_3N_2Cl disc relative to the KCl/S_3N_2Cl disc were noted whereas significant shifting in the bands occurred in the CsI/S_3N_2Cl disc, relative to the KCl/S_3N_2Cl disc. The infra-red spectrum of the CsI/S_3N_2Cl was compared with a series of standard infra-red spectra of sulphur-nitrogen systems and was concluded to be consistent with that of S_4N_4[66]. Thus a reduction of the thiodithiazyl cation appeared to have occurred.

There are very few examples of the reduction of sulphur-nitrogen cations, the only one being that reported by Muthmann and Clever (1896)[68] in which they reduced S_4N_3Cl to S_4N_4 and "S_5N_2" with zinc using methanol as a solvent. Reductions of S_4N_3Cl by HI and **KI** (in conc. HCl) were reported by Padma and Murthy[69] (1971) who reduced the $S_4N_3^+$ cation to sulphur or hydrogen sulphide, ammonia, hydrogen chloride and iodine.

It was therefore decided to investigate the reductions of the readily available sulphur-nitrogen cations ($S_4N_3^+Cl^-$, $S_3N_2^+Cl^-$ and $S_3N_2Cl^+Cl^-$) and trichlorotrithiatriazene $(NSCl)_3$.

3.3.1 The Reduction of Sulphur-Nitrogen Species by Iodide

Having observed the solid phase reduction of thiodithiazyl chloride (S_3N_2Cl) by iodide in an infra-red disc (experiment 3.2.1(i), page 114) preparative scale, solid phase reductions were investigated (experiment 3.2.1(ii), page 114). The product was separated by extraction using 1,4-dioxan, yielding a brown precipitate which was identified from its infra-red spectrum, to be S_4N_4[66]. Due to the low yield of product obtained by the solid phase reaction technique, solvents were sought in which solution reductions could be investigated. The relatively high dielectric constant of nitromethane ($\varepsilon = 35.9$)[70] and the absence of unsaturated centres and hydroxylic hydrogens, indicated that nitromethane would be a suitable solvent for the reduction of sulphur-nitrogen cations by iodides. Both S_4N_3Cl and S_3N_2Cl were successfully reduced by iodide in nitromethane solution yielding tetrasulphur tetranitride (experiments 3.2.1(iii),(iv), page 115). The yields recorded were not as high as initially expected. However these were improved by evaporating the solvent off using a stream of dry nitrogen, rather than pumping off the solvent under reduced pressure. The pumping off of the solvent under reduced pressure lowered the recorded yields due to S_4N_4 being removed with the solvent into the muck traps.

In an attempt to obtain high yields of S_4N_4 using cheap easily obtainable solvents, sulphur-nitrogen cations were reacted with saturated solutions of NaI in ice cold water, ethanol and methanol. In all cases hydrolysis of the S/N species occurred but some S_4N_4 was isolated. In the reaction of S_3N_2Cl with NaI in ice cold water (experiment 3.2.1(v), page 116), reduction was shown to occur by the formation of a red-purple carbon tetrachloride phase. The yield of S_4N_4 from experiment 3.2.1(v) was approximately 15% thus being a synthetically non-viable route to S_4N_4.

Sulphur dioxide was investigated as a possible solvent for the reduction of S_4N_3Cl by NaI (experiment 3.2.1(vi), page 116). The solubility of NaI in SO_2 is high (1.5g in 10g of SO_2 at $0^{o}C$)[71] and thus the NaI should be completely dissolved under the conditions employed in experiment 3.2.1(vi). The expected reduction did not however occur under these mild conditions, S_4N_3I being the only S/N product.

Although the reduction of S/N cations by iodide in nitromethane solution provided a useful route to crude S_4N_4, difficulty was found in separating the iodine, produced as a by-product of the reduction reactions, from the tetrasulphur tetranitride. Therefore reducing agents not producing a by-product that was difficult to separate from the reduced S/N species were sought.

3.3.2 Reduction of Sulphur-Nitrogen Species by the Sodium Salts of the Oxy-acids of Sulphur

The reduction of the sulphur-nitrogen cations ($S_4N_3^+Cl^-$, $S_3N_2^+Cl^-$ and $S_3N_2Cl^+Cl^-$) by sodium metabisulphite ($Na_2S_2O_5$) were investigated predominantly in nitromethane (CH_3NO_2) solutions (experiments 3.2.2(i)-(iii), pages 117-118). In all cases reduction of the cations to S_4N_4 occurred with the evolution of sulphur dioxide. The yields of S_4N_4 recorded were generally in the region 45-55%. Again yields of S_4N_4

were improved by the evaporation of the solvent at atmospheric pressure rather than at reduced pressure due to the removal of S_4N_4 into the muck traps with the solvent at reduced pressures. The lower than expected yields for the reduction reactions using sodium metabisulphite are thought to be due to the water of crystallisation possessed by the reducing agent ($Na_2S_2O_5 . 7H_2O$), which is difficult to remove without dissociating the salt into Na_2SO_3 and SO_2.

It is also noted that although sodium metabisulphite and sodium dithionite are generally regarded as reasonably strong reducing agents in aqueous solution, their reducing power is likely to be significantly modified in other solvents. This is typified by the reaction of S_3N_2Cl with sodium dithionite ($Na_2S_2O_4.2H_2O$) in CH_3NO_2, (experiment 3.2.2(v), page 119). No reduction reaction occurred using sodium dithionite as the reducing agent, the only reaction being the thermal cracking of S_3N_2Cl into S_4N_3Cl.[5]

The reduction of various sulphur-nitrogen systems by saturated, ice cold, aqueous solutions of sodium metabisulphite were investigated. The reaction of S_4N_3Cl with the aqueous reducing solution (experiment 3.2.2(iv), page 118) was the most successful, almost certainly due to the relative stability of the $S_4N_3^+$ cation to hydrolysis w.r.t. $S_3N_2^+$ and $S_3N_2Cl^+$. Tetrasulphur tetranitride was obtained in approximately 15% yields which, although significant due to the lack of complete hydrolysis of the reduction intermediates, was of little synthetic value.

Due to the problems of drying the metabisulphite and dithionite salts without their decomposition and due to their modified reducing power in aprotic solvents, no further investigations using these reducing agents were done. In order to avoid problems with water and unwanted side products the investigations were switched to the use of metals as reducing agents. Smith[72] and Fielder did however continue to study the reductions of S/N species by reducing anions e.g. $S_2O_3^{2-}$, $C_2O_4^{2-}$ and $H_2PO_2^{-}$, and recorded yields of S_4N_4 in the region of 40-60%.

3.3.3 The Reduction of Sulphur-Nitrogen Systems by Metals

There are numerous examples, in both main group and transition metal chemistry, of metals reacting with halogen containing organic species, forming the organometallic compound and the metal halide (equations 3.36-3.34).[73]

$$RX + 2Li \longrightarrow RLi + LiX \qquad (3.36)$$

$$4MeI + 2As \longrightarrow Me_4As^+I^- + AsI_3 \qquad (3.37)$$

$$ClSiMe_2CH_2Cl + Mg \longrightarrow (Me_2SiCH_2)_2 + MgCl_2 \qquad (3.38)$$

$$2CrCl_3 + 3Zn + 12CO \longrightarrow 2Cr(CO)_6 + 3ZnCl_2 \qquad (3.39)$$

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \longrightarrow 3\,(\pi\text{-}C_6H_6)_2Cr^+AlCl_4^- \qquad (3.40)$$

Hence it seemed likely that both main group and transition metals would reduce the sulphur-nitrogen cations and also trichlorotrithiatriazene, to S_4N_4 and the metal chloride. The postulated advantages of using metals as reducing agents were:

(a) the ease of removing all traces of moisture;

(b) the ease of separation of the excess metal and metal chloride from the reduced product;

(c) the expected non-participation of the metal chlorides in the reaction.

Various transition metals were successfully employed as reducing agents (Fe, Zn and Hg) in a number of organic solvents (CH_3NO_2, monoglyme, T.H.F. and 1,2-dichloroethane). Group I metals (Na and K) reacted with the sulphur-nitrogen species (experiment 3.2.3(a), page 119) initially producing S_4N_4 (identified from T.L.C.). Further reduction then occurred yielding initially a deep blue solution, then a purple solution which did not change colour on adding more reducing metal. It is likely that the blue and purple solutions observed are due to the presence of the $S_3N_3^-$ and $S_4N_5^-$ anions.[74] Due to their previous isolation and the highly explosive nature of the sulphur-nitrogen anions the salts were not isolated.

Probably the best synthetic routes to S_4N_4, by the reductions of S/N species using metals in organic solvents are:

(i) Reduction of $(NSCl)_3$ by Fe using monoglyme as a solvent.

(ii) Reduction of S_4N_3Cl by Fe using nitromethane as a solvent.

(iii) Reduction of S_4N_3Cl by Zn using T.H.F. as a solvent.

(iv) Reduction of S_3N_2Cl by Zn using T.H.F. as a solvent.

The reduction of S/N species by transition metals does, therefore present a convenient synthetic route to S_4N_4. There is however one major yield reducing factor. In certain cases the metal chloride produced as a by-product is Lewis acidic in nature. Thus it reacts with the chlorine containing S/N starting material, or an intermediate, forming the MCl_4^- anion which stabilises the S/N cation making the S/N species less prone to reduction (equation 3.41).

$$S_4N_3^+Cl^- + FeCl_3 \longrightarrow S_4N_3^+FeCl_4^- \qquad (3.41)$$

The formation of such salts is known to occur particularly when using CH_3NO_2 as a solvent, due to the isolation and characterisation of the salts from their infra-red spectra. Hence in the case of the reduction of S_4N_3Cl with Fe in CH_3NO_2, 25% of the S/N starting material is stabilised, w.r.t. reduction, as the $FeCl_4^-$ salt.

A second by-product formed in the reduction of $S_3N_2^+$, $S_3N_2Cl^+$ and $S_4N_3^+$ by metals is tetrasulphur dinitride (S_4N_2). Hence sulphur is not, as originally believed, formed in the primary reaction sequence. The overall equation for the reduction of $S_4N_3^+$ by Fe (in CH_3NO_2) must therefore take into account the formation of S_4N_4, S_4N_2 and $S_4N_3^+FeCl_4^-$ (equation 3.42).

$$\tfrac{16}{3}\ S_4N_3Cl + \tfrac{4}{3}\ Fe \xrightarrow[CH_3NO_2]{} 2S_4N_4 + 2S_4N_2 + \tfrac{4}{3}\ S_4N_3^+.FeCl_4^- \qquad (3.42)$$

The reduction of S_4N_3Cl by Fe using a coordinating ether as the solvent (monoglyme or T.H.F.) does not however produce an identical series of products. S_4N_4 and S_4N_2 are isolated but one species present in the insoluble products appears, from its infra-red spectrum (1280m, 1240m, 1180m, 1115m, 1065s, 1015s, 980m, 860s(sh), 850s, 800m, 555s, 410m, 370s, 355s cm^{-1}) to be the 1:1 adduct between $FeCl_3$ and monoglyme ($CH_3OCH_2CH_2OCH_3$).

(Infra-red spectrum of $FeCl_3:C_4H_{10}O_2$: 1282m, 1240m, 1200mw, 1181m, 1112m, 1065s, 1014vs, 980m, 862ms, 850s, 804m, 555m cm^{-1}).[75]

Hence the formation of the $S_4N_3^+FeCl_4^-$ salt is not observed due to the sequestering of the iron (III) chloride by the solvent. The effect of the solvent in determining the nature of the products is highlighted in the reduction of trichlorotrithiatriazene ($(NSCl)_3$) by iron, using as a solvent (i) monoglyme ($CH_3OCH_2CH_2OCH_3$) and (ii) nitromethane (CH_3NO_2). $(NSCl)_3$ was initially reduced by iron using monoglyme as the solvent and good yields of S_4N_4 were obtained (table 3.1, page 120). However subsequent work by Fielder, whilst attempting to increase the yield of S_4N_4, using CH_3NO_2 as the solvent, produced cyclopentathiapentazenium tetrachloroferrate (III) ($S_5N_5^+FeCl_4^-$) in yields of ca. 55%.

Hence the nature of the final product of the reaction was determined solely by the coordinating power of the monoglyme sequesting out the $FeCl_3$ which, in the case of the CH_3NO_2 reduction, entered into the reaction mechanism (equations 3.43, 44).

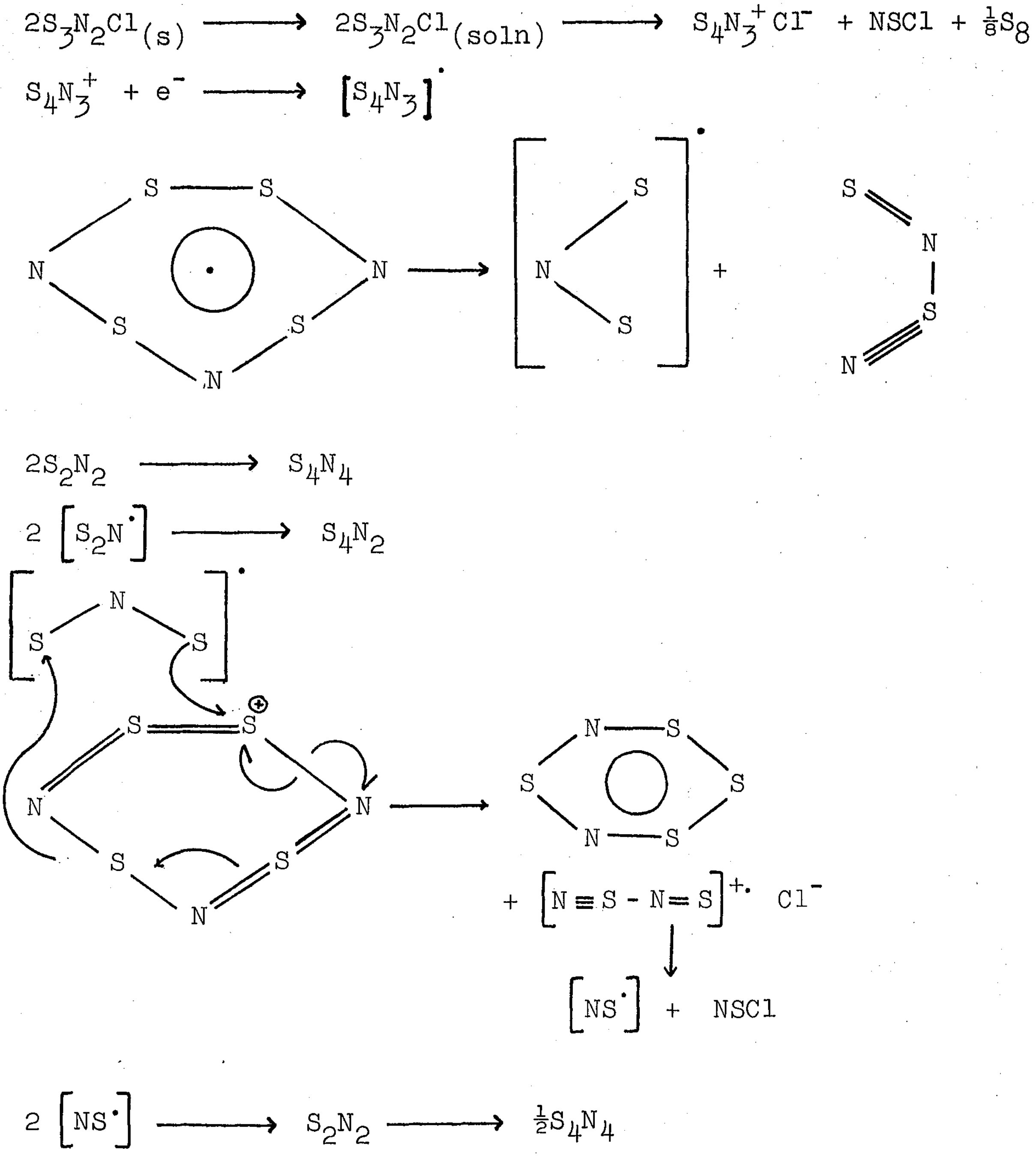
$$4(NSCl)_3 + 4Fe \xrightarrow[\text{monoglyme}]{} 3S_4N_4 + 4C_4H_{10}O_2 \cdot FeCl_3 \qquad (3.43)$$

$$5(NSCl) + 4Fe \xrightarrow[CH_3NO_2]{} 3S_5N_5^+FeCl_4^- + FeCl_3 \qquad (3.44)$$

The reaction of trichlorotrithiatriazene with tetrasulphur tetranitride and iron (III) chloride, has been reported by Banister and Dainty (1972),[31] to produce cyclopentathiapentazenium tetrachloroferrate (III). It can therefore be suggested that the initial reaction of iron with trichlorotrithiatriazene produces tetrasulphur tetranitride and iron (III) chloride, which in the presence of $(NSCl)_3$ reacts, by an identical mechanism postulated by Banister and Dainty, forming $S_5N_5^+FeCl_4^-$.

The reductions of S_4N_3Cl and S_3N_2Cl by metals are believed to follow essentially the same mechanistic route. It has been observed that on extracting S_3N_2Cl with refluxing CH_3NO_2, S_4N_3Cl is isolated as a fine yellow precipitate and $(NSCl)_3$ from solution. Hence it is concluded that the reductions of S_3N_2Cl in refluxing solvents probably proceed via S_4N_3Cl, the rate determining step being the rate at which S_4N_3Cl is produced. The first step in the mechanism in which both S_3N_2Cl and S_4N_3Cl are reduced by metals is, therefore, postulated to be a one electron reduction of the $S_4N_3^+$ cation. A suggested mechanism for the reduction of the $S_4N_3^+$ cation and subsequent formation of S_4N_4 and S_4N_2 is given in figure 3.5.

FIGURE 3.5 A possible mechanism for the reduction of $S_3N_2^+$ and $S_4N_3^+$ by metals and the subsequent rearrangement reactions.



$$2S_3N_2Cl_{(s)} \longrightarrow 2S_3N_2Cl_{(soln)} \longrightarrow S_4N_3^+Cl^- + NSCl + \tfrac{1}{8}S_8$$

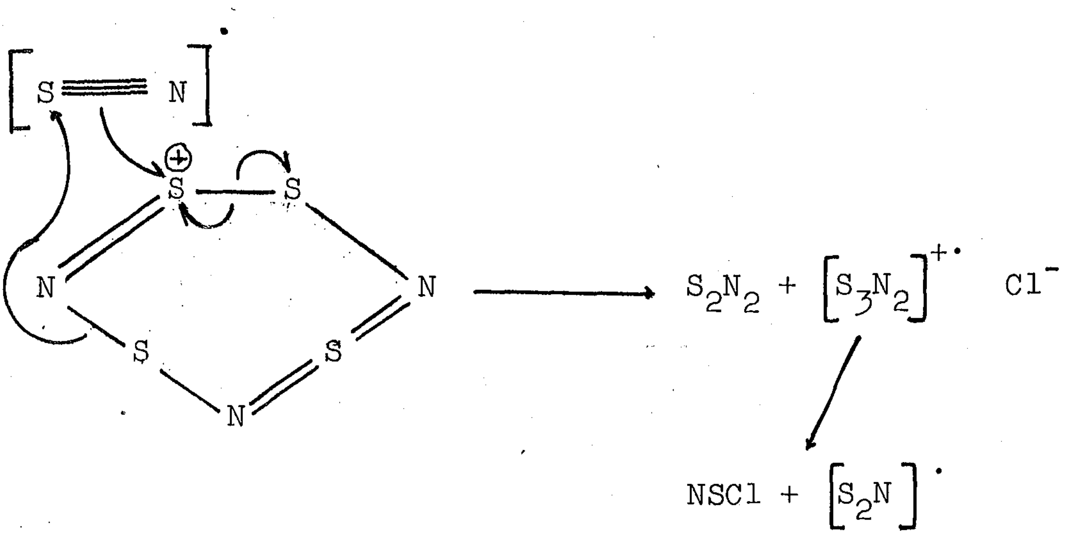
$$S_4N_3^+ + e^- \longrightarrow [S_4N_3]^{\bullet}$$

$$2S_2N_2 \longrightarrow S_4N_4$$

$$2\,[S_2N^{\bullet}] \longrightarrow S_4N_2$$

$$+\ [N\equiv S-N=S]^{+\bullet}\ Cl^- \longrightarrow [NS^{\bullet}] + NSCl$$

$$2\,[NS^{\bullet}] \longrightarrow S_2N_2 \longrightarrow \tfrac{1}{2}S_4N_4$$



$$4NSCl \xrightarrow{\text{Metal}} S_4N_4$$

$$2S_4N_2 \xrightarrow[\text{in solution}]{\Delta} S_4N_4 + 4S \qquad \text{(ref. 44)}$$

Smith[72] has shown that thermal cracking of S_4N_3Cl occurs in refluxing solutions of nitromethane, yielding S_4N_4 (cf. vapour phase cracking[76]).

The reactions of metals with sulphur-nitrogen species were, therefore, carried out in liquid sulphur dioxide at ambient temperatures in order to show that S_4N_4 is produced via a reduction mechanism and not via a thermal rearrangement process (section 3.2.3c, page 121). The main experiments of interest in this series of experiments are the reactions of chlorothiodithiazyl chloride ($S_3N_2Cl_2$) and trichlorotrithiatriazene ($S_3N_3Cl_3$) with the metals iron and mercury. Sulphur dioxide does not form stable isolatable complexes with Lewis acid chlorides (cf. monoglyme, THF[75]) and hence the formation of Lewis acidic chlorides will affect the course of the reaction to a greater or lesser extent depending upon the strength of the Lewis acid.

3.3 The Reactions of Sulphur Nitrogen Species with Metals using Sulphur Dioxide as a Solvent

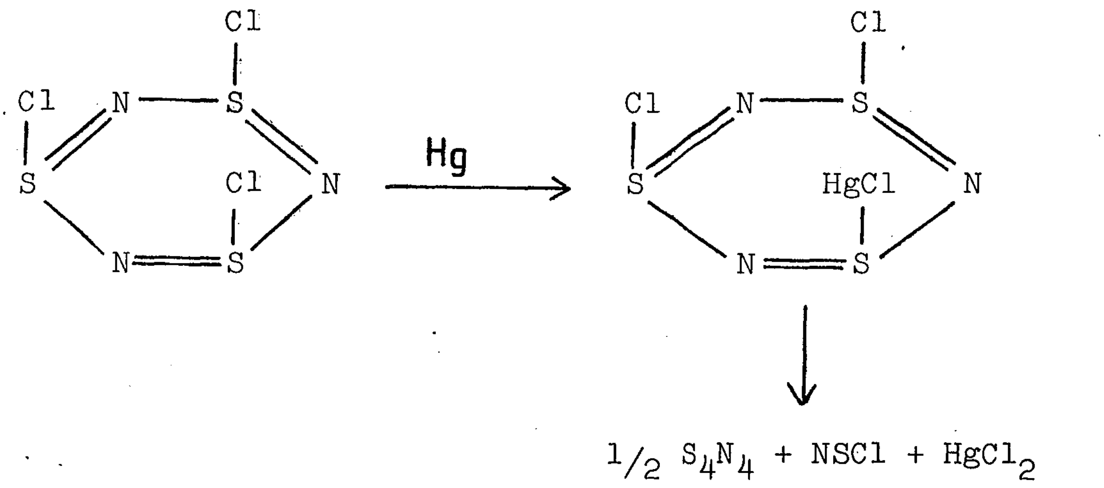
(i) The Reaction of Trichlorotrithiatriazene with Iron and Mercury

The reaction of trichlorotrithiatriazene with iron produced $S_5N_5^+FeCl_4^-$ (experiment 3.2.3(c,ii), page 121) in approximately 60% yields. The reaction was quite rapid being essentially complete within 30 min. The $S_5N_5^+$ salt is isolated in a virtually pure state, there being no S_4N_4 or S_4N_2 impurities. The salt is highly soluble in SO_2 crystallising out of the solvent as deep orange crystals.

The reaction of $S_3N_3Cl_3$ with excess mercury (experiment 3.2.3(c,vi), page 124) was very rapid, possibly due to the high surface area presented by the mercury. The product was filtered off from the excess mercury and identified by T.L.C. and infra-red spectroscopy as S_4N_4.

From the above results it is surmised that, as stated previously, the nature of the final products in the reduction of sulphur-nitrogen species by metals is a function of the Lewis acidic strength of the chloride formed as the by-product. The iron (III) chloride is a strong enough Lewis acid, in sulphur dioxide solution, to abstract chloride ions from either the sulphur-nitrogen starting material or an intermediate, thus forming an ionic product ($S_5N_5^+FeCl_4^-$). However mercury (II) chloride is not a powerful enough Lewis acid, in sulphur dioxide, to affect the basic reduction reaction and thus S_4N_4 is the sole sulphur-nitrogen product (figure 3.6).

Figure 3.6 A suggested mechanism for the reduction of trichlorotrithiatriazene by mercury



$$N \equiv S - Cl \xrightarrow{Hg} N \equiv S - Hg - Cl \xrightarrow{NSCl} {}^{1}/_{2}\ S_4N_4 + HgCl_2$$

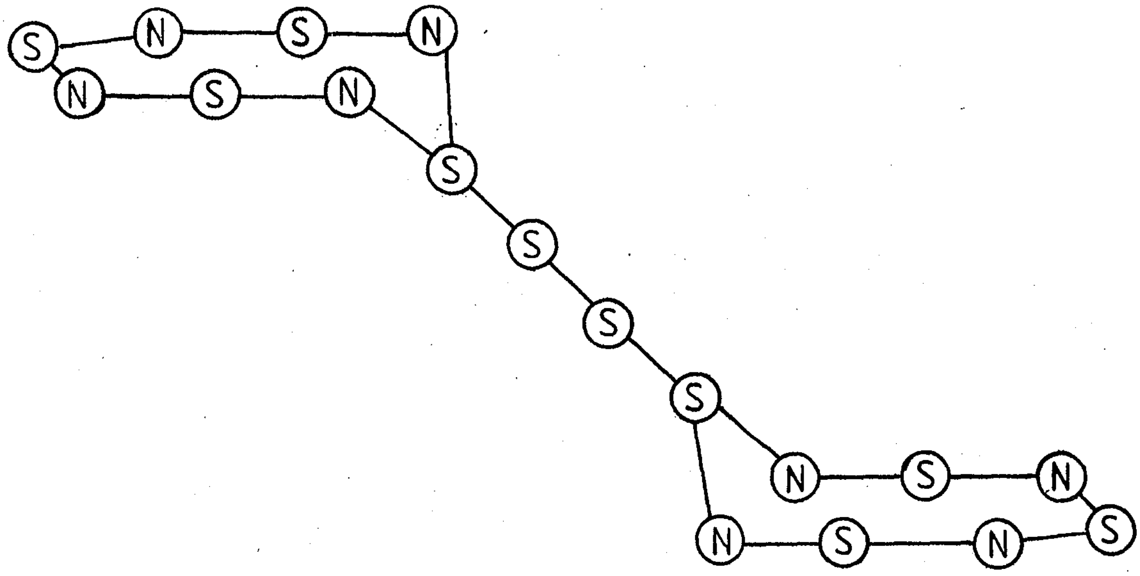
(ii) The Reaction of Chlorothiodithiazyl Chloride with Iron (experiment 3.2.3(c,iii), page 122)

As observed in the reaction of trichlorotrithiatriazene with iron, the formation of the iron (III) chloride intermediate plays a significant role in the determination of the overall mechanism of the reaction. The compound produced in the reaction of chlorothiodithiazyl chloride with iron is, as expected, by analogy with $S_3N_3Cl_3$/Fe reaction, the tetrachloroferrate (III) salt of a sulphur-nitrogen cation. The infra-red spectrum of the cation is however, significantly different from that of any of the sulphur-nitrogen cations previously synthesised. The compound was analysed as having the stoichiometry, $S_5N_4FeCl_4$. Using the guide-lines set down by Banister for calculating the number of π-electrons associated with sulphur-nitrogen heterocycles[77], it can be seen that the cation $S_5N_4^+$ is an odd electron species (cf. $S_3N_2^+$) and therefore the cation will probably exist as $S_{10}N_8^{2+}$.

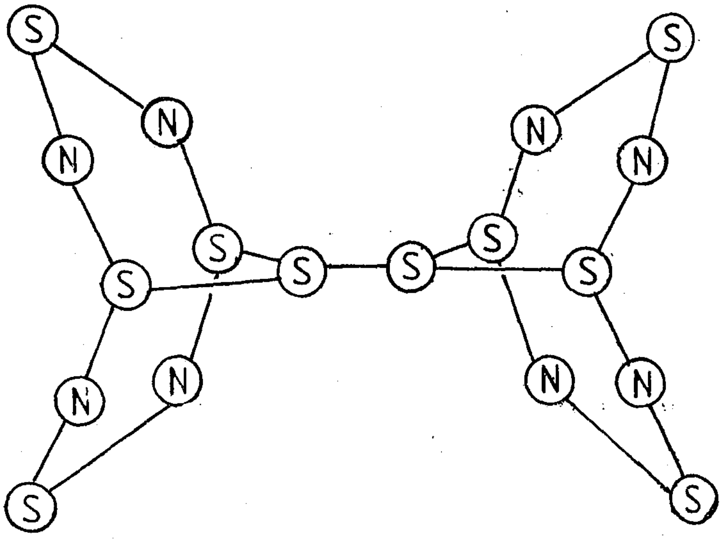
There are at least three possible structures for $S_{10}N_8^{2+}$. Two structures based on two $S_4N_4^+$ units connected by a disulphide bridge (figures 3.7a,b) and one structure based on a S_4N_4 cage and two $S_3N_2^+$ units (figure 3.7c).

Figure 3.7 Structures based on two $S_4N_4^+$ rings and a disulphide bridge

(a) Structure 1

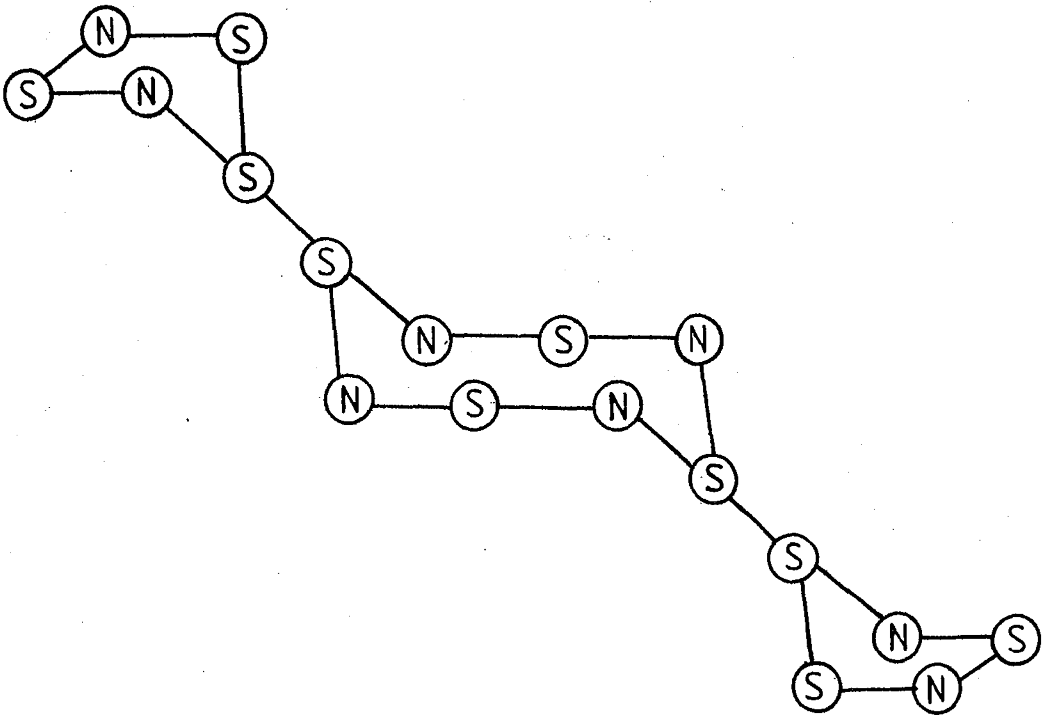


(b) Structure 2 (cf. $S_4N_5^+$)[78]



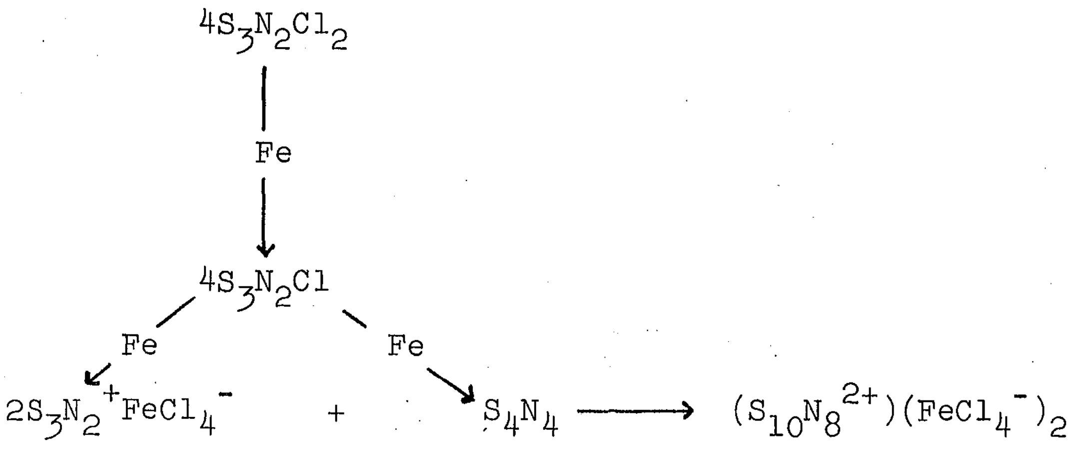
(c) Structure based on a S_4N_4 cage and two $S_3N_2^+$ units

Structure 3



Without an X-ray crystal structure of the compound it is impossible to arrive at a firm conclusion as to the configuration of the postulated $S_{10}N_8^{2+}$ cation. However certain structures seem more likely than others purely by virtue of the synthetic route used to prepare the species. In structure 3 the basic units upon which the structure is based are postulated to be $S_3N_2^+$ and S_4N_4. The $S_3N_2^+$ unit is readily formed by the dechlorination of the $S_3N_2Cl^+$ cation and the S_4N_4 unit by the subsequent reduction of the $S_3N_2^+$ cation by the metal, (cf. the reductions of S_3N_2Cl by metals, table 3.1, page 120). An overall reaction scheme may therefore be postulated for the reaction of $S_3N_2Cl_2$ with iron forming a species with structure 3 (equation 3.45).

Equation 3.45



i.e. $4S_3N_2Cl_2 + 2Fe \longrightarrow (S_{10}N_8^{2+})(FeCl_4^-)_2 + {}^2/8\ S_8$

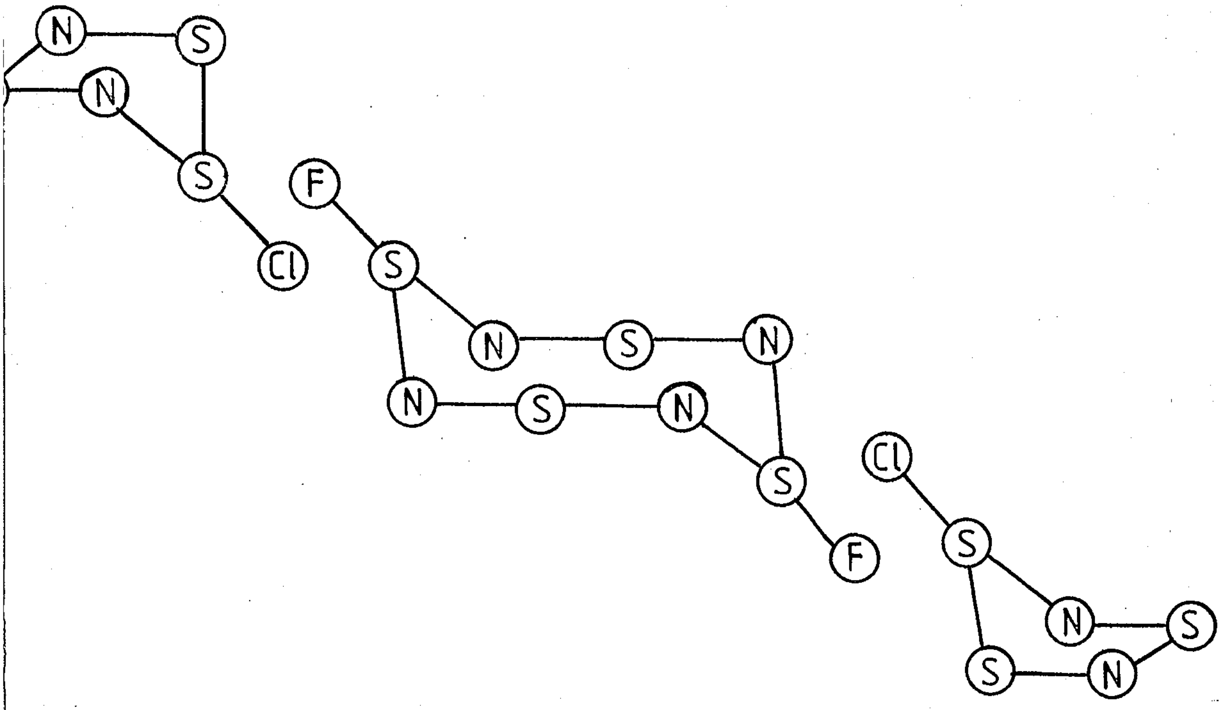
Mechanisms by which structures 1 or 2 could be formed can be devised. However due to the ease with which the reaction proceeds, it would appear unlikely that significant breakdown of the "S_3N_2" ring occurs, which would probably have to be invoked for a structure containing a disulphide bridge. Further support for the conclusion that $S_{10}N_8^{2+}$ is based upon an S_4N_4 cage and two $S_3N_2^+$ rings is drawn from the reactions of **G**roup VI polycations with S_4N_4 (Chapter **S**ix, page 276).

The basic unit around which all of the products are based in the reactions of $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratios 1:2 and 2:1) and in the reaction of $S_8^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 1:2), is the $S_3N_2^+$ or $Se_2SN_2^+$ unit.

The soluble product isolated from both the reactions of $S_8^{2+}(AsF_6^-)_2$ and $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (ratio 1:2) gave the same infra-red spectrum as that noted for the $S_{10}N_8^{2+}$ cation. In the case of the selenium reaction the analytical result implied a low selenium substitution into the cation. This is almost certainly due to the substitution of one or both of the "S_3N_2" units by "SSe_2N_2" units. The low percentage substitution of SSe_2N_2 rings for S_3N_2 rings in the $S_{10}N_8^{2+}$ cation (structure 3) is probably due to a sulphur-sulphur inter-ring bond being more favoured than a sulphur-selenium inter-ring linkage and thus the former is more prevalent.

The structure postulated for $S_{10}N_8^{2+}$ (structure 3) is based on two previously reported species, $S_3N_2Cl^+$ [49] and $S_4N_4F_2$.[78] The S_3N_2 rings will adopt the same structure as in $S_3N_2Cl^+$, the sulphur to which the chlorine would be attached in $S_3N_2Cl^+$ being bonded to the sulphur of the S_4N_4 ring. The S_4N_4 ring will adopt the same conformation as in $S_4N_4F_2$[78] the sulphurs to which the fluorines would be attached in $S_4N_4F_2$ being bonded to the S_3N_2 units (figure 3.8).

Figure 3.8 A Diagrammatic representation of the structural units from which $S_{10}N_8^{2+}$ may be regarded as being constructed.



Interpretation of the infra-red spectrum observed for the species $(S_{10}N_8^{2+})(FeCl_4^-)_2$, using the known infra-red spectra of the basic units ($S_3N_2Cl^+$ and $S_4N_4F_2$) is not feasible, due to the mass of the substituents on each ring. Hence whereas $S_4N_4F_2$ is an S_4N_4 ring with two substituents of M.W. = 19, in $S_{10}N_8^{2+}$ the substituents can be regarded as cations of M.W. = 124. The effects of the increase in mass of the substituents and the inherent charge will change the basic infra-red spectrum of $S_4N_4F_2$ very significantly but it is not possible to determine the overall effects of this change.

(iii) Reaction of Chlorothiodithiazyl Chloride with Mercury

The reaction of $S_3N_2Cl_2$ with mercury as the reducing metal and sulphur dioxide as the solvent, was studied with first, a great excess of mercury and second, with only a slight excess of mercury (experiment 3.2.3(c,vii), page 124). The reaction with a great excess of mercury proceeded rapidly producing S_4N_4 and S_4N_2 (cf. table 3.1, page 120). However in the second reaction in which less mercury was used, two distinct products were formed, one soluble and the other insoluble. The soluble product was readily identified from its infra-red spectrum and by its thin layer chromatogram (compared with standard S_4N_4 sample) as S_4N_4. However the insoluble component contained a species which gave an infra-red spectrum significantly different to any of the products previously isolated from the reductions of sulphur-nitrogen species by metals. By analogy with the reaction of mercury with trichlorotrithiatriazene it seems likely that the mercury chloride produced in the reaction will not affect the reduction mechanism by abstracting chloride ions from the sulphur-nitrogen starting material or an intermediate. Hence it is concluded that the species must either be a neutral sulphur-nitrogen species or a mercury thionitrosyl. The solubility of the species was tested in various solvents and was found to be, to all intents and purposes, negligible in non-polar or non-coordinating solvents (benzene, di-ethyl ether and hexane). Hence it is suspected that the species is not a neutral sulphur-nitrogen compound (cf. solubility of S_4N_4, S_4N_2 and $(NSCl)_3$ in benzene). It therefore appears as though the species is either a mercury thionitrosyl or a mercury chloride/sulphur-nitrogen heterocycle adduct. From the colour of the compound, pink-red, it can be deduced that the species is not $Hg(NS_7)_2$ (cream)[79] or $Hg_5(NS)_8$(green)[3]. It is known that the compound dissociates yielding S_4N_2 and S_4N_4 in tetrahydrofuran at room temperature. It may therefore be suggested that the compound is an $HgCl_2$ adduct which dissociates in T.H.F. with the formation of an $HgCl_2 \cdot THF$ adduct[80], S_4N_4 and S_4N_2. It has however been reported by Heal that $Hg(NS_7)_2$[79] dissociates, on heating, yielding S_4N_2. Hence the decomposition of both an adduct and a thionitrosyl can be postulated to give the observed products.

3.3 Attempts to product $(SN)_x$ by the Reduction of Sulphur-Nitrogen Species

Reactions of S_4N_3Cl with activated metal surfaces,(e.g. with Mg isolated from a Grignard reaction and with molten alkali metals) using solvents failed to produce $(SN)_x$.

The reported methods of producing $(SN)_x$ are by the vapour phase cracking of S_4N_4.[81] Hence the reduction of S_4N_3Cl by molten KNCS, *in vacuo*, was attempted (experiment 3.2.4, page 125). It was hoped that the S/N fragments formed in the reduction process would sublime on to a cold finger and thus polymerise. Although a very deeply coloured sublimate was formed the infra-red spectrum, recorded four months after its formation, indicated the presence of S_4N_3Cl and S_4N_4 only.

3.4 Conclusions

From work reported in this thesis and that of Smith,[72] it can be seen that S_4N_3Cl, S_3N_2Cl, $S_3N_2Cl_2$ and $(NSCl)_3$ are all reduced with ease by a wide range of reducing agents, yielding S_4N_4 and S_4N_2 as an impurity.

The formation of S_4N_4 by an *in situ* method allows a considerable number of synthetic reactions involving S_4N_4 to be done without the isolation of the intrinsically expolsive nitride. The reduction of sulphur-nitrogen species forming S_4N_4 *in situ*, may therefore, represent a useful industrial method of preparing the nitride for organic synthetic reactions.[82]

The use of sulphur dioxide as a solvent has facilitated the isolation of a series of intermediates and the determination of various aspects of the mechanism by which metals reduce sulphur-nitrogen species.

In work, subsequent to that reported in this thesis, Hauptman[83] and Smith[84] have concentrated on the vapour phase reduction of S_4N_3Cl using metals and sodium iodide and have isolated various halogen doped sulphur-nitrogen polymers.

Although solution reductions are no longer being investigated, the vapour phase work is continuing in earnest, as the route represents the first synthetically viable procedure for preparing analogues of $(SN)_x$ without the use of the potentially hazardous S_4N_4.

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CHAPTER FOUR

THE INVESTIGATION OF SYNTHETICALLY VIABLE ROUTES TO SULPHUR-NITROGEN-FLUORINE COMPOUNDS

4.1 Introduction

Little work had been done in the field of sulphur-nitrogen-fluorine chemistry until 1955 when Glemser synthesised a series of compounds, ($S_4N_4F_4$, SN_2F_2, and NSF), by reacting tetrasulphur tetranitride with silver difluoride.[1] Since then, a range of S/N/F compounds have been prepared, (mainly by Glemser *et al*[2-4]) and their spectral properties studied by many groups throughout the world.[5-9] Structural studies indicate that these species adopt both cyclic[10,11] and acyclic[5] configurations, in which delocalisation across the sulphur-nitrogen bonds occurs.[10,12] There are two main reviews by Mews and Glemser (1972[13], 1976[14]) which cover most aspects of sulphur-nitrogen-fluorine chemistry to date.

4.1.1 Thiazyl fluoride (N≡S-F)

Preparation

Thiazyl fluoride has been prepared by a variety of routes:

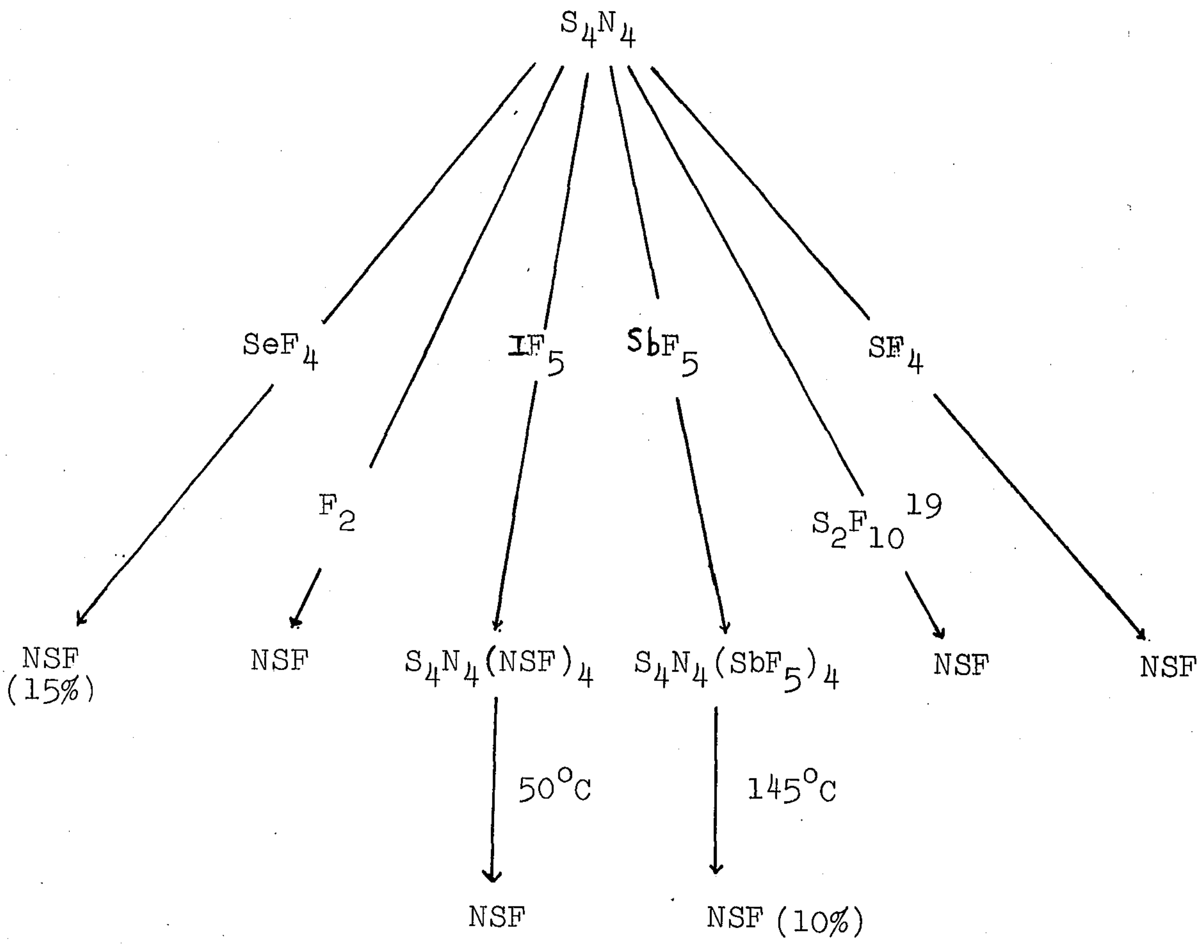
(a) NSF is produced by the oxidative fluorination of systems containing S-N bonds.

Tetrasulphur tetranitride is fluorinated by several powerful fluorinating agents, e.g. silver difluoride[15,16], cobalt trifluoride[15], and mercury difluoride[17](equation 4.1).

$$S_4N_4 + 4HgF_2 \longrightarrow 4NSF + 2Hg_2F_2 \qquad (4.1)$$

S_4N_4 may also be fluorinated using selenium tetrafluoride (SeF_4)[18], sulphur tetrafluoride (SF_4)[18,19] or iodine pentafluoride (IF_5)[18], or in a low temperature reaction with elemental fluorine[20], generally giving NSF in low yields (figure 4.1).

Figure 4.1 Fluorination of S_4N_4 to give thiazyl fluoride.[13]



(b) Ammonia reacts with sulphur-fluoride species to produce thiazyl fluoride (equation 4.3)[18,21]

$$SF_4 + 4NH_3 \xrightarrow[\text{flow system}]{20^{\circ}C} NSF + 3NH_4F \qquad (4.2)$$

(c) Reactions of nitrogen trifluoride with sulphur[21] or metal sulphides[23] (equations 4.3 and 4.4).

$$\underset{\text{molten}}{NF_3 + 3S} \xrightarrow{350-400^{\circ}C} \underset{30\%}{NSF} + S_2F_2 \qquad (4.3)$$

$$NF_3 + MoS_2 \xrightarrow{280^{\circ}C} NSF + MoF_3 \qquad (4.4)$$

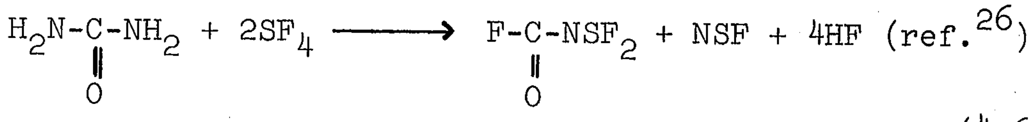
Thiazyl fluoride has also been observed as a product in flash photolysis reactions between nitrogen trifluoride and carbon disulphide or carbon oxide sulphide (COS)[24].

(d) Reactions of sulphur tetrafluoride (SF_4) with nitrogen containing species:

$$\begin{array}{l} Ph_3P = N\text{-}R + SF_4 \longrightarrow F_2S = N\text{-}R + Ph_3PF_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad N \equiv S\text{-}F + RF \end{array}$$

71% when R = $Si(CH_3)_3$; (ref.[25])

(4.5)

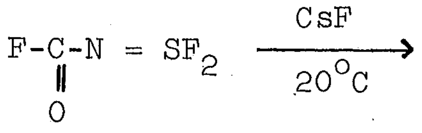


$$H_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH_2 + 2SF_4 \longrightarrow F\text{-}\underset{\underset{O}{\|}}{C}\text{-}NSF_2 + NSF + 4HF \quad (\text{ref.}^{26})$$

(4.6)

(e) Thiazyl fluoride is produced by the decomposition of S/N/F compounds, (equations 4.7 - 4.9).

$$S_4N_4F_4 \xrightarrow[\text{reflux}]{CCl_4} 4NSF \quad (\text{ref.}^{15}) \qquad (4.7)$$



$$F\text{-}\underset{\underset{O}{\|}}{C}\text{-}N = SF_2 \xrightarrow[20^{\circ}C]{CsF} COF_2 + NSF \quad (\text{refs.}^{26,27}) \qquad (4.8)$$

$$Hg(NSF_2)_2 \xrightarrow[\text{high vacuum}]{110^{\circ}C} HgF_2 + 2NSF \quad (\text{ref.}^{30}) \qquad (4.9)$$

Most of the reactions cited above produce thiazyl fluoride in relatively low yields, although reactions 4.5 and 4.9 are synthetically viable. Equation 4.9 is the route cited in most recent papers.[28,29] The production of thiazyl fluoride by the decomposition of the mercury salt is virtually quantitative, and little purification is required as no other volatile species are formed.

The mercury derivative, $Hg(NSF_2)_2$ was first prepared in 1969 by Glemser *et al*[30] from the reaction of mercury difluoride with N-fluoroformyliminosulphur difluoride ($SF_2 = NC(O)F$);the latter was synthesised by Clifford and Kobayashi[31] using silicon tetraisocyanate with SF_4:

$$SF_4 + Si(NCO)_4 \xrightarrow[\text{4 hr}]{100^{\circ}C} SF_2 = NCOF$$

sealed tube 60% yield

$$2SF_2 = NC(O)F + HgF_2 \xrightarrow[\text{room}]{\text{24 hr.}} Hg(NSF_2)_2 + COF_2$$

temp. 80% yield

The mercury derivative can be recrystallised from chloroform, yielding colourless, monoclinic needles, which decompose slowly in glass at room temperature.

The thermal cracking of the mercury species (equation 4.9), at 110°C *in vacuo* is the preferred route to thiazyl fluoride, being essentially quantitative. It is known that thiazyl fluoride cannot be stored at room temperature without decomposition.[13] Thus, the above method provides a useful synthetic route, as the mercury derivative may be stored indefinitely at low temperatures under nitrogen.

Structure

The structure of thiazyl fluoride (figure 4.2) has been elucidated from infra-red[32] and microwave spectra[33], and the force constants calculated[34](table 4.1).

Figure 4.2 Structure of thiazyl fluoride; (distances in pm).[33]

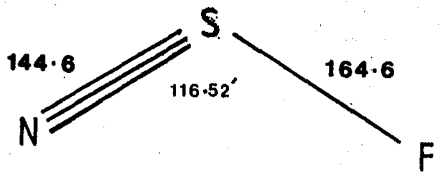
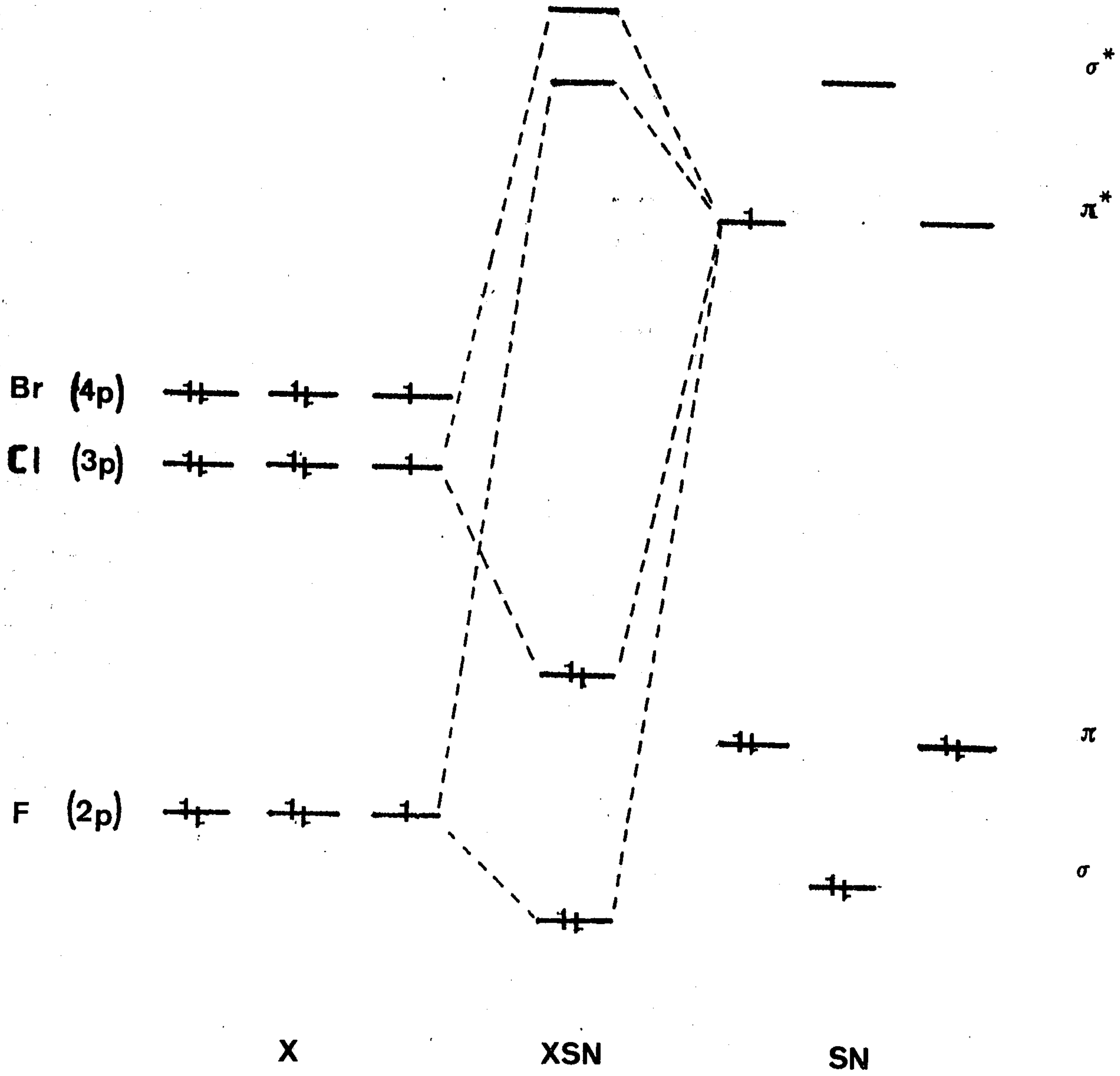


TABLE 4.1 Force constants, bond lengths and X-S-N bond angles for various sulphur-nitrogen species.[34]

Species	S-N stretching force constant k_{SN} ($N\ m^{-1}$)	S-N bond length (pm)	S-X stretching force constant k_{SX} ($N\ m^{-1}$)	S-X bond length (pm)	X-S-N bond angle
$N{\equiv}SF_3$	1255	141.6	449	155.2	
$N{\equiv}S^+$	1185	(143)	-	-	
N≡S-F	1070.9	144.6	287.1	164.6	116° 52′
N≡S-Cl	1009.5	145	138.0	216.1	117° 46′
N≡S-Br	987.5	(145)	129.4	(226)	118±3°

Peake and Downs[34] noted that the S-N stretching force constant (k_{SN}) was high in all thiazyl halides, the value of k_{SN} decreasing with decreasing electronegativity of the halide. The value of k_{SX} (the S-X stretching force constant) was noted as being low relative to that found in comparable systems. A simple qualitative molecular orbital treatment was invoked to explain these values, (figure 4.3). The interaction of the halogen with S≡N causes partial delocalisation of the odd electron of the $[S{\equiv}N^{\bullet}]$ radical,

Figure 4.3 Molecular orbital scheme for NSX



(contained in the $p\pi^*$ orbital), into the sulphur-halogen molecular orbital. The degree of delocalisation is directly related to the electronegativity of the halogen. Thus, when the halogen is fluorine, the sulphur-fluorine bonding MO is similar in energy to that of the p_z atomic orbital of fluorine. It is therefore suggested that there is a significant ionic contribution to the sulphur-fluorine bond. Hence, the S-F bond will have a rather low stretching force constant, whereas the partial removal of an electron from the $p\pi^*$ orbital of $\left[S\equiv N\right]^{\cdot}$ has the effect of enhancing the sulphur-nitrogen stretching force constant.

Spectral and Thermodynamic Data

(a) Gas phase infra-red spectrum[32]

TABLE 4.2 Gas phase infra-red data for thiazyl fluoride

Branch	Frequency cm^{-1}	Intensity	Assignment
P	356	s	
minimum	366		ν_3
R	380	s	
P	627	vs	
(Q)	640	vs	ν_2
R	651	vs	
	1000	w	$\nu_2 + \nu_3$
P	1270	m	
Q	1283	m	$\nu_2 + \nu_2$
R	1295	m	
P	1361	s	
Q	1372	s	ν_1
R	1387	s	
	1720	vw	$\nu_3 + \nu_1$
	1920	vw	$\nu_2 + \nu_2 + \nu_2$
	2020	vw	$\nu_1 + \nu_2$
	2730	w	$\nu_1 + \nu_1$

(b) ^{19}F n.m.r.[32]

$\bar{\nu}$ = 24071080 Hz

$\bar{\nu}_{reference}$ (KF) = 24062460 Hz

Chemical shift, (δ) = 3.58×10^4 ppm

Standard Heats of Formation and Bond Dissociation Energies

Date	ΔH^o_{f298} NSF(g) kJ mol^{-1}	D^o(N-S) kJ mol^{-1}	D^o(S-F) kJ mol^{-1}	Ref.
1968	+ 125	339	-	35
1970	+(172 ± 8)	297 ± 21		36
1973	-(20.9 ± 3.7)	526 ± 13.8	380±25.1	37

Chemical Reactions

Thiazyl fluoride (m.p. = -89°C; b.p. = 0.4°C) is highly moisture sensitive. It is recommended that the synthesis of NSF be carried out in quartz[4] or polythene[1] apparatus due to the reaction of thiazyl fluoride with glass to form silicon tetrafluoride.[15]

Due to the instability and difficulty of handling NSF, only a few reactions have been reported. (figure 4.4, page 159)

4.1.2 Oligmeric Forms of Thiazyl Fluoride: Trifluorotrithiatriazene ($S_3N_3F_3$)

Preparation

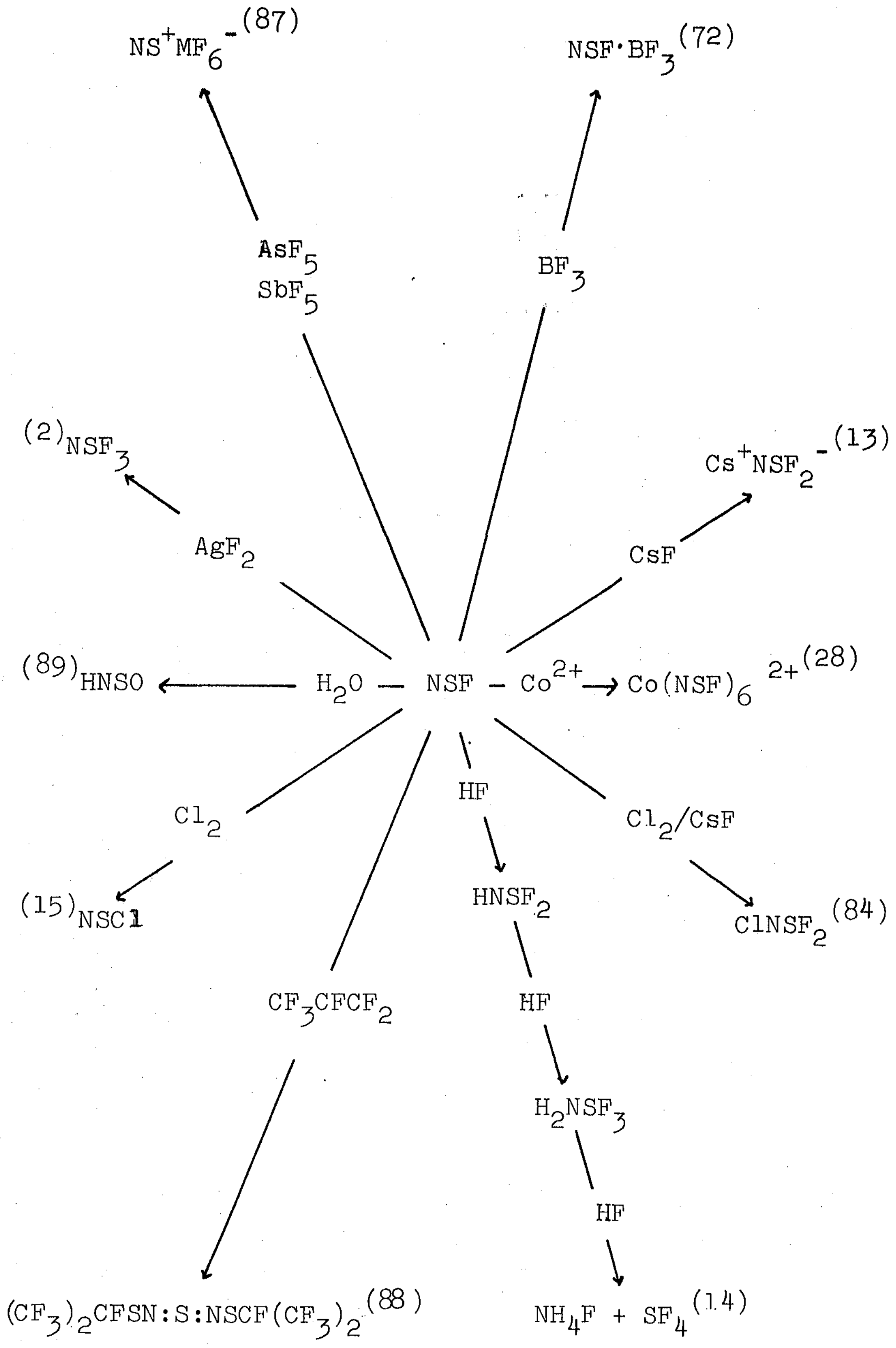
Trifluorotrithiatriazene ($S_3N_3F_3$) may be prepared by three routes:

(a) fluorination of S_4N_4 with fluorine at low temperatures[38]

(b) the exchange reaction between trichlorotrithiatriazene with silver difluoride (equation 4.10)

$$S_3N_3Cl_3 + AgF_2 \longrightarrow S_3N_3F_3 \quad (\text{ref.}^{39}) \qquad (4.10)$$

Figure 4.4 Reactions of Thiazyl Fluoride

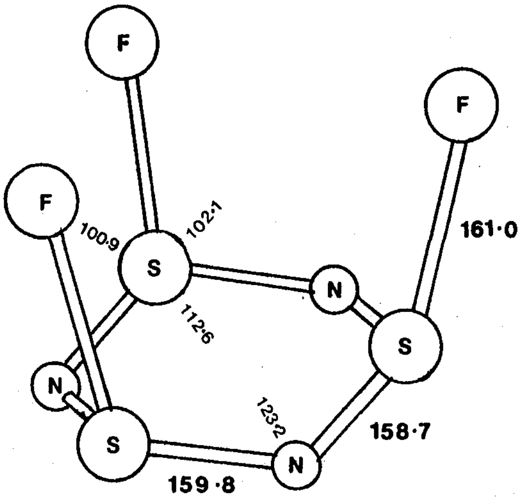


(c) polymerisation of thiazyl fluoride.[22]

Structure

Trifluorotrithiatriazene forms colourless, highly reactive crystals, which crystallise in the space group R$\bar{3}$ - C_{3i}, with a hexagonal cell,[40] (figure 4.5).

Figure 4.5 Crystal Structure of $N_3S_3F_3$.[40]



The equivalence of bond lengths implies extensive delocalisation of the π-system,[40] as observed in $(NSCl)_3$.[41]

Spectral Data

(a) Infra-red spectrum[17]

1080s, 720s, 650s cm^{-1}

(b) ^{19}F nmr

$\bar{\nu}$ = 24066220 Hz)
$\nu_{reference}$ (KF) = 24062680 Hz) ref.[32]
Chemical shift (δ) = 1.47×10^{4} ppm)

Chemical shift with $CFCl_3$ as external reference = -44.1 ppm.[13]

Chemical Reactions

(a) Reactions with Lewis acids[42-44] are summarised in equations 4.11 to 4.14.

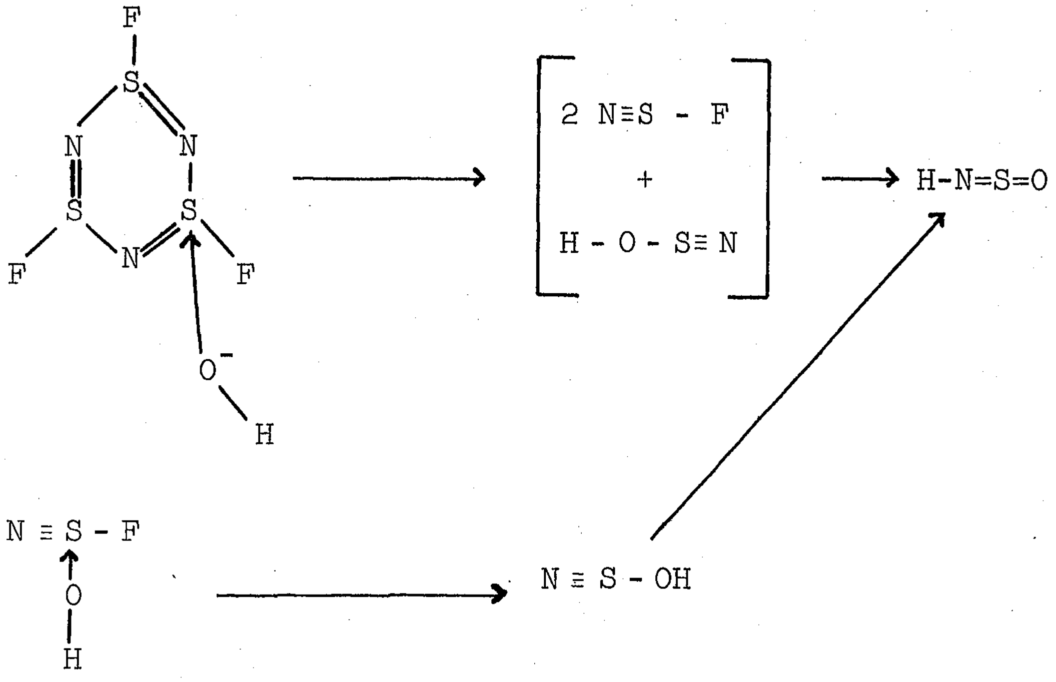
$$S_3N_3F_3 + BF_3 \xrightarrow{\text{liquid } SO_2} S_3N_3F_2^+BF_4^- \qquad (4.11)$$

$$S_3N_3F_3 + AsF_5 \xrightarrow{\text{liquid } SO_2} S_3N_3F_2^+AsF_6^- \qquad (4.12)$$

$$S_3N_3F_3 + SbF_5 \xrightarrow{\text{liquid } SO_2} S_3N_3F_2^+SbF_6^- \qquad (4.13)$$

$$S_3N_3F_2^+ \quad AsF_6^- \xrightarrow{85^oC} NS^+AsF_6^- + 2NSF$$

(b) Hydrolysis of $S_3N_3F_3$ [13]



4.1.3 Oligmeric Forms of Thiazyl Fluoride: Tetrafluorotetrathiatetrazocine ($S_4N_4F_4$)

Preparation

Tetrafluorotetrathiatetrazocine ($S_4N_4F_4$) is prepared by the fluorination of S_4N_4 using

(a) Silver fluoride, (equation 4.15)[1]

$$S_4N_4 + 4\ AgF_2 \xrightarrow{CCl_4} S_4N_4F_4 + 4\ AgF \qquad (4.15)$$

or

(b) fluorine at low temperatures, (equation 4.16)[38]

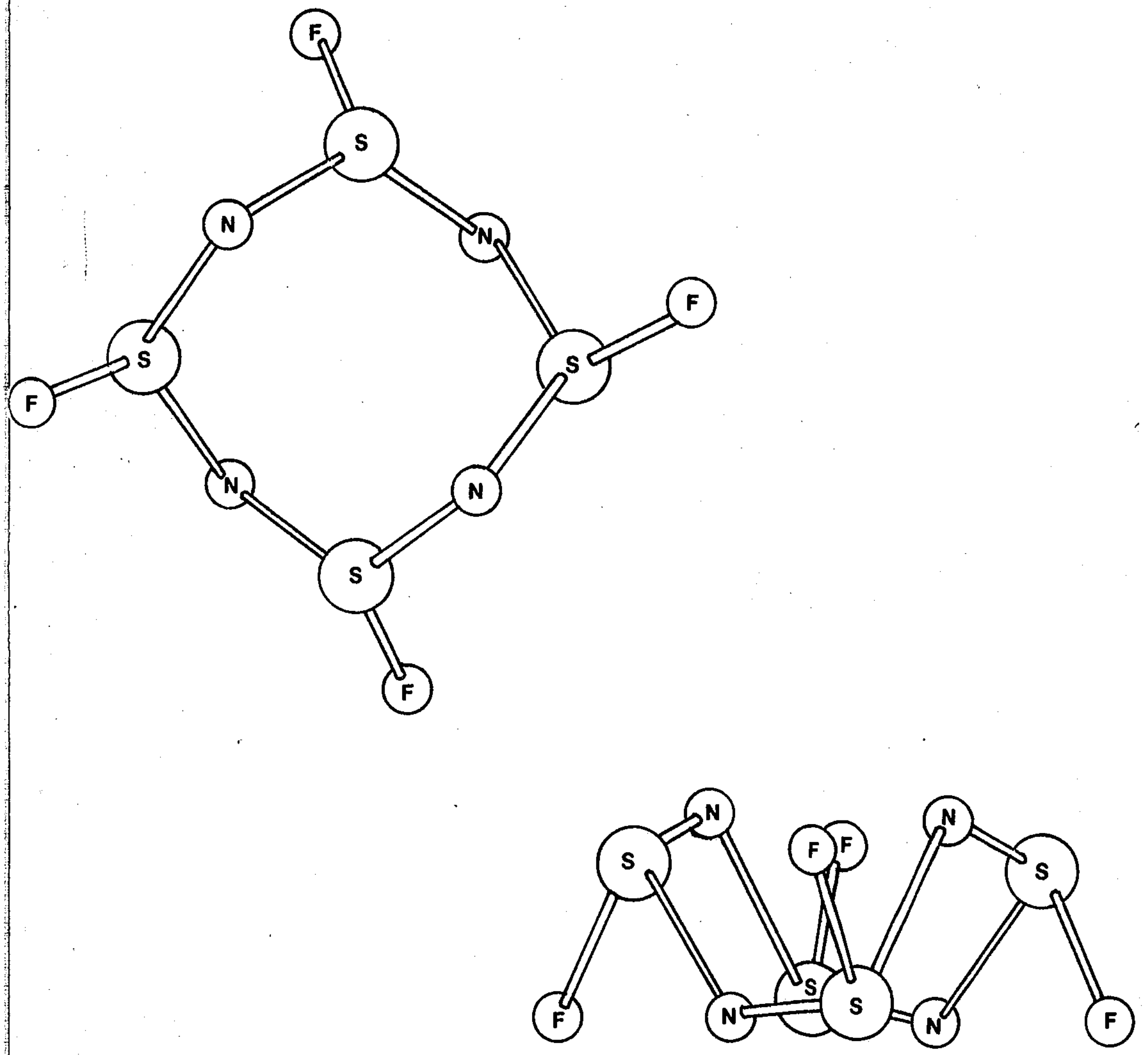
$$S_4N_4 + 2F_2 \xrightarrow{-78^\circ C} S_4N_4F_4 \qquad (4.16)$$

(It should be noted that, unlike $S_3N_3F_3$, $S_4N_4F_4$ cannot be prepared by the polymerisation of NSF).

Structure[11]

$S_4N_4F_4$ crystallises as white needles from carbon tetrachloride. The spacé group is $P_{42_1}c$.

Figure 4.6 Structure of $S_4N_4F_4$



From the X-ray structure (figure 4.6), it is seen that the π-system is localised in tetrafluorotetrathiatetrazocine.

This contrasts with the delocalised systems of trifluoro- and trichlorotrithiatriazene.

Physical Properties[46]

Some physical properties of $S_4N_4F_4$ are summarised in table 4.3.

TABLE 4.3 Physical Properties of $S_4N_4F_4$

Property	
Melting point	153°C; (decomposes at 128°C)
Sublimation temp.	80°C (high vacuum)
Solubility in CCl_4	3.448 gdm^{-3} at 20°C
Density	2.326 gcm^{-3} at 20°C

Spectral Data

(a) Infra-red spectrum[46]

1117, 786, 760, 645, 520 cm^{-1}

(b) ^{19}F n.m.r.

$$\left.\begin{array}{l} \bar{\nu} = 24066420 \text{ Hz} \\ \bar{\nu}_{\text{reference}} = (KF) = 24062680 \text{ Hz} \\ \text{Chemical shift } (\delta) = 1.55 \times 10^{4} \text{ ppm} \end{array}\right\} \text{(ref.}^{32}\text{)}$$

Singlet at -35 ppm; ($CFCl_3$ as external reference) (ref.[13])

Reactions

(a) Thermal decomposition (equation 4.17)

$$S_4N_4F_4 \xrightarrow{250^{\circ}C} 4\ NSF \quad \text{(ref.}^{13}\text{)}$$

(b) Hydrolysis (equation 4.18)

$$S_4N_4F_4 + 12\ H_2O \longrightarrow 4NH_4F + 4H_2SO_3 \quad \text{(ref.}^{13}\text{)}$$

(c) Reactions with Lewis acids are summarised in equations 4.19 and 4.20.

$$S_4N_4F_4 + \underset{\text{excess}}{4BF_3} \longrightarrow 4NSF + 4BF_3 \text{ (ref.}^{42}\text{)} \qquad (4.19)$$

$$\begin{tikzcd}
S_4N_4F_4 + 2AsF_5 \arrow[r] \arrow[d, "AsF_5"] & NS^+ AsF_6^- + S_3N_3F_2^+AsF_6^- \text{(ref.}^{45}\text{)} \\
S_4N_4F_3^+ AsF_6^- \arrow[r] & NS^+ AsF_6^- + N_3S_3F_3
\end{tikzcd} \qquad (4.20)$$

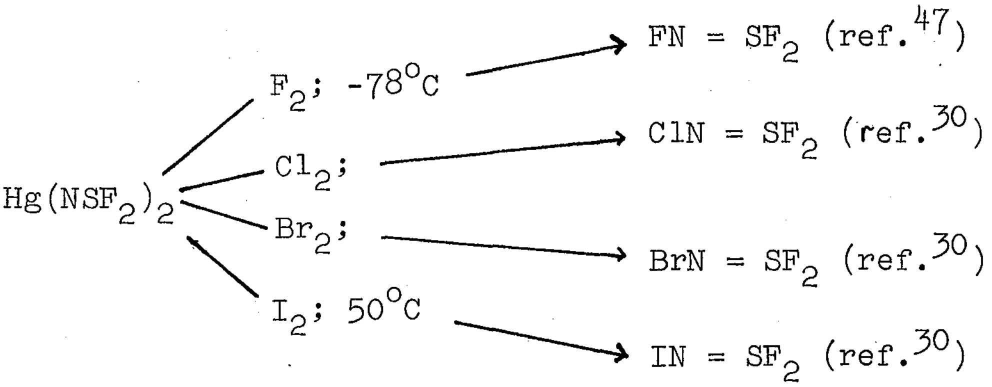
4.1.4 N-substituted Imido-Sulphurous Difluorides, (R-N=SF$_2$)

(I) R = Halogen; N-halo-imido-sulphurous difluoride

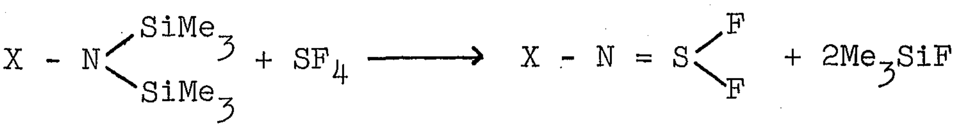
Preparation

All the N-halo-imido-sulphurous difluorides have been reported. The most synthetically viable route is via the mercury bis-imido-sulphurous difluoride, (figure 4.7)[30,47].

Figure 4.7 Formation of X-N=SF$_2$ (X = Halogen)



N-chloro- and N-bromo-imido-sulphurous difluorides may also be synthesised from N-halohexamethylsilanes and sulphur tetrafluoride,[48] (equation 4.21).

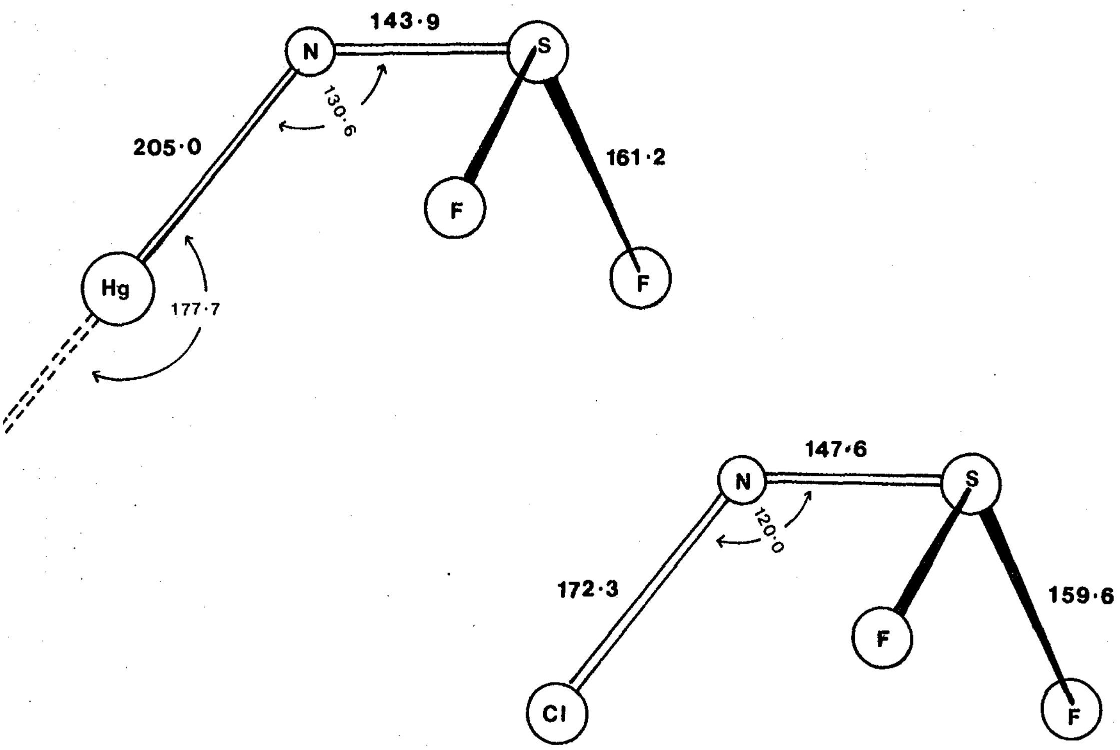


$$X - N(SiMe_3)_2 + SF_4 \longrightarrow X - N = SF_2 + 2Me_3SiF \qquad (4.21)$$

Structure

By comparing the electron diffraction results of N-chloro-imido-sulphurous difluoride[49] with results of an X-ray crystallographic study of $Hg(NSF_2)_2$ [50], it is deduced that both species adopt very similar configurations, (figure 4.8). The S-N bond distance in $Hg(NSF_2)_2$ is very short and is comparable[13] with that in thiazyl trifluoride (141.6 pm)[51] and thiazyl fluoride (144.6 pm).[33] The $S\text{-}\hat{N}\text{-}R$ bond angle in $Hg(NSF_2)_2$ is 130.6° which is significantly larger than the angle of 120.0° in the N-chloro-derivative. This is explained by the degree of participation of the nitrogen lone pair in the bonding which opens out the angle.[13]

Figure 4.8 Structures of $Hg(NSF_2)_2$ and $ClNSF_2$



Spectral Data

(a) Infra-red and Raman spectra for the N-Fluoro, N-Chloro-, N-Bromo-, and N-Iodo-Imido-Sulphurous Difluorides.[52]

The infra-red and Raman frequencies are summarised in table 4.4.

TABLE 4.4 Raman and Infra-red Data for X-N=SF_2; (I.R frequencies are in brackets); (all frequencies in cm^{-1})

F-N=SF_2	Cl-N=SF_2	Br-N=SF_2	IN=SF_2	Assignments
1133(1150)	1176(1200)	1208(1214.7)	(1235)	$A' \nu_s$ (N=S)
770(770)	741(752)	735(745)	(735)	ν_s (S-F)
809(822)	539(548.5)	465(468)	-	ν (N-X)
611(615)	640(644.5)	593	-	δ_s (SF_2)
435	409(409.6)	405	-	ω (SF_2)
200	165	135	-	δ_s (X-N-S)
696(712)	694	660(699)	(675)	$A'' \nu_{as}$ (S-F)
435	409(409.6)	405	-	ρ (SF_2)
150	145	135	-	δ_{as} (S-N-S)

(b) ^{14}N n.m.r. spectrum[53]

^{14}N chemical shifts relative to aqueous NH_4^+ are positive (i.e. downfield);   = 127 ppm for Cl-N=SF_2.

Reactions

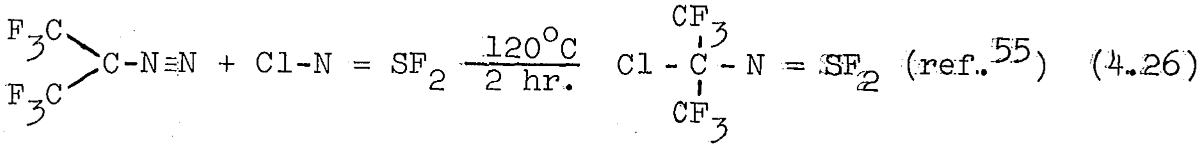
Reactions with unsaturated systems are summarised in equations 4.22 to 4.28.

$$Cl\text{-}N{=}SF_2 + F_2C = CF_2 \xrightarrow{h\nu} ClF_2CF_2NSF_2 \text{ (ref.}^{54}\text{)} \quad (4.22)$$

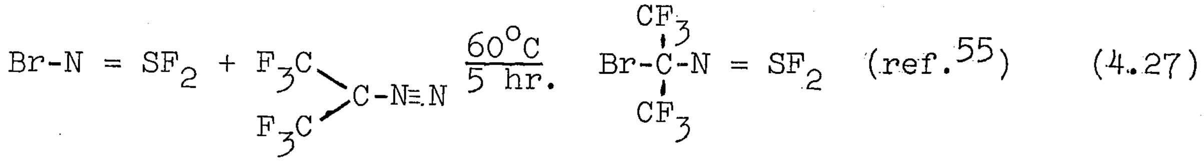
$$Cl\text{-}N = SF_2 + 2F_2C = CF_2 \xrightarrow{h\nu} ClF_2CCF_2CF_2CF_2NSF_2 \text{(ref.}^{54}\text{)} \quad (4.23)$$

$$Br\text{-}N = SF_2 + F_2C = CF_2 \xrightarrow{90^{\circ}C} BrF_2CCF_2NSF_2 \text{ (ref.}^{54}\text{)} \quad (4.24)$$

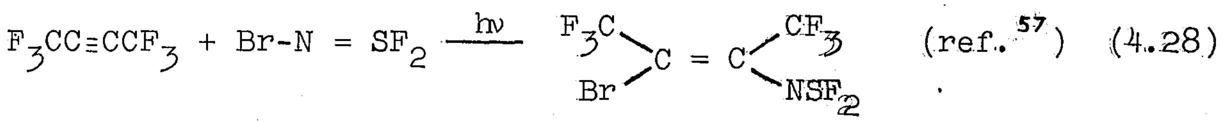
$$2Cl-N = SF_2 + 2F_3C-CF = CF_2 \xrightarrow{h\nu} \underset{(77\%)}{F_3CCFClCF_2NSF_2} + \underset{(23\%)}{F_3CCF(N = SF_2)CF_2Cl} \text{ (ref.}^{54}\text{)} \quad (4.25)$$



$$(F_3C)_2C-N{\equiv}N + Cl-N = SF_2 \xrightarrow[2\ hr.]{120^{\circ}C} Cl-C(CF_3)_2-N = SF_2 \text{ (ref.}^{55}\text{)} \quad (4.26)$$



$$Br-N = SF_2 + (F_3C)_2C-N{\equiv}N \xrightarrow[5\ hr.]{60^{\circ}C} Br-C(CF_3)_2-N = SF_2 \text{ (ref.}^{55}\text{)} \quad (4.27)$$



$$F_3CC{\equiv}CCF_3 + Br-N = SF_2 \xrightarrow{h\nu} (F_3C)(Br)C = C(CF_3)(NSF_2) \text{ (ref.}^{57}\text{)} \quad (4.28)$$

(trans- and cis-isomers)

Reactions 4.27 and 4.28 are believed to proceed by one of two mechanisms:

(i) via homolytic fission of the N-X bond and subsequent free radical attack.[56]

(ii) by an addition mechanism.[57]

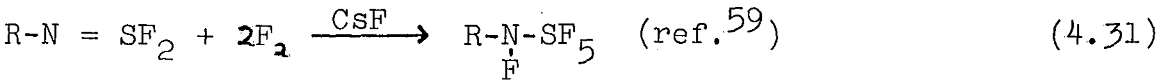
II R = Alkyl or Aryl; N-Substituted-Alkyl and Aryl Imido-Sulphurous-Difluorides

This large and varied group of compounds is covered in an excellent review by Glemser and Mews[39] (1972) and is therefore not discussed in detail in this thesis. Some reactions of the $R-N = SF_2$ system with various R groups are summarised in equations 4.29 to 4.32.

$$R-N = SF_2 + 2\ ClF \longrightarrow RNCl_2 + SF_4 \text{ (ref.}^{29}\text{)} \quad (4.29)$$

($R = FCO, CF_3CO, CF_3, (CF_3)_2CF$, and $F_2SN(CF_2)_2$)

$$R-N = SF_2 + 3HF \longrightarrow SF_4 + R-NH_3^{+}F^{-} \text{ (ref.}^{14}\text{)} \quad (4.30)$$



$$R-N = SF_2 + 2F_2 \xrightarrow{CsF} R-\underset{F}{N}-SF_5 \text{ (ref.}^{59}\text{)} \quad (4.31)$$

$$CH_3N = SF_2 + Cl_2 \xrightarrow{-HCl} CH_2ClN = SF_2 + CHCl_2N = SF_2 + CF_3N = SCl_2 \quad \text{(ref.}^{60}\text{)} \qquad (4.32)$$

(Note that chlorine does not add across the double bond).

4.1.5 Thiazyl Trifluoride ($N \equiv SF_3$)

Preparation

There are four main preparative routes to thiazyl trifluoride ($N \equiv SF_3$), (equations 4.33 to 4.36).

$$S_4N_4 + 12\ AgF_2 \xrightarrow[CCl_4]{reflux} NSF_3 \quad \text{(refs.}^{15,17}\text{)} \qquad (4.33)$$

$$NSF + 2\ AgF_2 \longrightarrow NSF_3 \quad \text{(refs.}^{2,15}\text{)} \qquad (4.34)$$

$$OCFNSF_2 + 2\ AgF_2 \xrightarrow[16\ hr.]{38^\circ C} NSF_3 \quad \text{(ref.}^{61}\text{)} \qquad (4.35)$$

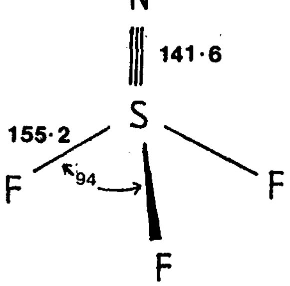
$$(-COF_2)$$

$$S_2F_{10} + NH_3 \xrightarrow[\text{flow system}]{150^\circ C} NSF_3 + SF_4 + 3HF \quad \text{(ref.}^{62}\text{)} \qquad (4.36)$$

Structure

The structure of thiazyl trifluoride has been determined from infra-red,[32] n.m.r.,[32] microwave[51] and photoelectron[63] spectra, (figure 4.9).

Figure 4.9 Structure of $N \equiv SF_3$ [51]



Spectral Data

(a) Vibrational spectrum[32,64]

The vibrational spectrum is summarised in table 4.5.

TABLE 4.5 Vibrational Spectrum of Thiazyl Fluoride; (Raman frequencies given in brackets)

Branch	Frequency (cm^{-1})	Intensity	Assignment	Calculated Frequency (cm^{-1})
P	324	m		
P	332	m		
Q	342(340 dp)	s	δ_{NSF} : ν_6 (E)	
R	351	m		
P	415	s		
Q	429(430 dp)	s	δ_{SF_3} : ν_5 (E)	
R	441	s		
P	510	s		
Q	521(520 dp)	s	$\delta_{S(SF_3)}$: ν_3 (A_1)	
R	535	s		
P	667	sh		
Q	678	w	$\delta_6 + \nu_6$	684
R	690	w		
P	769(768 p)	s	($\delta_{S(SF)}$ (A_1))	
Q	775	s	ν_2 (A_1)	
R	782	s		
Q	811(812 dp)	vs	$\nu_{as(SF)}$: ν_4 (E)	
-	861	m	$\nu_5 + \nu_5$ $\nu_3 + \nu_6$	858 863
P	940	sh		
Q	952	w	$\nu_3 + \nu_5$	950
R	965	w		
-	1155	w	$\nu_4 + \nu_6$	1153

TABLE 4.5 (contd.)

Branch	Frequency (cm^{-1})	Intensity	Assignment	Calculated Frequency (cm^{-1})
P	1241	w		
R	1256	w	$\nu_4 + \nu_5$	1240
P	1504	s		
Q	1515(1512 p)	s	$\nu_1(A_1)$: ν_{SN}	
R	1530	s		
P	1540	sh		
Q	1551	sh	$\nu_2 + \nu_2$	1550
R	1566	sh		
-	1582	m	$\nu_1 + \nu_4$	
-	1615	sh		
-	1625	sh		
Q	1635	m	$\nu_4 + \nu_4$	1622
-	1643	sh		
-	1860	w	$\nu_1 + \nu_6$	1857
P	1930	sh		
Q	1950	w	$\nu_1 + \nu_5$	1944
R	1966	w		
-	2040	w	$\nu_1 + \nu_3$	2036
-	2300	w	$\nu_1 + \nu_4$ $\nu_1 + \nu_2$	2290 2326
-	2420	vw	$\nu_4 + \nu_4 + \nu_4$	2433
-	3040	vw	$\nu_1 + \nu_1$	3030

(dp = depolarised; p = polarised)

(b) ^{19}F n.m.r.^{32}

$\bar{\nu}$ = 2406623 Hz for NSF_3

$\bar{\nu}_{reference}$(KF) = 24062128 Hz

Chemical shift (δ) = 1.87 x 10^4 ppm.

Thermodynamic and Physical Data

Some physical[13] and thermodynamic[36] properties of thiazyl trifluoride are summarised in table 4.6.

TABLE 4.6 Some physical and thermodynamic properties of $N \equiv SF_3$

Property	Value	
m.p.	$-72.6 \pm 0.5^\circ C$	
b.p.	$-27.1 \pm 1.0^\circ C$	
$\Delta H^o_{f298}(g)$	$-356.5 \pm$ kJ mol^{-1}	
D^o (N-S)	418 ± 8.4 kJ mol^{-1}	) calorimetric) measurements
D^o (S-F)	318 ± 29 kJ mol^{-1}	)

Selected Reactions of Thiazyl Trifluoride

NSF_3 is both chemically and thermally very stable; (c.f. sulphur hexafluoride as opposed to thiazyl fluoride). It does not react with dilute acids,[13] and reacts only at 300°C with metallic sodium.[13]

(a) Addition reactions to the sulphur-nitrogen multiple bond

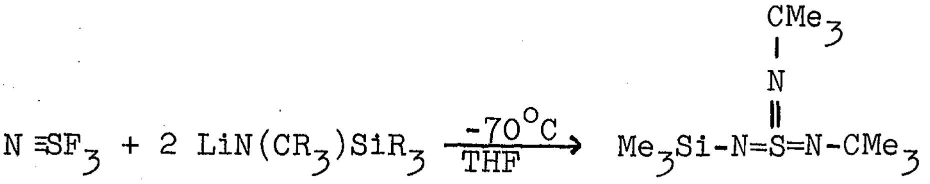
Some addition reactions to the S≡N triple bond in thiazyl trifluoride are summarised in equations 4.37 to 4.43.

$$N \equiv SF_3 + 2HF \xrightarrow{20^\circ C} H_2N - SF_5 \quad (\text{ref.}^{65}) \qquad (4.37)$$

$$N \equiv SF_3 + 2ClF \xrightarrow{-78^\circ C} Cl_2N\text{-}SF_5 \quad (\text{ref.}^{67}) \qquad (4.38)$$

$$N \equiv SF_3 + SF_4 \xrightarrow[BF_3]{180^\circ C} F_2SN\text{-}SF_5 \quad (\text{ref.}^{61}) \qquad (4.39)$$

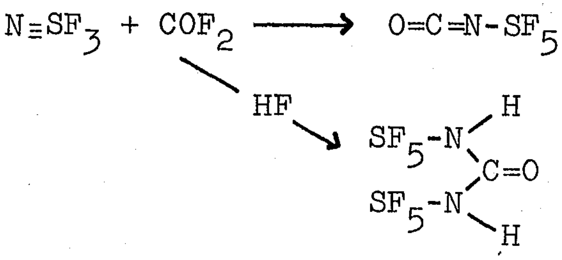
$$2\ N \equiv SF_3 + 3BCl_3 \xrightarrow{20^\circ C} \left[N(SCl_2)\right]^+ \left[BCl_4\right]^- + \frac{1}{2} N_2 + \frac{3}{2} Cl_2 + 2BF_3 \quad (\text{ref.}^{68}) \quad (4.40)$$



$$N{\equiv}SF_3 + 2\ LiN(CR_3)SiR_3 \xrightarrow[THF]{-70^{\circ}C} Me_3Si{-}N{=}\overset{\overset{CMe_3}{|}}{\overset{N}{\overset{\|}{S}}}{=}N{-}CMe_3$$

(ref.[69]) (4.41)

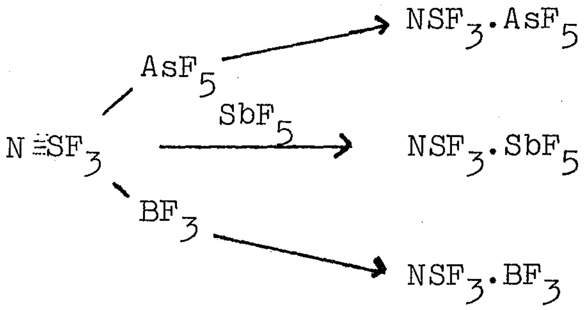
$$N{\equiv}SF_3 + CF_3{-}CF{=}CF_2 \xrightarrow[CsF]{90^{\circ}C} (CF_3)_2CF{-}N{=}SF_2$$ (ref.[70]) (4.42)



(ref.[71]) (4.43)

(b) Adduct chemistry

Thiazyl trifluoride forms adducts with BF_3, AsF_5 and SbF_5 (equations 4.44). The structures of the products have been elucidated from their vibrational spectra,[42,73] there being no evidence of fluoride ion abstraction by the Lewis acids.



(ref.[42])

(ref.[42]) (4.44)

(refs.[72,15])

4.2 Experimental

Fluorination of Sulphur-Nitrogen Species with Chlorine Monofluoride

(a) Tetrasulphur Tetranitride and Chlorine Monofluoride

(i) Tetrasulphur tetranitride and chlorine monofluoride (ratio 1:6)

Chlorine monofluoride (0.3267g, 5.99 mmole) was condensed, (in three aliquots) onto tetrasulphur tetranitride (0.1808g, 0.983 mmole) contained in a predried, vacuum tight, teflon vessel. The reaction was held at -78°C for 15 minutes between additions to allow a controlled reaction to occur. The system was warmed slowly, (over a period of 6 hours), to room temperature and kept there for 10 hours. The volatiles were sampled at various slush bath temperatures, and identified by their infra-red, Raman, and ^{19}F n.m.r. spectra (table 4.7). (The volatiles identified at one slush bath temperature were removed before sampling at a higher temperature).

TABLE 4.7 Volatiles observed at various slush bath temperatures after the reaction between S_4N_4 and ClF (1:6)

Temperature (°C)	Species identified
-196	N_2
-78	SF_5Cl; SF_4; (SOF_2); Cl_2
Room temp.	NSF; SF_4

(Standard spectra referenced in Appendix A, page 313)

The volatiles present at room temperature were completely removed and the infra-red and Raman spectra of the residue (0.1853g) were recorded.

Infra-red spectrum (nujol mull): 1100 m,br(sh), 1052 s,br(sh), 1015 vs, 970 s,br(sh), 695 s, 618 w, 588 m, 500 s,br, 465 m, 422 w, 388 m cm^{-1}.

Raman spectrum (green line): 1022 vs, 964 s, 718 w, 694 w, 595 m, 488 m, 482 m, 460 w, 432 w, 406 w, 380 m, 340 s, 324 m, 212 m, 208 m, 188 m, 182 m, 178 m, 110 s cm^{-1}.

^{19}F n.m.r. of the volatiles present at -78°C (reference CCl_3F):

Chemical shifts = 75.9 ppm and 81.1 ppm.

(ii) Tetrasulphur tetranitride and chlorine monofluoride (ratio 1:5)

Chlorine monofluoride (0.16g, 2.94 mmole) was condensed, (in four aliquots), on to S_4N_4 (0.11g, 0.60 mmole) contained in a Monel vessel. The system was warmed to -95°C for 15 minutes, and to -78°C for a further 30 minutes, between additions. After all the ClF had been added, the reaction was warmed slowly, (over a period of 6 hours), to room temperature. This temperature was maintained for 12 hours. The gas phase infra-red and Raman spectra of the volatiles were recorded at different slush bath temperatures (table 4.8). (At each slush bath temperature, the observed products were removed before further sampling).

TABLE 4.8 Volatiles observed at various slush bath temperatures after the reaction between S_4N_4 and ClF (1:5)

Temperature (°C)	Species identified
-196	N_2
-95	SF_4; SOF_2; SF_5Cl
-78	SF_4; Cl_2; SOF_2; SF_5Cl
-22	SOF_2; NSF ; SO_2ClF
Room temp.	NSF; SO_2ClF; SOF_2

(Standard spectra referenced in Appendix A, page 313)

The volatiles present at room temperature were completely removed and the infra-red spectrum of the residue (0.16g) recorded.

Infra-red spectrum (nujol mull): 1050 s,br(sh), 1017 vs, 970 s, 800 w, 698 s, 660 w, 632 m, 590 s, 553 w, 520 s, 508 m(sh), 468 m, 465 m, 422 w, 410 vw, 390 s cm^{-1}.

(iii) Tetrasulphur tetranitride and chlorine monofluoride (ratio 1:1.1)

ClF (0.12g, 2.20 mmole) was condensed on to S_4N_4 (0.37g, 2.01 mmole) contained in a predried, vacuum tight, Monel vessel. The reaction was warmed slowly from -78°C to room temperature (over a period of 4 hours) and maintained at room temperature for 10 hours. The volatiles were identified at various slush bath temperatures and the weight loss, on removal of the voltatiles at each slush bath temperature recorded (table 4.9).

TABLE 4.9 Volatiles observed at various slush bath temperatures after the reaction between S_4N_4 and ClF (1:1.1)

Temperature	Species identified	Weight of volatiles (g)
-196	N_2	< 0.01
-78	SF_4	0.04
-22 Room temp.	SF_4; NSF	0.05

(Standard spectra referenced in Appendix A, page 313)

All the volatiles present at room temperature were removed and the infra-red spectrum of the residue (0.38g) recorded.

Infra-red spectrum (nujol mull): 1080 m, 1018 s, 952 m(sh), 922 s, 895 m, 791 w, 776 w, 722 m, 700 s(sh), 698 s, 690 s(sh), 687 s(sh), 662 m, 630 w, 582 w, 558 s(sh), 550 s, 520 w, 510 w, 464 s cm^{-1}.

(^{19}F n.m.r. (reference perfluorobenzene): no signals).

(iv) Tetrasulphur tetranitride and chlorine monofluoride (ratio 1:16)

S_4N_4 (0.1988g, 1.08 mmole) was placed in a pre-dried vacuum tight, Monel vessel and pumped on for 2 hours. ClF (2 line atmos., 0.2740g, 5.03 mmole) was condensed into the vessel and the reaction warmed to -78°C for 20 minutes. On addition of a second aliquot of ClF (2 line atmos.) a reaction was observed to occur forming an incondensable gas. This gas was removed from the system and the reaction warmed to -55°C for 30 minutes. No further incondensable gas was formed. A third aliquot of ClF (2 line atmos.) was added and the formation of the same gas was noted. This was removed and the system held at -55°C for 30 minutes. The final aliquot of ClF (0.5 line atmos.) was then added, with the production of the non-condensable gas. After removal of this product, the system was warmed to room temperature and maintained there for 12 hours. The pressure, gas phase spectra, and weight loss on removal of the volatiles at the various slush bath temperatures were recorded (table 4.10).

Sulphur dioxide was added to the volatiles present at -78°C to test for ClF by the formation of sulphuryl chloride fluoride (SO_2ClF) which has a strong and distinctive infra-red spectrum.[74] No SO_2ClF was formed, implying that no chlorine monofluoride was present.

No residue was obtained from the reaction.

TABLE 4.10 Volatiles observed at various slush bath temperatures after the reaction between S_4N_4 and ClF (1:16)

Temperature (^{o}C)	Pressure (torr)	Species identified	Weight of volatiles (g)
-196	730	N_2	0.06
-78	290	SF_4; Cl_2	1.06
Room temp.	10	SF_4	0.01

(Standard spectra referenced in Appendix A , page 313).

(b) Trichlorotrithiatriazene and Chlorine Monofluoride

(i) Trichlorotrithiatriazene and chlorine monofluoride (ratio 1:3)

Chlorine monofluoride, (0.09g, 1.65 mmole), was condensed, (in three aliquots), onto trichlorotrithiatriazene ($(NSCl)_3$), (0.13g, 0.53 mmole), contained in a predried, vacuum tight, Monel vessel. The reaction was warmed to -78°C for 45 minutes between additions. After the final addition, the system was warmed to room temperature over a period of 6 hours. This temperature was maintained for 10 hours and the volatiles sampled at various slush bath temperatures (table 4.11).

TABLE 4.11 Volatiles observed at various slush bath temperatures after the reaction of $(NSCl)_3$ and ClF (1:3)

Temperature (^{o}C)	Pressure (torr)	Species identified
-196	40	N_2
-78	220	Cl_2; SF_4; SOF_2
Room temp.	0	-

(Standard spectra referenced in Appendix A, page 313)

The volatiles present at room temperature were completely removed, and the infra-red and Raman spectra of the residue (0.10g) were recorded.

Infra-red spectrum (nujol mull): 1017 vs, 698 m, 646 w, 618 w, 554 w, 519 s, 390 s cm^{-1}.

Raman spectrum (green line): 700 vw, 620 w, 495 m, 432 w, 376 s, 336 vs, 320 s, 211 w, 192 vs, 178 vs, 107 vs cm^{-1}.

(ii) Trichlorotrithiatriazene and chlorine monofluoride (ratio 1:3) at elevated temperatures

ClF (0.97g, 17.80 mmole) was condensed onto $(NSCl)_3$ (1.33g, 5.44 mmole) contained in a predried Monel vessel. The temperature of the vessel was increased slowly to room temperature and then to 60°C. This temperature was maintained for 35 hours. The system was cooled to -196°C, -78°C, -22°C and 0°C using a series of slush baths. The pressure, gas infra-red phase spectra, and weight of the volatiles present at each temperature were recorded (table 4.12).

TABLE 4.12 Volatiles observed at various slush bath temperatures after the reaction of $(NSCl)_3$ and ClF (1:3) at 60°C

Temperature (°C)	Pressure (torr)	Weight of volatiles (g)	Species identified
-196	100	0.03	N_2 (by discharge)
-78	200	1.09	$SF_4{}^*$; SF_5Cl; SF_6; $Cl_2{}^*$
-22	35	0.11	$SF_4{}^*$; SOF_2; SO_2ClF
0	10	0.03	$SF_4{}^*$; NSF
Room temp.	0	-	-

(* Main product)

(Standard spectra referenced in Appendix A, page 313)

The volatiles present at room temperature were completely removed and the infra-red and Raman spectra of the residual pale yellow, sublimed, crystals (1.03g) were recorded.

Infra-red spectrum (nujol mull): 1017 vs, 698 s, 514 s, 389 s cm^{-1}.

Raman spectrum (green line): 702 w, 691 w, 619 w,br, 495 m, 456 w, 438 w(sh), 432 m, 376 s, 336 vs, 320 s, 211 m, 192 vs, 178 vs, 107 vs cm^{-1}.

(iii) Trichlorotrithiatriazene and chlorine monofluoride (ratio 1:3) at prolonged elevated temperature

ClF (1.07g, 19.63 mmole) was condensed, (in two aliquots), on to $(NSCl)_3$ (1.42g, 5.81 mmole). The temperature was slowly raised from -78°C to 80°C. This final temperature was maintained for 94 hours. The system was then cooled and the volatiles collected in slush baths of varying temperatures. The pressure, gas phase infra-red spectra and weight of the volatiles at each temperature were recorded (table 4.13). There was no residue.

TABLE 4.13 Volatiles observed at various slush bath temperatures after the reaction of $(NSCl_3)$ and ClF (1:3) at 80°C

Temperature (°C)	Pressure (torr)	Weight of volatiles (g)	Species identified
-196	820	0.22	N_2
-78	165	0.39	SF_4^*; SOF_2; SF_6; SF_5Cl
-22	80	0.16	SF_4; $S_2Cl_2^*$
0	440	1.21	$S_2Cl_2^*$; SCl_2^*
Room temp.	210	0.50	SCl_2

(* Main product)

(Standard spectra referenced in Appendix A, page313)

(c) Investigation of the Mechanism of the Reaction of Chlorine Monofluoride with Tetrasulphur Tetranitride and Trichlorotrithiatriazene

(i) Thiazyl fluoride and chlorine monofluoride

Thiazyl fluoride (NSF) (100 torr, 0.33 mmole) was condensed into an infra-red gas cell. The spectrum was then recorded, the pressure in the cell being controlled by the condensation of the NSF into an isolatable side arm. The thiazyl fluoride was completely condensed into the side arm, isolated, and ClF (300 torr, 0.99 mmole) expanded into the cell. The valve on the side arm was opened to allow reaction between the gases to occur. The gas phase infra-red spectrum was recorded after 5 and 15 minutes. The spectra were identical.

Infra-red spectrum (gas phase): 894 m(sh), 884 s(sh), 870 s, 862 s, 856 s(sh), 858 s(sh), 732 vs, 723 vs, 712 vs(sh).

From the spectral data, the main infra-red active product was identified as SF_4 (standard spectrum referenced in Appendix A).

(ii) Thiazyl chloride and chlorine monofluoride

Thiazyl chloride (18 torr, 0.06 mmole) was expanded into an infra-red gas cell and the spectrum recorded. Aliquots of ClF were condensed into the cell and the gas phase infra-red spectrum was recorded after each addition. The variations in the spectrum were used to identify the products and hence the mechanistic pathway of the reaction (table 4.14).

TABLE 4.14 Species observed as products in the reaction between NSCl and ClF

Total pressure of ClF added (torr)	Approximate ratio of ClF: NSCl	Species observed in the gas phase infra-red spectrum
0	0 : 1	NSCl
20	1 : 1	NSCl; NSF*; $ClNSF_2$*
40	2 : 1	SF_4; $ClNSF_2$*
65	3.5 : 1	SF_4*; $ClNSF_2$; NCl_3*
90	5 : 1	SF_4*; NCl_3*
165	9 : 1	SF_4*; NCl_3*; ClF

(* Main product)

(Standard spectra referenced in Appendix A, page 313).

(iii) Thiazyl fluoride and chlorine

Thiazyl fluoride (10 torr, 0.033 mmole) was condensed into an infra-red gas cell and the spectrum was recorded. Three aliquots of chlorine were expanded into the gas cell giving total pressures of (a) 20 torr, (b) 100 torr, and (c) 300 torr. The infra-red spectrum was recorded after each addition, but no change from the spectrum of NSF was observed.

(Standard spectrum of NSF referenced in Appendix A, page 313).

(iv) Thiazyl fluoride and chlorine in the presence of sulphur dioxide

NSF (10 torr, 0.033 mmole) was expanded into a gas cell and its infra-red spectrum recorded. Sulphur dioxide (50 torr) was expanded into the same cell and the spectrum of the NSF/SO_2 mixture recorded. Chlorine (100 torr) was condensed into the gas cell and the infra-red spectrum of the reaction mixture was run 8 times over a period of 28 hours. The intensity of the bands due to sulphuryl chloride fluoride (SO_2ClF), thiazyl fluoride and thiazyl chloride were used as an empirical measure of their relative concentrations at any particular time. It was noted that a slow reaction occurred in which SO_2ClF and NSCl were produced, and the concentration of NSF decreased.

(Standard spectra referenced in Appendix A, page 313).

4.3 Discussion

4.3.a Fluorination of Sulphur-Nitrogen Species with Chlorine Monofluoride

Chlorine monofluoride is known to act as a mild fluorinating agent in a number of reactions. It has been particularly successful in the preparation of perfluoroalkyl derivatives of sulphur (IV), sulphur (VI),[75,76] selenium (IV) and selenium (VI).[77] The fluorination of certain sulphur-nitrogen species by chlorine monofluoride was therefore investigated as a possible route to thiazyl fluoride (NSF).

The envisaged reaction between tetrasulphur tetranitride (S_4N_4) and chlorine monofluoride (ClF) was the formation of thiazyl fluoride and chlorine (equation 4.3a),

$$S_4N_4 + 4ClF \longrightarrow 4\ NSF + 2Cl_2 \quad \Delta H^o = -503\ kJ\ mol^{-1} \qquad (4.3a)$$

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B, page 319).

It was however found that on reacting S_4N_4 with ClF, in an approximate ratio of 1:4 (experiments 4.2a(i,ii), pages 173, 174), sulphur tetrafluoride (SF_4) and trichlorothithiatriazene ($(NSCl)_3$) were the main products. The presence of large volumes of SF_4 and the low yield of NSF suggested that ClF was reacting by a mechanism in which one sulphur was completely fluorinated. The lack of fluorine in the residue and the presence of $(NSCl)_3$ and $(NSCl)_4$ (identified by their infrared spectra[78]) indicate that the only fluorinated product is SF_4. The weight of residue is consistent with the total fluorine component reacting with S_4N_4 forming SF_4 and nitrogen and the chlorine component reacting in the ratio 1:1 with the remaining NS units forming thiazyl chloride (NSCl), which then oligomerises producing $(NSCl)_3$ and $(NSCl)_4$, the observed products.

Due to the low yield of thiazyl fluoride from the reactions of chlorine monofluoride with tetrasulphur tetranitride, the exchange-fluorination reactions of chlorine monofluoride with trichlorotrithiatriazene were investigated.

The proposed reaction of ClF with $(NSCl)_3$ (ratio 3:1) was the formation of trifluorotrithiatriazene with chlorine as the by-product (equation 4.3b).

$$(NSCl)_3 + 3ClF \longrightarrow (NSF)_3 + 3Cl_2 \qquad (4.3b)$$

The initial reaction between $(NSCl)_3$ and ClF in the ratio 1:3 was carried out under moderate conditions, the temperature not rising above 22°C (experiment 4.2b(i) page 177). The products obtained indicated that the reaction had not gone to completion due to the presence of unreacted $(NSCl)_3$ and sulphuryl chloride fluoride (SO_2ClF). The presence of SO_2ClF was taken to indicate that ClF remained unreacted, as SO_2ClF is formed by the reaction of SO_2 with ClF,[74] (The SO_2 being produced as a hydrolysis product of SF_4, a major volatile product of the fluorination reaction). Hence in subsequent investigations the reaction temperature was raised in an attempt to ensure complete reaction. If however too high a temperature is employed for too long a period of time then complete degradation of the sulphur-nitrogen system occurs (experiment 4.2b(iii), page 179). Heating the reaction to 60°C for 35h (experiment 4.2b(ii), page 178) did not cause thermal degradation of the sulphur-nitrogen system but did ensure that complete reaction of the chlorine monofluoride occurred. The major products observed in experiment 4.2b(ii) (table 4.12, page 178) were identified by their vibrational spectra as

SF_4, Cl_2 and $(NSCl)_3$. Hence it was concluded that the proposed reaction (equation 4.3b) does not occur.

It was noted that, in both the reactions of S_4N_4 and $(NSCl)_3$ with ClF, the main volatile products were SF_4 and N_2 and the main product in the residue was $(NSCl)_3$. Thus it is suggested that the reaction of $(NSCl)_3$ with ClF should be regarded as a subsequent reaction to that of S_4N_4 with ClF (equation 4.3c,d).

$$S_4N_4 + 4ClF \longrightarrow SF_4 + (NSCl)_3 + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}N_2 \qquad (4.3c)$$

$$\Delta H^o = -1155 kJ\ mol^{-1}$$

$$\tfrac{1}{3}(NSCl)_3 + 4ClF \longrightarrow SF_4 + \tfrac{5}{2}Cl_2 + \tfrac{1}{2}N_2 \qquad (4.3d)$$

$$\Delta H^o = -585\ kJ\ mol^{-1}$$

Therefore if the ratio of ClF : S_4N_4 is greater than 4 : 1 then the reaction proceeds via equation 4.3d producing SF_4 (equation 4.3e).

$$S_4N_4 + 8ClF \longrightarrow 2SF_4 + \tfrac{2}{3}(NSCl)_3 + 3Cl_2 + N_2 \qquad (4.3e)$$

$$\Delta H^o = -1740\ kJ\ mol^{-1}$$

(Heats of reaction calculated from standard heats of formation of the gaseous species. See Appendix B, page 319).

The above postulate may be checked by calculating the theoretical weight of the residue from the known number of mmoles of both ClF and S_4N_4 or $(NSCl)_3$ (assuming that the ratio of ClF : $S_4N_4 \ngtr 4 : 1$ and the ratio of ClF : $(NSCl)_3 \ngtr 3:1$) (equation 4.3f,g).

Weight of residue in S_4N_4/ClF reactions =

$$\left(\text{No moles NS} - \frac{\text{No mole ClF}}{4}\right) \times \text{M.W. of NSCl} \qquad (4.3f)$$

Weight of residue in $(NSCl)_3/ClF$ reactions =

$$\left(\text{No moles NSCl} - \frac{\text{No mole ClF}}{4} \right) \times \text{M.W. of NSCl} \qquad (4.3g)$$

and comparing the theoretical weight with the observed (table 4.15):

TABLE 4.15 Comparison of the theoretical and observed residue weights for the reactions of S_4N_4 and $(NSCl)_3$ with ClF.

Sulphur-Nitrogen reactant (Expt. No.)	No mmoles S/N reactant	No mmoles ClF	Calculated Weight of residue	Observed Weight of residue
S_4N_4 (4.2a(ii))	0.60	2.94	0.14g	0.16g
$(NSCl)_3$ (4.2b(i))	0.53	1.65	0.10g	0.10g
$(NSCl)_3$ (4.2b(ii))	5.46	17.80	0.97g	1.03g

From the results listed in table 4.15 it can be seen that there is close agreement between the calculated and observed residue weights. The observed weights are marginally greater than the calculated. This is believed to be due to a low concentration of $(NSF)_3$ being present. Evidence for this is drawn from the presence of NSF in the volatiles of all the listed reactions. Hence it is suggested that on cooling the vessel to -196°C to test for nitrogen in the volatiles, polymerisation of the NSF occurs yielding $(NSF)_3$ which is not completely removed on pumping at room temperature.

If the postulate expressed in equation 4.3f and g is taken to its conclusion then when the ratio of ClF to S_4N_4 is greater than or equal to 16 : 1 and the ratio of ClF to $(NSCl)_3$ is greater than or equal to 12 : 1, no residue will be obtained, the only products being SF_4, N_2 and Cl_2 (equation 4.3h,i).

$$S_4N_4 + 16\,ClF \longrightarrow 4SF_4 + 2N_2 + 8Cl_2 \qquad (4.3h)$$

$$\Delta H^o = -2900 \text{ kJ mol}^{-1}$$

$$(NSCl)_3 + 12ClF \longrightarrow 3SF_4 + \frac{3}{2} N_2 + \frac{15}{2} Cl_2 \qquad (4.3i)$$

$$\Delta H^o = -1755 \text{ kJ mol}^{-1}$$

(Heats of reaction calculated from the standard heats of formation of the gaseous compounds. See Appendix B, page 319).

In order to verify that using excess ClF would produce only the gaseous products SF_4, N_2 and Cl_2 (equation 4.3h,i), ClF was reacted with S_4N_4 in a ratio of 17 : 1 (experiment 4.2a(iv) page 176). A highly exothermic reaction occurred yielding an incondensable gas (nitrogen), chlorine (identified from its Raman spectrum) and sulphur tetrafluoride (identified from its infra-red spectrum). No residue was obtained. From the weights of the volatiles and the lack of residue it was concluded that the reaction proceeds as outlined in equation 4.3h.

If the heat of reaction for the initially postulated reaction of S_4N_4 with ClF, in a ratio of 1 : 4 (equation 4.3a), is compared with that of the observed reaction (equation 4.3c), then it can be seen that the observed reaction is some 650 kJ mol^{-1} more exothermic than that postulated. Thus the primary reason for the difference between the postulated and observed reactions is the formation of the highly thermodynamically favoured sulphur tetrafluoride.

4.3.b Mechanism by which Thiazyl units react with Chlorine Monofluoride

It is known that chlorine monofluoride adds to unsaturated centres [29, 58, 67, 79], the fluorine attacking the more electropositive end of the multiple bond. Thus it seems likely the ClF would react with NSF by a multistage addition mechanism (cf. ClF/NSF_3 [67]) forming SF_4 as the final fluorinated product (equation 4.3j).

$$NSF + 3ClF \longrightarrow \frac{1}{2} N_2 + \frac{3}{2} Cl_2 + SF_4 \quad \Delta H^o = -600 \text{ kJ mol}^{-1} \qquad (4.3j)$$

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B, page 319).

In order to verify that NSF and ClF do react as postulated in equation 4.3j, NSF* and ClF, in a ratio of 1 : 3, were reacted in an infra-red gas cell. The reaction was very rapid forming SF_4 as the only infra-red active species. Hence it is believed that any NSF produced in a fluorination reaction will react readily with ClF forming SF_4, Cl_2 and N_2, as indicated by equation 4.3j.

If the reaction of chlorine monofluoride with thiazyl fluoride proceeds via an addition mechanism then the first addition product would be $Cl-N = SF_2$, a known compound,[84] and the second would be Cl_2N-SF_3 analogous to the species Cl_2N-SF_5.[67] Therefore a reaction was devised to observe the intermediates formed in the reaction of thiazyl chloride with chlorine monofluoride ultimately producing sulphur tetrafluoride. The reaction (experiment 4.2c(ii) page 180) was done in a gas phase infra-red cell, aliquots of ClF being added to the NSCl and the species produced being monitored by their infra-red spectra (table 4.14 page 181). After the addition of the first aliquot of ClF to NSCl (ratio 1 : 1), the species observed were NSCl, NSF and $ClN = SF_2$. Hence it is concluded that the mechanism must proceed by an exchange process followed by addition of ClF across the multiple bond of $N \equiv S-F$ (equation 4.3k).

$$NSCl \xrightarrow[(a)]{ClF} NSF \xrightarrow[(b)]{ClF} ClN = SF_2 \qquad (4.3k)$$

---

* (NSF was produced by the chlorine-fluorine exchange of thiazyl chloride on a cesium fluoride column, see experiment 4.4b,(v) page 205).

The presence of NSCl and $ClNSF_2$ in the gas phase infra-red spectrum indicates that step (a) and (b) must be of similar rates, rather than step (a) being very much faster than step (b). The presence of NSF in the volatiles implies that step (b) is not very much faster than step (a).

After the addition of the second aliquot of ClF (NSCl : ClF = 1 : 2) the main product was $ClNSF_2$ with traces of SF_4. Thus it is suggested that the thiazyl halides are more activated to attack by chlorine monofluoride than $ClN = SF_2$. If the rate of addition of ClF to $ClNSF_2$ was similar or faster than the rate of addition of ClF to N≡S-X then a higher concentration of SF_4 would be observed in the gas phase infra-red spectrum. Further addition of ClF to the system caused fluorination of the sulphur and chlorination of the nitrogen producing SF_4 and NCl_3. No $Cl_2N\text{-}SF_3$ was observed. (equation 4.3.l)

$$ClN = SF_2 \xrightarrow{ClF} \left[Cl_2N - SF_3\right] \xrightarrow{ClF} Cl_3N + SF_4 \qquad (4.3.l)$$

Hence an overall reaction mechanism can be suggested for the reaction of chlorine monofluoride with thiazyl chloride (figure 4.10).

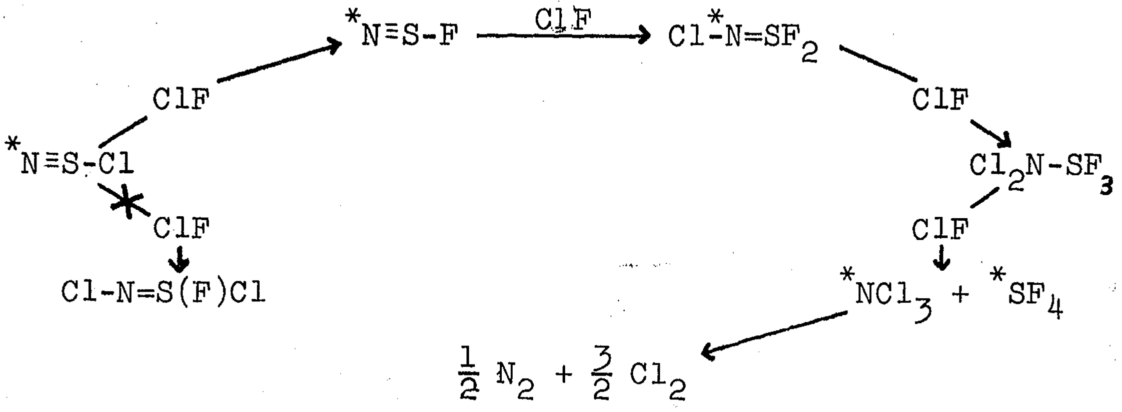
The overall reaction of NSCl with ClF is therefore the formation of sulphur tetrafluoride, nitrogen and chlorine (equation 4.3m).

$$NSCl + 4ClF \longrightarrow SF_4 + \frac{5}{2}Cl_2 + \frac{1}{2}N_2 \qquad (4.3m)$$

$$\Delta H^o = -650 \text{ kJ mol}^{-1}$$

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B, page 319).

Figure 4.10 The overall mechanism for the reaction of ClF with NSCl



(*denotes species observed in the gas phase infra-red spectrum).

Thus the above reaction scheme outlines the most likely route by which thiazyl units react with chlorine monofluoride to produce the observed products, SF_4, N_2 and Cl_2.

4.3.c The reaction of Thiazyl Fluoride with Chlorine

It has been reported by Glemser *et al* [15] that the reaction of thiazyl fluoride with chlorine, in a glass vessel, over a period of ten days, yields silicon tetrafluoride (SiF_4), thionyl fluoride (SOF_2), and thionyl chloride ($SOCl_2$) as volatiles and trichlorotrithiatriazene $(NSCl)_3$ as the residue. Hence from the above information it is concluded that the first step in the reaction sequence must be the formation of thiazyl chloride (equation 4.3n).

$$NSF + Cl_2 \rightleftarrows NSCl + ClF \quad \Delta H^o = + 50 \text{ kJ mol}^{-1} \quad (4.3n)$$

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B page 319).

As can be seen from equation 4.3n the proposed reaction step is thermodynamically unfavoured. It is also nown from this thesis (experiment 4.2c(ii) page 180) that he reverse reaction occurs readily. Hence initially it would appear unlikely that NSF reacts with chlorine, as suggested by Glemser. If however equation 4.3n is regarded as an equilibrium lying in favour of thiazyl fluoride and chlorine, then it could be regarded as the first step in a multistage reaction sequence in which ClF, produced in the first step, reacts with the NSF forming SF_4 (equation 4.3.o).

$$\begin{array}{l}3NSF + 3Cl_2 \rightleftharpoons 3NSCl + 3ClF \\ NSF + 3ClF \longrightarrow SF_4 + \tfrac{1}{2} N_2 + \tfrac{3}{2} Cl_2 \\ \hline 4NSF + \tfrac{3}{2} Cl_2 \longrightarrow 3NSCl + SF_4 + \tfrac{1}{2} N_2 + \tfrac{3}{2} Cl_2 \end{array} \qquad (4.3.o)$$

$$\Delta H^{o} = -455 \text{ kJ mol}^{-1}$$

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B page 319).

In order to show whether ClF is produced, as suggested by equation 4.3.o, a large excess of sulphur dioxide was added to the NSF/Cl_2 reaction (experiment 4.2c(iv) page 181). It is known that there is a rapid reaction between SO_2 and ClF[74] thus, any ClF produced by the reaction of NSF with Cl_2 will be removed as SO_2ClF, which is readily identifiable by its strong characteristic infra-red spectrum (equation 4.3p).

$$\begin{array}{lll}NSF + Cl_2 \longrightarrow NSCl + ClF & & \Delta H^{o} = +50 \text{ kJ mol}^{-1} \\ ClF + SO_2 \longrightarrow SO_2ClF & & \Delta H^{o} = -119 \text{ kJ mol}^{-1} \quad (4.3p) \\ \hline NSF + Cl_2 + SO_2 \longrightarrow NSCl + SO_2ClF & & \Delta H^{o} = -70 \text{ kJ mol}^{-1} \end{array}$$

The heats of reaction are calculated from the standard heats of formation of the gaseous species. See Appendix B page 319).

The rapid formation of SO_2ClF by the reaction of lF with SO_2 will cause the equilibrium (equation 4.3n) to be onstantly moved in favour of the production of NSCl and ClF.

Thus the observed concentration of SO_2ClF should increase with time. The above postulate was borne out by the results obtained from experiment 4.2c(iv) (page 181), in which the concentrations of both SO_2ClF and NSCl increased with time and the concentration of NSF decreased. Hence it is concluded that the gaseous products observed by Glemser were the products of hydrolysis, and the reaction with glass, of SF_4. The rate of the reaction between thiazyl fluoride and chlorine is very low, as indicated by both experiments 4.2c(iii, iv) (page 181). The low rate of reaction is probably due to the rate determining step being the thermodynamically unfavoured formation of ClF (equation 4.3n).

4.3.d The Mechanism by which Chlorine Monofluoride reacts with Tetrasulphur Tetranitride

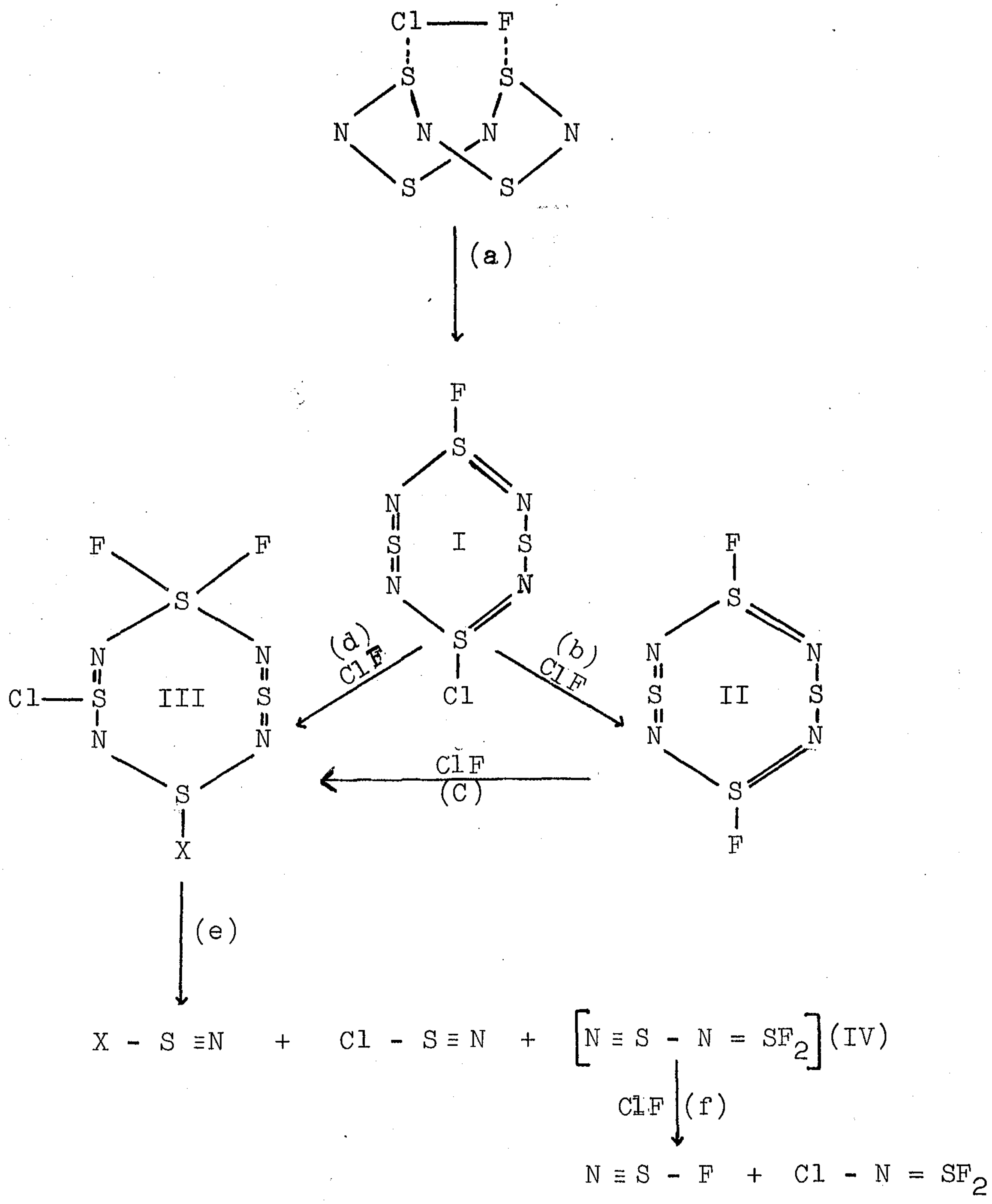
The reactions of S_4N_4 with halogens and interhalogens have been widely studied[39,78,80-83] and compounds of various skeletal arrangements synthesised. Recent work by Zborilova and Gebauer[83] has shown that the initial product in the chlorination of S_4N_4 by chlorine is $S_4N_4Cl_2$ and that the initial product in the fluorination of S_4N_4 by IF_5 is $S_4N_4F_2$. Hence it was postulated that the initial product in the reaction of S_4N_4 with ClF would be S_4N_4ClF.

In the reaction of ClF with S_4N_4, in a molar ratio of 1 : 1, (experiment 4.2a(iii) page 175), at low temperatures, no evidence was found for the existence of S_4N_4ClF as a stable isolatable species. From the weight and infra-red and ^{19}F n.m.r. spectra of the residue it was concluded that the species present in the residue were S_4N_4 and $S_4N_4Cl_2$. The presence of SF_4 in the volatiles implies that complete fluorination of one sulphur atom occurs at a higher rate than the addition of ClF to S_4N_4. Using basically the same equation as equation 4.3j but with modifications, (due to lack of chlorine to convert all "SN" units into NSCl), the theoretical weight of residue is calculated as 0.42g (observed = 0.38g). The discrepancy is believed to be due to prolonged pumping at room temperature removing all the $(NSF)_x$ species.

It is suggested that $S_4N_4Cl_2$ is formed by the reaction of chlorine, produced as a by-product of the fluorination reactions of ClF, with S_4N_4, (c.f. Zborilova[83]). A proposed reaction mechanism for the reaction of chlorine monofluoride with tetrasulphur tetranitride is presented in figure 4.11.

Step (a) in the mechanism is the addition of ClF to the S.......S bridge in S_4N_4. It seems likely that fluorine, chlorine and chlorine monofluoride will all add 1,5 across the relatively electropositive sulphurs rather than 1,2 across a sulphur-nitrogen bond. Thus the most stable disubstituted $S_4N_4X_2$ ring is formed with the least interaction between highly electronegative substituents. It is not known whether S_4N_4ClF (intermediate I) reacts with ClF by an exchange mechanism (step (b)) followed by an addition mechanism step (c), or by a single addition step (step (d)), to form intermediate III. It can only be surmised that because $S_4N_4Cl_2$ can be fluorinated to $S_4N_4F_2$[83] without the formation of SF_4, then step (b) and (c) may well be preferred to step (d). It is however likely that both routes operate to some extent in the actual mechanism. Intermediate III is then postulated as dissociating into substituted thiazyl units. Intermediate IV then reacts by an addition mechanism with chlorine mono-

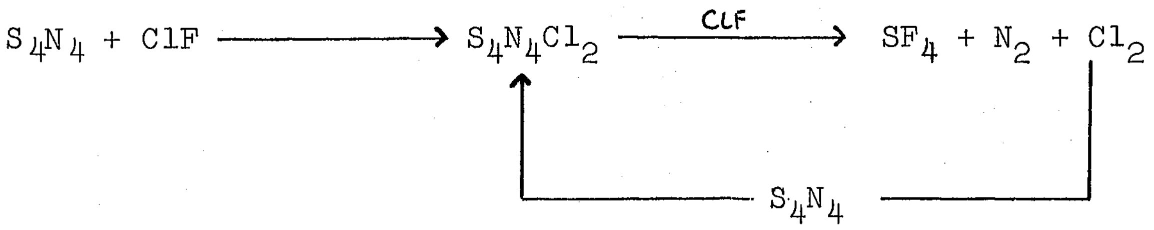
Figure 4.11 Proposed Mechanism by which ClF reacts with S_4N_4



fluoride forming NSF and ClN = SF_2. These latter species then react as previously indicated in equations 4.3k,1 forming SF_4, N_2 and Cl_2.

The species observed in the residue are, therefore, formed by the reaction of S_4N_4 with chlorine. It is suggested that once $S_4N_4Cl_2$ has been produced, then it is this compound that reacts with ClF in preference to S_4N_4 due to the substituted sulphurs being activated to attack by ClF, relative to the sulphurs in S_4N_4. Hence the initial step in the mechanism becomes the chloro-fluoro exchange between $S_4N_4Cl_2$ and ClF forming S_4N_4ClF (intermediate I) which subsequently reacts by the same mechanism as presented in figure 4.11. Therefore due to the homogeneous gas phase steps in the mechanism having a higher rate than the heterogeneous gas solid steps, a sufficient chlorine concentration is built up to maintain the presence of $S_4N_4Cl_2$ in the system (figure 4.12). However due to the basic reaction being heterogeneous and the concentration of ClF being initially much greater than that of Cl_2, the actual reaction mechanism will involve both attack on S_4N_4 and $S_4N_4Cl_2$ by ClF.

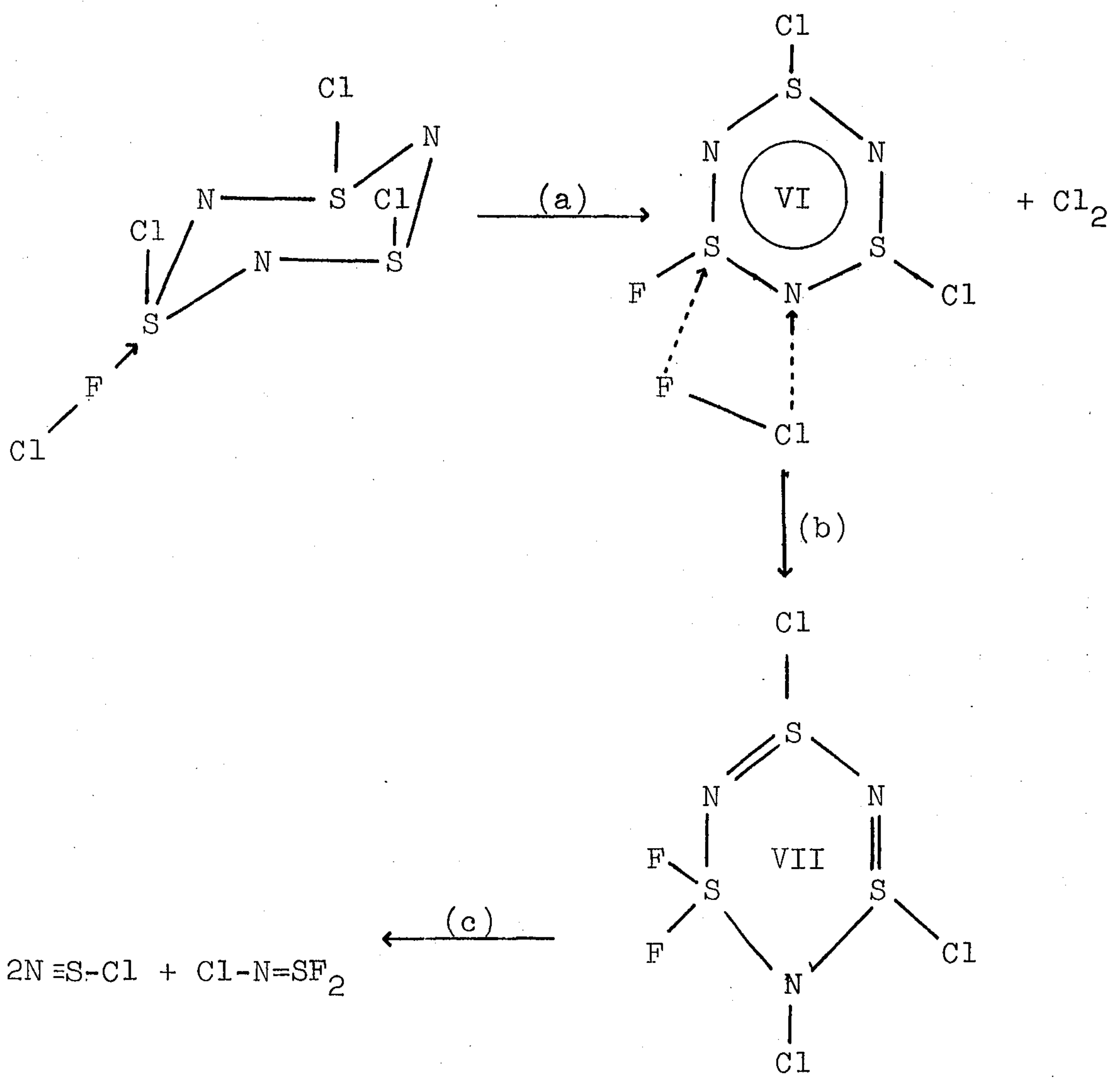
Figure 4.12 The Overall Reaction Cycle for the Reaction of S_4N_4 with ClF



4.3.e The Mechanism by which Chlorine Monofluoride reacts with Trichlorotrithiatriazene ($(NSCl)_3$)

In the reactions of $(NSCl)_3$ with ClF the main products observed are SF_4, Cl_2, N_2 and approximately 75% of the $(NSCl)_3$ starting material (experiment 4.2b(i,ii) pages 177, 178). It therefore appears as though the chlorine monofluoride reacts in such a way as to completely fluorinate one sulphur. A mechanism for the reaction of ClF and $(NSCl)_3$ is presented in figure 4.13.

Figure 4.13 Proposed Mechanism by which ClF reacts with $(NSCl)_3$



It is, therefore, suggested that the initial attack of ClF on $(NSCl)_3$ is by an exchange mechanism. The chlorine monofluoride attacks a sulphur from the opposite side to chlorines (probably an S_N2 mechanism). The effect of the equatorial S-F bond is to activate the fluorine substituted sulphur, relative to the chlorine substituted sulphurs, to further attack by ClF forming the intermediate VII. The intermediate VII then dissociates into two thiazyl chloride units and N-chloro-imido-disulphurous difluoride[84], which then react with ClF as indicated by figure 4.10. As postulated previously, the rate of the homogeneous gas phase reactions will be, on the whole, greater than the heterogeneous gas-solid reactions. Hence it seems likely that the majority of the ClF will react with NSCl(g) and $ClNSF_2$ forming SF_4, N_2 and Cl_2 thus leaving approximately 75% of the $(NSCl)_3$ starting material unreacted.

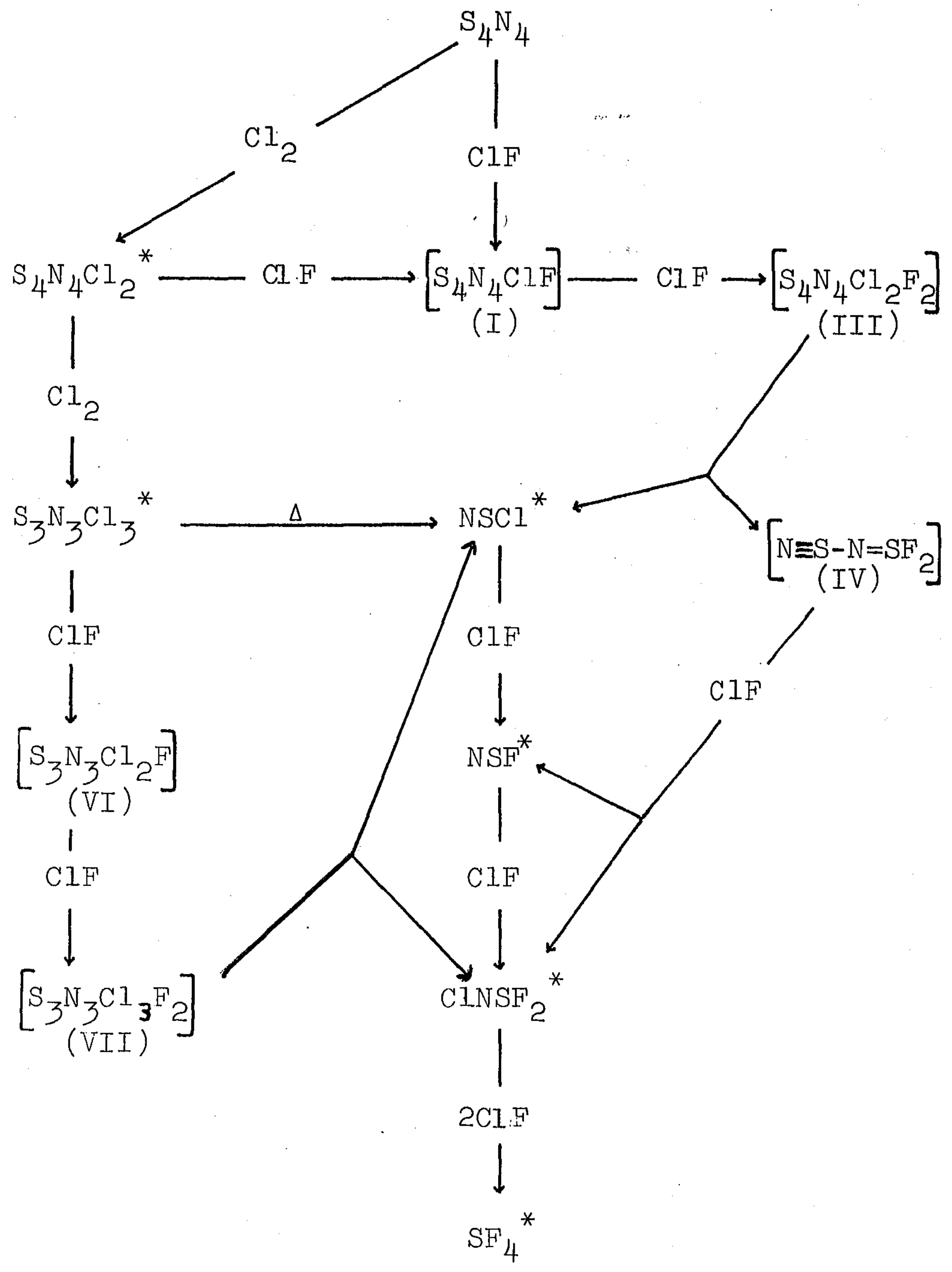
4.3.5 Overall Conclusion to the Reactions of ClF with S/N Compounds

The reactions of chlorine monofluoride with sulphur-nitrogen species do not provide a synthetically viable route to thiazyl fluoride. However should thiazyl chloride become a readily available starting material, then the reaction of NSCl with ClF in a 1 : 2 ratio might present a very useful synthetic route to N-chloro-imido-sulphurous difluoride ($Cl-N=SF_2$).

The over-riding factor which prevents the isolation of synthetically viable yields of NSF is the formation of SF_4 by the highly thermodynamically favoured addition of ClF across the multiple bond. Hence if any multiply-bonded sulphur-nitrogen species is formed in the presence of ClF, then addition across the multiple bond occurs with the eventual formation of SF_4.

An overall reaction scheme is presented in figure 4.14 for all the reactions investigated.

Figure 4.14 Overall Reaction Scheme for the Reactions of ClF with S/N Compounds



* Denotes species observed.

Roman numerals refer to intermediates postulated in figures 4.11 and 4.13.

4.4 Experimental

Exchange Reactions of Trichlorotrithiatriazene with Cesium Fluoride

4.4.a Exchange reactions using solvents

(i) Trichlorotrithiatriazene and Cesium Fluoride in Sulphur Dioxide

Trichlorotrithiatriazene (0.533g, 2.180 mmole) and powdered, anhydrous, cesium fluoride (3.300g, 21.71 mmole) were placed in a pre-dried, vacuum tight F.E.P. vessel (figure 1.3, page 15), and sulphur dioxide (12.136g) condensed in. The vessel was maintained at room temperature for 48h. and the high pressure infra-red spectrum of the volatiles present at room temperature recorded. The spectrum indicated that only sulphur dioxide and a very low concentration of sulphuryl chloride fluoride (SO_2ClF) were present. The volatiles present at room temperature were condensed into a holding vessel and the infra-red spectrum of the residue recorded.

Infra-red spectrum of the residue (nujol mull) 1296m,br, 1230 m(sh), 1185 s,br, 1105 s, 1174 m, 925 w, 750 w, 700 w, 650vw, 600 m(sh), 592 s, 500 s,br, cm^{-1}.

(ii) $(NSCl)_3$ and CsF in Arsenic trifluoride (AsF_3)

AsF_3 (10.134g) was condensed on to $(NSCl)_3$ (0.907g, 3.710 mmole) and powdered, anhydrous CsF (2.567g, 16.89 mmole), contained in a pre-dried vacuum tight pyrex vessel (figure 1.1, page 14). The reaction was warmed to room temperature. At ca. 0°C a vigorous reaction occurred in which the CsF bonded together forming a solid mass. The AsF_3 solution was filtered off and the insolubles washed several times with AsF_3 to remove all the solubles. On standing for 10h. at room temperature large colourless crystals were formed in the AsF_3 solution. The solvent was filtered off these crystals and the gas phase infra-red spectrum of the volatiles present at room temperature recorded prior, to the removal of the solvent. The infra-red spectrum indicated that a low concentration of NSF was present, the predominant species being the solvent. On removal of the solvent *in vacuo* the large colourless crystals gradually disappeared.

(iii) $(NSCl)_3$ and CsF in AsF_3 (Repeat of expt. 4.4a(ii))

AsF_3 (7.312g) was condensed on to $(NSCl)_3$ (0.614g, 2.511 mmole) and powdered, anhydrous, CsF (1.22g, 8.026 mmole) contained in a pre-dried vacuum tight F.E.P. vessel. The reaction was warmed slowly to room temperature from -22°C over a period of 2h, and maintained at room temperature for 60h. The gas phase infra-red spectra of the volatiles, at various slush bath temperatures were recorded and assigned (table 4.16).

TABLE 4.16 Volatiles at various slush bath temperatures for the reaction of $(NSCl)_3$ with CsF in AsF_3

Slush bath temperature (°C)	Pressure (torr)	Species identified
-196	10	N_2
-78	50	SF_4, AsF_3
-22	50	AsF_3, NSF
r.t.	160	SO_2ClF, AsF_3, NSF

(Species identified from their infra-red spectra. Standard spectra referenced in Appendix A, page 313).

The volatiles present at room temperature were removed but it was noted that on pumping the residue, AsF_3 was being constantly removed. Thus an accurate residue weight could not be recorded.

Infra-red spectrum of the residue (nujol mull) 1300 w, 925 w, 715 m, 695 m(sh), 672 s, 640 s, 596 s(sh), 675 vs, 383 s, 340 s, cm^{-1}.

(iv) $(NSCl)_3$ and CsF in Freon 11 (CCl_3F)

Freon 11 (5.0431g) was condensed into a pre-dried F.E.P. tube (figure 1.3, page 15) containing $(NSCl)_3$ (0.376g, 1.538 mmole) and powdered, anhydrous CsF (1.124g, 7.395 mmole). The reaction was warmed slowly to room temperature and maintained at this temperature for 24h. The gas phase infra-red spectra of the volatiles at various slush bath temperatures were then recorded and assigned (table 4.17).

TABLE 4.17 Species observed in the vapour phase of the $(NSCl)_3$/CsF reaction in CCl_3F

Slush bath temperature (°C)	Species observed
-78	CCl_3F
-22	CCl_3F, SOF_2
r.t.	CCl_3F, NSF, SOF_2

(Species identified from their infra-red spectra. Standard spectra referenced in Appendix A, page 313).

Sulphur dioxide was added to the volatiles present at -78°C to test for the presence of ClF by the formation of SO_2ClF, which is readily identified from its infra-red spectrum.[74] No evidence for the formation of ClF was noted.

The volatiles (5.163g) present at room temperature were removed and the infra-red spectrum of the residue (1.364g) recorded.

Infra-red spectrum of the residue (nujol mull) 2020 s,br, 1230 vs, br, 1130 w, 1105 w, 1090 w, 925 m, 830 w, br, 718 m, 698 m, 660 m, 607 m, 550 m, cm^{-1}.

(v) $(NSCl)_3$ and CsF in perfluorobenzene (C_6F_6)

Perfluorobenzene (3.33g) was condensed on to $(NSCl)_3$ (1.270g, 5.19 mmole) and CsF (2.730g, 17.96 mmole) contained in a pre-dried, vacuum tight, Monel vessel (figure 1. 4, page 15). The reaction was warmed slowly to room temperature and maintained at this temperature for 1h. The infra-red spectrum of the volatiles present at room temperature, was recorded indicating that only C_6F_6 was present. The reaction was then heated to 80°C for 2h. and the volatiles present at room temperature were retested for the presence of NSF. The infra-red spectrum indicated that NSF had been produced and thus the reaction was heated at 80°C for a further 40h. to ensure complete reaction. The gas phase infra-red spectrum of the volatiles was recorded at various slush bath temperatures and the species present identified by comparison with standard infra-red spectra (table 4.18), (standard spectra are referenced in Appendix A, page 313).

TABLE 4.18 Species identified in the volatiles at different slush bath temperatures from the reaction of $(NSCl)_3$ with CsF in C_6F_6

Slush bath temperature (°C)	Species identified
-196	N_2
-95	SF_4, SOF_2, NSF_3
-78	SOF_2, SF_4
-55	NSF, C_6F_6
-45	NSF, C_6F_6
-22	C_6F_6, NSF, SOF_2, SF_4
r.t.	C_6F_6, NSF

(Species listed in order of concentration in the gas phase infra-red spectrum)

The volatiles were completely removed at room temperature and the infra-red spectrum of the residue (3.34g) recorded.

Infra-red spectrum of the residue (nujol mull) 922 m, 917 m(sh), 720 s, 698 m, 550 s, 342 s, cm^{-1}.

4.4.b Exchange Reactions of Thiazyl Chloride with cesium fluoride without solvents

(i) The effect of temperature on the solid phase reaction between trichlorotrithiatriazene and cesium fluoride

$(NSCl)_3$ (0.845g, 3.46 mmole) and CsF (1.832g, 12.05 mmole), were placed in a pre-dried, vacuum tight Monel vessel (figure 1.4, page 15). The vessel was then connected to a Monel vacuum line, equipped with a vacuum-pressure gauge and the line and vessel put under static vacuum. The temperature was slowly raised and the pressure was then monitored with respect to both time and temperature (table 4.19).

TABLE 4.19 Variation in pressure w.r.t. temperature on heating the $(NSCl)_3$/CsF system

Temperature (°C)	Observed pressure (torr)	Time from commencement of experiment (minutes)
r.t.	45	40
30	50	55
40	75	65
43	1170	67
45	1040	75

As is noted in table 4.19 a large increase in pressure occurs at 43°C. The vessel was cooled to -196°C to observe the pressure of incondensable gas (470 torr, nitrogen). The incondensable gas was then removed and the reaction warmed to room temperature, at which temperature the gas phase infra-red spectrum of the volatiles present, was recorded. The infra-red spectrum indicated that SF_4, SOF_2 and NSF were the major volatile products.

The above experiment was repeated bringing the temperature very slowly up to the 43°C area. The same style of reaction occurred with the rapid increase on pressure occurring in the range 43-44°C.

(ii) The variation in observed pressure at a constant temperature for the solid phase reaction between trichlorotrithiatriazene and cesium fluoride.

Trichlorotrithiatriazene (0.700g, 2.86 mmole) and powdered anhydrous cesium fluoride were placed in a pre-dried, vacuum tight, F.E.P. vessel and the system put under a static vacuum (c f. experiment 4.4b(i)). The reaction was then heated to 35°C and the pressure within the system measured with time (table 4.20).

TABLE 4.20 Variation of the pressure of volatiles, generated by the reaction of $(NSCl)_3$ with CsF, at constant temperature, with respect to time

Pressure (torr)	Time from start of Expt.(minutes)
10	15
20	25
30	60
40	120

(volume of system = 60 cm^3)

(iii) Solid phase reaction between $(NSCl)_3$ and KF

$(NSCl)_3$ (0.432g, 1.77 mmole) and KF (0.942g, 16.24 mmole) were placed in a pre-dried, vacuum tight F.E.P. tube and placed under static vacuum (c f. experiment 4.4b(i)). The system was then heated and the volatiles produced were monitored by their pressure and gas phase infra-red spectrum. The reaction was heated to 120°C but no thiazyl fluoride was produced, the only product observed in the gas phase infra-red spectrum being NSCl .

(iv) Reaction of thiazyl chloride with cesium fluoride

$(NSCl)_3$(0.683g, 2.793 mmole) was placed in a pre-dried, vacuum tight, F.E.P. vessel and on top of this was placed a one inch layer of passivated F.E.P. chippings. A layer of powdered, anhydrous, cesium fluoride (7.073g, 46.53 mmole), 3 cm in length, was then placed on top of the F.E.P. chippings (figure 4.15, page 216). The vessel was then placed under static vacuum (c f. experiment 4.4b(i)) and heated slowly to 70°C. The gas phase infra-red spectra of the volatiles were monitored over a period of 4h. but no evidence for the formation of NSF was noted. Thiazyl chloride was the only species observed in the gas phase infra-red spectrum.

(v) The reaction of thiazyl chloride with cesium fluoride at 110°C

In a typical reaction $(NSCl)_3$ (2.436g, 9.96 mmole) was placed in a pre-dried pyrex vessel and connected to a Monel column ($\frac{1}{4}$" diam. 25 cm. in length) packed with powdered anhydrous CsF (8.10g, 53.29 mmole). The column was then connected to a vacuum line and the whole system evacuated (figure 4.16, page 217). The column was then heated to 160°C for 1h. in a dynamic vacuum to remove any water and then cooled to 110°C for the reaction. The system was then placed under static vacuum and the $(NSCl)_3$ heated slowly to 70°C, the thiazyl chloride being cryogenically pumped through the column, at 110°C, in to the collecting vessel at -196°C. The volatiles formed on the column were monitored by their gas phase infra-red spectrum. Initially the main products were SF_4 and NSF but after ca. 10 minutes the concentration of SF_4 in the volatiles had dropped to virtually zero. For the majority of the reaction the main product produced on the column was NSF but after approximately 75% of the $(NSCl)_3$ had sublimed, it was noted that the NSCl was passing through the column unreacted. The reaction was, therefore, terminated. The gas phase infra-red spectrum of the volatiles condensed in the collection vessel (1.66g) was recorded and indicated the presence of NSF, SOF_2 and SO_2ClF. The weight loss of the column and $(NSCl)_3$ bulb was recorded (1.64g) and also the weight of unreacted $(NSCl)_3$ (0.213g). Hence, assuming that all the volatiles are of the form $(NSF)_x$ (x = 1 or 3), a yield of 85% thiazyl fluoride is calculated.

(vi) The exchange reaction between thiazyl chloride and KF on a column

Experiment 4.4b(v) was essentially repeated using a KF column. The column was heated to 130°C in an attempt to obtain an exchange reaction. However, little or no exchange occurred, the major volatile products coming off the end of the column being NSCl, SF_4, N_2 and some NSF. A yield of only about 10% was obtained using KF as the exchange reagent.

4.5 Discussion

Exchange reactions of Trichlorotrithiatriazene with Cesium Fluoride

Thiazyl fluoride and its trimeric and tetrameric oligomers have been synthesised by the oxidation-fluorination of both tetrasulphur tetranitride (S_4N_4) and trichlorotrithiatriazene $(NSCl)_3$ by silver difluoride (AgF_2).[15-18,39,80] The direct exchange reaction of the chlorines in $(NSCl)_3$ for fluorines by the use of an ionic fluoride has, however, not been previously investigated (equation 4.5a).

$$(NSCl)_3 + 3MF \longrightarrow (NSF)_3 + 3MCl \qquad (4.5a)$$

In all the reactions of $(NSCl)_3$ at elevated temperatures there is a significant concentration of NSCl monomer.[85] Hence depending upon the temperature at which the exchange reaction occurs, the mechanism is either predominantly that of exchange with the trimer (equation 4.5a) or with the monomer (equation 4.5b).

$$3NSCl + 3MF \longrightarrow 3NSF + 3MCl \qquad (4.5b)$$

In order to find the most suitable metal fluoride for the exchange reactions (4.5a,b) it is necessary to be able to calculate the difference between the heats of formation of the chlorinated and fluorinated sulphur-nitrogen species. The heats of formation of the trihalotrithiatriazenes have not been reported and thus it is possible only to estimate the heat of reaction of the monomer exchange mechanism. The heat of formation of NSF is known but that of NSCl has been calculated from known S-Cl bond energies and the N≡S bond energy in thiazyl fluoride (see Appendix B, page 319). Hence in determining which ionic fluoride to use as the exchange reagent the criterion presented in equation 4.5c was used (table 4.21).

$$NSCl_{(g)} + MF_{(c)} \xrightarrow{\Delta H^{o}} NSF_{(g)} + MCl_{(c)}$$

$$\therefore \quad \Delta H^{o} = \Delta H_f^{o}NSF_{(g)} + \Delta H_f^{o}MCl_{(c)} - \Delta H_f^{o}NSCl_{(g)} - \Delta H_f^{o}MF_{(c)} \qquad (4.5c)$$

$$\Delta H^{o} = \Delta H_f^{o}MCl_{(c)} - \Delta H_f^{o}MF_{(c)} - 100 \text{ kJ mol}^{-1}$$

$\therefore \quad \Delta H_f^{o}MCl_{(c)} - \Delta H_f^{o}MF_{(c)} \geqslant 100$ kJ mol^{-1} for the exchange reaction to proceed readily.

TABLE 4.21 Thermodynamic comparison of a series of ionic fluorides w.r.t. the exchange reaction:

$$NSCl_{(g)} + MF_{(c)} \xrightarrow{\Delta H^o} NSF_{(g)} + MCl_{(c)}$$

Cation	$\Delta H^o_f MF_{(c)}$ kJ mol^{-1}	$\Delta H^o_f MCl_{(c)}$ kJ mol^{-1}	Heat of Exchange Reaction ΔH^o (kJ mol^{-1})
Li^I	-612	-408	+ 103
Na^I	-569	-411	+ 58
K^I	-562	-436	+ 27
Cs^I	-531	-433	-2
NH_4^I	-467	-315	+ 52
Ag^I	-203	-127	-24
Ba^{II}	-1200	-860	+ 71
Pb^{II}	-663	-359	+ 20
$Tl^I_{(g)}$	-138	-67	-28

(Standard heats of formation are referenced in Appendix B, page 319)

From table 4.21 it can be seen that, even allowing for a miscalculation of the heat of formation of thiazyl chloride of ca. 10 kJ mol^{-1} there are still only three feasible ionic fluorides for the exchange reaction, CsF, AgF and TlF. In no case is the exchange highly favoured but relatively speaking, AgF and TlF would be noticeably better exchange reagents than CsF. Due to the unavailability of both thalium and silver fluorides at the time of this work (though both are available from Alfa Vertron) the exchange reactions using cesium fluoride were investigated.

4.5.a The exchange reactions between Trichlorotrithiathiazene and Cesium Fluoride in solvents

The exchange reactions between $(NSCl)_3$ and CsF using sulphur dioxide (4.4a(i) page 199) and arsenic trifluoride (experiments 4.4a(ii,iii) pages 199, 200) proved unsatisfactory due to reaction of the solvent with the cesium fluoride forming $CsSO_2F$ and $CsAsF_4$. The reaction of cesium fluoride with arsenic trifluoride was highly exothermic (experiment 4.4a(ii), page 199) and it was found necessary to control the temperature of the reaction. Large colourless crystals were formed from the resulting AsF_3 solution in experiment 4.4a(ii) which disappeared on removal of the solvent from the system under reduced pressure. It is suggested that the crystals observed were $(NSF)_3$ which is known to sublime easily at room temperature[13] thus being removed with the solvent (AsF_3: Bpt. 63°C, vapour pressure at 13.4°C = 100 torr).[86] Low concentrations of thiazyl fluoride were observed in the gas phase infra-red spectrum of the volatiles present at room temperature. Hence it is believed that exchange does occur, forming $(NSF)_3$ but due to the similarities in vapour pressure of $(NSF)_3$ and the solvent, the isolation of the product is difficult.

In order to minimise the reaction of cesium fluoride with the exchange solvent, Freon II (CCl_3F) (experiment 4.4a(iv) page 201) and perfluorobenzene (C_6F_6) (experiment 4.4a(v) page 202) were employed. The exchange reaction between cesium fluoride and trichlorotrithiathiazene in these solvents was, however, slow. The low rate of reaction is almost certainly due to the low solubility of cesium fluoride in the solvents. However with sufficiently finely ground cesium fluoride and long reaction times significant yields of thiazyl fluoride and trifluorotrithiatriazene were obtained (yield (CCl_3F) : 41% ; (C_6F_6) : 65%). The yield of product is however artificially low due to the presence of a small quantity of a sulphur-nitrogen species in the residue. The sulphur-nitrogen compound in the residue appears, from its infra-red spectrum (925 s, 720 s, 698 s, 550 s, and 342 s cm^{-1}) to be S_4N_4. The mechanism by which both S_4N_4 and SF_4 (seen in the infra-red spectrum of the volatiles) are formed is thought to be highly complex involving the formation of ClF at some stage.

As can be seen from tables 4.17 and 4.18 the separation of thiazyl fluoride from the solvent presented a decided problem. During the evacuation of a vessel containing CsF and $(NSCl)_3$, prior to condensing in the solvent, it was noted that a gas was released that gave a blue discharge. The concentration of this gas was very low but it was suggested that it was thiazyl chloride or thiazyl fluoride. Hence due to this observation and the difficulty in separating thiazyl fluoride from solvents the solid phase reaction of cesium fluoride with trichlorotrithiatriazene was investigated.

4.5.b The Solid Phase Exchange Reactions between Cesium Fluoride and Trichlorotrithiatriazene ($(NSCl)_3$) or Thiazyl Chloride (NSCl)

In the initial investigative reaction, the mixture of cesium fluoride and trichlorotrithiatriazene was heated slowly, under static vacuum and the pressure above the solids monitored (experiment 4.4b(i) page 203). The pressure rose quite slowly up to approximately 43°C at which temperature a highly exothermic reaction occurred with the release of a considerable volume of gas, (table 4.19 page 203). The experiment was repeated to check whether the vigorous reaction was solely temperature dependent or if it was temperature and time dependent. The rate of heating in the second experiment was very much lower than that in the first experiment but it was noted that the reaction occurred at the same temperature (43-44°C). Thus it is concluded that the vigorous reaction occurs at ca. 43°C and is not dependent on how long the reaction has been at a certain temperature. The volatiles present after the sudden increase in pressure were identified as nitrogen, sulphur tetrafluoride and thiazyl fluoride. Hence the "solid phase" exchange had occurred. In order to observe the reaction products without the reaction going critical, the temperature was raised to only 35°C, some 7-8°C lower than that at which the decomposition reaction occurs. The pressure of volatiles above the reactants was monitored with respect to time at a constant temperature (35°C) (experiment 4.4b(ii) page 203). A very low rate of reaction occurred, the volatiles being identified, by infra-red spectroscopy as, NSF and NSCl.

In an attempt to avoid the highly exothermic reaction between cesium fluoride and trichlorotrithiatriazene, on which thermal breakdown of the S/N species occurs with the formation of nitrogen, potassium fluoride was employed as the exchange reagent (experiment 4.4b(iii) page 204). No exchange reaction was observed to occur. Hence it was concluded that exchange does occur between trichlorotrithiatriazene and cesium fluoride ($\Delta H^o \simeq -2$ kJ mol^{-1}) but not with potassium fluoride ($\Delta H^o \simeq + 27$ kJ mol^{-1}).

It is believed that the very high rate of reaction at 43°C is due to the rate of production of heat by a mildly exothermic reaction exceeding the activation barrier of a much more exothermic reaction. Hence once the second reaction has been initiated, a chain process is set up in which very high temperature, localised, regions occur due to the lack of a moderating solvent. The existence of these hot spots causes the thermal decomposition of the S/N species. Thus the reaction goes critical due to the rapid increase in temperature of the reaction, there being no solvent to dissipate any thermal energy.

From the results obtained from experiment 4.4b(i) (page 203) it is known that exchange does occur between $(NSCl)_3$ and CsF. Thus a reaction system was devised so that a chain reaction, caused by localised heating effects within the solid phase reactants, could not occur.

It has been known for many years that trichlorotrithiatriazene decomposes on heating *in vacuo* yielding the monomer, thiazyl chloride.[85] Hence in order to separate the cesium fluoride and trichlorotrithiatriazene it was decided to pass thiazyl chloride through a column of cesium fluoride (see figures 4.15, 4.16, pages 216, 217). Initially a relatively simple design was adopted in which the $(NSCl)_3$ and CsF were heated to the same temperature (70°C). The exchange reaction was however inefficient under these conditions, thiazyl chloride passing through the cesium fluoride column unreacted. To improve the exchange efficiency it was found necessary to heat the column and $(NSCl)_3$ independently. The most efficient exchange appeared to occur with the cesium fluoride column at 110°C and the trichlorotrithiatriazene container at 70°C. The products from the exchange reaction were monitored by expanding the volatiles, coming off the column, into a gas phase infra-red cell and identifying the products by their infra-red spectra. (Standard infra-red spectra are referenced in Appendix A, page 313). Initially it was noted that approximately equal concentrations of thiazyl fluoride and sulphur tetrafluoride were produced but this ratio rapidly altered, there being no sulphur tetrafluoride formed after ca. 10 minutes. The presence of SF_4 in the volatiles initially produced, is suggested to be due to the thermal decomposition of thiazyl chloride into nitrogen and disulphur dichloride, the latter then reacting with cesium fluoride forming SF_4 (equation 4.5d).

$$^{2}/_{3}\ (NSCl)_3 \underset{}{\overset{\Delta}{\rightleftharpoons}} 2NSCl \xrightarrow{\Delta} N_2 + S_2Cl_2 \qquad (4.5d)$$

$$S_2Cl_{2(l)} + 4CsF_{(s)} \longrightarrow 4CsCl_{(s)} + SF_{4(g)} + {^1/_8}S_{8(s)}$$

$$\Delta H^o = -323\ kJ\ mol^{-1}$$

The thermal decomposition of $(NSCl)_3$ in to N_2 and S_2Cl_2 is likely to occur to a small extent throughout the reaction but initially the rate of decomposition is likely to be higher due to non-uniform heating of the $(NSCl)_3$.

In the latter stages of the reaction exchange efficiency drops significantly with thiazyl chloride passing through the column unreacted. It is believed that the reason for the gradual decrease in efficiency of the column with time, is due to the surface coating of CsF by CsCl. Hence the effective exchange area presented by the cesium fluoride is decreased and therefore eventually "saturation" of the column occurs, there being little or no exchange area. Thiazyl chloride is thus observed in the volatiles.

The exchange reaction using potassium fluoride as the exchange reagent, and raising the column temperature to 130°C produced a low yield of thiazyl fluoride (experiment 4.4b(vi) page 206). It may therefore be suggested that, as the heats of formation of potassium fluoride and potassium chloride do not change significantly with temperature, then the term ΔH_f^t NSF$_{(g)}$ - ΔH_f^t NSCl$_{(g)}$ appears to become more negative. With the increase in temperature it is also likely that the entropy terms will start to play a significant role in the calculation of the free energy of the reaction. Thus the formation of thiazyl fluoride from thiazyl chloride using potassium fluoride as the exchange reagent at high temperatures may be due to the increased significance of the entropy terms and/or the variation with temperature of the heat of formation of the thiazyl halides.

4.5.c. Conclusion

The Exchange Reactions of Trichlorotrithiatriazene with Cesium Fluoride

The exchange reactions of trichlorotrithiatriazene with cesium fluoride yield, to a greater or lesser extent, thiazyl fluoride and trifluorotrithiatriazene. At ambient temperatures, using a solvent, a mixture of NSF and $(NSF)_3$ is produced whereas at elevated temperatures the majority of the fluorinated product is NSF.

From the heats of reaction presented in table 4.21 it can be seen that if exchange occurs using cesium fluoride, then it is likely that the rate of the conversion will be higher with silver or thallium fluoride. It is believed that $(NSF)_3$ would be readily produced in high yields on reacting $(NSCl)_3$ with either AgF or TlF in perfluorobenzene (C_6F_6), as under the same conditions CsF gave a 65% yield of NSF and its oligomers. The rate of conversion using a column of AgF or TlF with thiazyl chloride is also likely to be higher than in the case of a CsF column due to the conversion per unit area of exchange fluoride being greater.

The efficiency of the column exchange method is however a function of both the conversion efficiency of the column and the generation of thiazyl chloride. Little work has been done using thiazyl chloride as a reactant (Chapter Five, page 227) and thus the techniques for its continuous generation without a significant impurity level are not well documented.[85] Hence an improvement to the exchange procedure will almost certainly occur when a method for producing thiazyl chloride at a steady rate, over a period of hours, is found.

The efficiency of the column is a function of the exchange fluoride, the total surface area upon which exchange can occur and the temperature at which the column is maintained. In designing a column it is recommended that a long narrow bore column is used, so as to increase the path length of the thiazyl chloride through the exchange fluoride. The use of a non-participating dispersant within the column will probably increase the net surface area of the exchange reagent relative to the same mass of pure exchange fluoride. With the increased conversion rate per unit area of fluoride (AgF and TlF relative to CsF) it is likely that the column temperature can be lowered thus minimising any dissociation of thiazyl chloride in to nitrogen and disulphur dichloride (equation 4.5d) that may occur on the column.

Hence it is concluded that a high yield of thiazyl fluoride can be produced by the exchange reaction of thiazyl chloride with a suitable ionic fluoride on an efficient column.

Figure 4.15

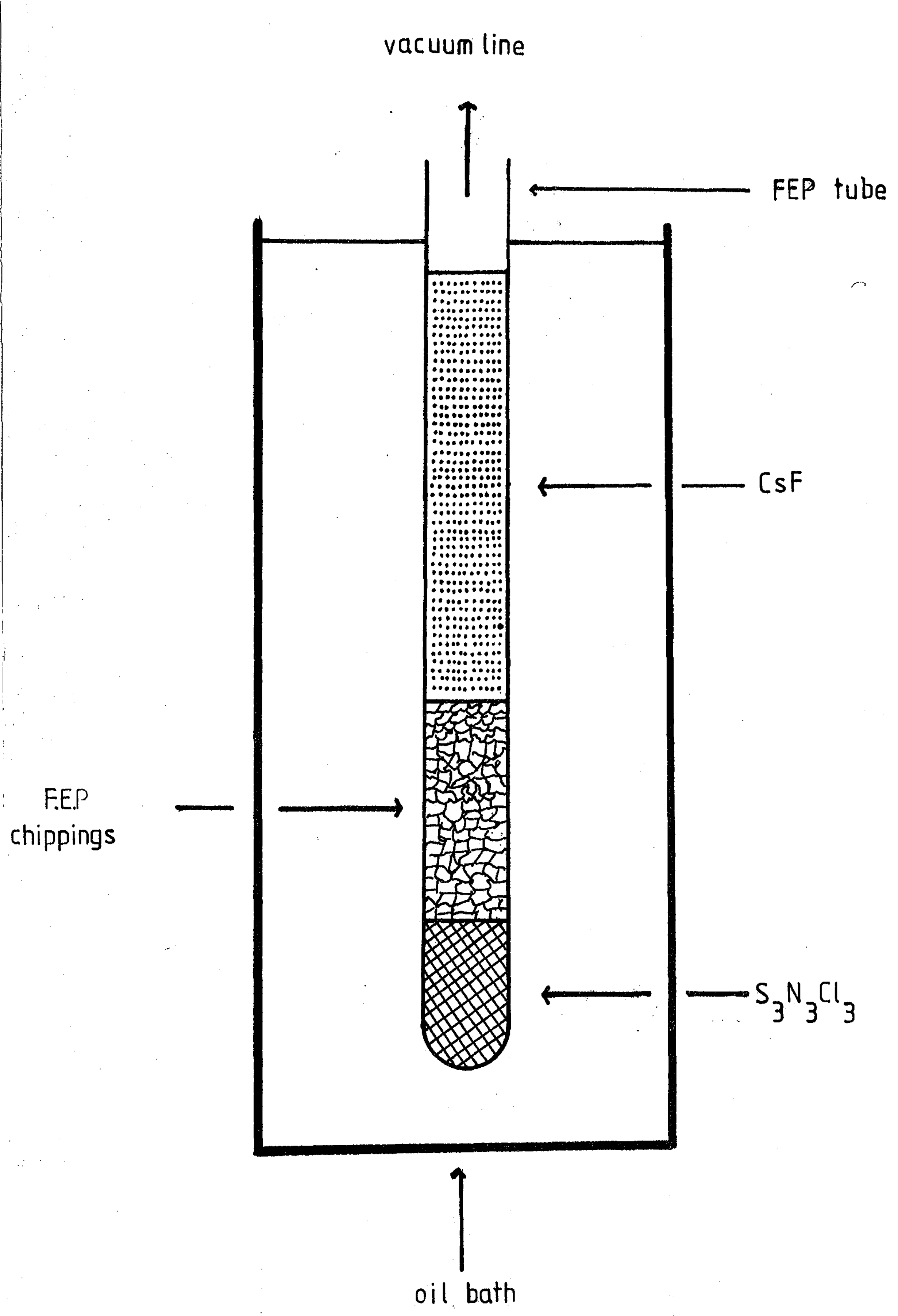
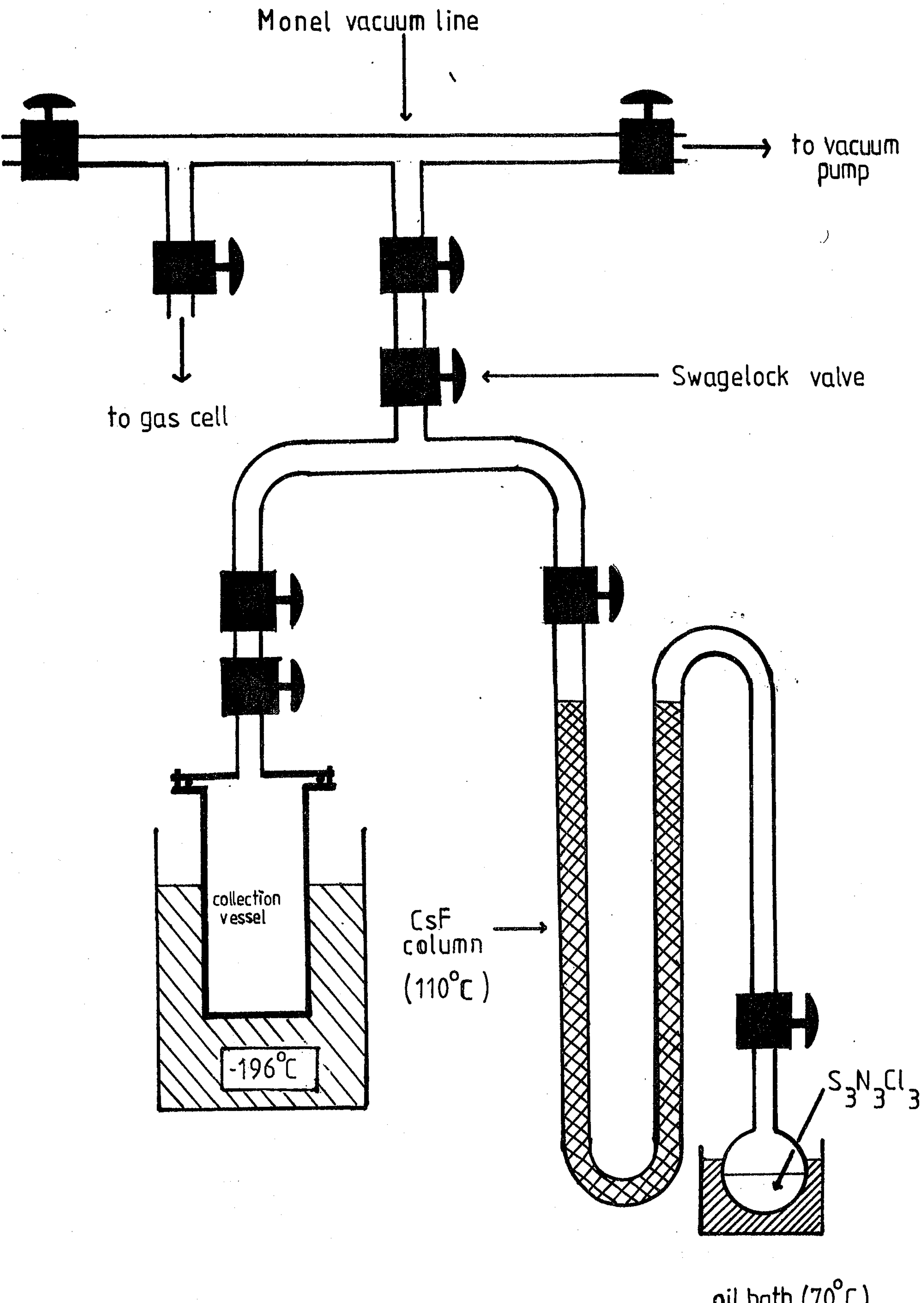


Figure 4.16


Monel vacuum line
to vacuum pump
to gas cell
Swagelock valve
collection vessel
-196°C
CsF column (110°C)
$S_3N_3Cl_3$
oil bath (70°C)

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CHAPTER FIVE

THE OXIDATION OF SULPHUR-NITROGEN SPECIES AND SOME REACTIONS OF THIAZYL CHLORIDE

5.1 Introduction

The oxidation of sulphur-nitrogen compounds covers a considerable area of chemistry which, for the most part, falls into four main categories.

(i) The reactions of tetrasulphur tetranitride with halogens.

(ii) The reactions of tetrasulphur tetranitride with Lewis acids.

(iii) The reactions of trichlorotrithiatriazene with Lewis acids.

(iv) The reactions of thiazyl halides with Lewis acids.

5.1.1 The Reactions of Tetrasulphur Tetranitride with Halogens and Inter-halogens

A considerable study has been made of the reactions of halogens and inter-halogens with S_4N_4.

(a) Fluorination of S_4N_4

The fluorination of S_4N_4 has been discussed in Chapter Four and is, therefore, not commented on further in this section.

(b) The Chlorination of S_4N_4

The chlorination of S_4N_4 has been the subject of much study over the last two decades.[1-5] The principal product formed in the reaction of S_4N_4 with chlorine is $(NSCl)_3$, although intermediate species and by-products have been isolated (e.g. $S_4N_4Cl_2$[3] and $(NSCl)_4$.[2])

(c) The Bromination of S_4N_4

The reaction of S_4N_4 with bromine has been studied both in solution and in the vapour phase. Zborilova *et al*[6-8] investigated the bromination of S_4N_4 in solution, isolating S/N/Br compounds (e.g. S_4N_3Br, $S_3N_2Br_2$). However Street *et al*[9,10] have studied the reactions of S_4N_4 with bromine in the vapour phase, obtaining modified $(SN)_x$ ($(SNBr_{0.4})_x$). Since 1977 there has been a considerable interest in the doping of $(SN)_x$ by halogens and inter-halogens[11-16] and this field is an expanding area of research in sulphur-nitrogen halogen chemistry.

(d) The Iodination of S_4N_4

Little or no work has been reported on the iodination of S_4N_4 by iodine.[9] However recent work by Banister and Smith[17] has led to the synthesis of a series of compounds $(SNI_y)_x$ where y is variable (cf. the doping of $(SN)_x$ by bromine).

5.1.2 The Reactions of Tetrasulphur Tetranitride with Lewis Acids

It is known that sulphur, selenium and tellurium can be oxidised by Lewis acids (AsF_5, SbF_5) to the homoatomic polycations (M_x^{y+}, Chapter Six, page 260).

Many reactions have been reported in which S_4N_4 forms adducts with Lewis acidic species.[18] The majority of reported adducts have the stoichiometry of 1:1 (S_4N_4: Lewis acid). Examples of adducts with stoichiometries of 1:X (X>1) are not that common, there being only two examples of 1:4 adducts, that of $S_4N_4{:}4SbF_5$[19] and $S_4N_4{:}4TiF_4$.[18]

The reaction of S_4N_4 with arsenic and antimony pentahalides has been studied by Gillespie *et al* who have isolated the species $S_3N_2^+AsF_6^-$ from the reaction of S_4N_4 with AsF_5 in SO_2[20] and in recent work (1977)[21] the cation $S_4N_4^{2+}$ (equation 5.1.2).

$$S_4N_4 + 3SbCl_5 \longrightarrow S_4N_4(SbCl_6)_2 + SbCl_3 \qquad (5.1)$$

$$S_4N_4 + 4SbF_5 \longrightarrow S_4N_4(SbF_6)(Sb_3F_{16}) \qquad (5.2)$$

The X-ray crystal structures of both the $S_3N_2^+$ (figure 3.2 , page 107) and $S_4N_4^{2+}$ cations have been determined which indicate that they are essentially planar. The formation of these cations from the reactions of the strongly oxidising Lewis acids (AsF_5, SbF_5 and $SbCl_5$) with S_4N_4 represent the first reported examples of Lewis acids oxidising S_4N_4 rather than forming adducts.

5.1.3 The Reaction of Trihalo-trithiatriazenes with Lewis acids

The reactions of trifluorotrithiatriazene ($S_3N_3F_3$) with Lewis acids have been discussed in Chapter Four (page 161).

Trichlorotrithiatriazene is known to form adducts with Lewis acids (e.g. $AlCl_3$, $FeCl_3$, $SbCl_5$, $SnCl_4$, $TiCl_4$ and BCl_3)[20-24] in a variety of solvents (thionyl chloride, sulphur dioxide and carbon tetrachloride) (equations 5.3-5).

$$(NSCl)_3 + TiCl_4 \longrightarrow (NSCl)_3 \cdot TiCl_4 \qquad (5.3)$$

$$2(NSCl)_3 + SnCl_4 \longrightarrow 2(NSCl)_3 \cdot SnCl_4 \qquad (5.4)$$

$$(NSCl)_3 + MCl_3 \longrightarrow (NSCl)_3 \cdot MCl_3 \longrightarrow (NSCl)_3 \cdot 2MCl_3 \quad \text{(ref.23)} \qquad (5.5)$$

$$(M = Fe,\ Al)$$

Special note is made of the reactions of BCl_3 and $SbCl_5$ with trichlorotrithiatriazene. The reaction of

$(NSCl)_3$ with BCl_3 in the presence of SCl_2 produces the cation $N(SCl)_2^+$ (equation 5.6).

$(NSCl)_3 + 3SCl_2 + 3BCl_3 \longrightarrow 3\ N(SCl)_2^+\ BCl_4^-$ (ref.25)(5.6)

The reaction of antimony pentachloride with trichlorotrithiatriazene has been reported on at least three different occasions, the products identified being different each time (equations 5.7-9).

$(NSCl)_3 + 3SbCl_5 \longrightarrow (NSCl)_3 \cdot xSbCl_5\ (x=1-3)$ (ref.22) (5.7)

$(NSCl)_3 + SbCl_5 \longrightarrow S_3N_3Cl_2^+SbCl_6^-$ (ref.24) (5.8)

$(NSCl)_3 + 3SbCl_5 \longrightarrow S_4N_4^{2+}(SbCl_6^-)_2 + SbCl_3$ (ref.21) (5.9)

5.1.4 The Reactions of Thiazyl Halides with Lewis Acids

Although some areas of the chemistry of thiazyl fluoride (NSF) have been investigated (Chapter Four, page 159), little or no chemistry of thiazyl chloride has been reported. As no previous reference has been made, in this thesis, to the preparation, physical properties, structure or reactions of thiazyl chloride, the chemistry of this compound is reviewed briefly in section 5.1.4(iii).

(i) The Formation and Reactions of Thiazyl Fluoride

The formation and reactions of thiazyl fluoride have already been discussed in Chapter Four (page 151), but particular note is made here of the reactions of thiazyl fluoride with the Lewis acids AsF_5 and SbF_5 (equations 5.10,11).

$NSF + AsF_5 \xrightarrow[SO_2]{} NS^+AsF_6^-$ (ref.26) (5.10)

$NSF + SbF_5 \xrightarrow[SO_2]{} NS^+SbF_6^-$ (ref.26) (5.11)

The thionitrosyl salts ($NS^+MF_6^-$) sublime readily at 40°C (M=As) or 100°C (M=Sb) and dissolve in sulphur dioxide.[27]

The S-N stretching frequency of the cation varies depending on the anion;[26] $NS^+SbF_6^-$ (1448 cm^{-1}), $NS^+AsF_6^-$ (1437 cm^{-1}).

(ii) The Chemistry of the Thionitrosyl Cation

The chemistry of the thionitrosyl cation has not been investigated in depth. However examples of three modes of reaction have been reported. (equations 5.12-14).

(a) Anion exchange.

$$NS^+AsF_6^- + NO^+CF_3SO_3^- \xrightarrow[SO_2]{} NS^+CF_3SO_3^- \quad \text{(ref.27)} \quad (5.12)$$

(b) Reactions with nucleophiles.

$$NS^+AsF_6^- + S_4N_4 \xrightarrow[SO_2]{} (S_5N_5{}^+AsF_6{}^-)_x \quad \text{(ref.27)} \quad (5.13)$$

(c) Reactions with polar bonds.

$$NS^+AsF_6^- + SCl_2 \xrightarrow[SO_2]{} N(SCl)_2{}^+AsF_6^- \quad \text{(ref.27)} \quad (5.14)$$

(iii) The Preparation, Structure, Physical Properties and Reactions of Thiazyl Chloride

(a) Preparation of Thiazyl Chloride

Thiazyl chloride can be produced by the dissociation of trichlorotrithiatriazene, $(NSCl)_3$, into monomeric thiazyl chloride units[28-31] and by the thermal decomposition of thiotrithiazyl chloride (S_4N_3Cl)[32] and chlorothiodithiazyl chloride ($S_3N_2Cl_2$).[33]

The vapour pressure of thiazyl chloride in equilibrium with solid trichlorotrithiatriazene in the temperature range 30-60°C is given by the equation

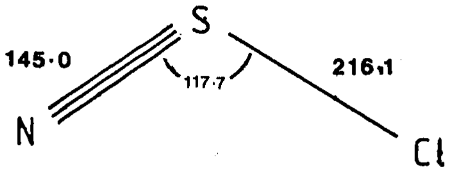
$$\log P_{NSCl(torr)} = 12.321 - 3360/T. \quad \text{(ref.29)}$$

$$(NSCl)_{3(S)} \longrightarrow 3NSCl_{(g)} \quad \Delta H^o = 193 \pm 6 \text{ kJ mol}^{-1} \quad \text{(ref.29)}$$
$$\Delta S^o = 524 \pm 20 \text{ J deg}^{-1}\text{mol}^{-1}$$

(b) Structure and Vibrational Spectrum of Thiazyl Chloride

The structure of thiazyl chloride was elucidated by Beppu *et al* (1970)[34] from the microwave spectrum. The molecule is bent with a $N - \widehat{S} - Cl$ of 117.7° (figure 5.1)

Figure 5.1 Structure of Thiazyl Chloride[24]



Infra-red spectrum of Thiazyl Chloride ($N^{14} \equiv S^{32} - Cl^{35}$)[32]

$\nu_1 = 1327.3\ cm^{-1}$

$\nu_2 = 403.75\ cm^{-1}$

$\nu_3 = 267.4\ cm^{-1}$

The photoelectron spectrum[35,36] and molecular constants[37-41] have been determined for the gas phase species but are not discussed in this thesis.

(c) Reactions of Thiazyl Chloride

There are no reported reactions in which gaseous thiazyl chloride is used as a reactant. The species has, however, been postulated as the reacting moiety in refluxing solutions of trichlorotrithiatriazene ($S_3N_3Cl_3$). There is however little or no evidence to substantiate whether the thiazyl chloride monomeric unit is the reactive species in the apple green refluxing solutions of $(NSCl)_3$ in carbon tetrachloride or benzene.

(iv) Other Thiazyl Halides

There is no reference made in the literature to the preparation, structure or reactions of thiazyl iodide. Thiazyl bromide has been synthesised and its infra-red spectrum analysed.[13] There are however no references made to any reactions of the bromide.

THE OXIDATION OF SULPHUR-NITROGEN SPECIES

5.2 Experimental

5.2.1 The Oxidation of Tetrasulphur Tetranitride

(i) The Oxidation of S_4N_4 by $(XeF^+)(Sb_2F_{11}^-)$

XeF_2 (0.2615g, 1.545 mmole) was placed in a pre-dried, vacuum tight, tube sealed with a Rotoflo valve and antimony pentafluoride (0.8345g, 3.856 mmole) condensed (*in vacuo*) in to the vessel. The reaction was warmed slowly to 90°C for 30 min. and then cooled to room temperature. A large quantity of colourless crystals in a pale green solution were formed. The excess SbF_5 was removed *in vacuo* and the weight of the product recorded (0.7878g, 1.306 mmole of $XeF^+Sb_2F_{11}^-$).

To the $XeF^+Sb_2F_{11}^-$ was added S_4N_4 (0.0711g, 0.386 mmole). The system was evacuated and the reaction slowly warmed to 90°C for 4h. A vigorous reaction occurred at ca. 45°C in which a blue compound was seen to be produced. After 4h. at 90°C the solution appeared to lighten and colourless crystals were formed. The reaction was cooled to -196°C and the volatiles present (300 torr), tested, by the colour of their discharge. Nitrogen and xenon were identified but no evidence for the presence of fluorine was noted. The reaction was then warmed to room temperature and the volatiles present at this temperature removed. The system was pumped on for 6h. and the majority of the SbF_5 was removed, however, even after this time SbF_5 could still be detected in the discharge. The product was isolated in a dry-box but residual SbF_5 made the material virtually impossible to work with. The reaction was terminated at this point as excessive pumping on the material at room temperature or elevated temperatures is likely to sublime any $NS^+SbF_6^-$ out of the system ($NS^+SbF_6^-$ sublimes readily at 100°C *in vacuo*).

(ii) Reaction of Tetrasulphur Tetranitride with Antimony Pentafluoride

S_4N_4 (0.5532g, 3.007 mmole) was placed in a pre-dried, vacuum tight vessel sealed by a Rotoflo valve and SbF_5 (7.8212g, 36.08 mmole) condensed in. The reaction vessel was then evacuated. On warming the reaction slowly to room temperature a vigorous reaction occurred which was highly exothermic and could not be controlled by submerging the vessel in liq.N_2. A blue product was formed which was soluble in the excess antimony pentafluoride (possibly $S_8^{2+}(SbF_6^-)_2$ or $S_4N_4^{2+}(SbF_6^-)(Sb_3F_{16}^-)$) and a white crystalline product was observed which coated the walls of the vessel. After the reaction had subsided the system was cooled to -196°C and the volatiles at this temperature tested (250 torr). Nitrogen was identified by its discharge. The reaction mixture was then warmed to room temperature and the excess SbF_5 removed *in vacuo*. The white microcrystalline product was isolated and its Raman spectrum recorded.

Raman spectrum of the white microcrystalline material (green line): 654s, 634s, 292w cm^{-1}.

(iii) The Reaction of Tetrasulphur Tetranitride with Antimony Pentafluoride at Elevated Temperatures

S_4N_4 (0.3531g, 1.919 mmole) was placed in a pre-dried, vacuum tight, pyrex vessel, sealed by a Rotoflo valve and SbF_5 (9.6177g, 4.437 mmole) condensed in. The reaction vessel was evacuated and then warmed very slowly, via slush baths at -45°C and -22°C, to room temperature over a period of 6h. The system was then stirred at room temperature for 2h. and then the temperature was raised slowly 150°C for 100h.

Colourless parallelepiped crystals were produced (main face ca. 3mm by 3mm) in a pale yellow SbF_5 solution. The reaction was then cooled slowly to room temperature. At ca. 120°C a pale yellow solid started to be deposited which coated the crystals. The reaction mixture virtually solidified into a cream mass on cooling to room temperature and the removal of excess antimony pentafluoride proved difficult. A few colourless crystals were isolated from the sticky mass and the Raman spectrum of these recorded.

Raman spectrum of the colourless crystals (green line): 654s, 634m, 292w cm^{-1}.

(iv) Reaction of Tetrasulphur Tetranitride with Antimony Pentafluoride in Arsenic Trifluoride

S_4N_4 (0.8414g, 4.57 mmole) was placed in a pre-dried vacuum tight, pyrex vessel and AsF_3 (7.2219g) and SbF_5 (4.0123g, 18.52 mmole) condensed in. The vessel was evacuated and on warming to room temperature a very deeply coloured solution was formed which did not change colour on heating to 125°C for 24h. After ca. 18h. colourless crystals were seen in the deep red solution. The reaction was slowly cooled to room temperature, the colourless crystals being coated with an orange-red precipitate. The solvent and excess antimony pentafluoride were removed under reduced pressure and the product isolated in a dry-box. The product was sorted by hand using a microscope fitted to the outside of the dry-box, the colourless crystals being loaded into a Raman tube for investigation.

Raman spectrum of the colourless crystals (green line):
686m, 664s, 644s, 626w, 607w, 292m cm^{-1}.
Infra-red spectrum of the colourless crystals (powder):
680m, 672m, 658s, 649s, 620m(sh), 475m, 450m,br; cm^{-1}.
Infra-red spectrum of the red non-crystalline material (powder):
1495m, 1220m, 1010w, 655vs,br, 475w,br, 436w, 378m cm^{-1}

5.2.2 The Oxidation of Trichlorotrithiatriazene ($(NSCl)_3$)

(i) Reaction of $(NSCl)_3$ with SbF_5 in AsF_3.

$(NSCl)_3$ (0.8389g, 3.431 mmole) was placed in a pre-dried, vacuum tight, pyrex vessel and arsenic trifluoride (5.7879g, 43.874 mmole) and antimony pentafluoride (4.3836g, 20.224 mmole) were condensed in. The reaction vessel was evacuated and then warmed slowly to room temperature yielding a deep green solution which, on refluxing under sealed system conditions for 72h. changed to deep red. After refluxing for 72h. a yellow solid was precipitated and on cooling the reaction to room temperature more of the same precipitate was formed. The system was cooled to -196°C to test for N_2 or F_2. No pressure of volatiles was recorded. The gas phase

infra-red spectrum of the volatiles present at room temperature was recorded and the spectrum indicated the presence of SbF_5, AsF_3, SiF_4 and SOF_2 (Appendix A, page 313).
Volatiles present at room temperature were completely removed and the product isolated under dry-box conditions. The product still contained some free SbF_5 and thus was recrystallised from sulphur dioxide (12.6341g). The product completely dissolved in the solvent forming a deep red solution. However on cooling the solution to ca. -63°C a creamy-white precipitate was noted. The solution was thus cooled to ca. -78°C and the precipitate isolated.

Raman spectrum of the precipitate (green line): 1208s, 692vw, 666w, 646s*, 620w, 564w*, 499vs, 296w(sh)*, 282m, 234s, 226vs, 142s cm^{-1} (*Denotes peaks assignable to SbF_6^-)[42].

Infra-red spectrum of the precipitate (powder): 815w, 800m, 670s(sh), 658vs, 650vs, 640s(sh), 570w, 465m, 382s cm^{-1}

Difficulty was found in drying the soluble red product (due to SbF_5) and thus an infra-red spectrum was not recorded.

(ii) Reaction of Trichlorotrithiatriazene and Arsenic Pentafluoride

$(NSCl)_3$ (1.21g, 4.95 mmole) was placed in a pre-dried, vacuum tight, Monel vessel and arsenic pentafluoride (4.13g, 24.32 mmole) condensed in. The vessel was evacuated and the reaction warmed slowly to room temperature and then to 70°C for 24h. The system was then cooled to -196°C and tested for nitrogen (50 torr, 0.01g). The excess AsF_5 was removed by pumping on the products at room temperature. The residue (4.59g) was isolated in a dry-box and the infra-red and Raman spectra recorded on the yellow solid.

Infra-red spectrum of the product (nujol mull): 700vs, 500s, 390vs cm^{-1}.

Infra-red spectrum of the product (fluorolube): 1445s, 500s, 390vs cm^{-1}.

No Raman spectrum could be obtained using the green line. The Raman spectrum recorded some two months after the experiment using a red laser is given below:

Raman spectrum (red line): 681m, 498m, 420vs, 396w, 371w, 185s, 154s.cm^{-1} (c f. $AsCl_4^+AsF_6^-$)[42]

(iii) The Reaction of Trichlorotrithiatriazene with Aluminium Trichloride

Anhydrous $AlCl_3$ (8.43g, 63.2 mmole) and $(NSCl)_3$ (3.24g, 13.25 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel. The system was evacuated, sealed under vacuum by a Rotoflo valve and the top of the vessel cooled with cold nitrogen gas, generated by placing a tube in a Dewar of liquid nitrogen. No product appeared to sublime. The reactants were then heated to 70°C resulting in the formation of a yellow sublimate which on warming became liquid then gaseous. On stabilising the whole vessel at room temperature the solid residue appeared to be "wet" with a yellow liquid. The volatiles were tested at various slush bath temperatures and identified from their infra-red and Raman spectra. At -196°C a low pressure of incondensable gas was noted which on removal from the system did not represent a great enough weight loss to be recorded on the balance (i.e. less than 0.01g). The volatiles, present at -63°C did not give an infra-red spectrum but were identified as being predominantly chlorine from their Raman spectrum. (The volatiles at -63°C were removed prior to the volatiles at room temperature being tested). The volatiles present at room temperature are believed to be mainly disulphur dichloride from the infra-red spectrum recorded.

The reaction was terminated at this point as complete degradation of the sulphur-nitrogen system appeared to have occurred.

5.2.3 Reactions of Thiazyl Chloride

(i) The Reaction of Thiazyl Chloride (NSCl) with Boron Trichloride

Thiazyl chloride (NSCl), generated by heating $(NSCl)_3$ *in vacuo*,[29] was expanded into a gas cell (figure 1.5 page 16). The pressure of NSCl in the gas cell was adjusted such that ca. 80% absorbance was recorded for the infra-red band at 1320 cm^{-1}. The complete gas phase infra-red spectrum of the volatiles within the cell was recorded between 4000 and 300 cm^{-1}) (KBr windows). BCl_3 contained in a sealable side arm was then expanded into the gas cell. An immediate reaction occurred yielding a yellow solid which coated the gas cell.

Infra-red spectrum of the products: 1468m(sh), 1460m, 1422s, 1375m, 1252m, 1245m, 1010-920vs,br,(xsBCl_3), 725m, 718m, 618m, 520m, 485m(sh), 475s, 462s, 454vs, 444s cm^{-1}.

The gas cell was pumped on for 10 min. and the spectrum re-run. No peaks were observed.

(ii) Reaction of Thiazyl Chloride with Tin(IV)Chloride

NSCl, generated by heating $(NSCl)_3$ *in vacuo*,[29] was expanded into a gas cell (figure 1. 5 , page 16). The gas phase infra-red spectrum of the volatiles present in the gas cell were recorded and tin(IV) chloride, contained in a sealable side arm, was then expanded into the cell. A series of infra-red spectra were recorded over a period of 16h. which indicated that a slow reaction was taking place, with the slow decrease in concentration of NSCl.

Gas phase infra-red spectrum recorded after 16h.: 1378s(sh)*, 1372s*, 1360vs*, 1350s*, 1342s*, 1260s(sh), 1255s, 1246s, 1165w*, 1135w*, 850m, 535w*, 505m*, 498m, 468s, 460s, 410vs cm^{-1} (* Denotes bands assignable to SO_2).

(iii) Reaction of Thiazyl Chloride with Antimony Pentachloride

NSCl, generated by heating $(NSCl)_3$ *in vacuo*,[29] was expanded into a gas cell and the gas phase infra-red spectrum of the species contained within the cell recorded. Antimony pentachloride, contained in a sealable side arm, was then expanded into the cell and the gas phase infra-red spectrum recorded. Due to coating of the gas cell windows by a white compound, a very low transmission of energy through the cell resulted, consequently no infra-red data of any significance were recorded.

(iv) Reaction of Thiazyl Chloride with Antimony Pentachloride (Preparative Scale)

The apparatus used for this experiment is shown in figure 5.2 (page 253). Trichlorotrithiatriazene (0.98g, 4.01 mmole) was placed in bulb A and antimony pentachloride (7 cm^3, 54.78 mmole) in bulb B. The apparatus was then completely evacuated and the inlet valve for the antimony pentachloride closed. The apparatus was then flamed out under dynamic vacuum, the $(NSCl)_3$ not being heated. The $(NSCl)_3$ was heated to 70°C under a dynamic vacuum and the volatiles condensed at -196°C in trap 2. After ca. 10 min. a green liquid was seen to condense in trap 2 (NSCl). Trap 1 was then cooled to -7°C and the antimony pentachloride inlet valve opened. A colourless crystalline material was readily formed which was contaminated by a green non-crystalline material. The majority of the product was deposited just prior to the -7°C trap (trap 1). After ca. 4h. the production of NSCl monomer appeared to have stopped and thus the reaction was terminated. The product was sublimed into trap 1 and traps 1 and 2 were sealed off under vacuum.

The product was isolated under dry-box conditions, loaded into a pre-dried vacuum tight vessel (figure 1.2 page 14) and washed with pre-cooled SO_2 (-63°C). The sulphur dioxide was then removed and the dry (no $SbCl_5$ present) pale yellow microcrystalline material isolated. The purified product was then placed in a pre-dried, sublimation tube and the product sublimed, *in vacuo*, to the upper reaches of the tube (80°C, 10^{-2} torr).

The product was then removed from the sublimation tube in a dry-box and the Raman and mass spectra recorded.

Raman spectrum of the product (red line): 1402vs, 1389w, 330s,* 284w,* 178m* cm^{-1} (* Denotes band assignable to the $SbCl_6^-$ anion)[42]

Mass spectrum (m/e (abundance) assignment) (spectrum run up to mass 226 only): 226(25) $SbCl_3$; 195(2) $SbCl_2$; 193(100) $SbCl_2$; 191(82) $SbCl_2$; 160(3) SbCl ; 158(12) SbCl ; 156(9) SbCl ; 123(9) Sb^{123} ; 121(13) Sb^{121} ; 48(6) SO ; 46(22) NS ; 38(46) HCl^{38} ; 37(3) Cl^{37} ; 36(72) HCl^{35} ; 35(30) Cl^{35} .

Analysis of the product.

Found: S, 8.04; N, 3.23; Cl, 57.0%

$NS^+SbCl_6^-$ requires: S, 8.40; N, 3.68; Cl, 55.94%

(v) Reaction of Thiazyl Chloride with Silver Metal (cf. experiment 3.2.3 (c, v) page 123)

$(NSCl)_3$ (0.34g, 1.39 mmole) contained in a break seal capsule, was placed in a pre-dried vacuum tight pyrex vessel (figure 5.3, page 254). Silver wool (0.9113g, 8.45 mmole) was also placed in the vessel, some 5 cm. from the $(NSCl)_3$ capsule. The complete vessel was then evacuated (10^{-6} torr) and flamed out (not the area containing the $(NSCl)_3$ capsule). The $(NSCl)_3$ capsule was then broken and the temperature in the vicinity of the $(NSCl)_3$ slowly raised to ca.60°C. The volatiles produced were passed over the pre-heated silver wool (200°C), in a dynamic vacuum of 10^{-5} torr and the volatile species formed condensed in either the -15°C trap or the -78°C trap. A deep blue film was rapidly formed, almost directly after the silver wool, which grew in intensity over a period of two hours. During this period of time evidence for the production of S_2N_2 was noted in the upper section of the -15°C trap. It was noted that whereas the silver becomes black (Ag_2S) when cracking S_4N_4 to yield S_2N_2, the silver from its reaction with thiazyl chloride has a white appearance (AgCl).

After ca. 2h. thiazyl chloride was noted in the -78°C trap and from this point onwards a multitude of colours were seen in both the -78°C and -15°C traps. A red compound was also formed which coated the blue (suspected polymer) film. The reaction was continued for 60h. but no further reaction appeared to occur, the only products observed being thiazyl chloride and sulphur chlorides. After 60h. the vessel was cooled to room temperature and the " U " tubes and tube containing the suspected polymer were sealed *in vacuo*. The infra-red spectrum of the yellow product isolated from the -78°C trap was consistent with the species being $(NSCl)_3$.

The suspected "polymer" coating gradually turned deep red over a period of a month and the silver surface became black.

Infra-red spectrum of the suspected polymer: 964m,* 944s,* 928s,† 725m,† 715m(sh),* 708s,* 698vs,* 582m,* 552s,† 430m,* 347s† cm^{-1}.

* Denotes peaks assignable to S_3N_2Cl.[46]

† Denotes peaks assignable to S_4N_4.[47]

5.2.4 Reactions of Thionitrosyl Hexachloroantimonate(V)

(i) The Reaction of $NS^+SbCl_6^-$ with liquid chlorine

$NS^+SbCl_6^-$ (0.3264g, 0.864 mmole) was loaded into a pre-dried vacuum tight pyrex tube (2mm inside diameter, 4m outside diameter) fitted with a Rotoflo valve. The vessel was evacuated and pre-dried chlorine (1.6348g, 23.03 mmole) condensed in. The reaction was agitated at room temperature for 10h. and then the chlorine removed. The Raman spectrum of the resulting compound was identical to that recorded for $NS^+SbCl_6^-$. Chlorine (1.2419g, 17.49 mmole) was again condensed into the vessel and the reaction heated to 80°C for 72h. The chlorine was removed and the Raman spectrum of the resulting yellow compound recorded.

Raman spectrum of the product (red line): 718vs, 654w, 508w, 333s,* 288w,* 220,* 202w, 176m,* cm^{-1}.

(* Denotes bands assignable to $SbCl_6^-$).[42]

Infra-red spectrum of the product (nujol mull): 1131m, 720m, 656m, 520vs, 495s, 340vs cm^{-1}.

(cf. $(SCl)_2N^+SbCl_6^-$: Infra-red spectrum 1130m, 735m(sh), 721m, 654s, 521s, 520s, 494s cm^{-1}).[55]

Analysis of the product.

Found: N, 3.12; S, 12.2; Cl, 59.5%.

NS_2SbCl_8 requires: N, 2.90; S, 13.23; Cl, 58.71%

(ii) Reaction of $SN^+SbCl_6^-$ with excess Elemental Sulphur

Sulphur (1.30g, 5.08 mmole) was loaded into the non-sealable section of a pre-dried, vacuum tight pyrex vessel (figure 1.2, page 14) and pumped on *in vacuo* for 36h. to remove all traces of moisture. $NS^+SbCl_6^-$ was then loaded into the sealable section of the vessel, whilst under dry-box conditions, and the whole system evacuated. Sulphur dioxide (13.41g) was then condensed in and the $NS^+SbCl_6^-$ solution filtered onto the sulphur. An immediate reaction occurred forming a deep red solution. After agitating for 2h. at room temperature the system was filtered. The insolubles were washed with recondensed sulphur dioxide removing all possible traces of the solubles. It was noted that a brown insoluble compound had been produced. The solvent was slowly evaporated from the filtrate and an orange-red precipitate was deposited. The solvent was finally removed and the products dried *in vacuo*. The vessel was then placed in the port of the dry-box and left for 1h. On admitting the vessel to the box it was noted that the brown insolubles had changed, yielding a pale yellow species, presumed to be sulphur due to its lack of an infra-red spectrum. The solubles were isolated and the infra-red spectrum recorded.

Infra-red spectrum of the solubles (nujol mull): 1495vs,* 1130m,† 1058m, 1020w, 974w, 942vs,ϕ 805w, 785w, 775w, 745w, 718m,† 692w, 654m,† 622w, 570s, 520vs,† 498s,† 470s, 440s,ϕ 425vs,ϕ 374s,*,ϕ 340vs($SbCl_6^-$) cm^{-1}.

(* Denotes bands assignable to $S_2N^+SbCl_6^-$. 43

† Denotes bands assignable to $(SCl)_2N^+SbCl_6^-$ 44

ϕ Denotes bands that may be assignable to
$S_3N_2Cl^+SbCl_6^-$). 45

THE OXIDATION OF SULPHUR-NITROGEN SPECIES AND SOME REACTIONS OF THIAZYL CHLORIDE

5.3 Discussion

The chemistry of thionitrosyl salts has not been developed significantly since their reported synthesis in 1970.[26] The reason for this is thought to be due to the difficulty in preparing the basic starting material thiazyl fluoride (NSF). As noted previously, Chapter Four (page 159), the chemistry of thiazyl fluoride is itself largely unexplored, probably due to the problems of handling the gas and the related problems of synthesising the compound. No other route to thionitrosyl salts has been reported other than via NSF and thus investigations were carried out to determine whether various sulphur-nitrogen species, which were readily available, could be oxidised under vigorous conditions to yield thionitrosyl salts.

5.3.1 The Oxidation of Tetrasulphur Tetranitride and Trichlorotrithiatriazene

The oxidation of tetrasulphur tetranitride by XeF^+, SbF_5 and SbF_5 in AsF_3 solution were studied. In all cases the results were disappointing due to the problems of removing the excess, relatively involatile, SbF_5 at the end of the reaction. Although obvious signs of reaction were noted and reduced products were obtained ($SbF_3 \cdot SbF_5$(Form A)[50] colourless crystals, experiment 5.2.1(iii), page 231) no definite identification of the oxidised products was made.

The investigation of the reactions of trichlorotrithiatriazene with arsenic trifluoride and antimony pentafluoride were carried out at elevated temperatures for prolonged periods of time (72h.) (experiment 5.2.2(i), page 232).

The reaction was designed with the intention that the thiazyl chloride would exchange with either AsF_3 or SbF_5 to yield thiazyl fluoride, which would then react with the excess SbF_5 to form $NS^+SbF_6^-$. Prolonged refluxing of the reaction did not decolourise the system, as would have occurred if the $NS^+SbF_6^-$ salt had been produced. The product obtained, on removing the solvent and excess SbF_5, was deep red and still contained appreciable quantities of SbF_5, even after drying *in vacuo* for 10h. In order to remove the excess SbF_5 the product was washed with sulphur dioxide. It was noted that on cooling the SO_2 to -63°C, a white compound was precipitated. The Raman spectrum of this species was remarkably simple consisting of bands assignable to SbF_6^- and three other bands at 1208, 499 and 266 cm^{-1}. The simplicity of the Raman spectrum implies that the cation must be relatively small and probably of quite high symmetry. Comparison of the spectrum with known sulphur-nitrogen species led to the conclusion that the 1208 cm^{-1} band is consistent with a species containing an S-N band of high bond order (cf. $ClN{=}SF_2$ 1178cm^{-1}).[51] The observed band at 499 cm^{-1} is very similar to that observed in the SCl_3^+ cation (SCl_3^+ $\nu_1(A_1)$: 498 cm^{-1} very strong).[52] Hence from the vibrational data it would seem plausible to suggest that the cation could be ($N{=}SCl_2^+$). Such a cation would be isoelectronic and isostructural to $O{=}SCl_2$. Thus a similar vibrational spectrum would be expected (table 5.1).

TABLE 5.1 <u>The Raman Spectrum of Thionyl Chloride</u>[53]

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
ν(S-O)	$\nu_s(SCl_2)$	δ(SOCl)	$\delta(SCl_2)$	$\nu_{as}(SCl_2)$	δ
1229	490	394	194	443	284

As seen from table 5.1 ν_1, ν_2 and possibly ν_6 correspond to the bands observed in the product at 1208, 499 and 266 cm^{-1}. It is therefore suggested that the reaction of $(NSCl)_3$ with SbF_5 (molar ratio 1:4) produces $NS^+SbF_6^-$ and $NSCl_2^+SbF_6^-$ (equation 5.15).

$$2/3(NSCl)_3 + 3SbF_5 \longrightarrow NS^+SbF_6^- + NSCl_2^+SbF_6^- + SbF_3 \quad (5.15)$$

The postulate was tested by reacting $(NSCl)_3$ with AsF_5 (molar ratio 1:4) (experiment 5.2.2(ii), page 233) and observing the weight of residue at the end of the reaction. The weight of residue was found to be consistent with that expected from equation 5.15 when using AsF_5 instead of SbF_5. The infra-red spectrum of the product, from the reaction of $(NSCl)_3$ with AsF_5, contained a band assignable to the $NS^+AsF_6^-$ salt (observed stretching frequency 1445 cm^{-1} reported 1437 cm^{-1}) and also contained a band at 500 cm^{-1}, that could possibly be assigned to the postulated species $NSCl_2^+AsF_6^-$. Hence it seems likely that the species $NSCl_2^+ MF_6^-$ could be formed in the reactions of $(NSCl)_3$ with SbF_5 or AsF_5. Analysis of the product isolated from the reaction of SbF_5 with $(NSCl)_3$, using AsF_3 as a solvent, was not however of any use in identifying the compound as more than one species appeared to be present. In an attempt to synthesise $NSCl_2^+SbF_6^-$ and isolate the salt in a pure state $NS^+SbCl_6^-$ was reacted with chlorine (see section 5.3.4, page 250), the product obtained did not however possess the same Raman spectrum as that of the supposed $NSCl_2^+$ cation.

5.3.2 The Reactions of Thiazyl Chloride with Lewis Acids

By direct analogy with the reactions of thiazyl fluoride with fluoro Lewis acids (BF_3, SbF_5 and AsF_5),[26,27] the reactions of thiazyl chloride with chloro Lewis acids

(BCl_3, $SbCl_5$, $SnCl_4$ and $AlCl_3$) were investigated. All the initial investigative reactions, except that with $AlCl_3$, were carried out using a gas cell, in order to monitor the reaction of the Lewis acid with thiazyl chloride and hence identify the products by their infra-red spectra. The procedure was successful in the cases of $SnCl_4$ and BCl_3 but with $SbCl_5$, coating of the gas cell windows occurred which virtually stopped all transmission of energy through the cell (experiment 5.2.3(iii), page 236). The products from the slow reaction of tin (IV) chloride with thiazyl chloride were SO_2 and an unidentified gaseous product (experiment 5.2.3(ii), page 235). It was therefore concluded that tin (IV) chloride and thiazyl chloride do not in fact react, the products observed in the gas phase infra-red spectrum being hydrolysis products of NSCl. The reaction between thiazyl chloride and boron trichloride (experiment 5.2.3(i), page 235) was however very rapid forming a series of compounds (deduced from the complexity of the spectrum) one of which gave an infra-red band at 1422 cm^{-1}, which would be consistent with a species $NS^+BCl_4^-$. However on removing the excess boron trichloride all the products were lost from the cell thus implying that the thionitrosyl salt, if produced, sublimes very easily or readily dissociates into BCl_3 and NSCl, which are then removed.

In order to increase the stability of the thionitrosyl, the syntheses of salts with larger anions were investigated in preparative scale reactions. The reaction of aluminium trichloride with trichlorotrithiatriazene at elevated temperatures (70°C) (effectively $AlCl_3$ and NSCl) produced no oxidised sulphur-nitrogen species only chlorine and disulphur dichloride, basically the thermal breakdown products of NSCl. However on reacting thiazyl chloride with gaseous $SbCl_5$ in a flow system, with pre-cooled traps, a virtually colourless crystalline material was formed which was contaminated by a deep green amorphous material (experiment 5.2.3(iv), page 236). The product readily sublimed and was found to trap out in a ca. -10°C trap. The main contaminant of the product, other than the aforementioned green material, was excess $SbCl_5$. Initially attempts were made to purify the product by sublimation but the vapour pressure, due to the $SbCl_5$, slowed the sublimation down. However $SbCl_5$ would have been a contaminant even if the sublimation were successful. Methods of removing the $SbCl_5$ as the first step in the purification procedure were therefore sought. The most convenient and effective method found, was to wash the crude product with cold sulphur dioxide and a sealed system sublimation of the washed product, *in vacuo*, at 80°C yielded virtually colourless crystals of the product. The deep green impurity did not sublime but was noted to change in colour to yellow after 5-10h. Raman spectra of both the impurity and the product were recorded. The product gave an excellent spectrum with a strong band at 1402 cm^{-1} and a very weak side band at 1389 cm^{-1}. The non-sublimed impurity did not give a Raman spectrum due to decomposition in the laser beam.

The Raman spectrum of the product is very simple, there being only the two bands at 1402 and 1389 cm^{-1} and bands assignable to the $SbCl_6^-$ anion. The simplicity of the spectrum and the position of the main band at 1402 indicates that the product is almost certainly $NS^+SbCl_6^-$. Mass spectral and analytical data confirm that the species is $NS^+SbCl_6^-$.

The main band at 1402 cm^{-1} is somewhat lower than that observed in $NS^+SbF_6^-$ (1448 cm^{-1}),[27] $NS^+AsF_6^-$ (1437 cm^{-1})[26] and $NS^+CF_3SO_3^-$ (1443 cm^{-1}).[27] It is suggested that greater cation-anion interactions occur in the $NS^+SbCl_6^-$ salt than in the SbF_6^- and AsF_6^- salts due to the higher polarisability of the $SbCl_6^-$ anion thus causing a drop in the observed stretching frequency of the $N \equiv S^+$ cation.

The side band at 1389 cm^{-1} is of the correct intensity for the $(N \equiv S^{34})^+$ cation, i.e. 5% of the intensity of the $(N \equiv S^{32})^+$ band (1402 cm^{-1}). The theoretical position of the $(N \equiv S^{34})^+$ band can be calculated knowing the reduced mass of each cation and the band position of $(N \equiv S^{32})^+$ (equation 5.16).

Equation 5.16

$$\bar{\nu}_{spec} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \qquad \text{(ref.55)}$$

(K = the force constant; μ = the reduced mass; c = the velocity of light).

For comparison of the stretching frequencies of the cations $(N \equiv S^{32})^+$ and $(N \equiv S^{34})^+$ the above equation may be simplified

$$\bar{\nu}_{spec} \propto \sqrt{\frac{1}{\mu}}$$

$$\mu = \left(\frac{1}{M_1} + \frac{1}{M_2}\right) \quad \text{i.e. } \mu_{(NS^{32})^+} = \left(\frac{1}{14} + \frac{1}{32}\right):\ \mu_{(NS^{34})^+} = \left(\frac{1}{14} + \frac{1}{34}\right)$$

Thus if the stretching frequency of the $(N^{14} \equiv S^{32})^+$ cation is known (x cm^{-1}) then the stretching frequency of the $(N^{14} \equiv S^{34})^+$ cation is given by

$$\nu_{N \equiv S^{34}} = x \cdot \sqrt{\frac{\mu_{(NS^{34})^+}}{\mu_{(NS^{32})^+}}} = 1402 \cdot \sqrt{\frac{0.1008}{0.1027}} = 1389\ cm^{-1}$$

The calculated and observed positions of the $(N \equiv S^{34})^+$ band are therefore coincident thus reinforcing the basic assumption that the 1402 cm^{-1} band is assignable to the $N \equiv S^+$ stretching vibration.

5.3.3 Further Reactions of Thiazyl Chloride

Several unsuccessful reactions were attempted in which thiazyl chloride was passed through columns of sodium hexafluorophosphate, sodium tetrafluoroborate and aluminium trichloride. In all cases the formation of the desired product, (NS^+ salts) was not observed, thiazyl chloride passing through the column unreacted or being dissociated in to N_2 and sulphur chlorides. Attention is however drawn to the reactions of thiazyl chloride with cesium fluoride in which thiazyl fluoride is formed (Chapter Four, page 205).

As noted in Chapter Three (page 123), when trichlorotrithiatriazene is placed under vacuum in the presence of silver wool it appears to be reduced forming the blue precursor to $(SN)_x$.[56] It was suspected that the actual sulphur-nitrogen reactant in the above reaction was thiazyl chloride (NSCl), which when reduced yields $[NS]^\bullet$ radicals which form short open chain species which, in turn, slowly polymerise to give $(SN)_x$. The reaction of thiazyl chloride with silver was therefore investigated.

Thiazyl chloride was passed over heated silver wool and the deep blue film of polymer precursor quickly formed (experiment 5.2.3(v), page 238). The film of polymer precursor grew rapidly over the first two hours virtually no thiazyl chloride passing through the silver unreacted. Evidence was seen in the first "U" tube trap (-15°C) of S_2N_2. However after two hours thiazyl chloride started to condense in the -78°C trap. It is believed that after ca. 2h. the surface of the silver wool had become coated with chloride and the transport of silver through the chloride coat was not rapid enough to cope with the flux of thiazyl chloride, hence thiazyl chloride was observed in the traps. The products finally isolated from the reaction proved to be S_3N_2Cl and S_4N_4 (the suspected polymer coating) and $(NSCl)_3$ from the -78°C trap. The presence of S_4N_4 and S_3N_2Cl can be explained by the cyclisation of the open chain polymer precursors and their reaction with thiazyl chloride.

It is therefore concluded that although the reaction of thiazyl chloride with silver reported in this chapter was not successful, with respect to the isolation of $(SN)_x$, the basic principle of passing thiazyl chloride over a silver surface to produce "SN" fragments, which act as polymer precursors, is valid. If a sufficiently large surface area of silver is used, such that no thiazyl chloride passes through without reaction, then a useful, non-hazardous method of coating substrates (e.g. ZnS, ZnSe) with $(SN)_x$ would be available for use under general laboratory conditions. (It should be noted that the silver can be easily regenerated by the passage of hydrogen over the heated surface thus removing the chlorine as hydrogen chloride).

One of the main problems encountered throughout the work with thiazyl chloride was its generation from trichlorotrithiatriazene. Although Patton and Jolly describe the method of production in detail, difficulty was found in practice when trying to produce large quantities at a steady rate. In an attempt to avoid this problem preliminary investigations into the possibilities of storing thiazyl chloride on a molecular sieve (4A) were carried out. The NSCl was generated in a gas cell and then a valve opened to allow the volatiles to come in contact with activated 4A molecular sieve. By observing the main bands in the infrared spectrum of thiazyl chloride (1328 cm^{-1}) the concentration of the thiazyl chloride could be monitored with respect to time.

It was found that the concentration of thiazyl chloride quickly decreased on exposure to the molecular sieve. The above procedure was repeated many times until the molecular sieve appeared saturated. The section containing the molecular sieve was then left opened to the gas cell and heated to drive off the absorbed thiazyl chloride. No traces of thiazyl chloride were seen in the gas phase spectrum. Thus it is concluded that thiazyl chloride is strongly absorbed on to the substrate. No further work was carried out on this problem but it is believed that a more thorough investigation into the storing of thiazyl chloride on substrates, such as molecular sieves, may solve the problem of continuous, controllable production of thiazyl chloride for gas phase reactions. If such a production should be found then thiazyl chloride could, as indicated by some of its reactions in this thesis, become a useful synthetic reagent.

5.3.4 The Reactions of the Thionitrosyl Cation (experiments 5.2.4(i,ii), pages 239,240)

(i) The Reaction of the Thionitrosyl Cation with Chlorine

As previously noted in this chapter (section 5.3.1, page 243), $(NSCl)_3$ reacts with SbF_5 forming a species, which from its Raman spectrum was deduced to be $NSCl_2^+SbF_6^-$.

In order to gain evidence as to the nature of this compound, an attempt to synthesise it from $NS^+SbCl_6^-$ and Cl_2 was carried out. The Raman spectrum of the product from the reaction of $NS^+SbCl_6^-$ and Cl_2 was compared with that of the postulated $NSCl_2^+$. The spectra were not identical, the product from the $NS^+SbCl_6^-/Cl_2$ reaction being identified as $(SCl)_2N^+SbCl_6^-$. Hence no further evidence as to the exact nature of the product from the $(NSCl)_3/SbF_5$ reaction was gained.

Mews has reported[27] that SCl_2 reacts with the thionitrosyl cation to form $(SCl)_2N^+$ salts. Therefore it would seem likely that during the reaction of $NS^+SbCl_6^-$ with chlorine at elevated temperatures, SCl_2 is formed as an intermediate which reacts with the thionitrosyl salt present, to form the observed $N(SCl)_2^+SbCl_6^-$ salt.

(ii) The Reaction of the Thionitrosyl Cation with Elemental Sulphur

The reactions of $S_8^{2+}(AsF_6^-)_2$ with azides have been studied in this thesis (Chapter Six), in order to synthesise cations of the form S_xN^+ ($x = 1$-7). It was found that the only sulphur-nitrogen cation present in the product of the S_8^{2+}/N_3^- reaction was S_2N^+. Hence in an attempt to prepare S_xN^+ cations from a different angle, the thionitrosyl cation was reacted with elemental sulphur. The products isolated were characterised, where possible, by their infra-red spectra. The main product from the reaction of SN^+ with sulphur was S_2N^+. Hence it appears as though all cations of the form S_xN^+ ($x > 2$) are unstable with respect to S_2N^+ and sulphur.

The other species identified in the products of the $NS^+SbCl_6^-/S_8$ reaction were $(SCl)_2N^+SbCl_6^-$ and $S_3N_2Cl^+SbCl_6^-$. These cations are probably formed by the reaction of $S_2N^+SbCl_6^-$ with chlorine and thiazyl chloride respectively.

Figure 5.2

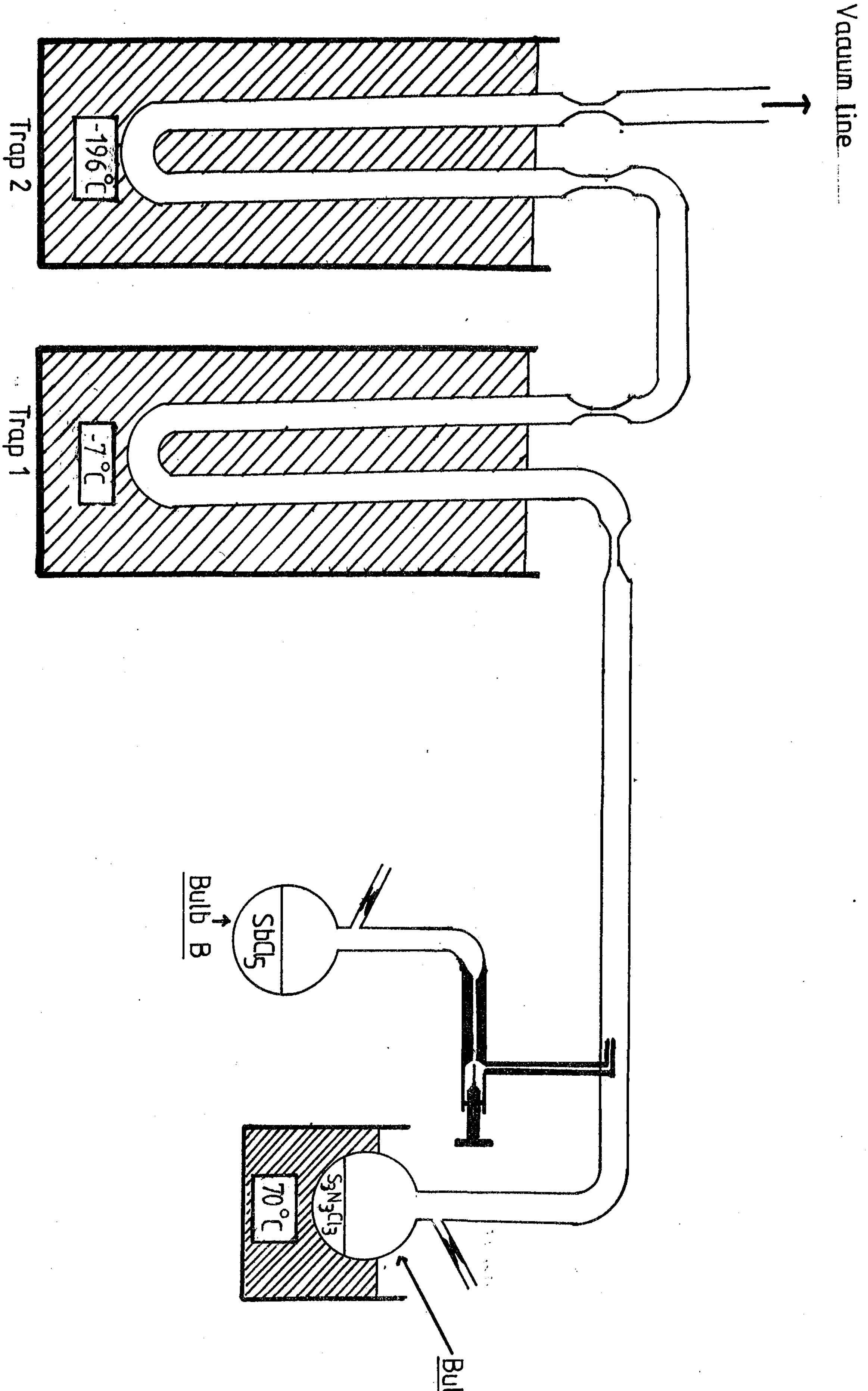
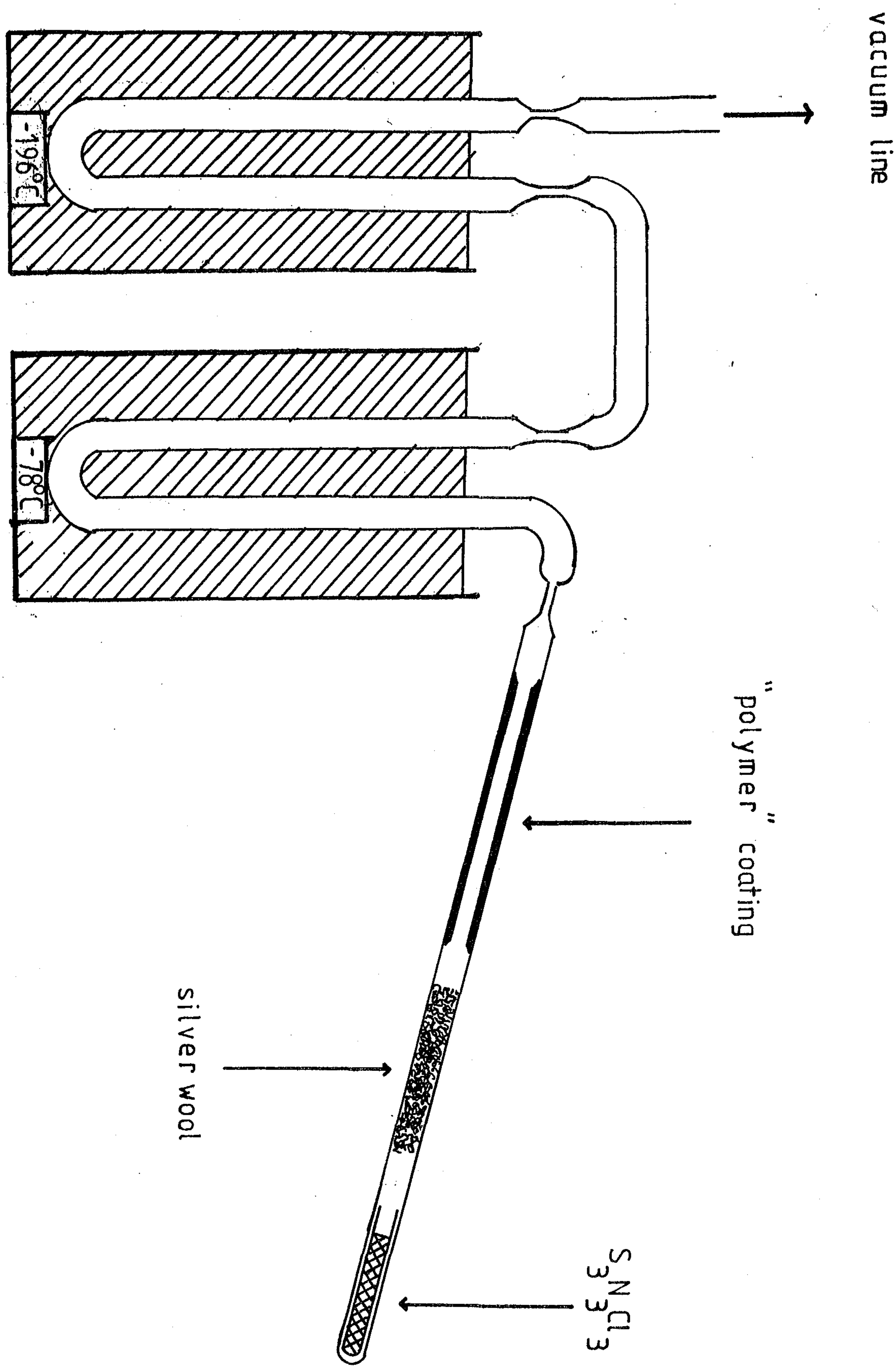

Vacuum line
Trap 2
-196°C
Trap 1
-7°C
SbCl5
Bulb B
S3N3Cl3
70°C
Bulb A

Figure 5.3



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CHAPTER SIX

THE REACTIONS OF GROUP VI POLYCATIONS WITH NITROGEN CONTAINING SPECIES

6.1 Introduction

Neutral and anionic homonuclear polyatomic species (e.g. P_4, O_3, S_8, Br_2 and I_3^- , I_5^- , O_2^- and S_4^{2-}) have been known for many years. Homonuclear aggregates of atoms are also present in cluster compounds such as $B_9H_9^{2-}$, Fe_3CO_{12} and $Ru_6(CO)_{18}$, in which the ligand donates electron density to the skeletal bonding. However, with the exception of Hg_2^{2+}, which has been known for many years,[1] it is only within the past decade that other stable, cationic homonuclear aggregates - "polycations" - have been synthesised and characterised.

By analogy with the mercury cation,there is substantial evidence for the existence of polyatomic cations in the reactions of metals with their corresponding metal chloride melts (e.g. Cd_2^{2+}, Zn_2^{2+}, Pb_2^{2+}, Mg_2^{2+}, Ca_2^{2+}, Sr_2^{2+} and Ba_2^{2+})[2-7]. The first firm evidence for a polyatomic cation M_x^{y+} (where $x>2$) came in 1963 when Hershaft and Corbett[8] proved,by X-ray crystallography the existence of Bi_5^{3+}, which was later followed by evidence for the existence of Bi_8^{2+}. Since 1963 there have been notable developments in anionic, cationic and neutral homonuclear catenates for the elements in Groups V, VI and VII.[9]

GROUP VI POLYCATIONS

6.1.1 Polycations of Oxygen

O_2^+ is the main example of the oxygen polycations[10-12] although O_3^+ has been observed in atmospheric studies.[13,14] The polycations of oxygen are reviewed by Gillespie and Passmore[26] and are mot discussed further in this thesis.

6.1.2 Synthetic Routes to Sulphur, Selenium and Tellurium Polycations

(i) Preparation of Sulphur Polycations

The existence of sulphur polycations has been known since 1804, when Bucholz[15] dissolved sulphur in oleum and obtained various coloured solutions, depending on the composition of the oleum and the relative concentration of the sulphur. Particular note was made of the intense blue colouration that could be produced and various possibilities were suggested as to the identity of the species responsible for this colouration, e.g. S_2O_3,[16] S_2,[17] $[X_2S\text{-}SX_2]^+$,[18] and also a species S_x.[19] It was not until 1969, when Gillespie and Passmore[20] isolated the first crystalline sulphur polycations $(S_8^{2+}(AsF_6^-)_2$ and $S_{16}^{2+}(AsF_6^-)_2)$ that it was realised that the intensely coloured solutions formed on dissolving S_8 in highly oxidising acid media, were due to the presence of sulphur polycations.

The oxidation of S_8 by arsenic or antimony pentafluorides (AsF_5, SbF_5) in the correct molar ratio, yields either the deep blue S_8^{2+} polycation or the deep red polycation, S_{16}^{2+} (equations 6.1-4).

$$2S_8 + 3AsF_5 \xrightarrow[HF/SO_2]{} S_{16}^{2+}(AsF_6^-)_2 + AsF_3 \quad \text{(ref.20,21)} \qquad (6.1)$$

$$2S_8 + 3SbF_5 \xrightarrow[HF/SO_2]{} S_{16}^{2+}(AsF_6^-)_2 + SbF_3 \quad \text{(ref.21,22)} \qquad (6.2)$$

$$S_8 + 3AsF_5 \xrightarrow[HF/SO_2]{} S_8^{2+}(AsF_6^-)_2 + AsF_3 \quad \text{(ref.20,21)} \qquad (6.3)$$

$$S_8 + 3SbF_5 \xrightarrow[SO_2]{} S_8^{2+}(SbF_6^-)_2 + SbF_3 \quad \text{(ref.21,22)} \qquad (6.4)$$

(sealed tube)

The cation S_4^{2+} was first isolated as S_4^{2+} $(SO_3F^-)_2$ from the reaction of S_8 with $S_2O_6F_2$, using sulphur dioxide as a solvent at -23°C[22] and then as S_4^{2+} $(Sb_2F_{11}^-)_2$ from the reaction of S_8 with SbF_5 at 140°C.[22]

(ii) Preparation of the Polycations of Selenium

As in the case of sulphur, highly coloured solutions had been observed (since the early eighteen hundreds (Magnus 1827)[23]) on dissolving selenium in oxidising acids. The nature of these solutions was not however elucidated until 1968 when Barr *et al* presented evidence for the existence of the Se_4^{2+} and Se_8^{2+} polycations from photometric, conductiometric and cryoscopy studies. Salts containing the selenium polycations have been isolated from a variety of reactions (table 6.1).

TABLE 6.1 Preparation of Salts containing Polycations of Selenium

Compound	Reaction	Conditions	Reference
$Se_4(HS_2O_7)_2$	Se+65% Oleum	50°-60°C. Soln. goes yellow-brown. Crystallisation on standing	25
$Se_4(AsF_6)_2$	$4Se+3AsF_5$	SO_2 solvent; 80°C for 8 days. Yellow solid from green solution	26
$Se_8(Sb_2F_{11})_2$	$8Se+5SbF_5$	Solvent SO_2: -23°C: 3 days	27
$Se_8(AsF_6)_2$	$8Se+3AsF_5$	Solvent HF: Warm from -78 to 0°C over 3 days	27
$Se_4(AlCl_4)_2$	$Se/SeCl_4/4AlCl_3$	Obtained from melts	28,29
$Se_8(AlCl_4)_2$	$Se/SeCl_4/2AlCl_3$	Fuse at 350° for 3h.	28

(iii) Preparation of the Tellurium Polycations

It has been known for 150 years that tellurium dissolves in sulphuric acid to give a deep red coloration[30] (cf. S_8, Se in highly oxidising acids). Bjerrum[31,32] postulated that the species responsible for the red colouration was of the form Te_{2n}^{2+}. Investigation of the solutions of tellurium in various acid media by conductometric and cryoscopic methods[33,34] supported the postulate made by Bjerrum and suggested that the species was in fact Te_4^{2+}. During the past decade various crystalline compounds containing tellurium polycations have been synthesised (table 6.2) and their X-ray crystal structure determined.

TABLE 6.2 Synthetic Routes to Compounds containing Tellurium Polycations

Compound	Synthesis	Conditions	Reference
$Te_4(Sb_2F_{11})_2$	$4Te+5SbF_5$	SO_2 solvent: stirred for several days at -23°C. SO_2 soluble products isolated	34
$Te_4(AsF_6)_2$	$4Te+3AsF_5$	Solvent SO_2: stirred 24h. at 25°C	34
$Te_6(AsF_6)_2$	$6Te+3AsF_5$	Solvent SO_2: stirred 24h. at 25°C	34
$Te_4(AlCl_2)_2$ $Te_4(Al_2Cl_7)_2$ $Te_6(AlCl_4)_2$	$Te/TeCl_4/$ $4AlCl_3$	Obtained from the melt	35
$Te_x(SO_3F)_x$	$4Te+S_2O_6F_2$	Yellow comp. Unstable above -20°C	34
$Te_6(AsF_6)_4\cdot 2AsF_3$	$6Te+6AsF_5$	Solvent AsF_3	36

6.1.3 The Structures of the Group VI Polycations

(i) Structures of the Cations containing Four Group VI Atoms

The X-ray crystal structures of both the Se_4^{2+}[37] and Te_4^{2+}[38] polyatomic cations have been determined and in both cases a close approximation to a square planar arrangement is found (figure 6.2, page 301). Knowing the structures of Se_4^{2+} and Te_4^{2+} it is possible to deduce from magnetic circular dichroism[39], visible U.V.[26], and solution Raman[26] data that a similar square planar arrangement is likely for S_4^{2+}.

(ii) Structures of the Cations containing Eight Group VI Atoms

Two homonuclear cations are known with the formulation X_8^{2+} (X = S, Se). The X-ray crystal structures of both these species have been determined and similar structures have been deduced (figure 6.3, page 301). The average bond distance in the S_8^{2+} ring is 204 pm.[40] which is identical to that found in the S_8[41] ring. However the cross ring distances are significantly reduced with respect to elemental S_8, implying significant cross ring interactions. This is supported by the reduction in the bond angles found in S_8 (109.7°) to the range 91.5° to 104.3°, as found in S_8^{2+}. In the Se_8^{2+} cation a similar skeletal arrangement is found.[28,29] The Se(3) - Se(7) cross ring distance (284pm) is however relatively shorter than the S(3)-S(7) distance (286pm) in S_8^{2+}. Whereas the Se(4)-Se(6) (329pm) and Se(2)-Se(8) (335pm) cross ring distances are relatively longer than the corresponding distances in S_8^{2+} (300 and 294pm respectively). Thus the canonical form shown in figure 6.3 (page 301) is more significant in the valence bond description of Se_8^{2+} than S_8^{2+}.[26] The bond lengths in Se_8^{2+} vary between 229pm and 236pm which are not that significantly different from those found in α or β selenium.[42,43] As in the case of S_8^{2+} the bond angles in the selenium polycation decrease with respect to those in α or β selenium, being in the range 89.8-103.6°.

(iii) Crystal Structure of $Te_6^{4+}(AsF_6^-)_4 \cdot 2AsF_3$.[36]

The Te_6^{4+} cation represents the first example of a hexa-atomic trigonal prism (figure 6.4, page 302) (cf. $C_6(CH_3)_6$,[44] Bi_9^{5+} [45]). The Te-Te bond lengths found within the triangles show significant multiple bond character being similar in length to those in Te_4^{2+} which may be described as having 25% double bond character.[46]

6.1.4 Reactions of the Group VI Polycations

There are very few reactions of the Group VI polycations reported in the literature. Those reactions published to date fall within three categories:

(i) The formation of heteronuclear Group VI polycations,

(ii) The reactions of Group VI polycations with Group VII elements.

(iii) The reaction of Group VI polycations with perfluorinated alkenes.

6.1.4 (i) The Formation of Heteronuclear Group VI Polycations

Since the isolation of the homonuclear polycations, in the early 1970s, there has been an interest in the preparation and structures of the inter-chalcogen (heteronuclear) analogues. No mixed sulphur-selenium cations have been reported to date but both tellurium-selenium and tellurium-sulphur cations have been prepared,[47,48] and their structures determined.

(a) Preparation and Structure of $Te_3S_3^{2+}$

$$\left.\begin{array}{l} Te_4^{2+}(AsF_6^-)_2 + S_8^{2+}(AsF_6^-)_2 \xrightarrow[SO_2]{} \\ \text{Te/S alloy (1:1)} + 3AsF_5 \xrightarrow[SO_2]{} \\ 3/8\ S_8 + 3Te + 3AsF_5 \xrightarrow[SO_2]{} \end{array}\right\rangle \rightarrow Te_3S_3^{2+}(AsF_6^-)_2 \text{(ref.48)}$$

The structure of $Te_3S_3^{2+}$ is given in figure 6.4 (page 302).

(b) Preparation and Structure of $Te_2Se_4^{2+}$

$$Te + Se \left\{\begin{array}{l} \xrightarrow[SO_2/AsF_5]{} Te_2Se_4^{2+}(AsF_6^-)_2 \\ \xrightarrow[SO_2/SbF_5]{} Te_2Se_4^{2+}(SbF_6^-)_2 \end{array}\right. \qquad \text{(ref.48)}$$

The structure of $Te_2Se_4^{2+}$ is given in figure 6.4 (page 302).

(c) Preparation and Structure of $Te_2Se_8^{2+}$

$$2Te + Se_8^{2+}(AsF_6^-) \xrightarrow[SO_2]{} Te_2Se_8^{2+}(AsF_6^-)_2 \qquad \text{(ref.47)}$$

The structure of $Te_2Se_8^{2+}$ is given in figure 6.4 (page 303).

(d) Preparation and Structure of $Te_{3.7}Se_{6.3}^{2+}(AsF_6^-)_2$

$$Se + Te + 3AsF_5 \xrightarrow[\substack{SO_2\\24h.}]{} Te_{3.7}Se_{6.3}^{2+}(AsF_6^-)_2 \qquad \text{(ref.47)}$$

The crystal structure of the species (figure 6.4, page 303) indicates that there is a mixture of $Te_3Se_7^{2+}$ and $Te_4Se_6^{2+}$ in approximately equal concentrations.

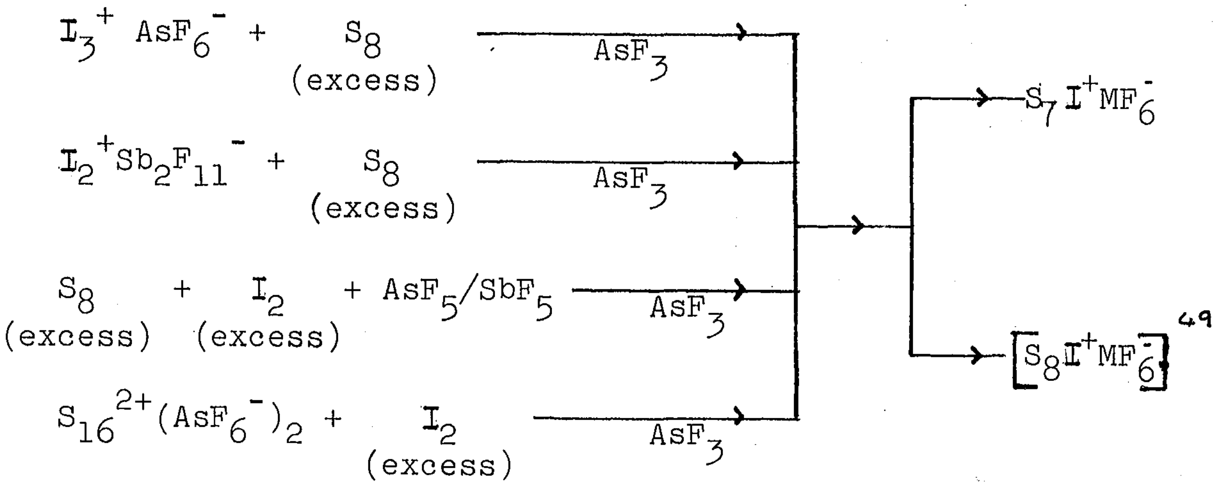
6.1.4(ii) The Reactions of the Group VI Polycations with the Halogens

There has only been one paper published in this area of chemistry, that of Passmore *et al*[49] in which they prepared $S_7I^+MF_6^-$ isoelectronic to S_8^{2+}, S_7[50,51] and S_8O[52,53].

and determined its crystal structure. The S_7I^+ cation was the first binary sulphur iodide isolated to be stable at room temperature.

The species S_7I^+ was prepared by a variety of routes (figure 6.1).

FIGURE 6.1 Preparative Routes to the S_7I^+ Cation



The structure of $S_7I^+SbF_6^-$ is given in figure 6.5 (page 304)

Recent attempts by Passmore and Sutherland to prepare S_8I^+ have failed. However in an attempt to prepare S_5I^+ from the reaction of sulphur with iodine and antimony pentafluoride, in the appropriate ratio, the species $(S_7I)_2I^{3+}(SbF_6^-)_3\cdot 2AsF_3$ was isolated,[54] (equation 6.5).

$$28/8\ S_8 + 3I_2 + 10SbF_5 \xrightarrow{AsF_3} 2\ (S_7I)_2I^{3+}(SbF_6^-)_3\cdot 2AsF_3 + (SbF_3)_3\cdot SbF_5 \qquad (6.5)$$

The structure of the $(S_7I)_2I^{3+}$ cation is given in figure 6.5, (page 304).

6.1.4(iii) The Reaction of the Group VI Polycations with Perfluoro-alkenes

Passmore *et al*[55-58] have reported the reactions of all the Group VI polycations (except Te_6^{4+}) with tetrafluoroethene (C_2F_4). The products of these reactions vary in nature depending on whether a solvent (normally sulphur dioxide) is present or not. The products of the above reactions are presented in tables 6.3a,b.

The reactions of S_4^{2+} and S_8^{2+} with perfluoropropene (C_3F_6) have also been studied by Passmore and Desjardins[58] and are found to proceed by a similar mechanism, yielding analogous organo-Group VI species to those isolated from the reactions of sulphur polycations with C_2F_4.

TABLE 6.3a <u>Reactions of Group VI Polycations with Perfluoroethene without solvents</u>

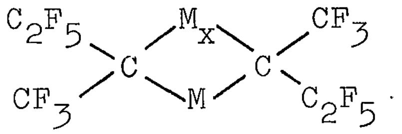
Group VI Polycation	S_8^{2+}	S_4^{2+}	Se_8^{2+}	Se_4^{2+}	Te_4^{2+}	Te_6^{2+}
Product Classification	value of x	value of x	value of x	value of x	value of x	value of x
$(C_2F_5)_2M_x$	2-6[55]	1-4[58]	2,3[56]	1-3[58]	1,2[57]	1,2[57]
$(C_4F_9)_2M_x$		2[58]	2[56]		1[57]	1[57]
$(C_4F_9)M_x(C_2F_5)$		1,2[58]	2,3[56]		1,2[57]	1,2[57]
$(C_2F_5)M_xC_3F_6C(O)F$					1[57]	1[57]
$(C_2F_5M_x)_2Hg$					1[57]	1[57]
		1,2[58]				

TABLE 6.3b Reactions of Group VI Polycations with Tetrafluoroethene using Sulphur Dioxide as a Solvent

Group VI Polycation	S_8^{2+}	Se_8^{2+}	Se_4^{2+}	Te_4^{2+}
Product Classification	value of x	value of x	value of x	value of x
$(CF_3)_2M_x$	3[58]	2[56]	2[58]	
$(C_2F_5)_2M_x$	2,3[55] 2,6[58]	2,3[42]		
$(C_4F_9)_2M_x$				1[57]
$C_2F_5M_xCF_3$	2,3[55] 3,5[58]	2[56]	2[58]	
$C_4F_9M_xC_2F_5$				1,2[57]
$(CF_3)M_xCF_2C(O)F$	3,4[58]		2[58]	
$(C_2F_5)M_xCF_2C(O)F$	2,3[55] 2,5[58]	2[56]	2[58]	
$(C_2F_5)M_xC_3F_6C(O)F$				1[57]
$(CF_2COF)_2M_x$	2,4[58]		2[58]	

6.2 Experimental

6.2.1 Reactions of Group VI Polycations with Azides

(i) Reaction of $S_8^{2+}(AsF_6^-)_2$ with Sodium Azide using Sulphur Dioxide as a Solvent

$S_8^{2+}(AsF_6^-)_2$ (0.3945g, 0.622 mmole) and NaN_3(0.0420g, 0.646 mmole) were placed in a pre-dried vacuum tight, pyrex vessel (figure 1.1 , page 14) and SO_2(4.5191g) condensed in. The reaction was allowed to warm slowly to room temperature. The initial deep blue colouration of the polycation solution gradually turned deep green then red. The reaction was agitated at room temperature for 12h. during which time precipitation of a pale yellow compound occurred. The product, soluble in sulphur dioxide, was filtered off leaving a pale yellow precipitate. The solvent was removed under reduced pressure and the weight due to the solvent and any other volatile species was recorded (4.5394g), corresponding to 4.5191g of SO_2 and 0.0203g of volatile product (nitrogen).

The infra-red and Raman spectra were recorded on both the soluble and insoluble products.

Infra-red spectrum of the insolubles (nujol mull): 695vs, br, 394vs cm^{-1}.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm^{-1}.

Infra-red spectrum of the solubles (nujol mull): 1498s, 695vs,br, 394vs cm^{-1}.

Raman spectrum of the solubles (red line): not obtained.

(ii) Reaction of $S_8^{2+}(AsF_6^-)_2$ with Sodium Azide using Arsenic Trifluoride as a Solvent

$S_8^{2+}(AsF_6^-)_2$ (2.8248g, 4.455 mmole) was loaded into an isolatable bulb of a pre-dried, vacuum tight, pyrex vessel (figure 1.2, page 14) and NaN_3 (0.2916g, 4.486 mmole) into the second bulb. The AsF_3 (17.4813g) was condensed on to the polycation and the deep blue solution was added to the azide, with the resulting formation of a green then deep red solution. The reaction was stirred at 0°C for 54h. An orange-red precipitate was formed in a deep red solution. The solution was filtered off and the insolubles were washed with recondensed solvent yielding an orange solution and a pale yellow precipitate.

Slow removal of the AsF_3 solvent from the solution did not yield crystals but gave an amorphous mass which "foamed" when pumped on at reduced pressure. The weight loss recorded after the removal of all the volatiles present at room temperature corresponded to a loss of the solvent and 0.1228g of volatile product (nitrogen). The vessel was broken under dry-box conditions and the soluble product (0.910g) and insoluble product (2.024g) isolated.

Infra-red spectrum of the insolubles (nujol mull): 695vs, 394vs cm^{-1}.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm^{-1}.

Infra-red spectrum of the solubles (nujol mull): 1495s, 695vs, 394vs cm^{-1}.

(iii) Reaction of $S_8^{2+}(AsF_6^-)_2$ with CsN_3 using SO_2 as a Solvent

$S_8^{2+}(AsF_6^-)_2$ (0.8886g, 1.402 mmole) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1. 2, page 14) and sealed. CsN_3 (0.2546g, 1.455 mmole) was loaded into the second bulb and SO_2 (15.1364g) condensed in. The cesium azide solution was then filtered on to the polycation solution. An immediate reaction occurred forming a deep red solution and a pale yellow precipitate. The reaction was agitated for 4h. at room temperature and then the soluble product filtered off. The solvent was slowly removed from the filtrate leaving an intensely coloured red oil which "foamed" when the vessel was pumped on under reduced pressure.

The weight loss recorded on removal of the volatiles at room temperature corresponded to the weight of solvent and 0.0529g of volatile product (nitrogen). The vessel was broken under dry-box conditions and the solubles and insolubles isolated. The Raman and infra-red spectra of the products were recorded.

Infra-red spectrum of the solubles (nujol mull): 1495m, 695vs,br, 395vs cm^{-1}.

Raman spectrum of the solubles (red line): not obtained.

Infra-red spectrum of the insolubles (nujol mull): 695vs,br, 392vs cm^{-1}.

Raman spectrum of the insolubles (red line): 152, 220, 243, 434, 472 cm^{-1}.

Analysis of the soluble product.

Found: S, 50.47; N, 1.65; As, 19.3%.

$S_{13}NAs_2F_{12}$ requires: S, 51.48; N, 1.73; As, 18.57%.

(iv) Reaction of $Se_4^{2+}(AsF_6^-)_2$ with Cesium Azide (CsN_3)

$Se_4^{2+}(AsF_6^-)_2$ (0.8537g, 1.230 mmole) was loaded into the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1. 2, page 14) and sealed. Cesium azide (0.2250g, 1.286 mmole) was placed in the second bulb and SO_2 (15.6314g) condensed into the vessel (approx. 50% of the SO_2 in each bulb). The yellow CsN_3 solution was then filtered on to the green selenium polycation solution. An immediate reaction occurred forming a deeply coloured solution and a brown precipitate. The reaction was agitated for 4h. and then the solubles were filtered off leaving a tan coloured insoluble residue. The solvent was slowly removed from the solution yielding a black precipitate. On complete removal of the solvent a weight loss corresponding to the weight of solvent and 0.0364g of volatile product (nitrogen) was recorded.

The solubles (0.1443g) and insolubles (0.8198g) were isolated under dry-box conditions and their infra-red spectra recorded.

Infra-red spectrum of the insolubles (nujol mull): 695vs,br, 392vs cm^{-1}.

Infra-red spectrum of the solubles (nujol mull): 720s(sh), 695vs, 395vs cm^{-1}.

Analysis of the insolubles.

Found: N, 0.38%.

(v) Reaction of $Se_8^{2+}(AsF_6^-)_2$ with $Et_4N^+N_3^-$

$Se_8^{2+}(AsF_6^-)_2$ (3.1009g, 3.071 mmole) was loaded into a pre-dried, vacuum tight, pyrex vessel and sealed off by a Rotoflo valve. Et_4NCl (0.5732g, 3.463 mmole) and NaN_3 (0.3071g, 4.725 mmole) were placed in a second sealable section and SO_2 (10.4834g) was condensed into both bulbs (similar to figure 1.2, page 14 but with three bulbs, two of which are sealable). The resulting deep yellow $Et_4N^+N_3^-$ solution was then filtered on to the deep green polycation solution forming a red-brown solution and an insoluble black precipitate. The reaction was stirred at room temperature for 15h. and then the soluble product filtered off. The solvent was then slowly evaporated off the solution leaving a deep brown microcrystalline material (3.064g) and a black insoluble product (0.289g).

Infra-red spectrum of the insolubles (nujol mull): 1080w, 1015w cm^{-1}.

Infra-red spectrum of the solubles (nujol mull): 1400m, 1305m, 1180s, 1145w, 1072w, 1028s, 1000s, 930m, 789s, 720-670vs, 630s(sh), 580m, 452m, 400-380vs cm^{-1}.

(The solubles contain an $Et_4N^+X^-$ salt, identified from the above infra-red spectrum).

(vi) Reaction of $Te_4^{2+}(AsF_6^-)_2$ with Sodium Azide

$Te_4^{2+}(AsF_6^-)_2$ (1.2595g, 1.418 mmole) was placed in a pre-dried, vacuum tight, pyrex vessel and sulphur dioxide (11.4386g) condensed in. To this deep cherry red solution was added anhydrous NaN_3 (0.1103g, 1.697 mmole). A rapid reaction occurred in which the cherry red coloration disappeared with the formation of a colourless solution and a black precipitate. The solubles were filtered off and the precipitate washed several times with sulphur dioxide to remove all traces of the solubles. The solvent was then slowly removed leaving a creamy-white "tar" which, when pumped on under reduced pressure at room temperature, lost solvent forming a white compound. The vessel was separated in the dry-box and the insolubles (0.8833g) isolated. On scraping out the soluble product an explosion occurred which was forceful enough to break the containing glass bulb. The experiment was terminated.

The weight of the insolubles corresponds to 1.418 mmoles of $NaAsF_6$ and 3 x 1.418 mmoles of Te.

(vii) Reaction of $Te_4^{2+}(AsF_6^-)_2$ with $Et_4N^+N_3^-$

Experiment 6.2.1(vi) was essentially repeated. $Te_4^{2+}(AsF_6^-)_2$ (3.7069g, 4.173 mmole) and $Et_4N^+N_3^-$ (4.300 mmoles) (formed *in situ* from $Et_4N^+Cl^-$ (0.7117g, 4.300 mmoles) and NaN_3 (0.3388g, 5.212 mmoles) cf. experiment 5.2.1(v)) were reacted together in SO_2 (10.2233g). The cherry red coloration rapidly disappeared with the formation of a colourless solution and a black precipitate. The creamy-white solubles (1.622g) and insolubles (2.775g) were isolated under dry-box conditions.

Analysis of the solubles:

Found: C, 23.71; H, 5.50; N, 3.65%

$Et_4N^+AsF_6^-$ requires: C, 30.1; H, 6.27; N, 4.39%

6.2.2 Reaction of Group VI Polycations with Tetrasulphur Tetranitride

(i) Reaction of $S_8^{2+}(AsF_6^-)_2$ with S_4N_4 (Ratio 2:1)

$S_8^{2+}(AsF_6^-)_2$ (0.6543g, 1.032 mmole) and S_4N_4 (0.0961g, 0.522 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel (figure 1.1, page 14) and arsenic trifluoride (7.7088g) condensed on to the reactants. The reaction was warmed to room temperature, rapidly forming a red-brown solution. The system was agitated for 12h. at room temperature during which time a yellow precipitate was formed which floated on the surface of the solvent (indicative of sulphur). The reaction mixture was filtered and the insoluble product washed with recondensed solvent to remove all traces of the soluble product. The solvent was then slowly evaporated from the system yielding a red-orange microcrystalline product which, on close examination using a microscope, was seen to be a yellow crystalline material coated by a red amorphous material.

The solubles (0.927g) and insolubles (0.249g) were isolated and their infra-red and Raman spectra recorded.

Infra-red spectrum of the insolubles (nujol mull): Only peaks assignable to the mulling agent were observed.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm^{-1}.

The mass spectrum of the insolubles gave a break down pattern consistent with the species S_8.

Infra-red spectrum of the solubles (nujol mull): 1498s, 695vs,br, 394vs cm^{-1}.

Raman spectrum (red line): no bands observed.

(ii) Reaction of $S_8^{2+}(AsF_6^-)_2$ with S_4N_4(Ratio 1:2)

$S_8^{2+}(AsF_6^-)_2$ (0.99g, 1.56 mmole) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1.2 , page 14) and S_4N_4 (0.60g, 3.26 mmole) in the second bulb. SO_2 (8.36g) was condensed in (some into each bulb) and the resulting deep blue polycation solution filtered slowly into the S_4N_4 solution. An immediate reaction occurred forming a deep red solution and a finely divided, pale coloured precipitate. All the polycation was washed over on to the S_4N_4 solution and the reaction was agitated at room temperature for 4h. The solubles were filtered off and the insolubles were repeatedly washed to remove the soluble product. The solvent was then slowly evaporated from the solution yielding an orange-red microcrystalline precipitate. The insoluble product (0.29g) and soluble product (1.28g) were isolated and the Raman and infrared spectra recorded where applicable.

Infra-red spectrum of the solubles (nujol mull): 1329w, 1298w, 1280w, 1260w, 1215w, 1068w, 1036m, 1018m, 995ms, 970vw, 928m, 865vs, 750m, 740s, 700vs,br, 594w, 578m, 569m(sh), 560w(sh), 525vw, 495m, 395vs cm^{-1}.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm^{-1}.

(iii) Reaction between S_8, S_4N_4 and AsF_5

S_4N_4 (0.2063g, 1.121 mmole) and S_8 (1.5830g, 6.184 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel (figure 1.1 , page 14) and SO_2 (5.7452g) and AsF_5 (1.3357g, 7.857 mmole) condensed on to the reactants. The reaction was slowly warmed to room temperature. At ca. -60°C a reaction occurred forming a deep blue solution which, on warming further, went first green then deep red. The reaction was stirred for 2h. at room temperature and then the soluble products were filtered off, the pale yellow residue being washed several times with recondensed solvent. Slow evaporation of the solvent from the solution did not yield a crystalline material but a red amorphous mass which, when pumped on under reduced pressure, "foamed" (cf. S_{16}^{2+} when pumped on under reduced pressure). Recrystallisation of the product from a 1:5 mixture of $SO_2ClF:SO_2$ (by weight) did not produce crystalline material.

Infra-red spectrum of the solubles (nujol mull): 1495m, 1020w, 695vs,br, 394vs cm^{-1}.

Raman spectrum of the solubles (red line): no spectrum observed.

Infra-red spectrum of the insolubles (nujol mull): peaks assignable to mulling agent only.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm^{-1}.

(iv) Reaction of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (Ratio 2:1)

$Se_4^{2+}(AsF_6^-)_2$ (1.5800g, 2.277 mmole) and S_4N_4 (0.2160g, 1.174 mmole) were loaded into a pre-dried, vacuum tight, pyrex vessel (figure 1.1 , page 14) and SO_2 (9.1483g) condensed on to the reactants. A rapid reaction occurred in which a black precipitate was formed in a deep green solution. The precipitate was washed, with the recondensed solvent, several times to remove all traces of the soluble product. The solvent was then slowly evaporated from the solution leaving a small quantity of orange crystalline product and a deep green mass ($Se_8^{2+}(AsF_6^-)_2$).

Infra-red spectrum of the orange crystalline product (nujol mull): 1035w, 995vw, 928w, 860m, 740m(sh), 700vs, 580vw, 500w, 400s cm^{-1}. (cf. experiment 3.2.3(iii), page 122).

Infra-red spectrum of the insolubles (nujol mull): 998m, 954s, 715vs, 690s, 665s, 620s, 580w, 547m, 398vs, 354m cm^{-1}.

(v) Reaction of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (Ratio 1:2)

$Se_4^{2+}(AsF_6^-)_2$ (2.0689g, 2.982 mmole) and S_4N_4 (1.1546g, 6.275 mmole) were loaded into a pre-dried, vacuum tight, pyrex vessel (figure 1. 1, page 14) and sulphur dioxide (8.9321g) condensed in. On warming to room temperature a rapid reaction occurred with the formation of a deep red solution and the deposition of a purplish precipitate. The reaction was stirred for 24h. and then the solubles were filtered off, the residue being washed several times to remove all traces of the solubles. The solvent was then slowly evaporated off from the solution yielding a deep orange crystalline material (0.843g).

The soluble and insoluble products (1.273g) were isolated under dry-box conditions and their vibrational spectra and analyses recorded.

Infra-red spectrum of the soluble product (nujol mull): 1036m, 995w, 927w, 864vs,br, 748m(sh), 738s, 700vs, 580m, 550w, 500m, 470w, 397vs, 380s cm^{-1} (cf. experiment 3.2.3(iii), page 122).

Raman spectrum of the solubles (red line): 1036w, 680m, 620m, 572w, 514vw, 372w, 350m, 268s, 242w, 222m, 182s, 162m, 62vs cm^{-1}.

Infra-red spectrum of the insolubles (nujol mull): 996m, 952s, 924m, 610w, 688s, 670m(sh), 664s, 630w(sh), 620s, 550m, 404s(sh), 395vs cm^{-1}.

Analysis of the insolubles:

Found: S, 11.27; N, 6.44, Se, 43.9%.

Mass spectrum of the solubles (m/e,(abundance) assignment).

151(100) AsF_4 ; 132(19) AsF_3 , 113(27) AsF_2 ; 94(13) AsF ; 92(75)S_2N_2 ; 78(10) S_2N ; 65(26) NSF ; 46(44) NS .

Mass spectrum of the insolubles (m/e (abundance) assignment):

158(8) S_2NSe^{80} ; 156(4) S_2NSe^{78} ; 151(11) AsF_4 ; 138(25) S_3N_3 ; 132(5) AsF_3 ; 113(6) AsF_2 ; 94(9) AsF ; 92(100) S_2N_2 ; 80(4) Se^{80} ; 78(9) S_2N,Se^{78} ; 64(21) S_2,SO_2 ; 48(11) SO ; 46(82) NS; 32(12) S; 28(67) N_2.

A diagrammatic representation of the above mass spectra are given in figure 6.6(a) and (b) respectively, pages 305,306.

(vi) Reaction of $Te_4^{2+}(AsF_6^-)_2$ with S_4N_4 (Ratio 1:2)

$Te_4^{2+}(AsF_6^-)_2$ (0.8615g, 0.970 mmole) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1. 2, page 14) and sealed off with the Rotoflo valve. S_4N_4 (0.3592g, 1.952 mmole) was placed in the second bulb and SO_2 (14.6439g) condensed in (approx. 75% on to the Te_4^{2+} and 25% on to the S_4N_4). The deep cherry red solution of the polycation was then filtered on to the S_4N_4 solution. An immediate reaction occurred forming a black precipitate in a deep orange solution. The tellurium polycation was completely dissolved and filtered over onto the S_4N_4 solution. The reaction was then agitated for 4h. at room temperature without any obvious signs of further reaction. The deep orange solution was then filtered off and the black precipitate washed with recondensed solvent. The solvent was then slowly evaporated from the solution (using a 2°C temperature gradient across the vessel) yielding a bright orange crystalline material.

Infra-red spectrum of the insolubles (nujol mull): Only peaks assignable to the mulling agent were observed.

Infra-red spectrum of the solubles (nujol mull): 1329w, 1200vs, 1155w, 1068w, 1035s(sh), 1025s, 1010s, 948s, 935s, 838m, 705vs, 772s(sh), 582s, 532vw, 522vw(sh), 494m, 482m, 398vs, 375w, 368w, 332w, cm^{-1}

Analysis of the solubles:

Found: S, 26.7; N, 9.71, Te, 23.33; As, 15.05%.

$Te_2S_8N_8As_2F_{12}$ requires: S, 25.57; N, 11.18; Te, 25.48; As, 14.98%.

$Te_2S_8N_7As_2F_{12}$ requires: S, 25.93; N, 9.94; Te, 25.85; As, 15.19%.

$TeS_4N_3AsF_6$ requires: S, 26.31; N, 8.63; Te, 26.22; As, 15.41%.

Mass spectrum of the soluble product (m/e(abundance) assignment):

132(15) AsF_3 ; 113(16) AsF_2 ; 94(4) AsF ; 92(33) S_2N_2; 78(5) NS_2 ; 76(2) CS_2 ; 64(100) S_2 ; 63(13) CSF ; 48(33) SO ; 47(3) NSH ; 46(26) NS ; 44(3) CS .

A diagrammatic representation of the above mass spectrum is given in figure 6.6c, page 307.

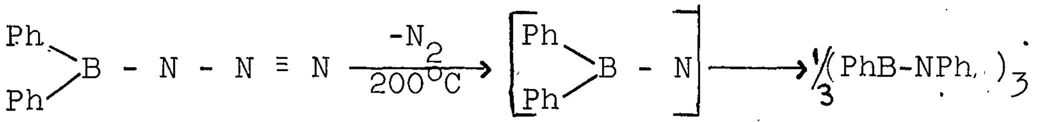
FORMATION OF GROUP VI - NITROGEN CATIONS FROM GROUP VI POLYCATIONS AND NITROGEN CONTAINING MOIETIES

6.3 Discussion

6.3.1 The Reactions of Group VI Polycations with Azides

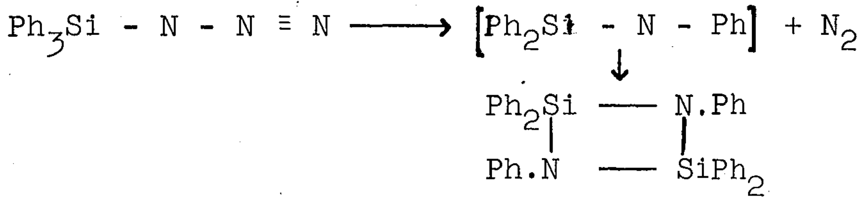
The use of azide intermediates as a route to main group - nitrogen heterocycles is well documented (equation 6.3.1(a-f)).

Boron-Nitrogen Heterocycles[59,60]



$$Ph_2B-N-N\equiv N \xrightarrow[200^{\circ}C]{-N_2} [Ph_2B-N] \longrightarrow \tfrac{1}{3}(PhB\text{-}NPh)_3 \qquad (6.3.1a)$$

Silicon-Nitrogen Heterocycles[61]



$$Ph_3Si-N-N\equiv N \longrightarrow [Ph_2Si-N-Ph] + N_2 \qquad (6.3.1b)$$

Phosphorus-Nitrogen Heterocycles[52,63]

$$R_2PCl + R_3'SiN_3 \longrightarrow 1/3\ (R_2PN)_3 + R_3'SiCl \qquad (6.3.1c)$$

$R = Me,$[62] Ph[62,63]

Sulphur-Nitrogen Heterocycles[64-66]

$$2S_2Cl_2 + 4MN_3 \longrightarrow S_4N_4 + 4MCl + 4N_2 \qquad (6.3.1d)$$

($M = Li,$[64] $Al(N_3)_3$[65]).

$$PhS(O)Cl + NaN_3 \longrightarrow PhS(O)N_3 \xrightarrow{0^{\circ}C} (Ph(O)SN)_3 \text{ (ref.66)} \qquad (6.3.1e)$$

$$S_4N_3Cl + MN_3 \longrightarrow S_4N_4 + N_2 + MCl \quad \text{(ref.65)} \qquad (6.3.1f)$$

Hence by analogy with work done by Passmore and Sutherland, in which they have isolated a range of compounds from the reactions of S_8^{2+} with halides and pseudohalides

(CNS^-) the reaction of S_8^{2+} with N_3^- was investigated. It was suggested that an intermediate of the form $S_8N_3^+$ may exist which, on thermal decomposition, would yield a sulphur-nitrogen cation of the form S_xN^+ (x = 1-7).

6.3.1(i) Reaction of Sulphur Polycations with Azides

The reactions of $S_8^{2+}(AsF_6^-)_2$ with both NaN_3 and CsN_3, using sulphur dioxide and arsenic trifluoride as solvents, were studied. All the reactions proceeded in the same manner, forming deep red solutions which, on evaporation of the solvent deposited an orange-red material which "foamed" on pumping under reduced pressure. The foaming of the product is very reminiscent of the effect that pumping at reduced pressure has on $S_{16}^{2+}(AsF_6^-)_2$.[67] Therefore it is thought likely that some $S_{16}^{2+}(AsF_6^-)_2$ is formed as a by-product in the reaction. The reaction was found to produce measurable quantities of nitrogen but a quantitative measure of nitrogen, from the weight loss on its removal, was not accurate enough to determine whether one mole of azide evolved one mole or 3/2 moles of nitrogen. The Raman spectrum of the insoluble product was consistent with that of sulphur, the infra-red spectrum indicating only the presence $Na^+AsF_6^-$.

The analysis of the soluble product from the reaction of $S_8^{2+}(AsF_6^-)_2$ with cesium azide in sulphur dioxide indicates that a compound or mixture of the overall formulation $S_{13}NAs_2F_{12}$ is produced. From this analytical result and the assumption that $S_{16}^{2+}(AsF_6^-)_2$ is present in the soluble product, it is suggested that the solubles are a mixture of $S_xN^+(AsF_6^-)_2$ and $S_{16}^{2+}(AsF_6^-)_2$. The presence of $S_{16}^{2+}(AsF_6^-)_2$ can be readily explained by the reaction of S_8 (formed in the initial reaction of S_8^{2+} with azide (equation 6.3.1g)) with $S_8^{2+}(AsF_6^-)_2$ (equation 6.3.1h).

$$\begin{array}{lll} S_8^{2+}(AsF_6^-)_2 + Cs^+N_3^- \longrightarrow & CsAsF_6 + \left[S_8N^+AsF_6^-\right] + N_2 & \\ & \qquad\qquad\downarrow & (6.3.1g) \\ & \qquad S_xN^+AsF_6^- + 1-{}^x/8\ S_8 & \end{array}$$

$$S_8^{2+}(AsF_6^-) + S_8 \longrightarrow S_{16}^{2+}(AsF_6^-)_2 \qquad (6.3.1h)$$

The presence of the S_{16}^{2+} polycation in the product indicates that either the azide anion does not react with S_{16}^{2+} or that the azide becomes deactivated during the reaction thus changing the apparent reaction ratio. The latter explanation is most likely to be correct because the solubility of both sodium azide and hexafluoroarsenate is low in sulphur dioxide and thus coating of the azide, by the virtually insoluble hexafluoroarsenate salt, inhibits further reaction. Consequently the $S_8^{2+}(AsF_6^-)_2$ reacts with the sulphur by-product (equation 6.3.1g), producing the observed $S_{16}^{2+}(AsF_6^-)_2$.

In an attempt to overcome the problem of the azide being coated, an azide of higher solubility (in SO_2 or AsF_3) was employed (CsN_3). It was, however, found that the solubility of cesium azide in SO_2 was not significantly better than that of sodium azide, and the same products were obtained (i.e. S_8, $M^+AsF_6^-$, $S_{16}^{2+}(AsF_6^-)_2$ and $S_xN^+AsF_6^-$).

The nature of the species $S_xN^+AsF_6^-$ was elucidated from its infra-red spectrum (1498s, 695vs,br, 394vs cm^{-1}). The infra-red spectrum of the cation is very simple consisting of only one observed band (1498 cm^{-1}), the other two observed bands being due to AsF_6^-(ν_3: 700 cm^{-1}, ν_4: 400 cm^{-1}).[68] Comparison of the observed S-N stretching frequency with those of other sulphur-nitrogen cations in the literature (table 6.4) indicates that the compound is not the AsF_6^- salt of a previously synthesised cation.

TABLE 6.4 <u>The Infra-red active stretching modes for some Sulphur-Nitrogen multiple bonds</u>

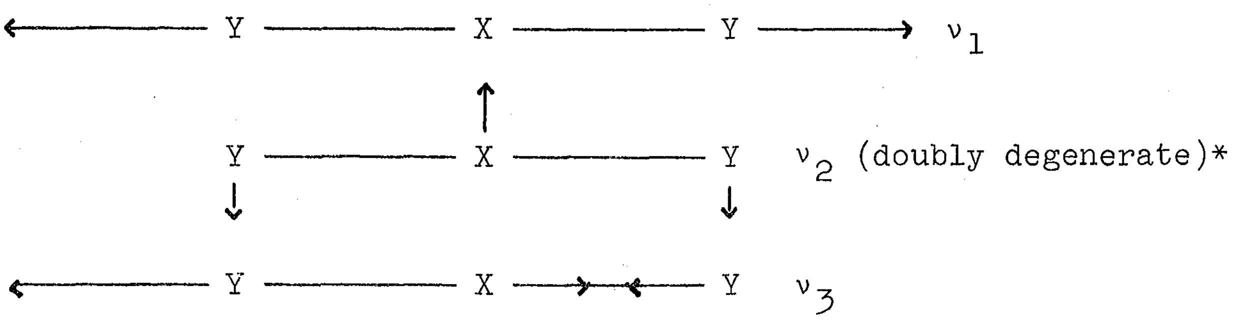
Species	S-N Stretching frequency (cm^{-1})	Reference
$N \equiv SF_3$	1515	69
$N \equiv S^+$	1447 (SbF_6^- salt)	70
$N \equiv S - F$	1372	69
$ClN = SF_2$	1204	71

As noted in table 6.4 the species has a stretching frequency higher than that recorded for NS^+ and only slightly lower than that of NSF_3. However, due to the preparative route, the formation of a sulphur-nitrogen cation containing $S^{(VI)}$ is highly unlikely.

Comparison of the stretching frequencies of the species NO^+ ($2220\ cm^{-1}$)^{68} with NO_2^+ (ν_3: $2360\ cm^{-1}$)^{68} and CO($2143\ cm^{-1}$)^{68} with CO_2 ($2349\ cm^{-1}$)^{68} indicates that the formation of a linear triatomic molecule (XY_2) increases the observed stretching frequency by up to ca. 10% relative to the diatomic (XY). Hence it was suggested that the most probable structure for the species S_xN^+ based on vibrational frequency data, is S_2N^+, a linear triatomic, isoelectronic and isostructural to CS_2.

A linear triatomic of the form XY_2 has three normal modes of vibration (figure 6.7).

Figure 6.7 Normal modes of vibration of a linear triatomic(XY_2)



*(There are an infinite number of vibrations of the type ν_2 which differ only in their directions perpendicular to the molecular axis. Any of these vibrations can be resolved into two mutually perpendicular base vibrations ν_{2a} and ν_{2b}. Thus the ν_2 mode in a linear triatomic is said to be "doubly degenerate").

The ν_1 mode in the species XY_2 is infra-red inactive, there being no net change in dipole moment, but is Raman active. The modes ν_2 and ν_3 are infra-red active and hence, as a consequence of the mutual exclusion principle, are not Raman active. By comparison with the bands in CS_2, the band observed in the infra-red spectrum of S_xN^+ at 1498 cm^{-1} is probably comparable with the ν_3 band in $CS_{2(l)}$ (1510 cm^{-1}). Hence the ν_2 band in S_xN^+ would be expected to occur at slightly lower frequencies than that in CS_2 (397 cm^{-1}),[68] probably in the region of 370-390 cm^{-1}.

The identity and the structure of the S_xN^+ cation was subsequently clarified by comparison of the vibrational spectrum of the above species with that reported by Faggiani *et al*[71] for the cation S_2N^+ (figure 6.8 and table 6.5).

Figure 6.8 Structure of the S_2N^+ Cation [71]

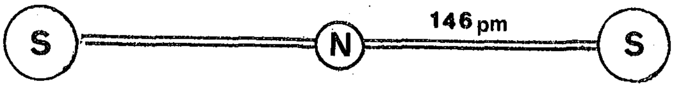


TABLE 6.5 Vibrational Spectrum of the Species $S_2N^+SbCl_6^-$.[71]

Infra-red Spectrum $S_xN^+(cm^{-1})$	Infra-red Spectrum $S_2N^+(cm^{-1})$	Raman Spectrum $S_2N^+(cm^{-1})$	Assignment of the band
1498s	1498m		ν_3 S_2N^+
		766m	$2\nu_2$ S_2N^+
		688m	ν_1 S_2N^+
	374m		ν_2 S_2N^+
		333vs	ν_1 $SbCl_6^-$
	320s		ν_3 $SbCl_6^-$
		293w	ν_2 $SbCl_6^-$
		283w	
		180m	ν_5 $SbCl_6^-$
		175m	
		167vw	
		778vs	lattice modes
		67s	

Hence it is concluded that the reaction between S_8^{2+} and N_3^- (molar ratio 1:1) yields the linear triatomic $S_2N^+AsF_6^-$ and $S_{16}^{2+}(AsF_6^-)_2$. (The latter compound prevents the Raman spectrum of the former being recorded).

The apparent stability of the S_2N^+ cation implies that it is highly unlikely that intermediates of the form $S_xN^+AsF_6^-$ (x = 3-7) will be isolated from the reaction of S_8^{2+} with azide. If however intermediate cyclic species are to be isolated then it is believed essential that the reaction be between solutions of azide and polycation thus avoiding the coating problems associated with less soluble azides.

6.3.1(ii) Reaction of Selenium and Tellurium Polycations with Azides.

By analogy with the reactions of S_8^{2+} with azides, in which S_2N^+ was formed, it was proposed that the species Se_2N^+ and Te_2N^+ may be synthesised by reaction of the appropriate polycation with an azide.

The reactions of $Se_4^{2+}(AsF_6^-)_2$ (experiment 6.2.1(iv), page 277), $Se_8^{2+}(AsF_6^-)_2$ (experiment 6.2.1(v), page 278) and $Te_4^{2+}(AsF_6^-)_2$ (experiment 6.2.1(vi), page 279) with azides were, therefore investigated. In all cases reaction occurred with the evolution of nitrogen and a noticeable change in colour of the solution. The reactions of selenium polycations with azides produced deep brown solutions and brown precipitates. Due to the infra-red spectrum of the solubles possessing only bands assignable to the mulling agent and AsF_6^-,[68] it is suggested that the soluble product is likely to be a higher selenium polycation (e.g. $Se_{10}^{2+}(AsF_6^-)_2$ cf. $S_{16}^{2+}(AsF_6^-)_2$ in the reactions of $S_8^{2+}(AsF_6^-)_2$ with azides). The insoluble tan-brown precipitate also gives essentially no infra-red spectrum. Analysis of the insoluble product from the reaction of CsN_3 with $Se_4^{2+}(AsF_6^-)_2$ indicates that the compound, to all intents and purposes, does not contain nitrogen. (Analysis of insoluble product $CsN_3/Se_4^{2+}(AsF_6^-)_2$: N, 0.38%). It is, therefore, concluded from the above evidence that the reaction between selenium polycations and azides produces two ionic compounds neither of which contain nitrogen and must therefore be homoatomic selenium polycations with the AsF_6^- anion.

The reactions of tellurium polycations ($Te_4^{2+}(AsF_6^-)_2$) with azides are very rapid, quickly decolouring the cherry red Te_4^{2+} solutions yielding colourless solutions with a black precipitate (elemental tellurium). The product is highly soluble in sulphur dioxide and has a great affinity for the solvent, forming creamy-white oils or tars, from which it is very difficult to remove the remaining sulphur dioxide. It was noted that the creamy-white product tends to explode with friction. Hence although there is no firm evidence for the formation of a tellurium nitrogen cation, in the reaction of $Te_4^{2+}(AsF_6^-)_2$ with azide, it is strongly suspected, from the weights of residual elemental tellurium, the affinity for sulphur dioxide, the colour of the compound and the tendency to explode with friction, that a species of the form $(TeN^+)_x$ has been produced.

Investigations into the reactions of selenium and tellurium polycations with azides are being undertaken, at the present time, by MacLean and Passmore at the University of New Brunswick.

6.3.2 The Reactions of Group VI Polycations with Tetrasulphur Tetranitride

(i) The Reactions of $S_8^{2+}(AsF_6^-)_2$ with Tetrasulphur Tetranitride

In the reaction of $S_8^{2+}(AsF_6^-)_2$ with tetrasulphur tetranitride (ratio 2:1) (experiment 6.2.2(i), page 275) both the soluble and insoluble products are readily identified from their vibrational spectra as S_8 (insoluble) and $S_2N^+AsF_6^-$ (soluble product).[71] There is also evidence for the formation of $S_{16}^{2+}(AsF_6^-)_2$, from the foaming of the soluble product when pumped on under reduced pressure.

In the reaction of $S_8^{2+}(AsF_6^-)_2$ with tetrasulphur tetranitride (ratio 1:2) (experiment 6.2.2(ii), page 275) the reaction appears to proceed in the same way as that of the 2:1 reaction, forming a deep red solution and a pale yellow insoluble material. The pale yellow insoluble material is identified from its Raman spectrum as S_8. The soluble product is not however S_2N^+. The infra-red spectrum of the soluble product has major peaks and 865, 740, 700 and 395 cm^{-1}. From this evidence it is readily concluded that an ionic species is present in the solubles containing the AsF_6^-[68] anion (700, 395 cm^{-1}). Comparison of the rest of the spectrum, particularly the 865 cm^{-1} band, with other recorded infra-red spectra of sulphur-nitrogen cations leads to the conclusion that the compound produced in the reaction of $S_8^{2+}(AsF_6^-)_2$ with S_4N_4 (ratio 1:2), is identical to that formed in the reaction of Fe with $S_3N_2Cl_2$, using SO_2 as a solvent ($S_{10}N_8^{2+}$) (Chapter Three, experiment 3.2.3(iii), page 122).

Hence overall equations for the reactions of $S_8^{2+}(AsF_6^-)_2$ with S_4N_4 can be written (equations 6.3.2(a,b)

Ratio 2:1

$$S_8^{2+}(AsF_6^-)_2 + \tfrac{1}{2}\, S_4N_4 \longrightarrow 2S_2N^+AsF_6^- + 6/8\ S_8 \qquad (6.3.2(a))$$

Ratio 1:2

$$S_8^{2+}(AsF_6^-)_2 + 2S_4N_4 \longrightarrow (S_{10}N_8^{2+})(AsF_6^-)_2 + 6/8\ S_8 \quad (6.3.2(b))$$

(ii) The Reactions of Selenium Polycations with Tetrasulphur Tetranitride

It has been found that the reaction of $S_8^{2+}(AsF_6^-)_2$ with tetrasulphur tetranitride in a ratio of 2:1 yields the cation S_2N^+ and that in a ratio of 1:2 the species postulated to be $(S_{10}N_8^{2+})(AsF_6^-)_2$ is formed. Hence by analogy with the reactions of $S_8^{2+}(AsF_6^-)_2$ with S_4N_4, the reactions of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 were investigated with a view to preparing the previously unsynthesised $SeNS^+AsF_6^-$ salt and the selenium substituted analogue of $(S_{10}N_8^{2+})(AsF_6^-)_2$. The reactions of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 were therefore investigated using a molar ratio of 1:2 and 2:1 (experiments 6.2.2(iv,v), pages 277,278).

It was found that the insoluble products in both the 2:1 and 1:2 reactions gave the same infra-red spectrum whereas the soluble products were not identical. The soluble product from the 2:1 reaction was identified as being mainly $Se_8^{2+}(AsF_6^-)_2$ but a few orange crystals were isolated which gave the same infra-red spectrum as the soluble component of the 1:2 reaction. The infra-red spectrum of the solubles formed in the 1:2 reaction was compared with infra-red spectra of known sulphur-nitrogen species and was found to be identical to that recorded for the cation $S_{10}N_8^{2+}$ From the analytical data obtained on the soluble product and the lack of any significant shifting in the infra-red bands, it is concluded that the soluble product, from the reaction of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (in a molar ratio of 1:2) is $(S_{10}N_8^{2+})(AsF_6^-)_2$, with a low percentage of a selenium substituted analogue.

The insoluble products of both the 2:1 and 1:2 reaction gave an infra-red spectrum consistent with the product being ionic and probably containing a selenium analogue of a cyclic sulphur-nitrogen cation. It was, therefore, surprising that the salt was not soluble to some extent in sulphur dioxide, as it has been found throughout this thesis that, in general, all sulphur-nitrogen salts, with the exception of S_3N_2Cl, dissolve readily in sulphur dioxide.

The colour of the compound is also noted, as virtually all sulphur-nitrogen salts are red, orange or yellow. The main exception to the above statement is S_3N_2Cl which is green-black. Hence from purely physical evidence it would appear reasonable to suggest that the salt isolated in the insolubles could be an analogue of the $(S_3N_2^+)_2$ system. The infra-red spectrum of the insoluble product was compared with that of S_3N_2Cl,[72] and the recently reported species $(SSe_2N_2^+)_2(X^-)_2$ (X = Cl, Br)[72], (table 6.6).

It is observed that the antisymmetric S-N stretching frequencies, occurring in the 900-1000 cm^{-1} region of the spectrum, are very similar in S_3N_2Cl, SSe_2N_2Cl and the product. Two strong bands occur in this region which move to higher wave numbers in the order S_3N_2Cl lower than SSe_2N_2Cl lower than the insoluble product. The splitting in the two main bands in the 900-1000 cm^{-1} region is also noted to increase in the same order as observed above, being greatest for the insoluble product (splitting of 44 cm^{-1}). It is suggested that the effects noted in the infra-red spectra when comparing S_3N_2Cl with SSe_2N_2Cl would be amplified when comparing S_3N_2Cl with $SSe_2N_2^+AsF_6^-$. The AsF_6^- anion is likely to interact much less strongly with the cation than

TABLE 6.6 Comparison of the Infra-red Spectra of S_3N_2Cl, SSe_2NCl[72] and that of the insoluble product from the reactions of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4.

S_3N_2Cl (cm^{-1})	SSe_2N_2Cl (cm^{-1})	Insoluble Product (cm^{-1})
964s	972s	998m
944vs	941s	954s
745w	801w	
716s(sh)		720s(sh)
708vs	720w	710vs,br (AsF_6^-)[68]
699s(sh)		690s
		655s
	617vs	617s
583s	588m	548m
569w		
456w	472w	
		398vs (AsF_6^-)[68]
	356vs	354s

the chloride anion and will therefore increase the effective positive charge on the ring, hence tending to move the observed antisymmetric ring modes to higher wave numbers. The effect of lowering the degree of anion-cation interaction is also likely to cause a greater splitting in the observed bands. (SSe_2N_2Cl splitting 31 cm^{-1}, product splitting 44 cm^{-1}). Hence by comparison of the bands occurring in the region 900-1000 cm^{-1} it appears that the product could be the AsF_6^- salt of $SSe_2N_2^+$. However on examination of the infra-red spectrum of the product in the region 650-750 cm^{-1} it is noted that a large number of strong bands are observed, the main one of which (710 cm^{-1}) is assignable to the AsF_6^-[68] anion. The bands occurring between 650 and 750 cm^{-1} are not thought to be due to Se-N vibrations as the major bands in Se_4N_4 occur below 580 cm^{-1}.[73] Comparison of this area of the spectrum with that of S_3N_2Cl shows up certain similarities. However the bands observed below 700 cm^{-1} occur at noticeably lower wave numbers than those in S_3N_2Cl, the band at 617 cm^{-1} being similar to that observed in SSe_2N_2Cl. Hence from spectroscopic evidence it would seem likely that the product is either $(SSe_2N_2^+)_2$ $(AsF_6^-)_2$ or $(SSe_2N_2^+)(S_3N_2^+)(AsF_6^-)_2$. The latter species could explain the number of bands observed in the region 650-750 cm^{-1} and their similarity to those observed in the spectrum of S_3N_2Cl.

The analytical data on the insoluble species, although not giving an exact stoichiometry of the compound, indicates a sulphur:nitrogen ratio of 3:4. Hence as there are very few cationic species in which the ratio of sulphur:nitrogen is less than 1:1 $(S_4N_5^+)$[74], it is thought likely that selenium is substituted into the ring in place of sulphur, therefore giving a Group VI to nitrogen ratio of greater than or equal to 1:1.

From the physical properties, infra-red spectrum and analytical data of the insoluble compound it is suggested that a selenium analogue of S_3N_2Cl has been produced. The exact nature of the compound is not known, as a pure sample has not been isolated and thus without accurate analytical data no firm conclusion as to the structure of the product is drawn. However it is thought that the two most likely structures for the product are $(SSe_2N_2^+)$ $(AsF_6^-)_2$ and $(SSe_2N_2^+)(S_3N_2^+)(AsF_6^-)_2$ both of which will probably adopt a similar structure to $(S_3N_2^+)_2(AsF_6^-)_2$.[75]

(iii) The Reaction of $Te_4^{2+}(AsF_6^-)_2$ with S_4N_4 (Ratio 1:2) (experiment 6.2.2(vi), page 279)

By analogy with the reactions of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 it was postulated that a tellurium analogue of $S_3N_2^+$ may be synthesised by the reaction of $Te_4^{2+}(AsF_6^-)_2$ with S_4N_4.

On reacting together $Te_4^{2+}(AsF_6^-)_2$ and S_4N_4 in a ratio of 1:2 a rapid reaction occurred forming an orange-red solution and a black precipitate. Investigation of the solubles and insolubles revealed that the insolubles consisted of only elemental tellurium and sulphur. The infra-red spectrum of the soluble species was compared with the spectra of known sulphur-nitrogen species but was found to be significantly different. A series of spectra were run on different parts of the sample to discover whether the product was a mixture or not. It was noted that significant changes in the intensity of some bands occurred with differing spectra thus implying that the product was indeed a mixture. The band at 1338 cm^{-1} was noted to vary in intensity from spectrum to spectrum. A band at 1338 cm^{-1} is generally regarded as being high for a sulphur-nitrogen system (except for NS^+, S_2N^+ and NSF) but the band could be in approximately the correct position for $TeSN^+$. If the difference in the position of the ν_3 bands in CS_2 (ν_3 = 1510 cm^{-1})[68] and S_2N^+ (ν_3 = 1498 cm^{-1})[71] is used as the basis on which to deduce the ν_3 band position of $TeSN^+$, from the ν_3 band in TeSC (ν_3 = 1347 cm^{-1})[76], then a shift to lower wave numbers, of ca. 10-15 cm^{-1} is expected. Therefore the ν_3 band in $TeSN^+$ is postulated as occurring between 1337 and 1332 cm^{-1} (c f. observed band 1338 cm^{-1}).

The majority of the other bands in the observed infra-red spectrum occur between 450 and 1250 cm^{-1}. It is likely that these bands are assignable to S-N modes as Te-N and Te-S stretching vibrations will probably occur at wavenumbers lower than 450 cm^{-1}. The main peak of interest, in the above region of the spectrum, is the 1200 cm^{-1} band, which is very strong. The position of this band is similar to, but slightly higher than that observed in $ClN=SF_2$ (1176 cm^{-1})[77]. Hence it is concluded that the structure of one compound in the product possesses a sulphur-nitrogen grouping with a high bond order. The remainder of the spectrum between 450 and 1050 cm^{-1} is similar to the spectrum expected for a cyclic sulphur-nitrogen cation. The analysis of the solubles although indicating that the overall stoichiometry is either $TeS_4N_3AsF_6$ or $Te_2S_8N_8As_2F_{12}$ does not help significantly in deducing the nature of the species present in the mixture. The experiment is regarded as an initial investigative reaction. The above results will hopefully be followed up either at the University of Durham (England) or at the University of New Brunswick (Canada).

6.3.3 SUGGESTED MECHANISM BY WHICH GROUP VI POLYCATIONS REACT WITH TETRASULPHUR TETRANITRIDE

In the reactions of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (ratio 2:1 and 1:2) and $S_8^{2+}(AsF_6^-)_2$ with S_4N_4 (ratio 1:2) the primary intermediate species, around which all the products appear to be built, is the $X_3N_2^+$ unit (X = S and/or Se). The isolation of a product suspected of containing the $Se_2SN_2^+$ cation (insolubles $Se_4^{2+}(AsF_6^-)_2/S_4N_4$), indicates that the polycation probably attacks the S_4N_4 cage across the nitrogens, producing the $SSe_2N_2^+$ which dimerises yielding $(S_2Se_4N_4^{2+})(AsF_6^-)_2$. In the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 1:2) reaction the soluble product was identified as basically $(S_{10}N_8^{2+})(AsF_6^-)_2$ with a low selenium substitution, i.e. $(S_3N_2 \cdot S_4N_4 \cdot Se_2SN_2)^{2+}(AsF_6^-)_2$. As mentioned briefly in Chapter Three (page 141) it is believed that $S_3N_2^+$ units will add to S_4N_4 more readily than $SSe_2N_2^+$ units, as in the former case a sulphur-sulphur inter-ring linkage is formed which is likely to be stronger, and therefore more thermodynamically favoured than the sulphur-selenium linkage if $SSe_2N_2^+$ bonds to the S_4N_4 ring. Hence an overall mechanism can be suggested to explain the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 1:2) reaction (equation 6.3.2(c)).

Equation 6.3.2(c)

$$\begin{tikzcd}
2Se_4^{2+}(AsF_6^-)_2 + 2S_4N_4 \arrow[r] & 2Se_2SN_2^+AsF_6^- \arrow[dl, "\text{dimerises}"'] + 2S_3N_2^+AsF_6^- \arrow[d, "S_4N_4"] + 4Se \\
(Se_4S_2N_4^{2+})(AsF_6^-)_2 & (S_{10}N_8^{2+})(AsF_6^-)_2
\end{tikzcd}$$

If the above mechanism is correct then the insoluble product isolated from the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 2:1) must be $(Se_4S_2N_4^{2+})$ $(AsF_6^-)_2$. It was noted in the reaction of $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 1:2) (experiment 6.2.2(iv), page 277) that the $Se_4^{2+}(AsF_6^-)$ was in excess for the observed reaction. It is therefore suggested that the reaction stoichiometry to produce the proposed $(Se_4S_2N_4^{2+})(AsF_6^-)_2$ salt is in fact 1:1. Hence it is proposed that the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ reaction (ratio 1:1) proceeds via a transition state in which "Se_4" ring interacts with all four nitrogens of the S_4N_4 unit, which adopts a similar configuration to that in $S_4N_4^{2+}$.[78]

The transition state then dissociates into two $SSe_2N_2^+$ units which dimerise yielding $(S_2Se_4N_4^{2+})(AsF_6^-)_2$, the observed product, and 2/8 S_8 (equation 6.3.2(d)).

$$S_4N_4 + Se_4^{2+}(AsF_6^-)_2 \longrightarrow (S_2Se_4N_4^{2+})(AsF_6^-)_2 + 2/8\ S_8 \tag{6.3.2(d)}$$

Hence from a mechanistic point of view it is concluded that the insoluble product in the reactions of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (ratios 1:2 and 2:1) is $(S_2Se_4N_4^{2+})(AsF_6^-)_2$.

The mechanism by which $S_8^{2+}(AsF_6^-)_2$ reacts with S_4N_4 (ratio 1:2) is almost certainly via the attack of the polycation on the nitrogens of the S_4N_4 unit, with the formation of two $S_3N_2^+$ units which subsequently attack an S_4N_4 unit producing $(S_{10}N_8^{2+})(AsF_6^-)_2$, the observed product (cf. the proposed mechanism for the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ reaction (ratio 1:2) equation 6.3.2(c)).

In the reaction of $S_8^{2+}(AsF_6^-)_2$ with S_4N_4(ratio 2:1) the S_2N^+ cation is produced. There is a possibility of at least two mechanisms by which $S_2N^+AsF_6^-$ could be formed. The first assumes that the initial reaction of S_4N_4 with $S_8^{2+}(AsF_6^-)_2$ produces two $S_3N_2^+$ units and elemental sulphur. Subsequent reaction of $S_3N_2^+$ with $S_8^{2+}(AsF_6^-)_2$ then yields two S_2N^+ units and $S_{16}^{2+}(AsF_6^-)_2$. The $S_{16}^{2+}(AsF_6^-)_2$ then attacks the S_4N_4 forming two $S_3N_2^+$ units and the cycle is continued. The second possibility is that in the initial attack of $S_8^{2+}(AsF_6^-)_2$ on the S_4N_4 cage, two S_2N^+ cations are produced along with an S_2N_2 unit and elemental sulphur. The S_2N_2 unit then reacts further with the $S_8^{2+}(AsF_6^-)_2$ forming S_2N^+ units and elemental sulphur.

The latter mechanism appears the most feasible as the former invokes the attack of a doubly charged cation on an $S_3N_2^+$ ring whereas in the latter case $S_8^{2+}(AsF_6^-)_2$ is postulated to attack only neutral entities (i.e. S_2N_2). It is also suggested that the S_2N^+ cation is thermodynamically highly favoured due to the delocalised linear configuration and thus, as seen from the reactions of azides with $S_8^{2+}(AsF_6^-)_2$ and $NS^+SbCl_6^-$ with S_8(experiment 5.2.4(ii), page 240), the species is very readily produced. Hence it would seem likely that the $S_8^{2+}(AsF_6^-)$ /S_4N_4 intermediate would dissociate forming the thermodynamically favoured S_2N^+ units.

6.4 Conclusion

The reactions of Group VI polycations with azides and tetrasulphur tetranitride provide useful inroads into the previously little explored area of homo-Group VI-nitrogen and hetero-Group VI-nitrogen cation chemistry.

The S_2N^+ cation as synthesised by Gillespie[78] is not a viable synthetic reagent due to the difficulty of preparing the starting materials and also what are suspected to be rather poor yields of the product. However as an extension to the work described in this thesis, Maclean and Passmore[79] reacted sulphur with tetrasulphur tetranitride and arsenic pentafluoride (in the correct stoichoimetry) in the presence of catalytic quantities of bromine and isolated quantitative yields of $S_2N^+AsF_6^-$ (cf. experiment 6.2.2(iii), page 276). Hence using $S_8/S_4N_4/AsF_5/Br_2$ as the synthetic route to $S_2N^+AsF_6$, S_2N^+ is a viable and potentially useful sulphur-nitrogen reactant. MacLean[79] has prepared the $N(SCl)_2^+AsF_6^-$ and $N(SBr)_2^+AsF_6^-$ salts by the reaction of $S_2N^+AsF_6^-$ with the respective halogens and is presently investigating the reactions of $S_2N^+AsF_6^-$ further.

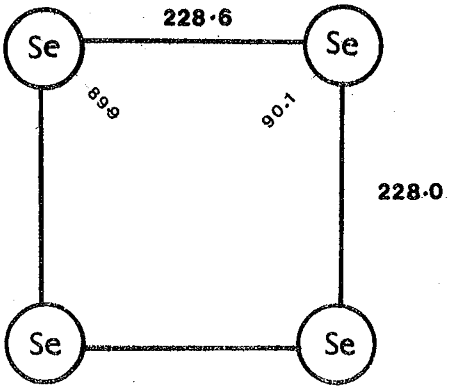
From the reactions of $S_8^{2+}(AsF_6^-)_2$ and $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (ratio 1:2), the salt $(S_{10}N_8^{2+})(AsF_6^-)_2$ has been produced. The formation of this salt via the above routes provides conclusive evidence that the compound that analysed as $S_5N_4FeCl_4$ (experiment 3.2.3c(iii), page 122) is an ionic species. The salt $(S_{10}N_8^{2+})(X)_2^-$ has not been reported and thus from work in this Chapter and that in Chapter Three, two completely independent synthetic routes have been found to this postulated multi-cyclic system.

The reactions of $Se_4^{2+}(AsF_6^-)_2$ with S_4N_4 (ratio 1:2 and 2:1) produced the same insoluble product which is postulated to be $(S_2Se_4N_4)(AsF_6^-)_2$. The AsF_6^- salt of the $S_2Se_4N_4^{2+}$ cation can not be synthesised by the route described by Wolmershäuser *et al*[72] and thus the reactions of selenium polycations with S_4N_4 provide a useful route to the $Se_4S_2N_4^{2+}$ salts with anions such as AsF_6^-, SbF_6^-, $SbCl_6^-$ and $AlCl_4^-$. The potential of these salts could be great in the field of modified sulphur-nitrogen polymers. If the $SSe_2N_2^+$ cation is reduced, as in Chapter Three (cf. reductions of the $S_3N_2^+$ cation), mixed sulphur selenium nitrides of the form X_4N_2 and/or X_4N_4 (X = S and or Se) could be formed. The cracking of the X_4N_4 species on silver metal (cf. S_4N_4 splitting[80]) may well yield $(XN)_x$, a selenium doped sulphur-nitrogen polymer.

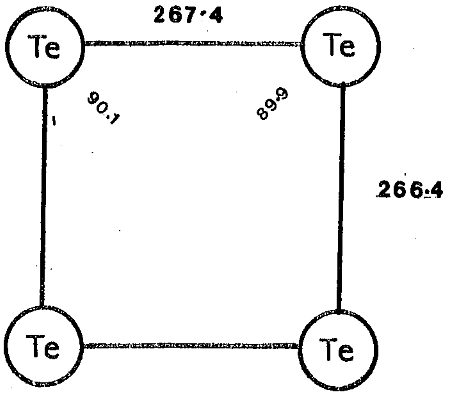
Gillespie is also believed to be working on the reactions of selenium polycations with tetrasulphur tetranitride and is thought to have isolated $(Se_4S_2N_4^{2+})(AsF_6^-)_2$[81]

Although the reactions of $Te_4^{2+}(AsF_6^-)_2$ with azides and tetrasulphur tetranitride did not yield products that were easily characterised, it is believed from these initial investigative reactions that tellurium-nitrogen and tellurium-sulphur-nitrogen cations should be isolatable. Maclean (University of New Brunswick) is, at present, investigating the Te_4^{2+}/N_3^- reaction and has isolated crystals for X-ray structure determination.

Figure 6·2

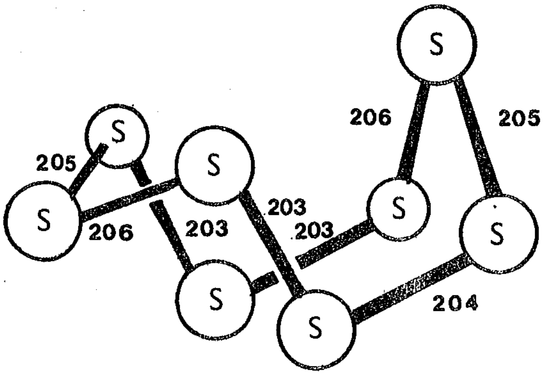


$Se_4^{2+}(HS_2O_7^-)_2$

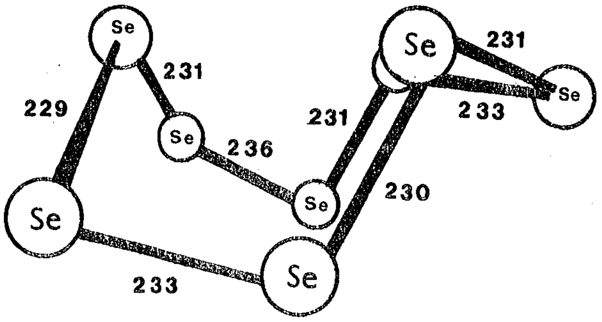


$Te_4^{2+}(Al_2Cl_7^-)_2$

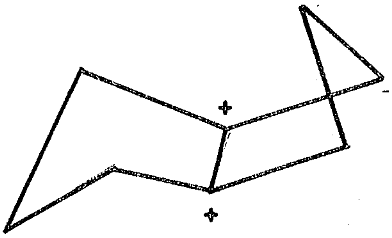
Figure 6·3



$S_8^{2+}\cdot(AsF_6^-)_2$

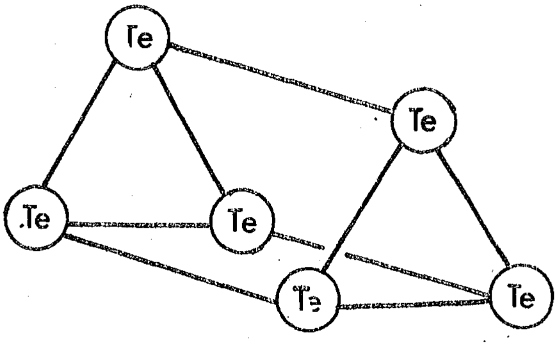


$Se_8^{2+}(AlCl_4^-)_2$

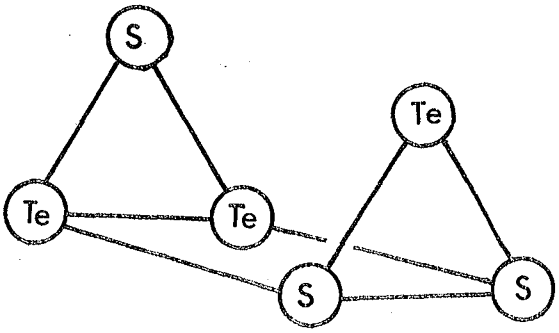


A significant resonance canonical structure for the Se_8^{2+} cation

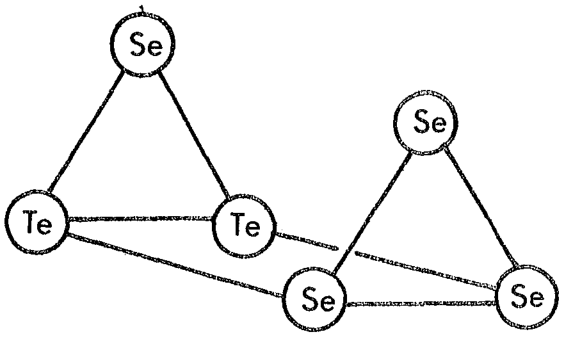
Figure 6·4



$Te_6^{4+}(AsF_6^-)_2$

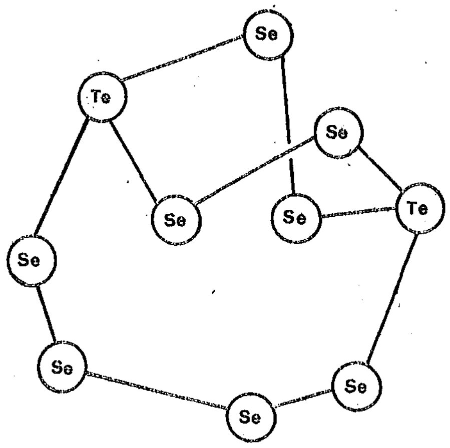


$Te_3S_3^{2+}(AsF_6^-)_2$

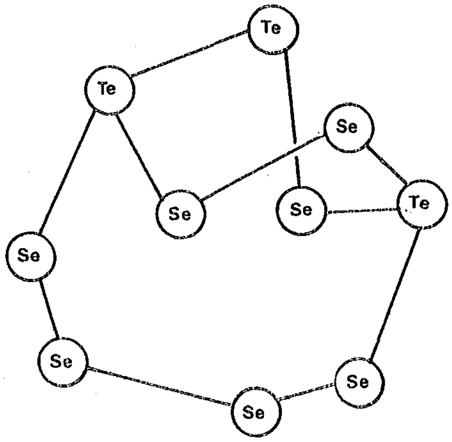


$Te_2Se_4^{2+}(AsF_6^-)_2$

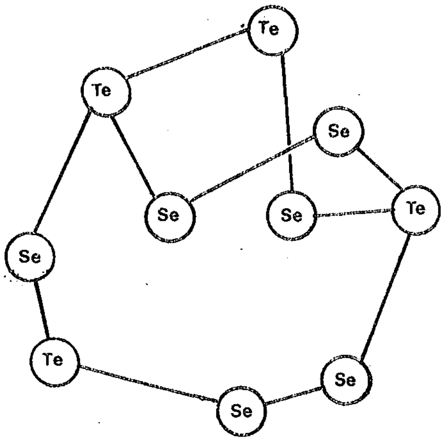
Figure 6.4



$Te_2Se_8^{2+}$

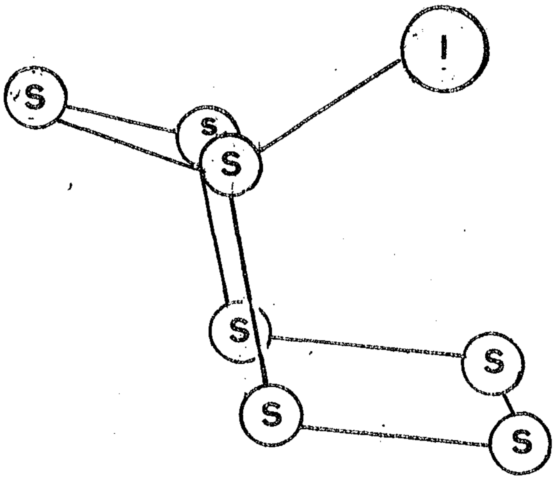


$Te_3Se_7^{2+}$

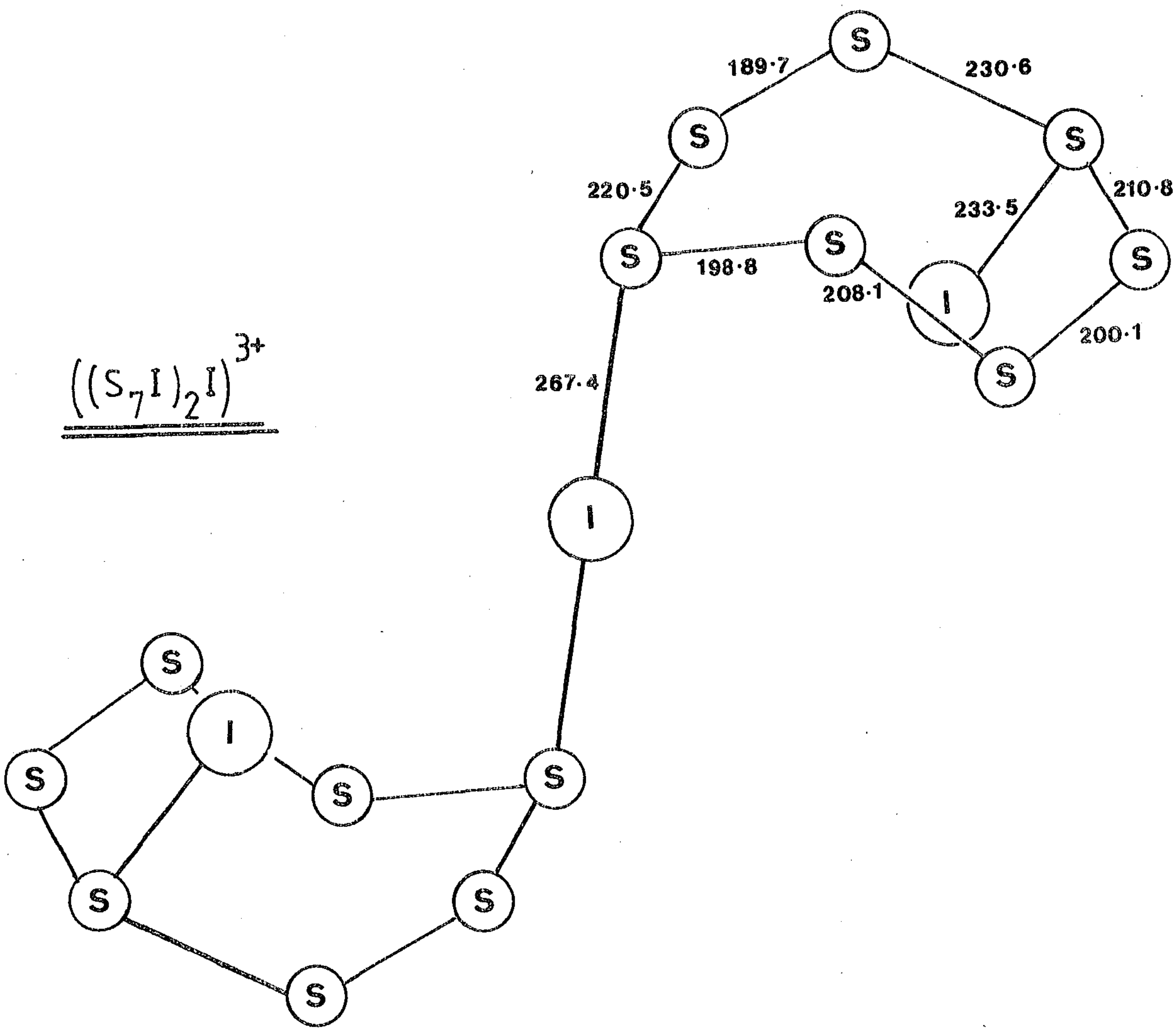


$Te_4Se_6^{2+}$

Figure 6.5



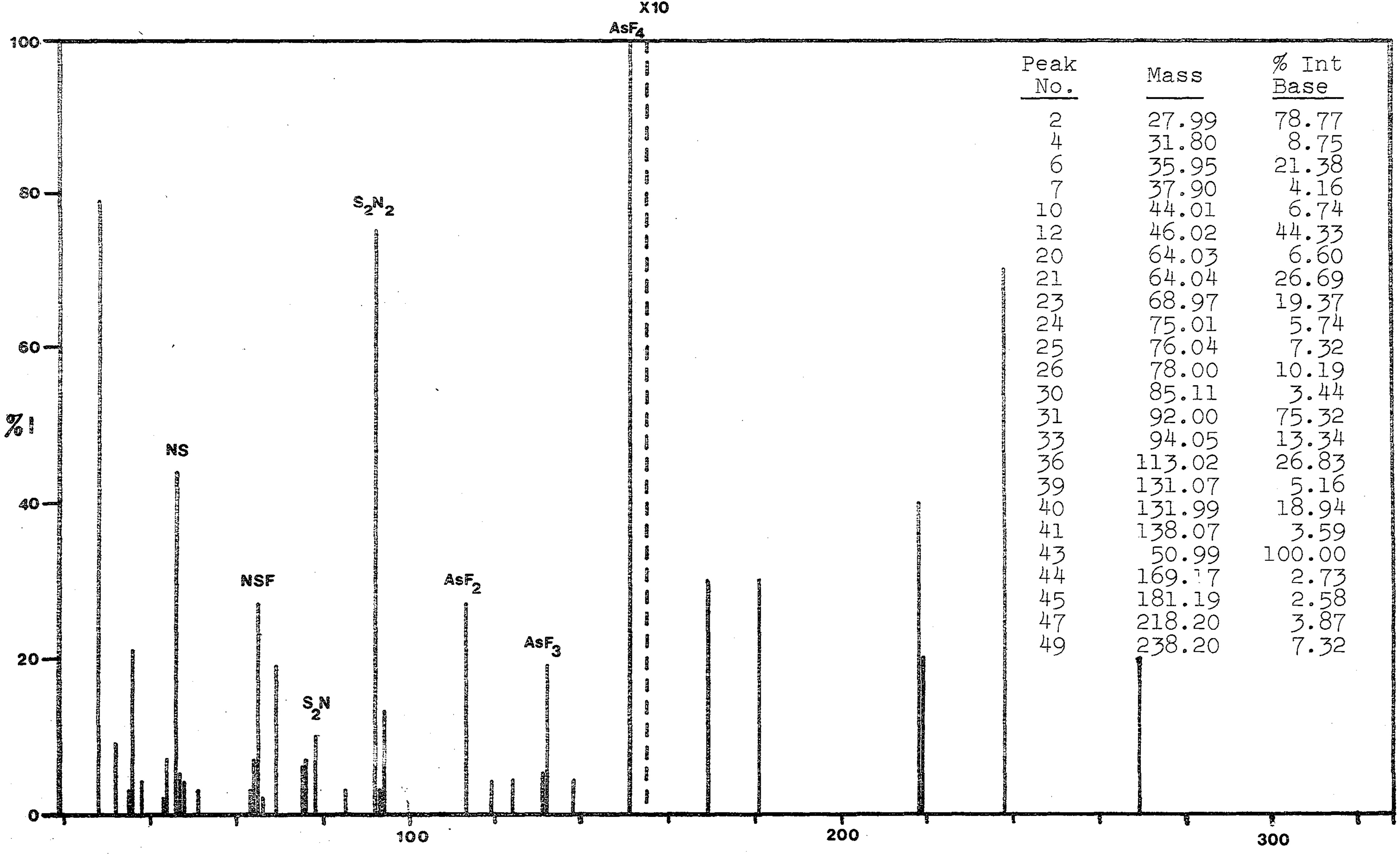
S_7I^+



$((S_7I)_2I)^{3+}$

RHS14/2

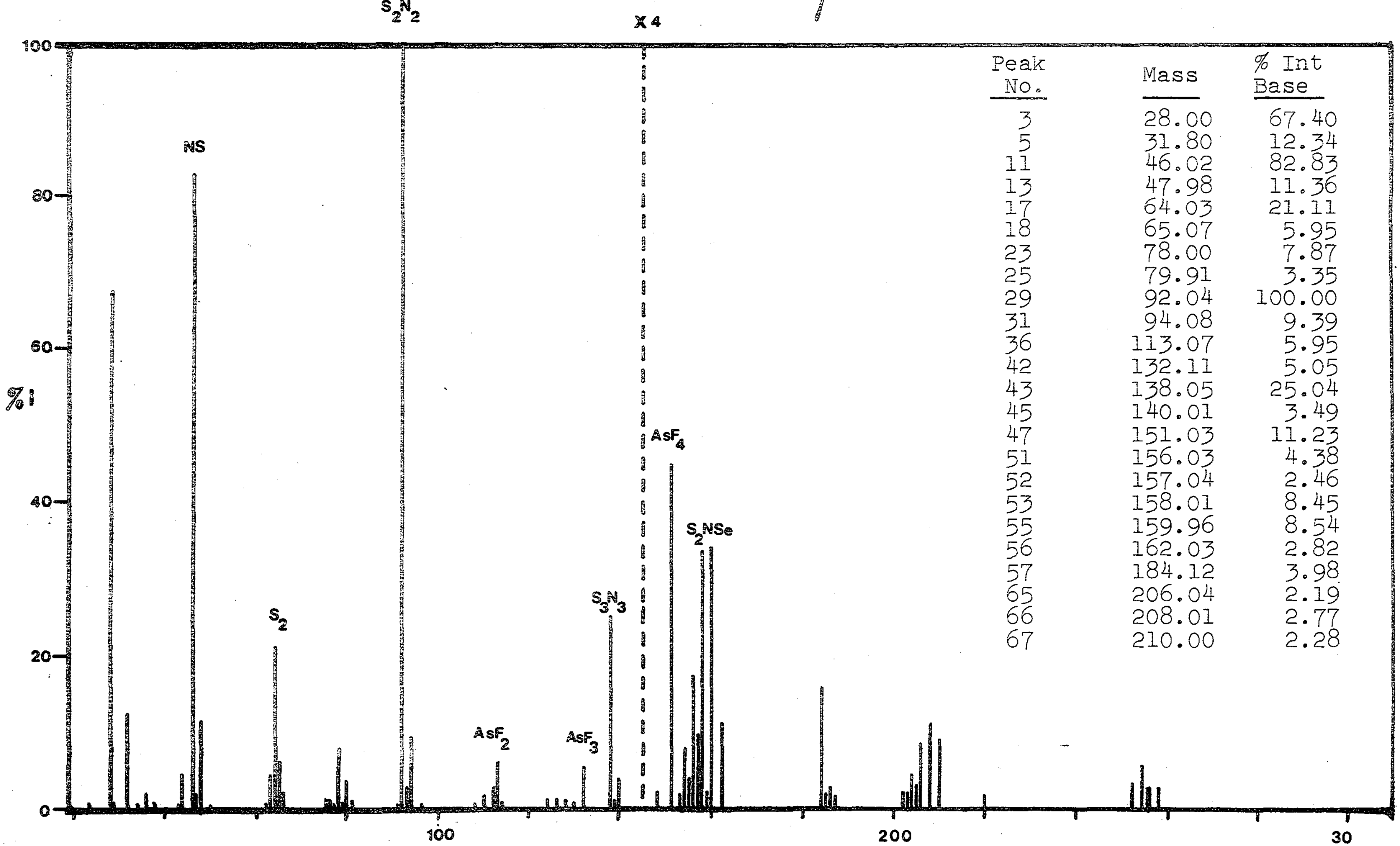
Figure 6.6.a Se^{2+}(AsF$_6^-$)$_2$/2S$_4$N$_4$ (Solubles)



Peak No.	Mass	% Int Base
2	27.99	78.77
4	31.80	8.75
6	35.95	21.38
7	37.90	4.16
10	44.01	6.74
12	46.02	44.33
20	64.03	6.60
21	64.04	26.69
23	68.97	19.37
24	75.01	5.74
25	76.04	7.32
26	78.00	10.19
30	85.11	3.44
31	92.00	75.32
33	94.05	13.34
36	113.02	26.83
39	131.07	5.16
40	131.99	18.94
41	138.07	3.59
43	50.99	100.00
44	169.17	2.73
45	181.19	2.58
47	218.20	3.87
49	238.20	7.32

RHS14/1

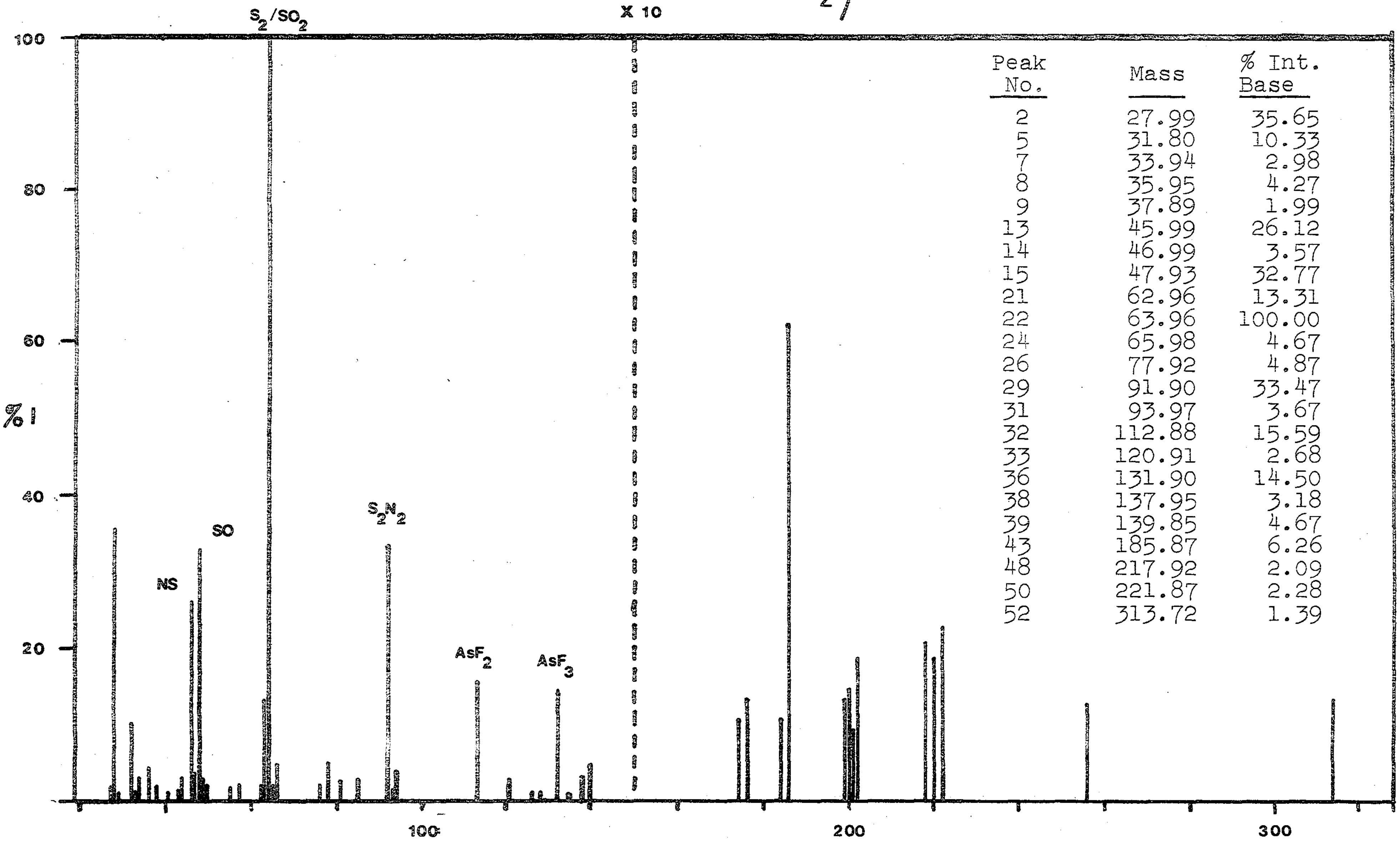
Figure 6.6.b $Se^{2+}(AsF_6^-)_2/2S_4N_4$ (Insolubes)



Peak No.	Mass	% Int Base
3	28.00	67.40
5	31.80	12.34
11	46.02	82.83
13	47.98	11.36
17	64.03	21.11
18	65.07	5.95
23	78.00	7.87
25	79.91	3.35
29	92.04	100.00
31	94.08	9.39
36	113.07	5.95
42	132.11	5.05
43	138.05	25.04
45	140.01	3.49
47	151.03	11.23
51	156.03	4.38
52	157.04	2.46
53	158.01	8.45
55	159.96	8.54
56	162.03	2.82
57	184.12	3.98
65	206.04	2.19
66	208.01	2.77
67	210.00	2.28

RHTe2/14

Figure 6.6.c $Te^{2+}[AsF_6^-]_2/2S_4N_4$ (Solubles)



Peak No.	Mass	% Int. Base
2	27.99	35.65
5	31.80	10.33
7	33.94	2.98
8	35.95	4.27
9	37.89	1.99
13	45.99	26.12
14	46.99	3.57
15	47.93	32.77
21	62.96	13.31
22	63.96	100.00
24	65.98	4.67
26	77.92	4.87
29	91.90	33.47
31	93.97	3.67
32	112.88	15.59
33	120.91	2.68
36	131.90	14.50
38	137.95	3.18
39	139.85	4.67
43	185.87	6.26
48	217.92	2.09
50	221.87	2.28
52	313.72	1.39

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APPENDIX A

STANDARD INFRA-RED AND RAMAN SPECTRA

TABLE 1 Sulphur-Nitrogen Species

S/N Species	Reference
$S_5N_5^+$	1
S_4N_4	2
$S_4N_3^+$	3
S_4N_2	4
$S_3N_3Cl_3$	5
$S_3N_2Cl^+$	1
$S_3N_2^+$	6
$N(SCl)_2^+$	7
$ClNSF_2$	8
NSCl	9
NSF	10
NS^+	11

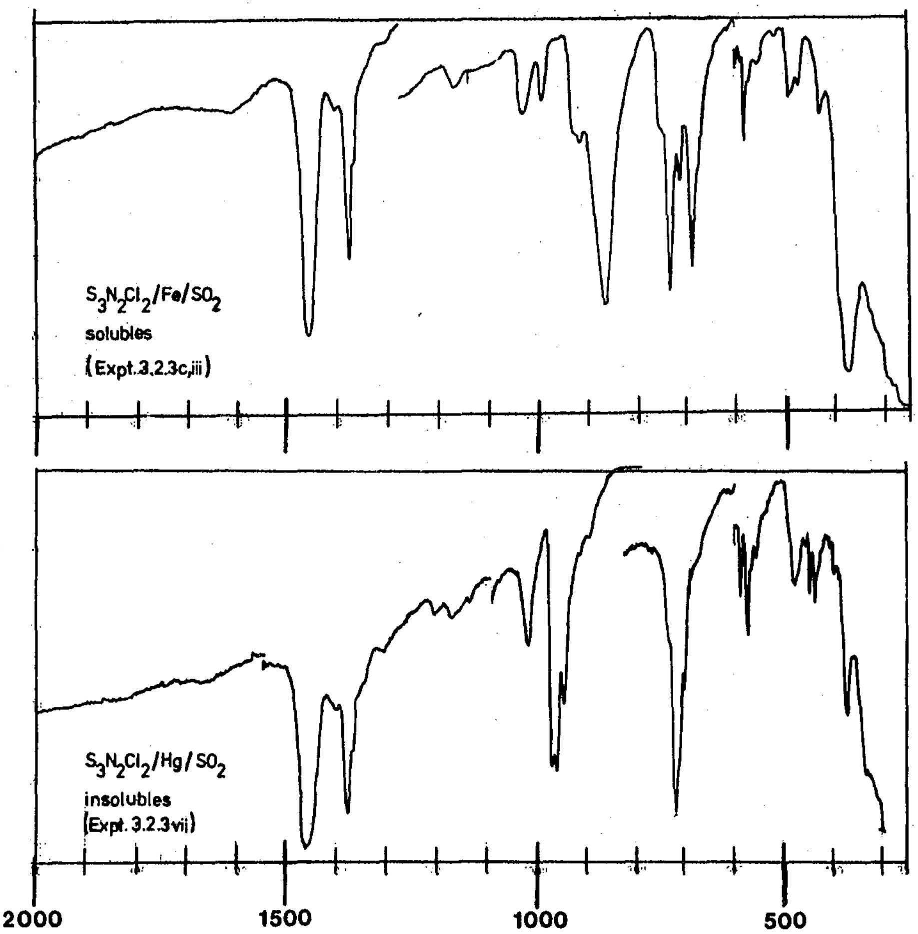
TABLE 2 Sulphur-Halogen Species

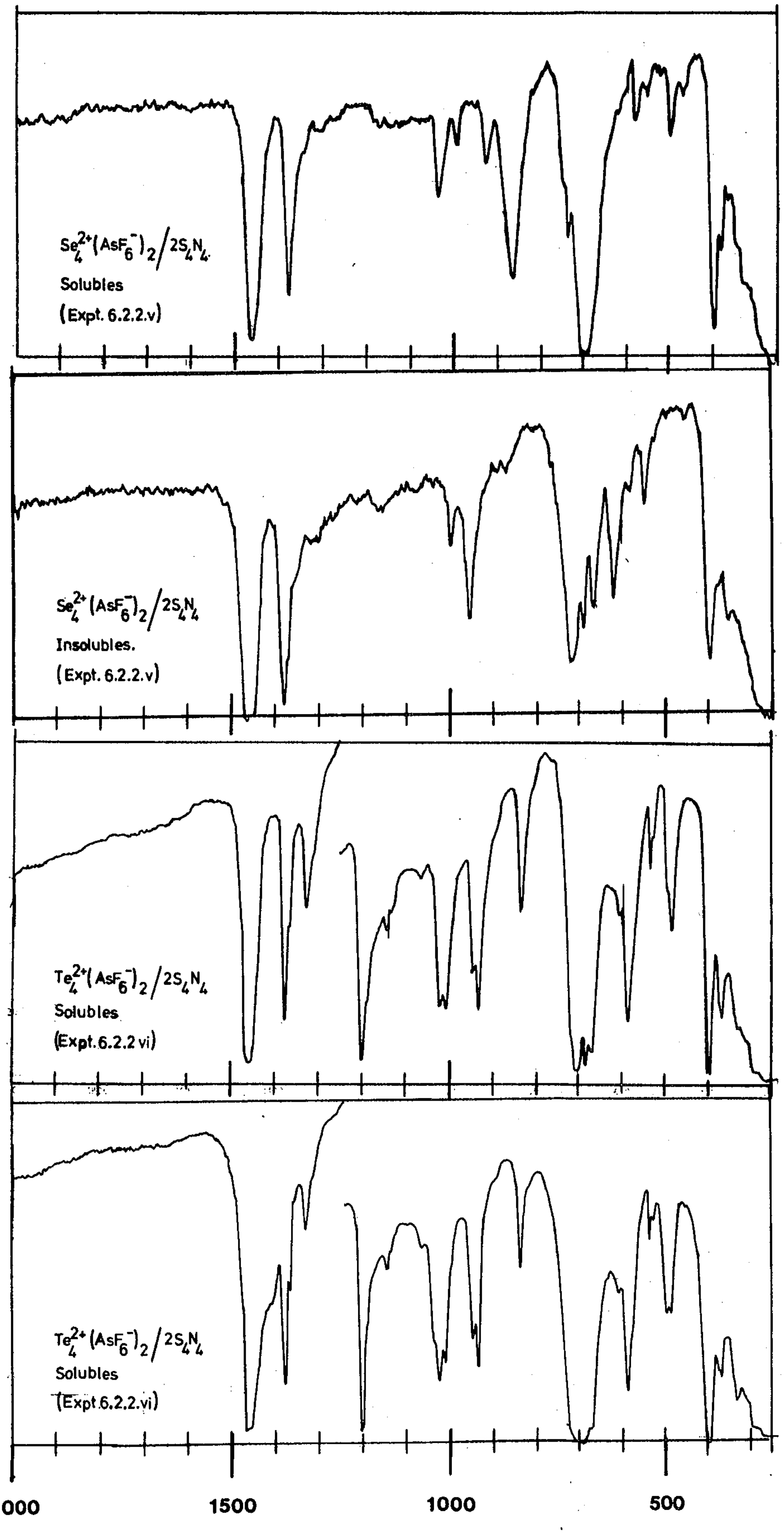
Sulphur-Halogen Species	Reference
SCl_2	12
S_2Cl_2	13
$SOCl_2$	14
SO_2Cl_2	14
SF_4	15
SF_5Cl	16
SF_6	17
SOF_2	18
SOF_4	19
SO_2F_2	20
SO_2ClF	21

TABLE 3 Other Species Referenced in the Text

Species	Reference
ClF	22
Cl_2	23
BCl_3	24
$SnCl_4$	25
AsF_3	26
SO_2	27

Photographic representations of various infra-red spectra referenced in this thesis




Se$_4^{2+}$(AsF$_6^-$)$_2$/2S$_4$N$_4$
Solubles
(Expt. 6.2.2.v)
Se$_4^{2+}$(AsF$_6^-$)$_2$/2S$_4$N$_4$
Insolubles.
(Expt. 6.2.2.v)
Te$_4^{2+}$(AsF$_6^-$)$_2$/2S$_4$N$_4$
Solubles
(Expt. 6.2.2 vi)
Te$_4^{2+}$(AsF$_6^-$)$_2$/2S$_4$N$_4$
Solubles
(Expt. 6.2.2.vi)
2000
1500
1000
500

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APPENDIX B

THERMODYNAMIC DATA RELEVANT TO THIS THESIS

$\Delta H^{o}_{f}\ (S_4N_4) = +536$ kJ mol^{-1} (ref.1)

$\Delta H^{343}_{sub}(S_4N_4) = +\ 89$ kJ mol^{-1} (ref.2)

$\Delta H^{o}_{f}(ClF) = -\ 51$ kJ mol^{-1} (ref.3)

$\Delta H^{o}_{f}(NSF) = -\ 21$ kJ mol^{-1} (ref.4)

$\Delta H^{o}_{f}(SF_4) = -775$ kJ mol^{-1} (ref.5)

The standard heats of formation of the metal chlorides and fluorides (table 4.2, page 157) were referenced from the "G.R.C. Handbook Chemistry and Physics", 57th Ed. 1976-77.

(a) Calculation of the Heat of Formation of $(NSCl)_g$

The following assumptions were made in this calculation

(1) The $D^{o}_{N\equiv S}$ in N≡S-F and N≡S-Cl is the same.

(2) That $D^{o}_{S-F} - D^{o}_{S-Cl}$ for NSCl and NSF respectively, is the same as $D^{o}_{S-F} - D^{o}_{S-Cl}$ for SOF_2 and $SOCl_2$ respectively.

$D^{o}_{N\equiv S}\ (NSF) = 526$ kJ mol^{-1} (ref.4)

$D^{o}_{S-Cl}(SOCl_2) = 265$ kJ mol^{-1} (ref.5)

$D^{o}_{S-F}\ (SOF_2) = 322$ kJ mol^{-1} (ref.6)

(Equ.A) $\Delta H^{o}_{disrupt.}(NSF)_g = \Delta H^{o}_{f}(\tfrac{1}{2}N_2)_g + \Delta H^{o}_{f}(S)_s + \Delta H^{o}_{f}(\tfrac{1}{2}F_2)_g - \Delta H^{o}_{f}(NSF)_g$

(Equ.B) $\Delta H^{o}_{disrupt.}(NSCl)_g = \Delta H^{o}_{f}(\tfrac{1}{2}N_2)_g + \Delta H^{o}_{f}(S)_s + \Delta H^{o}_{f}(\tfrac{1}{2}Cl_2)_g - \Delta H^{o}_{f}(NSCl)_g$

(Equ.C) $\Delta H^{o}_{disrupt.}(NSF)_g = D^{o}_{N\equiv S} + D^{o}_{S-F}$

(Equ.D) $\Delta H^{o}_{disrupt.}(NSCl)_g = D^{o}_{N\equiv S} + D^{o}_{S-Cl}$

$\therefore$ Equ.B-Equ.A $= \Delta H^{o}_{disrupt.}(NSCl)_{g} - \Delta H^{o}_{disrupt.}(NSF)_{g}$

$= \Delta H^{o}_{f}(NSF)_{g} - \Delta H^{o}_{f}(NSCl)_{g}$

Equ.D-Equ.C $= \Delta H^{o}_{disrupt.}(NSCl)_{g} - \Delta H^{o}_{disrupt.}(NSF)_{g}$

$= D^{o}_{S-Cl} - D^{o}_{S-F}$

$\therefore$ $D^{o}_{S-Cl} - D^{o}_{S-F} = \Delta H^{o}_{f}(NSF)_{g} - \Delta H^{o}_{f}(NSCl)_{g}$

$265-322 = -21-\Delta H^{o}_{f}(NSCl)_{g}$

$\therefore$ $\Delta H^{o}_{f}(NSCl)_{g} = +78\ kJ\ mol^{-1}$

(b) Calculation of the Heat of Formation of $(NSCl)_3$

$(S_3N_3Cl_3)_s \xrightarrow{\qquad} 3NSCl_g \quad \Delta H^{o} = +193 \pm 6\ kJ\ mol^{-}$

(ref.7)

$\therefore$ $\Delta H^{o}_{f}(S_3N_3Cl_3)_s = 3(\Delta H^{o}_{f}(NSCl)_{g}) - 193\ kJ\ mol^{-1}$

$\therefore$ $\Delta H^{o}_{f}(S_3N_3Cl_3)_s = +\ 41\ kJ\ mol^{-1}$

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APPENDIX C

The Board of Studies in Chemistry requires that each postgraduate research thesis should contain an appendix listing all research colloquia, seminars and lectures (by external speakers) arranged by the Department of Chemistry during the period when research for the thesis was carried out.

Research Colloquia, Seminars and Lectures Arranged by the Department of Chemistry between October 1976 and September 1979

20 October 1976

Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur"

10 November 1976

Dr. J.S. Ogden (University of Southampton), "The Characterisation of High Temperature Species by Matrix Isolation"

17 November 1976

Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable Inorganic Solids"

24 November 1976

Dr. M.I. Page, (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions"

8 December 1976

Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals"

26 January 1977

Dr. A. Davis (E.R.D.R.), "The Weathering of Polymeric Materials"

2 February 1977

Dr. M. Falk (N.R.C. Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases"

9 February 1977

Professor R.O.C. Norman (University of York), "Radical Cations; Intermediates in Organic Reactions"

23 February 1977

Dr. G. Harris (University of St. Andrews), "Halogen Adducts of Phosphines and Arsines"

25 February 1977

Professor H.T. Dieck (Frankfurt University), "Diazadienes - New Powerful Low-Valent Metal Ligands"

2 March 1977

Dr. F. Hibbert (Birkbeck College, University of London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids"

4 March 1977

Dr. G. Brink (Rhodes University, South Africa), "Dielectric Studies of Hydrogen Bonding in Alcohols"

9 March 1977

Dr. I.O. Sutherland (University of Sheffield), "The Stevans' Rearrangement: Orbital Symmetry and Radical Pairs"

18 March 1977

Professor H. Bock (Frankfurt University), "Photoelectron Spectra and Molecular Properties: A Vademecum for the Chemist"

30 March 1977

Dr. J.R. MacCallum (University of St. Andrews), "Photo-oxidation of Polymers"

20 April 1977

Dr. D.M.J. Lilley (Research Division, G.D. Searle), "Tails of Chromatin Structure - Progress Towards a Working Model"

27 April 1977

Dr. M.P. Stevens (University of Hartford), "Photocycloaddition Polymerisation"

4 May 1977

Dr. G.C. Tabisz (University of Manitoba), "Collision Induced Light Scattering by Compressed Molecular Gases"

11 May 1977

Dr. R.E. Banks (U.M.I.S.T.), "The Reactions of Hexafluoropropene with Heterocyclic N-Oxides"

18 May 1977

Dr. J. Atwood (University of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates"

25 May 1977

Professor M.M. Kreevoy (University of Minnesota), "The Dynamics of Proton Transfer in Solution"

1 June 1977

Dr. J. McCleverty (University of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten"

6 July 1977

Professor J. Passmore (University of New Brunswick, Canada), "Adducts Between Group V Pentahalides and a Postscript on S_7I^+"

27 September 1977

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