Cyclic sulphur inides and thiazenes: synthetic studies and some structural correlations

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CYCLIC SULPHUR IMIDES AND THIAZENES: SYNTHETIC STUDIES AND SOME STRUCTURAL CORRELATIONS.

by

JAMES ALAN DURRANT, B.Sc.

A thesis submitted for the degree of Doctor of Philosophy
in the University of Durham.

September 1977

Acknowledgements

I wish to express my warmest thanks to Dr. A.J. Banister, under whose supervision this research was carried out, for his constant encouragement and sound advice during the whole period of study.

My thanks are also due to the Science Research Council for providing a research grant and the University of Durham for research facilities. Thanks too, to the whole of the Chemistry department technical staff especially Mr. R. Coult, Mr. B. Hall and Mr. J. Lincoln.

I am very grateful to Dr. D.B. Adams, Dr. I. Rayment, Dr. H.M.M. Shearer and Dr. K. Wade for their invaluable assistance and to Miss A.B. Daly for the many hours spent in typing this thesis.

Memorandum

The work described in this thesis was carried out in the University of Durham between September 1974 and September 1977. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference. Parts of this thesis have been the subject of the following publications:-

1. A.J. Banister, J.A. Durrant, I. Rayment and H.M.M. Shearer. "Reactions of Tetrasulphur Tetranitride with Halides. Part VI. The Preparation and Structure of Cyclopentathiazenium Pentachloro(phosphoryl chloride)stannate(IV)." J.C.S. Dalton, 1976, 928.

2. A.J. Banister and J.A. Durrant. "Nitrogen Bond Angle - Sulphur Nitrogen Bond Distance Correlations." J. Chem. Research, 1977 (in press).

3. A.J. Banister and J.A. Durrant. "Sulphur Bond Angle - Sulphur Nitrogen Bond Distance Correlations." J. Chem. Research, 1977 (in press).

Parts of this thesis have been presented by Dr. A. J. Banister at the following conferences.

1. Amer. Chem. Soc. Centennial Symposium, "Sulphur and its Binary Inorganic Compounds", New York, April 1976.
2. Berlin Technical University, Chemistry Dept., Invitation Lecture, January 1977.

3. Second Reunion of the First International Symposium of Inorganic Heterocyclic Chemistry, Opening Plenary Lecture, Madrid, June 1977.

In each case a review lecture was presented which included a portion devoted to rationisations of SN structures e.g. d_{SN}/ bond angle correlations.

Lectures

From October 1976 the University Board of Studies requires that postgraduate students list the lectures offered by the Chemistry Department and mark those lectures attended by the student.

University of Durham, Chemistry Colloquia.

Michaelmas Term, 1976

Wednesday, 20th October

Professor J.B. Hyne (University of Calgary, Canada)

"New Research on an Old Element - Sulphur." (Attended)

Wednesday, 10th November

Dr. J.S. Ogden (Southampton University)

"The Characterisation of High Temperature Species by Matrix Isolation." (Attended)

Wednesday, 17th November

Dr. B.E.F. Fender (University of Oxford)

"Familiar but Remarkable Inorganic Solids." (Attended)

Wednesday, 24th November

Dr. M.I. Page (Huddersfield Polytechnic)

"Large and Small Rate Enhancements of Intermolecular Catalysed Reactions."

Wednesday, 8th December

Professor A.J. Leadbetter (University of Exeter)

"Liquid Crystals" (Attended)

Epiphany Term 1977

Wednesday, 26th January

Dr. A. Davis (ERDR) "The Weathering of Polymeric Materials." (Attended)

Wednesday, 2nd February

Dr. M. Falk (NRC Canada)

"Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases."

Wednesday, 9th February

Professor R.O.C. Norman (University of York)

"Radical Cations; Intermediates in Organic Reactions."

Wednesday, 23rd February

Dr. G. Harris (University of St. Andrews)

"Halogens Adducts of Phosphines and Arsines." (Attended)

Wednesday, 2nd March

Dr.F. Hibbert (Birkbeck College, London)

"Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids."

Wednesday, 9th March

Dr. I.O. Sutherland (Sheffield University)

"The Stevans' Rearrangement: Orbital Symmetry and Radical Pairs."

Friday, 18th March

Professor Hans Bock

Wednesday, 30th March

Dr.J.R. MacCallum (University of St. Andrews)

"Photooxidation of Polymers." (Attended)

Easter Term 1977

Wednesday, 20th April

Dr. M.J. Lilley (G.D. Searle, Research Div.)

"Tails of Chromatin Structure - Progress Towards a Working Model."

Wednesday, 27th April

Dr. M.P. Stevens (University of Hartford)

"Photocycloaddition Polymerisation." (Attended)

Wednesday, 4th May

Dr. G.C. Tabisz (University of Manitoba)

"Collision Induced Light Scattering by Compressed Molecular Gases." (Attended)

Wednesday, 11th May

Dr. R.E. Banks (UMIST)

"Fluorocarbon and Related Chemistry."

Wednesday, 18th May

Dr. J. Atwood (University of Alabama)

"Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates." (Attended)

Wednesday, 25th May

Prof. M.M. Kreevoy (University of Minnesota)

"The Dynamics of Proton Transfer in Solution."

Wednesday, 1st June

Dr. J. McCleverty (University of Sheffield)

"Consequences of Deprivation and Overcrowding of the Chemistry Molybdenum and Tungsten." (Attended)

Wednesday, 6th July

Prof. J. Passmore (University of New Brunswick)

"Adducts between Group V Pentahalides and a Postscript on S_7I^+." (Attended)

Durham University Chemical Society

Tuesday, 19th October

Dr. J.A. Salthouse

"Chemistry and Energy." (Attended)

Tuesday, 26th October

Dr. R.E. Richards

"NMR Measurements on Intact Biological Tissue." (Attended)

Tuesday, 2nd November

Mr. R.G. Ficken

"The Chemical Bond as a Figment of the Imagination." (Attended)

Tuesday, 30th November

Dr. R.J. Donovan

"The Chemistry of the Stratosphere." (Attended)

Tuesday, 18th January

Prof. I. Fells (University of Newcastle-upon-Tyne)

"Energy Storage and the Chemist's Contribution to the Problem."

Tuesday, 8th February

Dr. M.J. Cleare (Johnson Matthey)

"Platinum Group Metal Compounds as Anti-Cancer Agents." (Attended)

Tuesday, 1st March

Prof. J.A.S. Smith (Queen Elizabeth College, London)

"Double Resonance." (Attended)

Tuesday, 8th March

Prof. C. Eaborn (University of Sussex)

"Structure and Reactivity." (Attended)

There were also approximately twenty seminars given by each research member of the Inorganic and Physical Groups.

To my family, friends and O.B.

"...and he shall be tormented with fire and brimstone..."

Revelation 14, v.10.

Abstract

This thesis describes the work carried out by the author between September 1974 and September 1977.

The shapes of known sulphur-nitrogen species are rationalised by linear interpolation and the probable structures of sulphur-nitrogen species, as yet uncharacterised, are discussed. Correlations between sulphur-nitrogen and sulphur-oxygen stretching frequencies and bond lengths are presented and predictions of shapes from infra-red data are discussed.

Preparation of derivatives of sulphur chlorides using methyleneamino-lithium proved to be an excellent route to old and new sulphur-nitrogen compounds.

Reactions of $(SNCl)_3$ were studied with a view to reaction mechanisms involved and the first fully characterised derivatives of 3-phenylcyclodithiadiazolium chloride were prepared.

The reactions of sulphur-nitrogen-oxygen species especially hexaoxocyclotrithiazenide (3-) anions are reported including the preparation of new salts.

Attempts were made to prepare new members of the "electron rich" aromatic series of sulphur nitrogen compounds. Although unsuccessful in the original aim, the new compounds S_7NCOCF_3, $(S_5N_5)(SnCl_5(OPCl_3))$ and $S_4N_4.POCl_3.SnCl_4$ were prepared and the use of phosphoryl chloride as a solvent was investigated.

The crystal structure of $(S_5N_5)(SnCl_5(OPCl_3))$ is discussed and a series of CNDO/2 calculations with and without "d" orbital basis sets have been carried out on a series of "aromatic" sulphur-nitrogen compounds.

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Reactions of 4 - phenyl - 1,2,3,5 - dithiadiazolium chloride

Chapter 6 Sulphur - Nitrogen - Oxygen Compounds

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Experimental

Results and Discussion

Chapter 8 Theoretical Considerations of Structure and Bonding in Some Cyclic Sulphur-Nitrogen Species

Introduction

There is no large introductory review to this thesis as it was felt that each chapter is, to a large extent, separate from the others. Hence a small introduction is given to each chapter. Further information may be obtained from the many excellent reviews of sulphur-nitrogen chemistry listed below (table (i)).

Table (i)

Reviews of SN Chemistry

Date	S_4N_4	SN-Hal	SNO	S-N
1976		Mews[1]		Roesky[2]
1975				Banister[3]
1973	Emeléus[4]			Horn[5]
1972	Heal[8]	Glemser[7]		Armitage[6]
				Garcia-Fernandez[9]
1970	Becke-Goehring[10]			Haiduc[11]
1969		Glemser[12]		
1968	Heal[14]		Burton[13]	
1967	Allen[16]	Glemser[17]		Allcock[15]
1966	Becke-Goehring[18]			Becke-Goehring[19]
1963				Gmelin[20]
1959	Becke-Goehring[21]			
1956	Goehring[22]			

Nomenclature

Acyclic Compounds

There is still much confusion in nomenclature in inorganic chemistry, for example, HNSO may be called thionyl imide, thionylamide, sulphinyl imide or sulphinylamide. However in this thesis the conventions adopted in Chemical Abstracts will be used except where the nomenclature is too lengthy, then the more manageable trivial names will be adopted (table ii).

Table ii

SII

S_2Cl_2, disulphur dichloride
HONS, thionitrous acid
$S(NH_2)_2$, sulphoxilic diamide

SIV

HNSO, thionyl imide
$SOCl_2$, thionyl chloride
H_2SNH, sulphilimine
$SO(NH_2)_2$, sulphurous diamide
$S(NH)_2$, sulphur diimide

SVI

NH_3SO_3, sulphamic acid
$SO_2(NH_2)_2$, sulphamide
$SO_2(NH_2)Cl$, sulphamoyl chloride
SO_2NH, sulphuryl imide
$H_2S(O)NH$, sulphoximine
$S(NH)_3$, sulphur triimide
SO_2Cl_2, sulphuryl chloride
$S(Me)_2(NH)_2$, dimethyl sulphur diimide

Mixed Oxidation Number

$S(NSO)_2$, sulphur bis(sulphinylamide)
$(N(SCl)_2)^+$, bis(chlorothio) nitrogen cation
$(N(SMe_2)_2)^+$, bis(dimethylthio) nitrogen cation

Cyclic Compounds

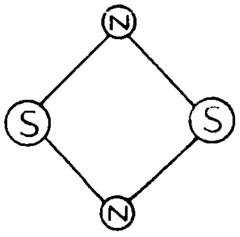
Many cyclic sulphur-nitrogen compounds are still called by their trivial names, for example, sulphanuric chloride $(SNOCl)_3$, was originally proposed because of its analogy with cyanuric chloride[23] and the name tetrasulphur tetranitride (S_4N_4) comes directly from the molecular formula.

The limitations of trivial names are that they frequently do not convey

a) the cyclic or acyclic nature of the compound,
b) the degree of polymerisation or
c) the presence of unsaturated bonds.

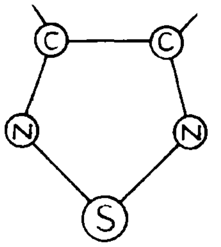
It is possible to describe these rings accurately using the 1970 set of definitive rules established by I.U.P.A.C.[24], but these can tend to become unwieldy, for example, $(MeNSO_2)_3$ would be called 1,1,3,3,5,5 -hexaoxo-2,4,6-trimethyl-cyclo-1,3,5,2,4,6-trithia(1,3,5,S^{VI}) triazine. This system will be used when the ring does not contain repeating units since it describes the molecules unambiguously, however, a simpler system based on the one used by Haiduc[11] will be used whenever possible (table iii).

The ending -ium implies positive charge and -ide negative charge. The terms -azene and -azane are used for unsaturated and saturated nitrogen respectively.



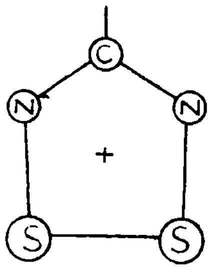
S_2N_2

cyclodithiadiazene



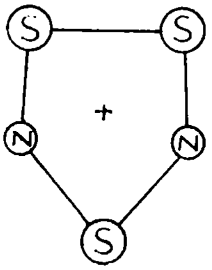
$R_2C_2N_2S$

1,2,5-cyclothiadiazole



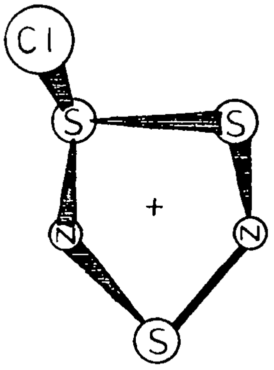
$[RCN_2S_2]^+$

cyclodithiadiazolium cation



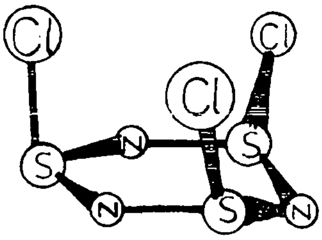
$[S_3N_2]^+$

cyclotrithiadiazenium cation



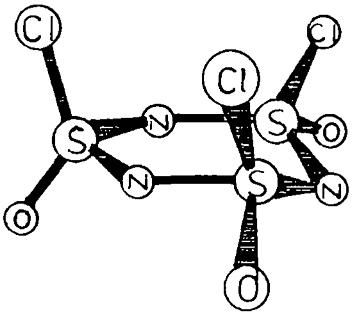
$[S_3N_2Cl]^+$

chlorocyclotrithiadiazenium cation



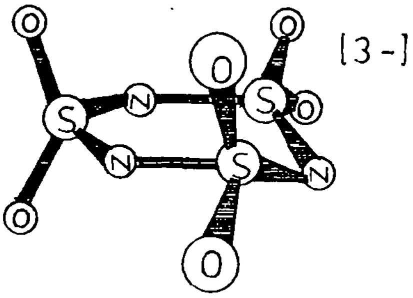
$(SNCl)_3$

trichlorocyclotrithiatriazene



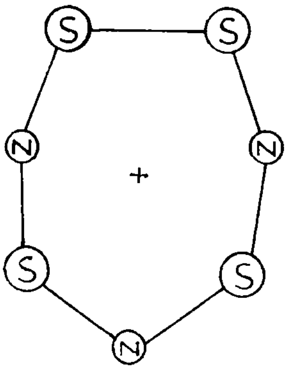
$(SNOCl)_3$

trichlorotrioxocyclotrithiatriazene



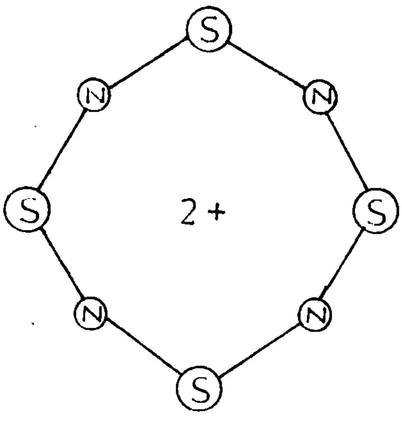
$[SNO_2]_3^{3-}$

hexaoxocyclotrithiatriazenide(3-) anion



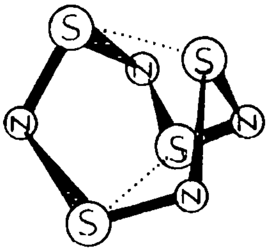
$[S_4N_3]^+$

cyclotetrathiatriazenium cation

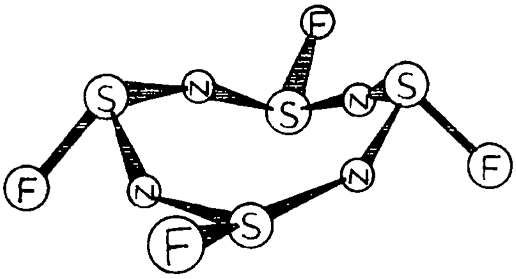


$[S_4N_4]^{2+}$

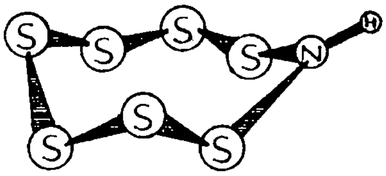
cyclotetrathiazenium-(2+) cation



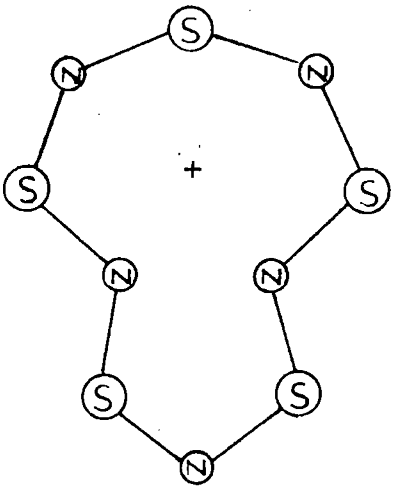
S_4N_4
cyclotetrathiazene



$(SNF)_4$
tetrafluorocyclotetrathiatetrazene



S_7NH
cycloazaheptasulphane



$[S_5N_5]^+$
cyclopentathiazenium cation

CHAPTER 1

Nitrogen and Sulphur Bond Angles - Sulphur Nitrogen Bond Distance Correlations

(A) Nitrogen Bond Angle - Sulphur Nitrogen Bond Distance Correlations.

In this chapter the simple relationships between nitrogen bond angles and sulphur-nitrogen bond lengths in inorganic and organic compounds containing two-coordinate nitrogen are discussed. This work was undertaken because such correlations would provide a means of assessing the reliability of X-ray structural data when large or no estimated standard deviations are provided.

Correlations involving vibrational spectral data and structural parameters such as bond lengths and bond angles have proved valuable for assigning stretching frequencies and deducing the structures of several types of sulphur -nitrogen compounds. For many SN systems smooth relationships exist between SN bond length and bond order[25-27], SN bond length and force constant[27], SN bond length and SN stretching wavelength[28] or frequency[29] and between SN bond distance or bond order and the sulphur oxidation state[29]. For compounds containing the sequence NSO, there is a linear relationship[28] between ν_s NSO and ν_{as} NSO which is similar to the ν_s- ν_{as} correlation found by Robinson[30] for compounds containing the SO_2 group.

For cyclic sulphur imides it has been noted that an increase in the number of nitrogen atoms opens out the $S\hat{N}S$ angle[29,31](and to a lesser extent $N\hat{S}N$ [31]) and contracts not only the SN bonds[29,31] but also the cross ring SS distances[31]. These changes were interpreted in terms of increasing bonding interactions between the nitrogen (or sulphur) lone pairs and the empty sulphur d orbitals. Hecht, Reinhardt, Steudel and Bradaczek similarly rationalise the SNHS planarity in S_7NH, in terms of 3 centre π-bonding[32]. On the other hand, the X-ray photoelectron spectra of all the known cyclic sulphur imides $S_{8-x}(NH)_x$ have been examined[33] and the small magnitudes of the sulphur atomic charges deduced from the chemical shifts, gave no evidence for any π interaction due to nitrogen lone pair donation into sulphur d orbitals. Perhaps σ-bond polarisation, due to the higher electronegativity of nitrogen compensates for this π-electron drift (cf. borazines[34]). This is another example of the perennial problem of trying to assess when d orbitals are likely to be involved significantly in bonding in sulphur compounds. Gathering together the available structural data on a wide variety of SN compounds allows a more detailed examination of the relationship between SNS bond angle and mean SN bond length. A smooth curve has been found for $S\text{-}N\text{-}S^{IV}$ species which approximates to a straight line. Species containing five membered rings, negatively charged nitrogen atoms or $S^{VI}\text{-}N\text{-}S^{VI}$ links, give points off the curve, but lie on a line of their own: points for re-entrant nitrogen atoms lie off both lines. Major causes of these effects appear to be changes in hybridisation, bond polarisation due to the higher electronegativity of nitrogen, and N lone pair -S d orbital π bonding. It is shown that for $S\text{-}N\text{-}S^{IV}$ species stereochemical inactivity of the N lone pair due to π-bonding (i.e., linear SNS) would correspond to an SN distance of about 151 pm. Variations in SN bond distances in the aromatic thiazenes will also be discussed.

TABLE 1.1

Mean Bond Distances and Nitrogen Angles in Sulphur Nitrogen Compounds

Group 1 - Non Cyclic $S\text{-}N\text{-}S^{IV}$ Groups

Compound	Mean d_{SN}pm†	$S\hat{N}S^{o}$	Reference
$(N(SMe_2)_2)(Br)$	163.5(4.0)	110.8(2.0)	35
Me_2SNSO_2p-tolyl	161.4(8)	113.4(5)	36
Ph_2SNSO_2p-tolyl	161.3(7)	113.4(5)	37
(nPr)PhSNSO$_2$p-tolyl	161.9(7)	115.7(4)	38
Me_2SNSO_2Me	160.7(9)	116.2(6)	39

Compound	Mean d_{SN} pm†	$S\hat{N}S^{o}$	Reference
R_2SNSO_2p-tolyl	160.2(5)	116.3(4)	40
$(SN)_x$	161.0(6)	119.4(4)	41
$S_3N_2NSO_2F$	159.5	124.3	42
$(Ph_2CN)_2S_3N_2$	160.1(6) x2	126.4(4) x2	43
$Ph_2S_3N_2$	159.4(5)	126.7(4)	44
$(pClC_6H_4)_2S_3N_2$	159.8(1.7)	126.0(2.0)	45
"	161.1(1.8)	129.0(2.0)	45

Group 2 - Cyclic $S-N-S^{IV}$ Groups.

Compound	Mean d_{SN} pm†	$S\hat{N}S^{o}$	Reference
$(S_4N_5O)(NH_4)$	161.1(4) x2	111.2(2) x2	46
"	161.9(5)	114.1(3)	46
"	162.7(4) x2	114.8(3) x2	46
S_4N_4	161.8(1.6)	112.3(6)	47
"	161.8(1.6)	112.6(7)	47
"	162.2(1.6)	112.8(7)	47
"	160.6(1.8)	113.6(7)	47
S_4N_4CuCl	162.3(4)	113.6(2)	48
"	162.4(5)	113.7(2)	48
$(S_4N_5)(nBu_4N)$ *	162.5(2.0)	113.0(1.0)	49
"	162.5(2.0)	114.0(1.0)	49
"	162.0(2.0)	114.0(1.0)	49
"	161.5(2.0)	115.0(1.0)	49
$S_3N_5PF_2$	162.2(6)	115.9(5)	50
"	162.1(9) x2	122.9(4) x2	50
$C_{14}H_{16}S_4N_4$	161.0(2.0)	118.5(1.3)	51
"	163.0(3.0)	126.4(1.3)	51
$(S_5N_5)(S_3N_3O_4)$ (anion)	160.1(3)	121.9(2)	52
"	160.2(3)	121.0(2)	52
$(SNCl)_3$	160.7(7) x2	123.0(4) x2	53

Compound	Mean d_{SN} pm†	$S\hat{N}S^{o}$	Reference
$(SNCl)_3$	160.2(7)	124.9(4)	53
$(NSON(CF_3)_2)_4$ *	159.0(1.0) x4	123.4(1.0) x4	54
$(SNF)_3$ *	159.3(3) x3	123.2(1) x3	55
$(SNF)_4$ *	160.0(1.0)x4	123.9(6) x4	56
$S_3N_3NA_sPh_3$(in plane)	162.3(6)	124.0(3)	57
$S_3N_3NPPh_3$(in plane)	158.0(1.4)	127.3(9)	58
$S_4N_4.BF_3$	157.1(6)	137.3(4)	59
"	156.9(6)	137.6(4)	59
"	158.4(6)	137.9(4)	59
$(S_4N_3)_2(SbCl_5)$	157.7(9)	137.2(6)	60
"	156.0(9)	147.3(7)	60
"	155.3(9)	147.6(7)	60
$(S_5N_5)(S_3N_3O_4)$	158.0(3)	133.0(2)	52
"	157.0(3)	149.9(2)	52
"	156.4(3)	152.1(2)	52
$(S_5N_5)(SnCl_5OPCl_3)$	158.4(1.4)	131.5(9)	61
"	155.8(1.5)	148.1(1.0)	61
"	156.7(1.4)	154.0(9)	61

Group 3 - Small Strained Rings.

Compound	Mean d_{SN} pm†	$S\hat{N}S^{o}$	Reference
S_2N_2	165.4(1) x2	90.4(1) x2	41
$S_3N_2NSO_2F$	160.0	117.2	42
"	161.1	119.1	42
$S_3N_2NP_3N_3F_5$	157.5(4)	117.6(4)	62
"	160.5(4)	119.7(4)	62
$(S_6N_4)(S_2O_6Cl)_2$	158.7(3)	119.1(2)	62
"	158.6(3)	119.6(2)	62
$(S_3N_2)(AsF_6)$	157.7(7)	119.8(4)	63
"	158.7(7)	119.9(4)	63

Compound	Mean d_{SN} pm†	$S\hat{N}S$°	Reference
$(S_3N_2Cl)(FeCl_4)$	159.0(6)	119.6(4)	64
"	156.6(6)	121.5(4)	64

Group 4 - Cyclic S^{VI}-N-S^{VI} groups.

Compound	Mean d_{SN} pm†	$S\hat{N}S$°	Reference
$(SNOF)_2(SNOPh)$	158.5(1.0)	118.9(3)	65
"	155.5(1.0)	119.3(3)	65
"	154.5(1.0)	122.5(1.0)	65
$(S_5N_5)(S_3N_3O_4)$ (anion)	158.0(3)	119.2(2)	52
$(SNOCl)_2(PNCl)_2$	157.8(1.3)	120.3(8)	66
$(SNOF)_2(PNCl_2)$	156.8(9)	120.9(6)	67
$(SNOCl)_3$	157.0(1.0)	119.5(5)	68
"	157.6(1.1)	120.9(6)	68
"	157.6(1.3)	120.9(6)	68

Group 5 - Re-entrant Nitrogen Atoms.

Compound	Mean d_{SN} pm†	$S\hat{N}S$°	Reference
$(S_5N_5)(S_3N_3O_4)$	155.3(3)	136.8(2)	52
"	154.5(3)	139.8(2)	52
$(S_5N_5)(SnCl_5OPCl_3)$	155.2(1.3)	135.5(8)	61
"	152.7(1.4)	146.1(9)	61

Group 6 - Negatively Charged Nitrogen Atoms.

Compound	Mean d_{SN} pm†	$S\hat{N}S$°	Reference
$(S_4N_5)(nBu_4N)$	166.0(2.0)	112.0(1.0)	49
$(SNO_2)_3Ag_3$	163.6(6) x3	115.0(3) x3	69
$S_3N_3NPPh_3$(out of plane)	164.0(1.0)	117.1(6)	58
"	163.7(1.0)	117.9(6)	58
$S_3N_3NAsPh_3$(out of plane)	165.0(5)	118.2(4)	57

Compound	Mean d_{SN}†	SNS^{o}	Reference
$S_3N_3NAsPh_3$(out of plane)	163.1(6)	120.1(4)	57
	Others		
Compound	Mean d_{SN}†	SNS^{o}	Reference
$(SN)_x$	165.0(8.0)	113.5(5.0)	70
$S(NSO)_2$	163.5 x2	120.0 x2	71
$(N(SCl)_2)(BCl_4)$	153.5(8)	149.2(6)	72

† Arithmetic mean of adjacent d_{SN} (and mean of the quoted e.s.d.'s)

* See original paper for significance of quoted errors (sometimes not given for the separate bonds).

Data and Discussion

Compounds containing the S-N-S grouping have been subdivided into structural types (data in Table 1.1). $S\hat{N}S$ angles and mean SN bond distances are given (and the mean of the two e.s.d.'s, described below as the e.s.d. in bond distance). The e.s.d.'s in bond angle are quoted in Table 1.1, but are not referred to in the discussion because the gradients of the graphs render these errors insignificant compared to the errors in bond distance. Groups of points clearly belonged together and the common factor was the oxidation number of the sulphur atoms. This simple classification can be adopted until new data or understanding force modification.

Open chain structures (group 1, S-N-S^{IV} species, represented by '+' in Fig.1.1) are assumed to be unstrained at nitrogen. The 13 points lie within two e.s.d.'s in bond distance of the best straight line (from a least squares treatment): (1) $d_{SN} = 176.2 - 0.128\ \hat{N}$ Correlation coeff. - 0.7189. $\hat{N}$ is the S-N-S bond angle in degrees and d_{SN} (pm) is the mean of the two SN distances. Many of the Group 2 species (cyclic S-N-S^{IV}species) may also be unstrained;

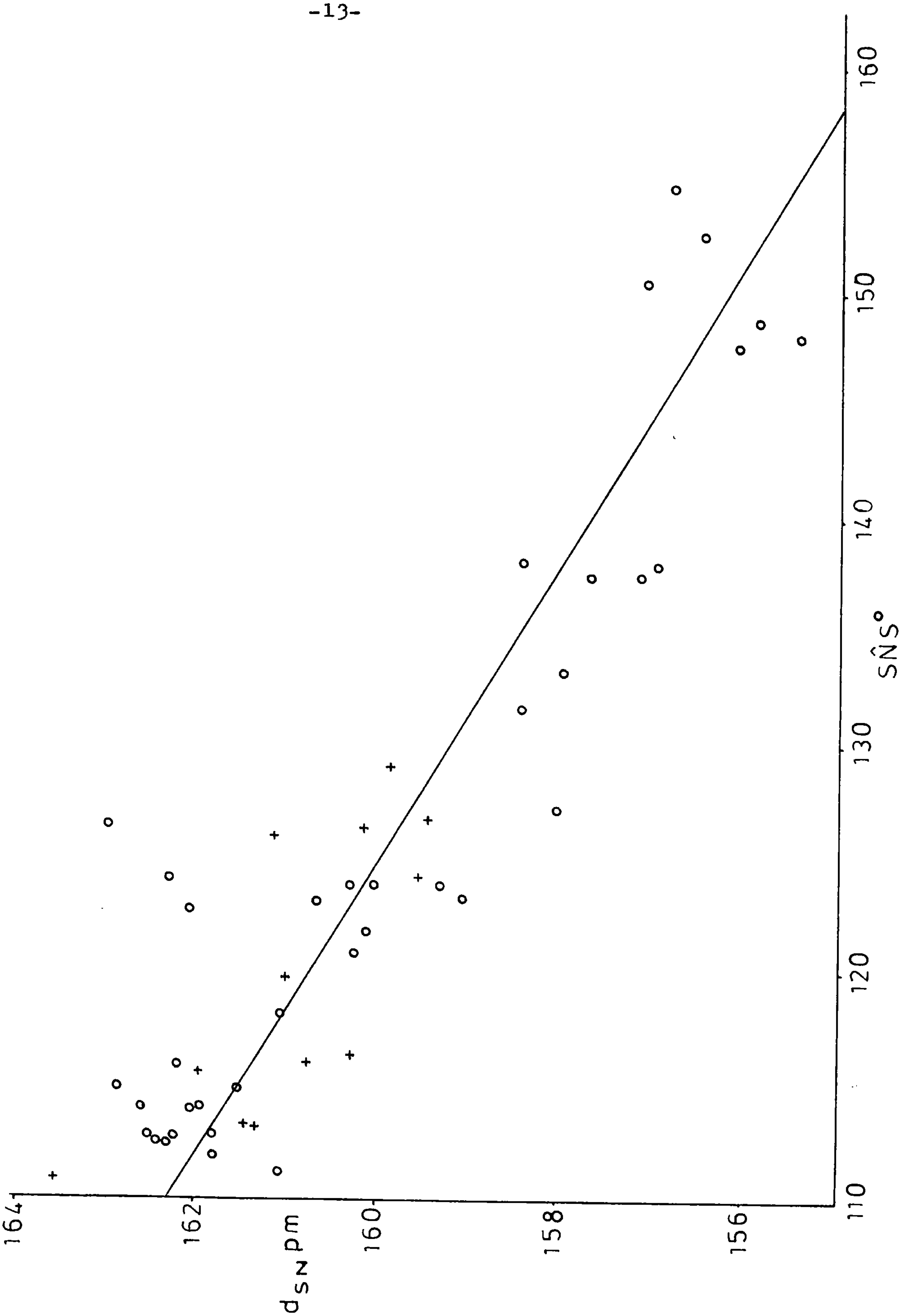


Figure 1.1 Sulphur-nitrogen distance/nitrogen bond angle correlation for $S\text{-}N\text{-}S^{IV}$ species, ($d_{SN} = 179.8-0.158\hat{N}$).

for this Group (represented in Fig.1 by open circles) lie within 2e.s.d's (in bond distance) of the polynomial (determined by a least squares treatment):

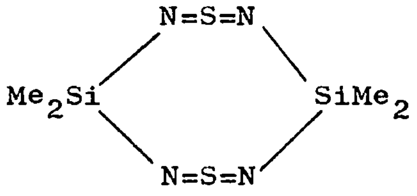
$$(2) \quad d_{SN} = 174.0 - (7.76 \times 10^{-2})\hat{N} - (2.87 \times 10^{-4})\hat{N}^2$$

This curve deviates very little from the following best straight line (determined by a least squares treatment):

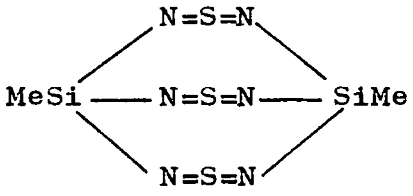
$$(3) \quad d_{SN} = 179.8 - 0.158\hat{N} \quad \text{Correlation coefficient - 0.8724}$$

All points from Groups 1 and 2 lie within three e.s.d's (in bond distance) of this line (shown in Fig.1) except one (the unique ring N atom in $S_3N_3NAsPh_3$ but the deviation is only 3.5 e.s.d's).

Extrapolation of curve (2) (or line (3)) to linear $S{=}\overset{+}{N}{=}S$ gives an anticipated $d_{S=N}$ of 150.9 pm (or 151.3 pm). This compares well with the SN double bond distances (150.7 pm) found in both compounds (I)[73] and (II)[42] :



I



II

and the SN double bond distance of 152.1 pm predicted by Nyburg[25] from the bond order (N_{SN}) - bond distance relationship:

$$N_{SN} = 0.429 + (6.85 \times 10^{-2})d_{SN} - (3.825 \times 10^{-4})d_{SN}^{\ 2}.$$

A distance of ~151 pm must only be regarded as a typical S=N distance. Even in linear SNS configurations some variation in $d_{S=N}$ will arise due to changes in atomic charge distributions and in sulphur hybridisation. A similar variation in the characteristic SN single bond distance has been discussed earlier.[28]

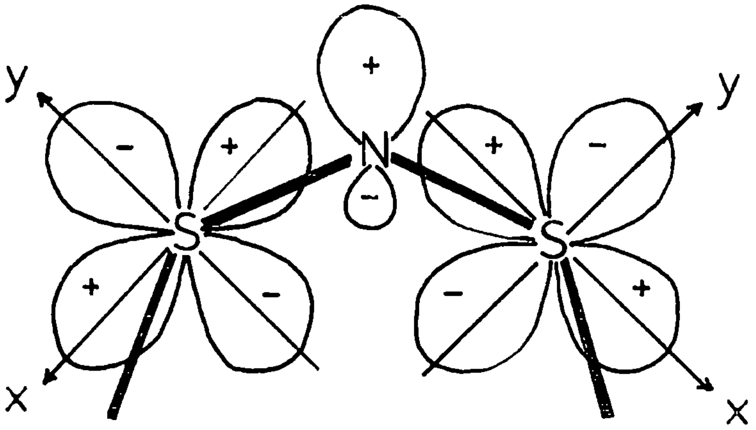
Wide variations in nitrogen bond angle are also found in cyclophosphazenes (ca. 120-160° which compares with 110-155° in SN compounds). In phosphazenes this is generally rationalised[74] taking into account two systems of delocalisation: in one, the participating orbitals are antisymmetric to reflection in the molecular plane (π_a system) and in the other they are symmetric (π_s system). If the X axis is taken to point into the ring and the Y axis is tangential, then the nitrogen $2p_z$ and $3d_{yz}$ orbitals are of the appropriate symmetry for the π_a system. For a π_s system nitrogen s and p_y orbitals and phosphorus $3d_{x^2-y^2}$, $3d_{xy}$ and $3d_{z^2}$ are all able to participate. The nitrogen lone pairs are involved in the π_s system.

A similar approach can be adopted for sulphur-nitrogen compounds. As illustrated in Fig.1.2, the nitrogen lone pair can donate into the sulphur $d_{x^2-y^2}$ and d_{xy} orbitals producing (because of the nodes at sulphur) three centre islands of π_s charge. It is therefore likely that the effect of lone pair donation would be mostly felt by the two adjacent SN bonds. As nitrogen lone pair donation increases, its stereochemical activity diminishes (so that $S\hat{N}S$ opens out) and strengthening of the adjacent SN bonds arises from two factors. First, the sulphur d orbital lobes overlap more effectively with the N lone pair hybrid and, secondly, the change in hybridisation at nitrogen (increasing s character $sp^2 \rightarrow sp$) strengthens both the σ and π_s components.[74,75]

Groups 3,4, and 6 contain four, five and six membered rings that are generally strained and together fall on a straight line (from least squares treatment), in which the nitrogen angle is only weakly responsive to changes in SN distance.

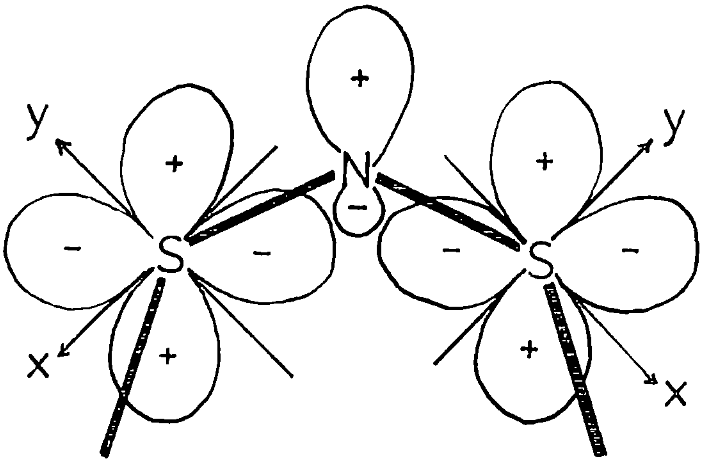
(4) $d_{SN} = 191.9 - 0.272\hat{N}$ Correlation coefficient - 0.6146

In the species of Group 3 (planar or close to planar four or five membered rings). π delocalisation leads to shorter SN bonds but the ring strain imposed by the ring prevents the nitrogen angle from expanding and the points lie many e.s.d's (in distance) below the curve of equation (2).



(a)

Overlap of Sulphur $d_{x^2-y^2}$ Orbital with Nitrogen Lone Pair



(b)

Overlap of Sulphur d_{xy} Orbital with Nitrogen Lone Pair

Figure 1.2

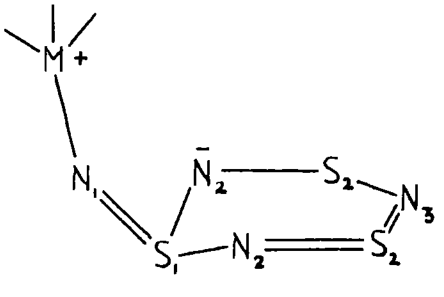
Group 4 contains species with the nitrogen atom adjacent to two 4-coordinate sulphur atoms in the +6 oxidation state. For any specific nitrogen angle the sulphur (VI) -nitrogen distance is about 4 pm shorter than for sulphur(IV)-nitrogen. Further ligands change the sulphur hybridisation and when strongly electronegative they increase the effective positive charge at sulphur. This strengthens the ionic and p_π-d_π components of the SN bonds and indirectly affects the σ hybridisation. This can be compared with the situation in cyclophosphazenes where contraction of ring bonds by highly electronegative ligands is well established[74]. However, in Group 4 type SN species, the extent to which the nitrogen angle can open out in response to bond contraction is restricted by ring strain, and so again the points lie below the unstrained line.

In Group 5, which refers to re-entrant nitrogen atoms in azulene-shaped $S_5N_5^+$ cations, the nitrogen angle is too small for the observed SN distances. This may indicate 'non-bonded' in plane SS interactions due to d-d overlap and in-plane sulphur lone pair sulphur d orbital σ overlap. The latter is no longer possible in the absence of re-entrant angles. Evidence for cross-ring bonding involving phosphorus or sulphur d orbitals has also been found for cyclophosphazenes, cyclothiazenes and $(SO_3)_3$[76-82].

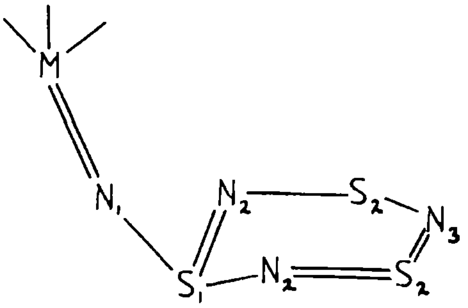
Group 6 includes four species where there appears to be good reasons for the points to lie above lines (1) and (3).

One SNS group in $(S_4N_5)^-$ and three in $(NSO_2{}^-)_3$ probably contain strained negatively charged nitrogen. Negative nitrogen leads to relatively little π bonding and hence long d_{SN}. The six membered rings are unable to accommodate the associated small $S\hat{N}S$ and strain ensues.

Each of the compounds $S_3N_3NMPh_3$(M=P,As) contains two nitrogen atoms N_2 which connect a planar delocalised system and an out of plane 3-coordinate sulphur atom[57,58]. Although valence bond structures can be misleading as a means of describing the bonding in delocalised, and especially Hückel, SN species[83], it seems as if the compounds $S_3N_3NMPh_3$ can be described adequately using two main canonical forms of types I and II:



(I)



(II)

Ylid structures of type I are expected to lead to long $d_{S_1N_2}$ in both P and As compounds and $d_{S_1N_1}$ shorter for the arsenic compound than for the P compound. The negative nitrogen leads to relatively little π-bonding (as discussed above for $(S_4N_5)^-$ and $(NSO_2)_3^{3-}$) and hence long $d_{S_1N_2}$ and $d_{S_2N_2}$. An unstrained S_1-N_2-S_2 group would need small angles at nitrogen (~98°) with d_{SN} ~164pm and so ring buckling occurs to help alleviate the strain at N_2. Structural data for both compounds (Table 1.1) support this interpretation. Thus all four members of Group 6 appear to be of a similar type, viz. strained negatively charged nitrogen.

There are four compounds which do not come under Groups 1-5 and, for no clear reasons, give points that deviate markedly from lines (1) and (3). These are $\beta(SN)_x$, $S(NSO)_2$, $(N(SCl)_2)^+$ and heart shaped $(S_5N_5)^+$. The last of these species will be discussed later in this chapter.

The estimated standard deviations for the electron diffraction study of $\beta(SN)_x$ are so large that it is hardly surprising that the point for this compound deviates so much from line (1). Parry and Thomas[84] in a semi-empirical calculation of the valence electron band structure reported that on attempting to evaluate the coordinates of the atomic positions, the $\beta(SN)_x$ structural data were marginally inconsistent and so, for their calculations, modified the $\beta(SN)_x$ data (in fact, selecting N and d_{SN} which gave points even further from line (1)). The problem has now been resolved by a more accurate structure determination[41] which gives a point almost exactly on line (1).

The accuracy of the structural data for $S(NSO)_2$ is also doubtful. No e.s.d. values were quoted[71] and the SO distance (137 pm) is one of the shortest values reported for any SO compound.[85] A comparable distance (137.1(1.3) pm) is found in $(SO_3)_3$[86] but sulphur(IV) normally shows longer distances than sulphur(VI), e.g. above the value (141.2(1) pm in SOF_2[87]). In compounds X-NSO, the higher NSO stretching frequency is normally associated largely with the SO bond[88]. In $S(NSO)_2$ this occurs at 1180 cm^{-1} and (from the d_{so}/λ_{so} correlation for S^{IV} compounds[89]) this corresponds to $d_{SO} \approx 145$ pm, rather than 137 pm found by X-ray diffraction[71]. A value close to 145 pm is typical of X-NSO compounds (cf. ClNSO, $d_{SO} = 144.5(4)$ pm[90] and HNSO, $d_{SO} = 145.1(5)$ pm[91]).

Like $S(NSO)_2$, $(N(SCl)_2)^+$ (see Fig.1.3) can be treated as an unstrained system. Line (1) for unstrained systems correlates $S\hat{N}S$ with d_{SN} over the range $d_{SN} = 164$-159 pm and $\hat{N} = 110$-130°. Extrapolation of this line to the region $d_{SN} = 153$ pm (as in $N(SCl)_2^+$) would introduce indeterminate errors in the estimation of angle. Line (3) on the other hand contains all S-N-S^{IV} species which appear to be unstrained (or largely so), including all the points from line (1). The range of this line ($d_{SN} = 164$-155 pm, $\hat{N} = 110^\circ$-155° probably makes extrapolation to $d_{SN} = 153$ pm more reliable. Thus for $(N(SCl)_2)^+$ ($d_{SN} = 153.2(8)$ and $153.7(8)$ pm) we would expect an $S\hat{N}S$ angle of ~166°, which contrasts with the nitrogen angle found ($S\hat{N}S = 149^\circ$). However, there may be some distortion due to lattice forces. Glemser <u>et al</u>[72] also quote i.r. data for $(N(SCl)_2)(BCl_4)$ but the highest frequency strong absorptions

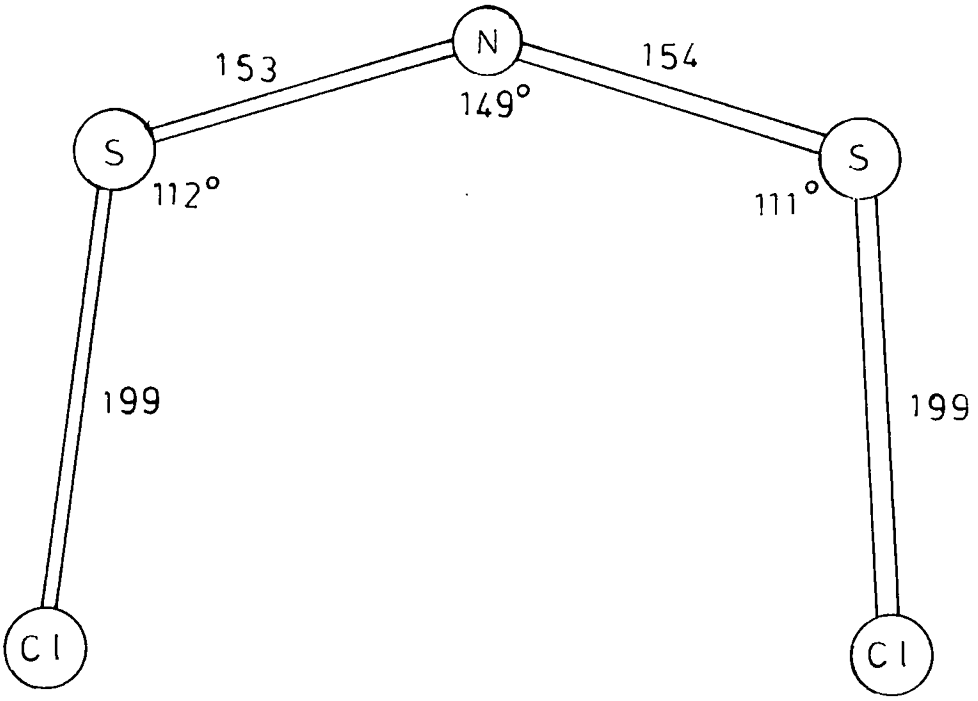


Figure 1.3

Structure of $(N(SCl)_2)^+$ in $(N(SCl)_2)(BCl_4)$; bond distances in pm[72].

(1380, 1340 and 1325 cm^{-1}) which should be due to ν_{SN} are typical[93] of $d_{SN} \leq 145$ pm. Perhaps the i.r. spectrum reported[92] for $(N(SCl)_2)(AlCl_4)$ with highest frequency strong absorption (1130 cm^{-1}) is more characteristic of $(N(SCl)_2)^+$. This frequency corresponds to $d_{SN} \approx 154$ pm[93] and hence $S\hat{N}S$ of 163° from line 3; these values are closer to the structural data reported for $(N(SCl)_2)(BCl_4)$.

The conclusions that can be drawn from the correlation between $\hat{N}$ and d_{SN} are that the structures of $S(NSO)_2$ and $(N(SCl)_2)^+$ and the vibrational spectra of $(N(SCl)_2)^+$ salts deserve reinvestigation.

(B) Sulphur Bond Angle - Sulphur Nitrogen Bond Distance Correlations.

As recently as 1971, Jolly[94] rightly observed that sulphur nitrogen compounds had frustrated and mystified chemists because various structure determinations had often shown that structures predicted for these compounds were wrong. In this section one can see that it is possible to rationalise the shapes of a wide variety of SN compounds, including cyclic species. The available structural data on inorganic and organic sulphur nitrogen compounds containing two-coordinate nitrogen have been collected and it is found that when compounds are allocated to structural classes, there is for each class an inverse relationship between the mean SN distance (d_{SN}) and the N-S-N angle. In delocalised rings the N-S-N angle is found to be largely governed by ring size.

It has already been shown that for various sulphur nitrogen species there are inverse relationships between d_{SN} and $S\hat{N}S$, and so by combining the $d_{SN}/N\hat{S}N$ and $d_{SN}/S\hat{N}S$ equations for unstrained sulphur and nitrogen, preferred angles can be determined for sulphur nitrogen distances between ca. 152 and 169 pm. Using these equations and the basic geometry of flat rings, it is possible to rationalise the shapes of some known sulphur nitrogen compounds and to deduce probable structures of some unknown species.

Data and Discussion

The available X-ray data, arranged in Tables 1.2-1.5 according to structural type, are also presented in Figures 1.4 and 1.5. In each table sulphur bond angles and mean SN bond distances are given (and the mean of the two e.s.d.'s in bond distance, described below as the e.s.d. in bond distance). Relatively few compounds are unstrained (Table 1.2 and Fig. 1.4); they are of four types, i) S^{II}, $S-(N{=}X)_2$, ii) S^{IV}, sulphur di-imides $S{=}(N-Y)_2$, iii) the delocalised chain $(SN)_x$ and iv) sulphur(VI) di-imides $R_2S{=}(N-Z)_2$. Despite the variation in chemical type all points lie within three e.s.d.'s of the best straight line given by (d_{SN} in pm in all equations):

(1) $d_{SN} = 219.2 - 0.531\hat{S}$ Correlation coefficient - 0.9746

Fig. 1.5 and Table 1.3 refer to points for all cyclic sulphur(VI) compounds (except anions) and to cyclic sulphur di-imides; again there is a variety of structural type but all points (except compound 8 Table 1.3, which is the only point for four coordinate sulphur(VI)) lie within one e.s.d. of the best straight line:

(2) $d_{SN} = 223.0 - 0.584\hat{S}$. Correlation coefficient - 0.9519

In Table 1.4 are rings containing three coordinate sulphur(IV) or cyclic sulphur(VI) anions; these points lie on a line:

(3) $d_{SN} = 228.1 - 0.606\hat{S}$. Correlation coefficient - 0.8893

The final structural category (highly delocalised species with two coordinate sulphur, (Table 1.5)) is discussed later in this chapter.

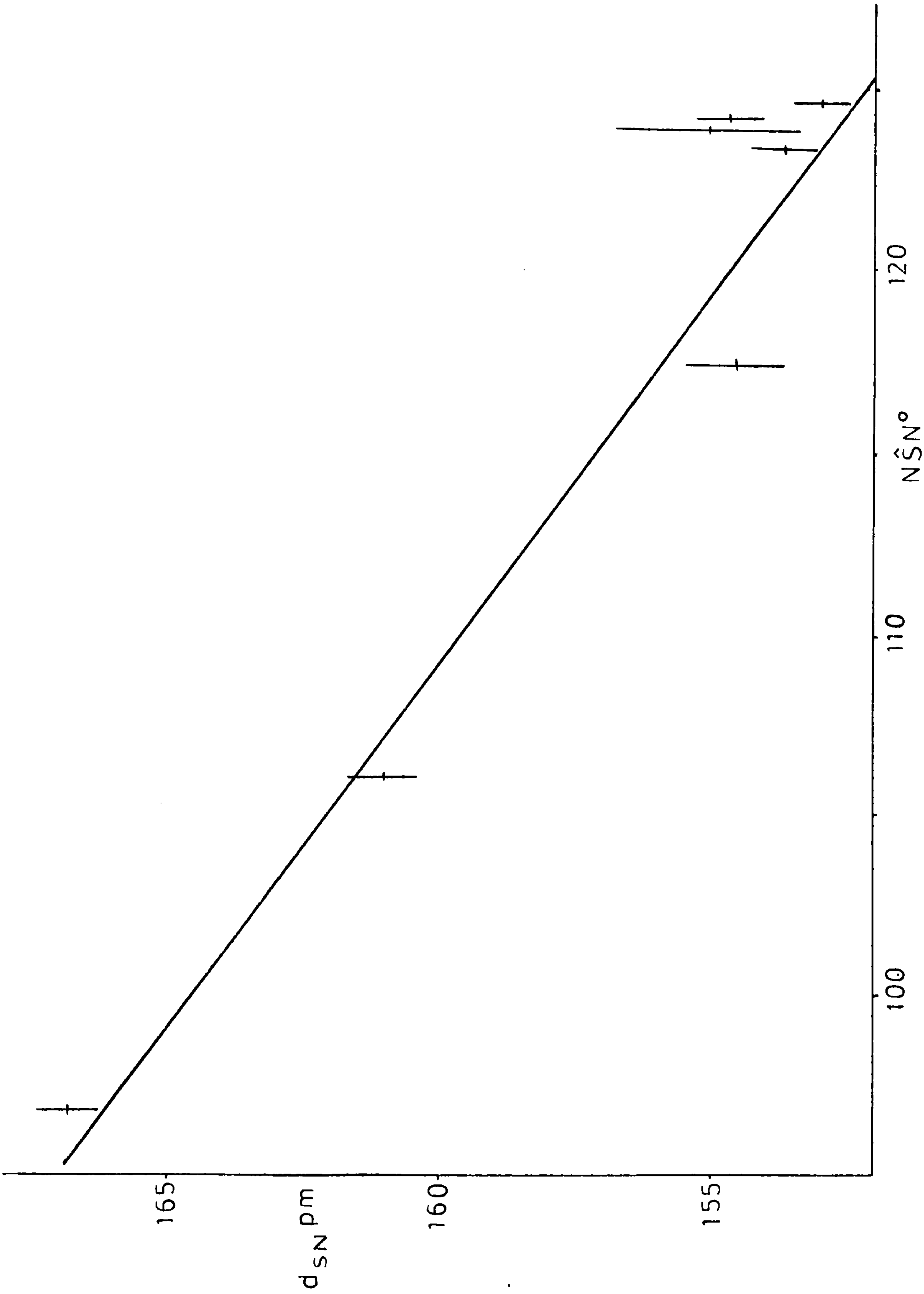
Table 1.2

Non-cyclic molecules

Compound	Mean d_{SN}(pm) †	$N\hat{S}N$°	Reference
1. $Ph_2CNSNSN\text{-}S\text{-}NCPh_2$	168.8(6) x2	96.8(4) x2	43
2. $(SN)_x$	161.0(6)	106.2(4)	41
3. $S(N\text{-}p\text{-}tolyl)_2$	154.5(9)	117.2(4)	95
4. $S(Me)_2(NH)_2$	153.6(6)	123.4(8)	96
5. $S(NSC_6H_4Cl)_2$	155.0(1.7)	124.0(1.0)	45
6. $S(NSNCPh_2)_2$	154.6(6)	124.2(4)	43
7. $S(NSPh)_2$	152.9(5)	124.7(4)	44

† Arithmetic mean of adjacent d_{SN} (and mean of the quoted e.s.d.'s).

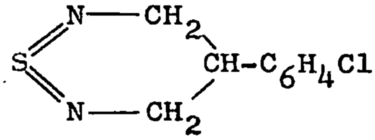
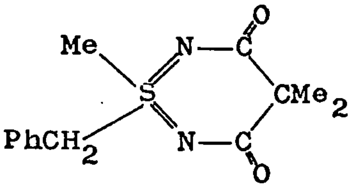
Figure 1.4



Sulphur-nitrogen distance/sulphur bond angle correlation for unstrained compounds given in Table 1.2 (errors:- 1 e.s.d. in d_{SN})

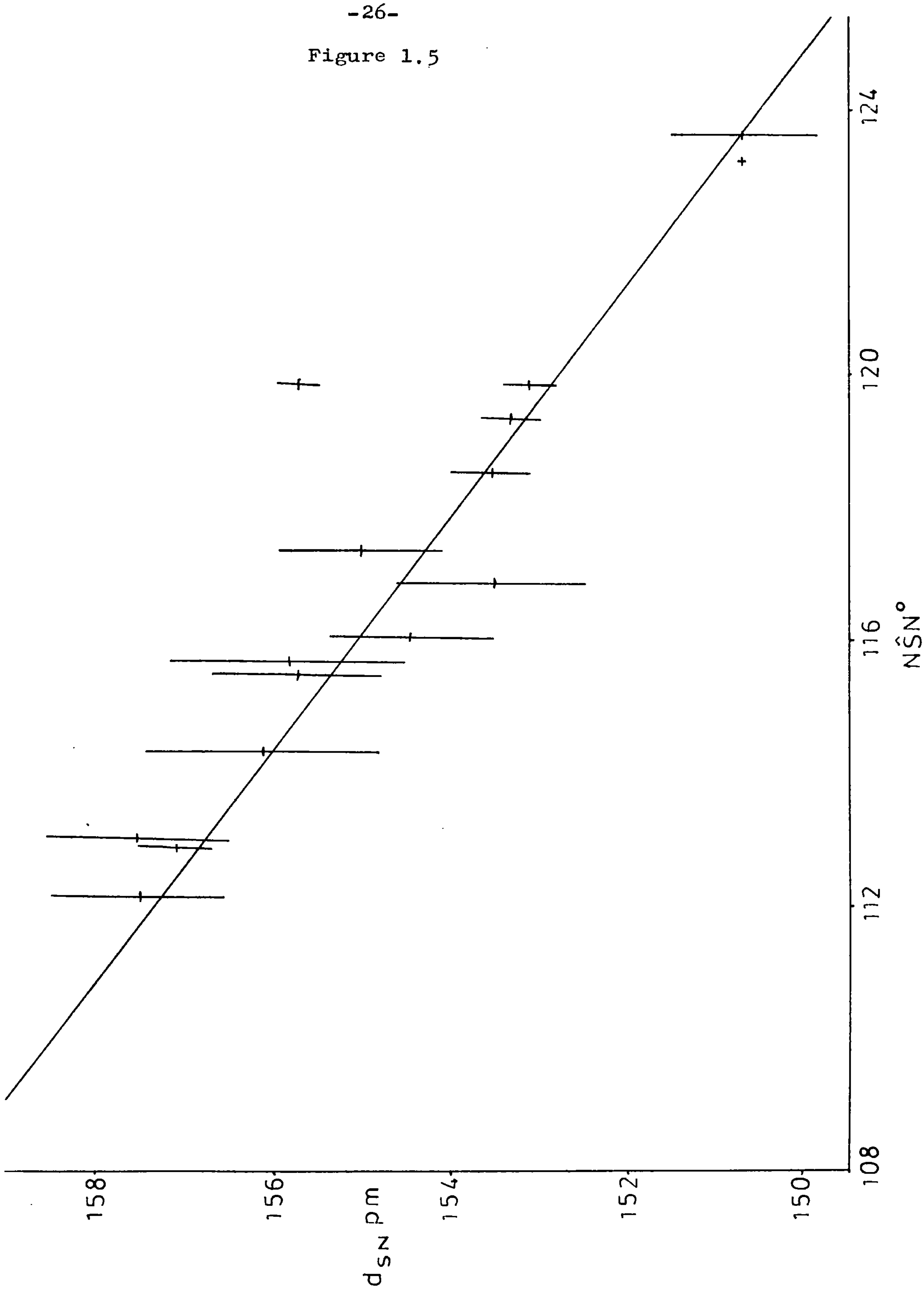
Table 1.3

Cyclic sulphur di-imides and cyclic sulphur(VI) compounds

Compound	Mean d_{SN} (pm)†	$N\hat{S}N$°	Reference
1. $(SNOCl)_3$	157.3(1.1) x2	111.7(9) x2	68
"	157.6(1.3)	113.7(6)	68
2. $(SNOF)_2SNOPh$	157.5(1.0)	112.1(6)	65
"	157.5(1.0)	112.9(6)	65
"	153.5(1.0)	116.8(8)	65
3. $(SNOCl)_2PNCl_2$	156.1(1.3)	114.3(7)	66
"	155.8(1.3)	115.6(7)	66
4. $(SNOF)_2PNCl_2$	155.7(9)	115.4(4)	67
"	154.4(9)	116.0(5)	67
5. $S_3N_5PF_2$	155.0(9)	117.3(4)	50
6. 	153.5(4)	118.5(3)	97
7. $SN_2P_4N_4F_6$	153.3(3)	119.3(2)	98
8. 	155.7(2)	119.8(3)	99
9. $(S_5N_5)(S_3N_3O_4)$ (anion)	153.1(3)	119.8(2)	52
10. $MeSi(NSN)_3SiMe$	150.7 x3	123.2 x3	42
11. $Me_2Si(NSN)_2SiMe_2$	150.7(8) x2	123.6(5)x2	73

† Arithmetic mean of adjacent d_{SN} (and mean of the quoted e.s.d.'s).

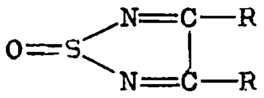
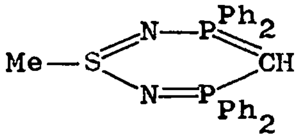
Figure 1.5



Sulphur-nitrogen distance/sulphur bond angle correlation for cyclic compounds in Table 1.3 (errors:- 1 e.s.d. in d_{SN}).

Table 1.4

Three coordinate sulphur(IV) and cyclic sulphur(VI) anions

Compound	Mean d_{SN} (pm)†	N$\hat{S}$N^{o}	Reference
	169.2(4)	97.2(2)	100
$(NH_4)(S_4N_5O)$	165.3(4)	104.6(2)	46
$Ph_3PNS_3N_3$	165.4(1.0)	106.2(5)	58
$Ph_3AsNS_3N_3$	163.6(4)	106.3(3)	57
$(nBu_4N)(S_4N_5)$ *	165.7(2.0)	106.3(1.0)	49
"	163.7(2.0)	107.3(1.0)	49
$S_3N_5PF_2$	163.6(7)	106.4(4)	50
$(Ag)_3(SNO_2)_3$	163.6(6) x3	106.1(3) x3	69
$(S_5N_5)(S_3N_3O_4)$ anion	163.2(3)	106.0(1)	52
"	162.5(3)	106.5(1)	52
$(NH_4)(S_4N_5O)$	158.8(3)	109.1(1)	46
$(NSON(CF_3)_2)_4$ *	159.0(1.0)x4	111.8(1.0) x4	54
$(SNF)_4$ *	160.0(1.0)x4	112.0(6) x4	56
$S_3N_2NP_3N_3F_5$	160.1(4)	112.0(2)	62
$S_3N_2NSO_2F$	162.4	112.4	42
$(SNF)_3$ *	159.3(3) x3	112.6(2) x3	55
	161.2(3)	113.2(2)	101
$(SNCl)_3$	160.1(7) x2	113.6(3) x2	53
"	161.4(7)	113.2(5)	53

† Arithmetic mean of adjacent d_{SN} (and mean of the quoted e.s.d.'s).

* See original paper for significance of quoted errors (sometimes not given for the separate bonds).

Table 1.5

Delocalised rings containing two-coordinate sulphur(IV)

Compound	Ring size	Mean d_{SN}(pm)†	Mean $N\hat{S}N^{o}$	Ref.
S_2N_2	4	165.4(1)	89.6(1)	41
$H-\overline{C=N-S-N=C}-H$	5	162.0	98.7	102
$R-\overline{C=N-S-N=C}-R$	5	162.0	98.8	103
$R'-\overline{C=N-S-N=C}-R'$	5	166.0(1.0)	98.9	104
$Ph-\overline{C=N-S-N=C}-H$	5	163.3(4)	99.2	105
$H-\overline{C=N-S-N=C}-H$	5	162.8(8)	99.4(2)	106
"	5	163.1(3)	99.6(2)	107
$R'-\overline{C=N-S-N=C}-R'$	5	165.0(1.0)	99.7	104
"	5	164.5(1.0)	99.9	104
S_4N_4	5	161.6(1.0)	103.7	47
$S_4N_4.CuCl$	5	162.3(5)	104.2(2)	48
$(S_3N_2Cl)(FeCl_4)$	5	158.9(6)	105.8(4)	64
$(S_3N_2)(AsF_6)$	5	158.0(7)	107.2(3)	63
$(S_3N_2)_2(S_2O_6Cl)_2$	5	158.7(5)	108.0(2)	108
$S_3N_2NP_3N_3F_5$	5	159.7(3)	109.7(4)	62
$(NH_4)(S_4N_5O)$	6	161.7(4)	111.7(2)	46
$(nBu_4N)(S_4N_5)$	6	162.0(2.0)	114.0(1.0)	49
$Ph_3PNS_3N_3$(planar section)	6	159.0(1.2)	114.5(7)	58
$Ph_3AsNS_3N_3$(planar section)	6	160.4(6)	115.5(3)	57
$(S_4N_3)_2(SbCl_5)$	7	156.6(9)	118.8(7)	60
"	7	156.0(9)	120.0(7)	60
$S_4N_4.BF_3$	8	156.5(6)	120.8(3)	59
$(S_5N_5)(S_3N_3O_4)$	10	156.3(3)	124.5(2)	52

Continued on next page.

Table 1.5 continued

Compound	Ring size	Mean d_{SN}(pm)†	Mean $N\hat{S}N^{\circ}$	Ref.
$(S_5N_5)(SnCl_5OPCl_3)$	10	156.5(1.5)	124.6(8)	61
Sulphurs joined to re-entrant nitrogen atoms.				
$(S_5N_5)(S_3N_3O_4)$	10	156.2(3)	109.2(2)	52
$(S_5N_5)(SnCl_5OPCl_3)$	10	155.8(1.5)	110.9(7)	61

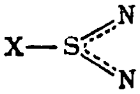
† Arithmetic mean (and mean of the quoted e.s.d.'s).

In all compounds (Tables 1.2-1.5) sulphur atoms are joined to two-coordinate nitrogen. Some species (e.g. $S_3N_2NSO_2F$ and $S(NSNCPh)_2$) have sulphur atoms which appear in more than one Table but for each separate type of sulphur atom there is only a small range of NSN angle and S-N distance. Table 1.6 (summarising data from Tables 1.2-1.4) shows that two-coordinate sulphur, bond distances and angles vary as expected viz. S^{II}: $d_{SN} \approx 167$ pm, $\hat{S} = 97^{\circ}$; S^{IV}: d_{SN} 150 - 155 pm, $\hat{S} = 125 - 117^{\circ}$. As SN bond order increases, so does the mutual repulsion between adjacent SN bonds. A similar correlation and rationalisation has been described by Gillespie and Robinson[109] for SO_2 systems. For sulphur(IV) species SN bonds weaken and $N\hat{S}N$ angles decrease, with (i) increase in coordination number and (ii) decrease in formal π-bond order. In the sulphur (VI) compounds (Table 1.6) the change in formal SN π-bond order appears (despite the great variation in compound type) to be sufficient to account for the changes in bond angles and distances: (i) sulphur di-imides (formal SN π-bond order of 1) (ii) sulphanuric compounds (formal SN π-bond order of $\frac{1}{2}$) and (iii) sulphimide species (formal SN

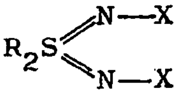
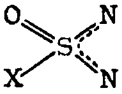
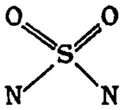
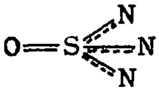
Table 1.6

Typical structural parameters in sulphur-nitrogen compounds

Sulphur coordination number

	2	3	
	to 2N	to 2N	to 3N
S^{II}	167pm, 97° X=N-S-N=X		
S^{IV}	150-155pm, 125-117° X-N=S=N-X	i) 169pm, 97° X-C=N-S(O)-N=C-X ii) 159-163pm, 114-111° 	163-166pm, 108-104° 

Sulphur coordination number

	4	
	to 2N	to 3N
S^{VI}	i) 153-156pm, 125-119°  ii) 153-158pm, 117-112°  iii) 162-164pm, 107-106° 	159pm, 109° 

π-bond order of $\frac{1}{4}$)[78]. The bonding in $S_4N_5O^-$ is more complex so that it is not possible to give a meaningful estimate of formal π-bond order or a detailed rationalisation of distances and angles. However, the distances and angles are typical of 4 coordinate sulphur(VI).

If we compare (Table 1.6) the S^{VI} compounds formed by replacing the lone pair on the three-coordinate S^{IV} compounds by oxygen, we find that the SN distances are appreciably shorter (cf $(SNOCl)_3$, 157.1(4) pm[68]; $(SNCl)_3$, 160.5(7) pm[53]). Inserting a highly electronegative atom increases the sulphur Lewis acidity and hence donation by the ring nitrogen lone pairs. Further, by removing electron density from the sulphur, electrostatic contributions to the SN bonds increase. However, large increases in $N\hat{S}N$ are prevented by ring strain.

For highly delocalised species,(Table 1.5)as ring size increases (4-8 atoms), the average d_{SN} decreases and the angles $\hat{S}$ and $\hat{N}$ open out. These variations are consistent with change in hybridisation at sulphur and nitrogen and increased overlap between the nitrogen lone pair orbitals and the empty sulphur d orbitals. Larger rings e.g. $(S_5N_5)^+$ require re-entrant atoms to reduce ring strain. Data for compounds with 5 membered rings (Table 1.5.) indicate that d_{SN} decreases with increasing positive charge at sulphur; this contraction can be attributed to increased bond polarity and stronger sulphur overlap provided by stabilised sulphur d-orbitals. The accuracy of the data is insufficient to reveal any contraction in d_{SN} specifically associated with (4n + 2)π electrons. This suggests that such a complement of π electrons helps to rationalise similar SN distances and a planar or close to planar geometry[110], but is not associated with any large stabilisation energy. A corollary of this is that a low strain non-planar system such as $(S_3N_3O)^-$ (8π) may well be stable without being aromatic.

Deduction of Structures for Minimum Strain

In this treatment we ignore intermolecular and interionic forces and assume that in the most stable structure of a molecule or ion there is minimum strain of bond distances and angles so that in the preferred structure, equations 4 and 5 below are obeyed. Equation 4 (with 7 points) relates d_{SN} and $\hat{S}$ for the unstrained NSN species given in Table 1. Equations 5 and 6 relate to data given previously. Equation 5 (13 points) relates d_{SN} and $\hat{N}$ for unstrained $S-N-S^{IV}$ species over the range 164-159 pm (110-130°). Equation 6 with 63 points holds for a wider variety of $S-N-S^{IV}$ compounds (most of which appear to be largely unstrained) and over a larger structural range (164-155 pm, 110-155°) and so for $d_{SN} < 159$ pm the deductions rely on equations 4 and 6.

(4) $d_{SN} = 219.2 - 0.531\hat{S}$

(5) $d_{SN} = 176.2 - 0.128\hat{N}$

(6) $d_{SN} = 179.8 - 0.158\hat{N}$

Combining relationships 4 and 6, we can relate the nitrogen angle directly to the sulphur angle:

(7) $\hat{N} = 3.361\hat{S} - 249.4^{\circ}$

The method of prediction is illustrated by considering the planar species $(S_4N_3)^+$. In the absence of crystallographic data on unstrained delocalised -N-S-S- system the assumption, that the $N\hat{S}S$ angle can be treated like the $N\hat{S}N$ angle, is made. Only then is it legitimate to state:-

(8) $4\hat{S} + 3\hat{N} = 900^{\circ}$

Combining equations 7 and 8 gives $\hat{S} = 117.0^{\circ}$, $\hat{N} = 144.0^{\circ}$ and substituting these angles in equation 4 or 6 gives $d_{SN} = 157.1$ pm.

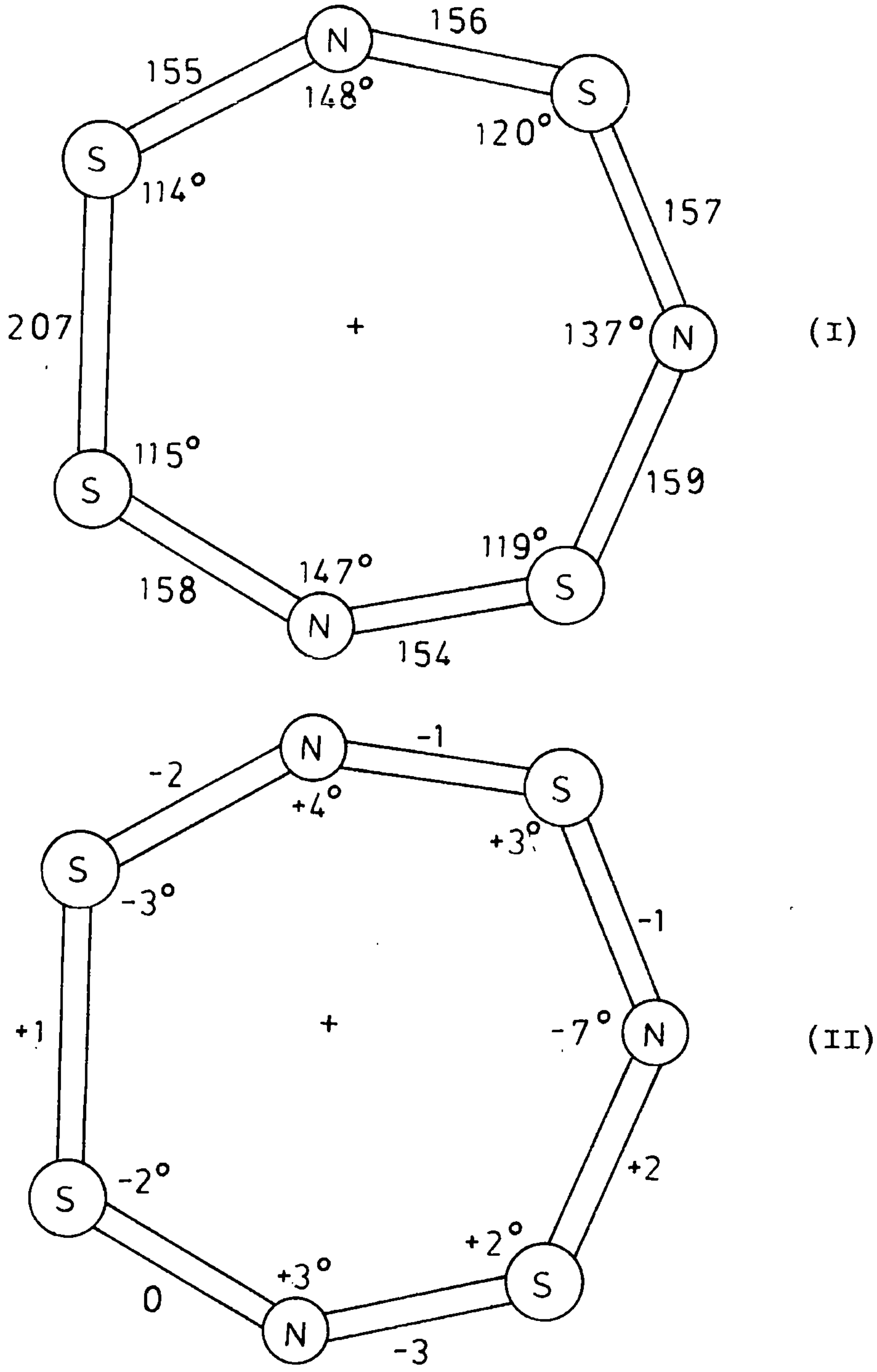


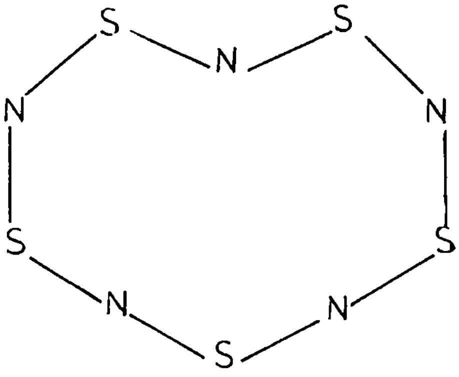
Figure 1.6 $(S_4N_3)^+$

(I) X-ray structural data[60].

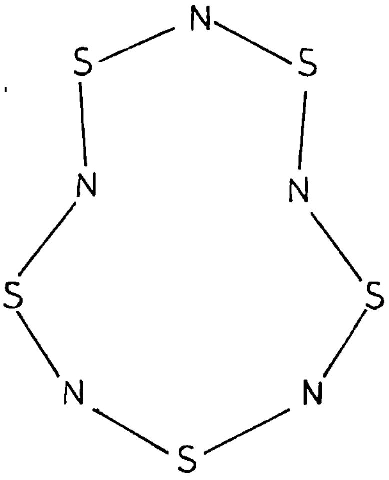
(II) Each quoted value = Found (X-ray) - "deduced" value.

Fig.1.6 shows X-ray structural data,[60] together with the differences from the predicted angles and bond lengths. The experimental (X-ray) average values (with e.s.d.'s in parentheses), $\hat{S} = 117.0(7)^\circ$, $\hat{N} = 144.0(7)^\circ$ and $d_{SN} = 156.3(9)$ pm, show that the predicted data lie within the X-ray experimental errors; also the calculated S-S distance (205.3 pm) compares well with the X-ray value (206.6(4) pm)[60]. Thus the special stability of $(S_4N_3)^+$ can be attributed to π delocalisation and an unstrained structure (or nearly so).

For $(S_5N_5)^+$, three X-ray studies have been published; one structure (I) has one re-entrant nitrogen atom[111] and two (II) have two re-entrant nitrogen atoms.[52,61]



(I)



(II)

We now attempt to determine which conformation bears the least strain. For this we use equation 4 (unstrained $\hat{S}$) and equation 9 (which is equation 6 for $S\text{-}N\text{-}S^{IV}$ species without points for $(S_5N_5)^+$).

(9) $d_{SN} = 179.8 - 0.159\hat{N}$ Correlation coefficient - 0.7630

With one re-entrant nitrogen atom (i.e. planar heart shaped $(S_5N_5)^+$):

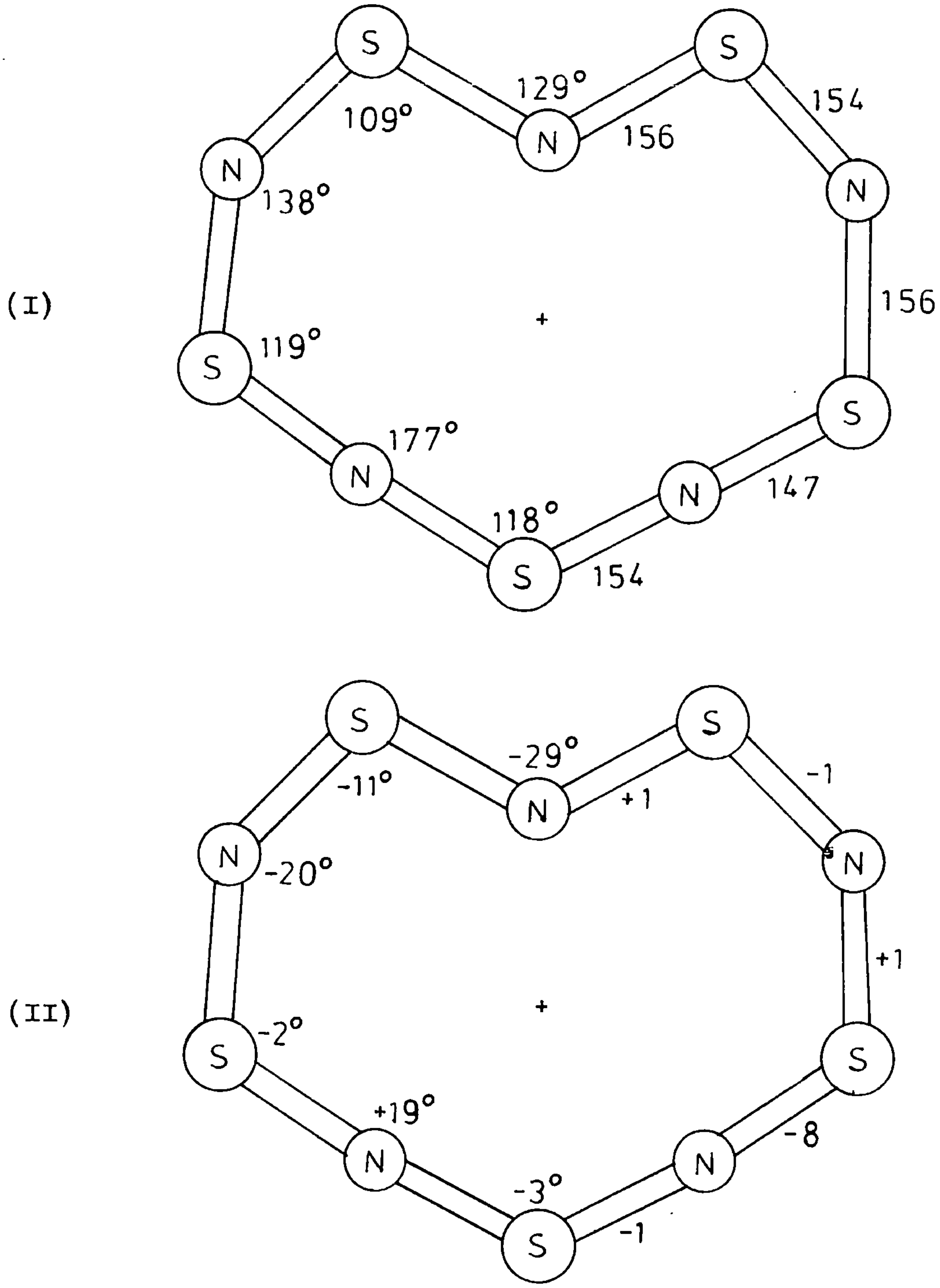


Figure 1.7 $(S_5N_5)^+$

(I) X-ray structural data[111].

(II) Each quoted value = Found (X-ray) - "deduced" value.

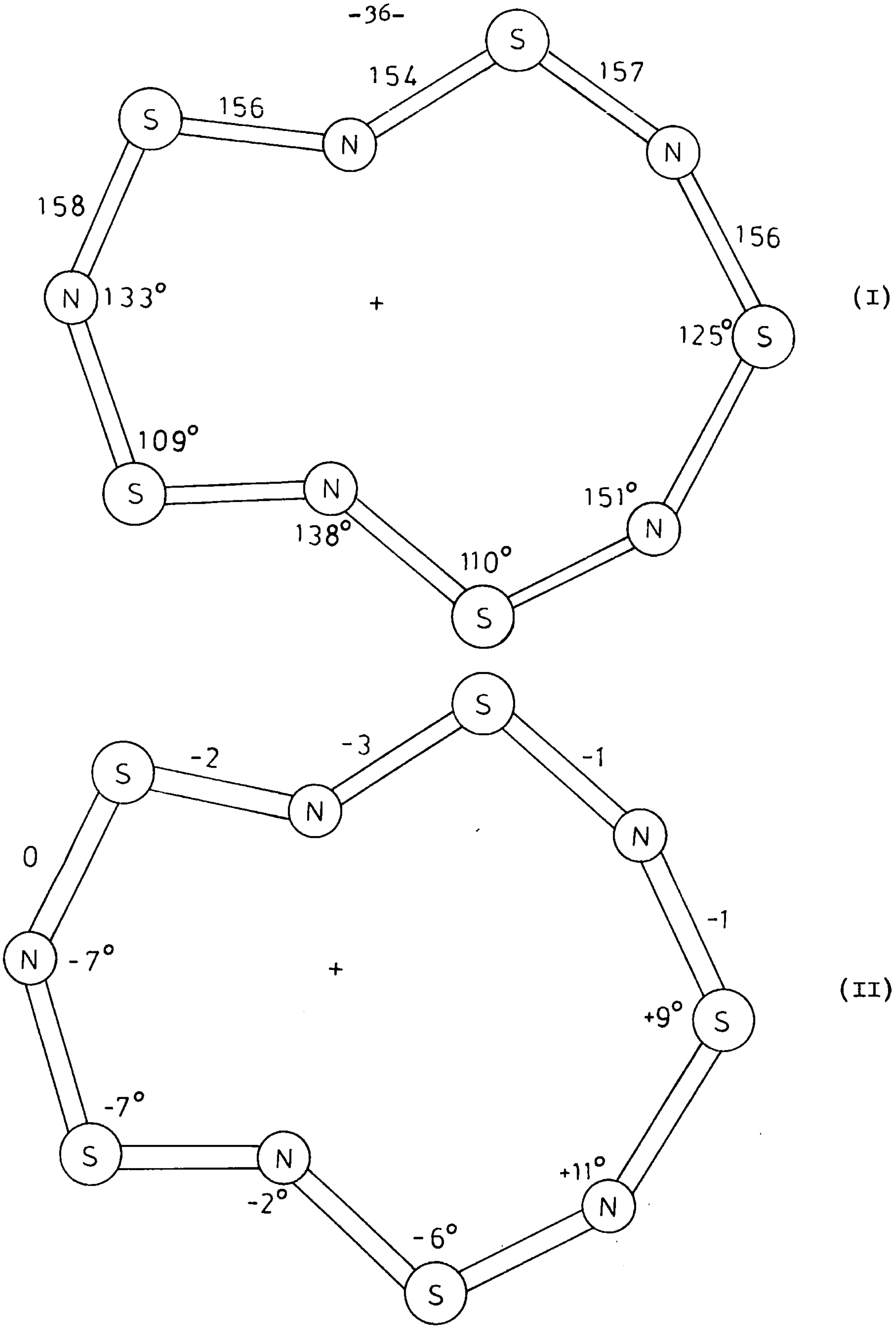


Figure 1.8 $(S_5N_5)^+$

(I) X-ray structural data[52].

(II) Each quoted value = Found (X-ray) - "deduced" value.

(10) $5\hat{S} + 4\hat{N} + (360^\circ - \hat{N}) = 1440^\circ$

Combining equations 4 and 9 gives:

(11) $\hat{N} = 3.340\hat{S} - 247.8^\circ$

and combining equations 10 and 11 gives $\hat{S} = 121.4^\circ$ and $\hat{N} = 157.7^\circ$. Substituting these values in either equation 4 or equation 9 gives $d_{SN} = 154.7$ pm.

Fig. 1.7 shows the structure found by X-ray diffraction[111] with the differences between predicted and experimental bond lengths and angles. The X-ray average value with e.s.d.'s in parentheses are $\hat{S} = 114.9(7)^\circ$, $\hat{N} = 151.9(7)^\circ$ and $d_{SN} = 153.9(9)$ pm.

For $(S_5N_5)^+$ with two re-entrant nitrogen angles, $5\hat{S} + 3\hat{N} + (720^\circ - 2\hat{N}) = 1440^\circ$. Following the same procedure as before, $\hat{S} = 116.0^\circ$, $\hat{N} = 140.0^\circ$ and $d_{SN} = 157.5$ pm.

Fig. 1.8 shows the structure found by X-ray diffraction[52] with the differences between predicted and experimental bond lengths and angles. The average experimental values with e.s.d.'s in parentheses are $\hat{S} = 112.2(2)^\circ$, $\hat{N} = 142.4(2)^\circ$ and $d_{SN} = 156.0(3)$pm.

The differences between predicted and X-ray data in $(S_5N_5)^+$ are considerably less for two re-entrant angles and so this appears to be the preferred conformation. It must also be noted that the experimental bond lengths and angles for the heart shaped $(S_5N_5)^+$ structure provide points that are many e.s.d.'s from the unstrained lines: (Table 1.7).

Table 1.7

Difference between predicted and experimental heart-shaped $(S_5N_5)^+$

X-ray Structure		Predicted d_{SN}	X-ray Structure		Predicted
S°	d_{SN} (pm)†	d_{SN}(pm)	N°	d_{SN}(pm)†	d_{SN}(pm)
110.1(4)	154.7(8)	160.7	138.4(6)	154.7(9)	157.8
118.5(5)	151.2(1.0)	156.3	177.1(8)	150.1(1.0)	151.6
118.4(6)	150.1(1.0)	156.3	177.3(7)	152.4(1.0)	151.6
118.6(5)	158.6(1.0)	156.2	137.7(5)	156.8(9)	157.9
109.4(4)	155.0(8)	161.1			

† Arithmetic mean of adjacent d_{SN}(and mean of the quoted e.s.d.'s).

It is perhaps significant that bond distances and angles (and thermal parameters for most atoms) can be simulated by superimposing two $(S_5N_5)^+$ azulene shapes one on top of the other (Fig. 1.9)[112]. It therefore seems likely that there is disorder of azulene-shaped $(S_5N_5)^+$ at the cation sites of $(S_5N_5)(AlCl_4)$.

Now consider likely structures of $S_4N_4{}^{2+}$. The cation $S_4N_4{}^{2+}$ has been proposed[61,114] as a new 10π aromatic system and so should prefer a planar or close to planar conformation, if this can be achieved without undue strain. Four of the most likely structures with planar rings are (i) no re-entrant atoms (ii) one re-entrant atom (iii) two re-entrant atoms and (iv) two fused five membered rings with common S-S (an 8π system).

If $(S_4N_4)^{2+}$ has no re-entrant atom, $4\hat{S} + 4\hat{N} = 1080^\circ$ and with equations 7 and 4 this gives $\hat{S} = 119.1^\circ$, $\hat{N} = 150.9^\circ$ and $d_{SN} = 156.0$ pm (structure III). If the ring has one re-entrant nitrogen atom, $4\hat{S} + 3\hat{N} + (360^\circ - \hat{N}) = 1080^\circ$ and in combination

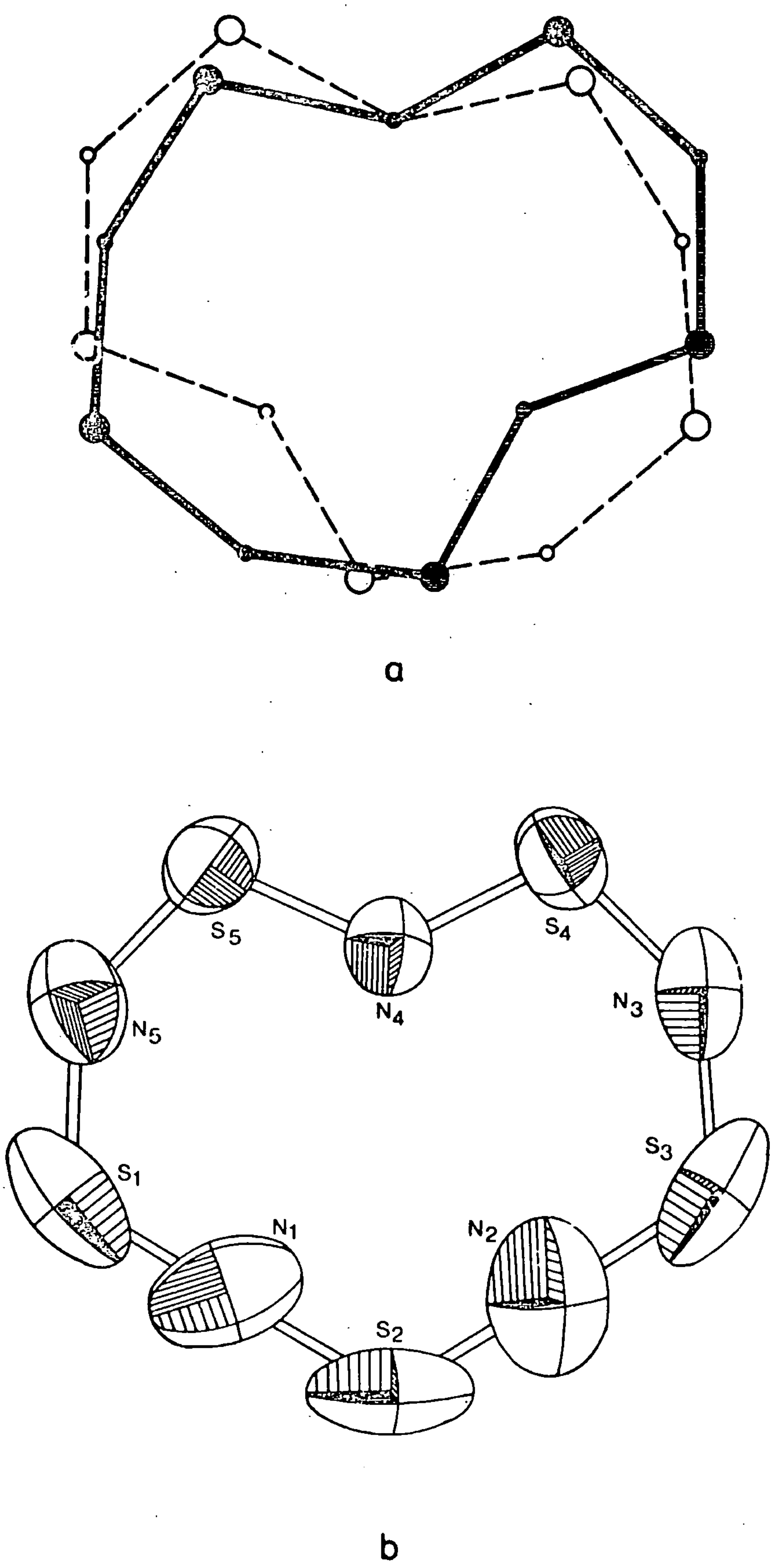


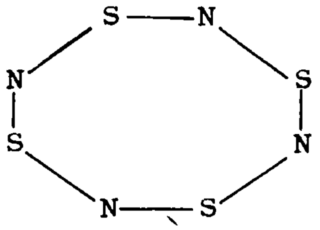
Figure 1.9

(a) Superposition of two $S_5N_5^+$ cations as found in $S_5N_5^+S_3N_3O_4^-$.

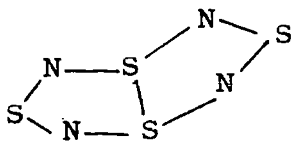
(b) Thermal elipsoids for $S_5N_5^+$ in $S_5N_5^+AlCl_4^-$

with equation 7 this gives $\hat{S} = 113.7^{\circ}$, $\hat{N} = 132.6^{\circ}$ and $d_{SN} = 158.8$pm. A similar approach for one re-entrant sulphur atom gives $S = 111.2^{\circ}$, $\hat{N} = 124.4^{\circ}$ and $d_{SN} = 160.2$ pm. However, the structures with re-entrant N or S cannot be drawn with equal bond lengths.

Using the same approach for two re-entrant atoms, deduced angles are unrealistic ($\leq 90^{\circ}$) and re-entrant atoms are much closer than van der Waals contact.



III



IV

If $S_4N_4^{2+}$ consists of two fused five-membered rings (IV), it becomes an 8π rather than a 10π system and so one cannot assume that each ring will be planar. However, at the bridgehead the two three-coordinate sulphur(IV) atoms should have $N\hat{S}N \approx 111^{\circ} - 114^{\circ}$ (Table 5) and $d_{SS} \geq 200$ pm (SS bonds are usually 200 - 220 pm)^{115}. Such a structure is completely impossible if the two rings are coplanar but it can be drawn consistent with the above and with mean $d_{SN} \approx 158$-159 pm, mean $N\hat{S}N \approx 105^{\circ}$-$108^{\circ}$, mean $S\hat{N}S \approx 118^{\circ}$- 121° (parameters typical of positively charged five membered rings - see Table 4), if the angle between the planes of the two rings is $\sim 100^{\circ}$. Some buckling of each of the two rings is possible to enhance cross-ring SS interactions (cf. the weak SS interaction adjacent to re-entrant N atoms in $S_5N_5^{+}$ which gives smaller $S\hat{N}S$ than expected at these points); but the buckling should be only slight since it would add further strain to the rings.

Fortunately structural data are available for some related compounds $S_4N_4.SbCl_5$[116], $S_4N_4.BF_3$[59] and $S_4N_4.CuCl$[48]. The geometry of the S_4N_4 group in $S_4N_4.CuCl$ differs very little from that of free S_4N_4 and the Cu-N distances (210 and 212 pm) are long for N → Cu(I) (e.g. 199 pm in $(Cu(CH_3CN)_4)(ClO_4)$[117]) and so $S_4N_4.CuCl$ appears to be a very weak complex or a clathrate. The SbN(217 pm) and BN (158 pm) distances in $S_4N_4.SbCl_5$ and $S_4N_4.BF_3$ respectively are more characteristic of nitrogen base adducts (_cf._ d_{SbN}= 223 pm in $CH_3CNSbCl_5$[118] and d_{BN} = 158 pm in Me_3NBF_3[119]), so it is useful to compare $(S_4N_4)^{2+}$ with $S_4N_4^{+}\text{——}SbCl_5^{-}$ and $S_4N_4^{+}\text{——}BF_3^{-}$ the latter being the more accurate structure determination. In the region remote from the three coordinate nitrogen atom (which has lost its capacity for lone pair NS π-bonding), the S_4N_4 geometry is closer to III than IV. In both adducts, sulphur atoms are coplanar and there are no close SS cross-ring distances.

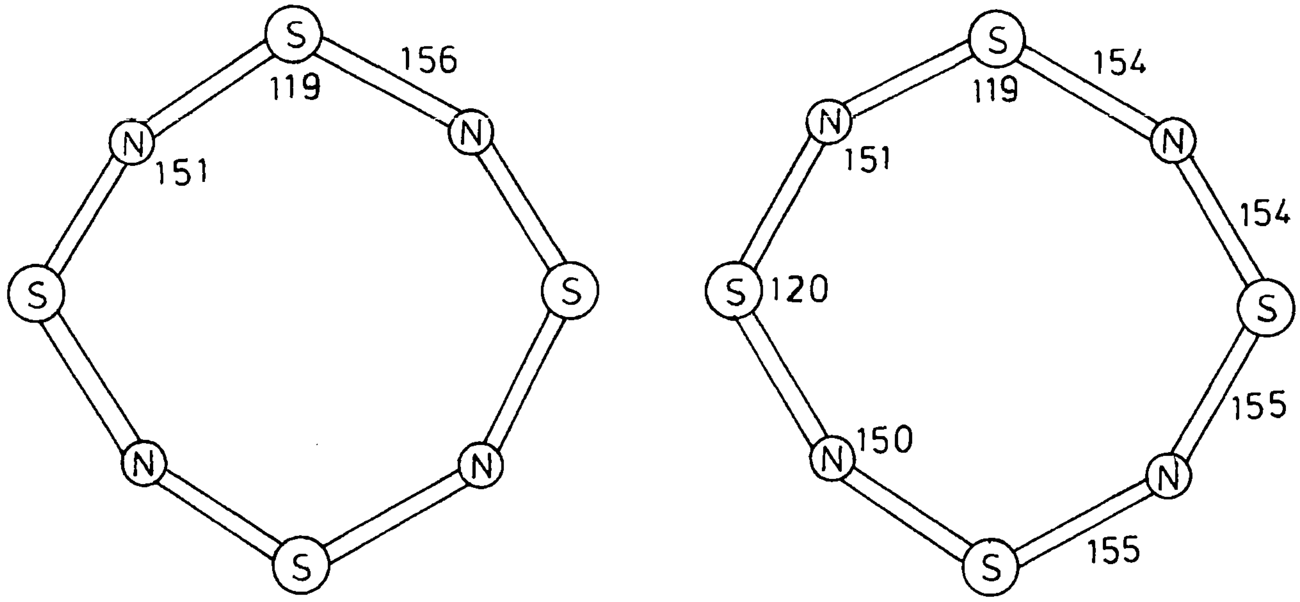
Table 1.8

Structural parameters for S_4N_4 rings

	S_4N_4	$S_4N_4.BF_3$	$S_4N_4^{2+}$ prediction (structure III)
Mean $\hat{S}^o$	104.5	115.5	119.1
Mean $\hat{N}^o$	113.0	131.4	150.9
Mean d_{SN} (pm)	161.6	159.5	156.0

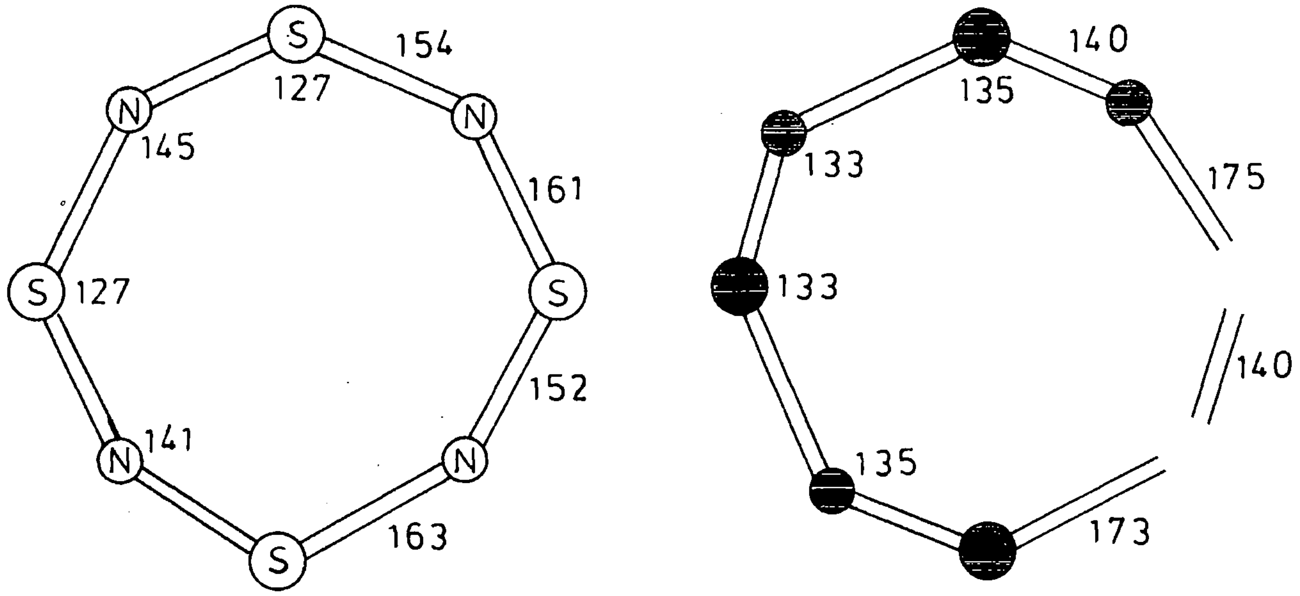
In Table 1.8 $\hat{S}$, $\hat{N}$, and d_{SN} are compared for S_4N_4, $S_4N_4^{+}\text{——}BF_3^{-}$ and octagonal $S_4N_4^{2+}$(III). The increasing positive charge and approach to planarity are accompanied by increases in $\hat{S}$ and $\hat{N}$ and decrease in d_{SN}.

We therefore conclude that $S_4N_4^{2+}$ is probably close to planar with no re-entrant atoms. However, the unusually large nitrogen



Predicted

A



B

C

Figure 1.10

(A) Structure of ring in $(S_4N_4)(SbF_6)(Sb_3F_{14})$.

(B) Structure of ring in $(S_4N_4)(SbF_6)(Sb_3F_{14})$.

(C) Structure of ring in $(S_4N_4)(SbCl_6)_2$ viewed down the S_4 axis S atom and N atom disorder (hence equal bond angles).[120]

angles involved might cause slight buckling of the ring at nitrogen. An alternative structure consisting of two fused close-to-planar 5-membered rings, and with the angle between planes of the two rings at 100°, seems less likely.

After this work had been submitted for publication an X-ray crystallographic study was carried out on the $(S_4N_4)^{2+}$ cation[120]. It was found that the cyclic cation had different structures in different molecular environments (Figure 1.10). Unfortunately, no e.s.d.'s are given and structure (C) shows considerable disorder.

However, the predicted structure is virtually the same as structure (A) and this structure has been shown to be more stable than (B), from CNDO/2 calculations (Chapter 8).

This method of predicting structures has thus been shown to be remarkably accurate.

CHAPTER 2

Sulphur Nitrogen and Sulphur Oxygen Stretching Wavelength Correlations with Bond Distance

Introduction

Since sulphur nitrogen bonds can have formal bond orders from 1 to 3, there is a wide range of bond distances (141-178 pm), vibrational stretching frequencies (590-1690 cm^{-1}) and force constants (179-1268 Nm^{-1}). A survey of these parameters for organic and inorganic sulphur-nitrogen compounds has shown that there are linear correlations between $\nu_{asym}(SN_2)$ and $\nu_{sym}(SN_2)$ for NSN systems, and between the sulphur-nitrogen stretching wavelength and the bond distance for acyclic SN compounds. The SN distances derived from the SN stretching wavelength are compared with those predicted from force constants. A linear relationship between the SO stretching wavelength and the SO bond length is also reported. Using these correlations and the relationships derived in Chapter 1 between the nitrogen and sulphur angles and the SN distance, the structures of some sulphur-nitrogen and sulphur-nitrogen-oxygen compounds are deduced from vibrational data.

Discussion

$\nu_{asym}(SN_2) - \nu_{sym}(SN_2)$ Relationship.

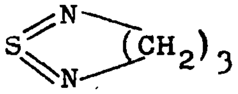
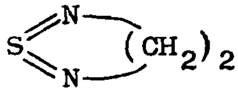
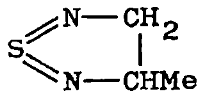
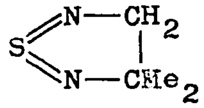
In sulphur-nitrogen chemistry, the frequencies of the S=N vibrations often overlap and may be confused with S=O or C-F bond vibrations and SN single bond absorptions often occur in the same region as ν_{S-F}. Consequently empirical guides can be of value in locating these vibrations especially if they are largely associated with particular bonds and these can be used in deducing structural parameters.

Robinson[30] has shown, for inorganic and organic sulphuryl compounds, that there is a linear correlation between the symmetric and asymmetric $> SO_2$ stretching frequencies because the $> SO_2$ stretching vibrations were found to be essentially free from mass and coupling effects[30]. It has been shown that there is a linear relationship between symmetric and asymmetric -NSO stretching frequencies[28] although the correlation is not as good as for the $> SO_2$ groups. A variety of S^{VI},S^{IV} and S^{II} di-imides give rise to symmetric and asymmetric stretching frequencies. The data for these compounds are reported in Table 2.1 and plotted in Fig.2.1.

Table 2.1

Table of the Asymmetric and Symmetric Stretching Frequencies for SN Compounds.

Compound	ν_{asym} cm^{-1}	ν_{sym} cm^{-1}	ref.
$S(F_2):(NSiMe_3)_2$	1430	1258	121*
$S(F_2):(NC_2F_5)_2$	1429	1242	122*
$S(F_2):(NCF_3)_2$	1404	1235	122*
$S(F_2):(NSF_5)_2$	1350	1280	123
$Me_3SiN:S:nCl$	1315	1225	124
MeSi(N:S:N)SiMe	1312	1190	125
$S:(NP_3N_3F_5)_2$	1270?	1185	126
$S:(NSiCl_2Me)_2$	1258	1177	127
$Me_3SiN:S:NSNR_2$	1255	1187	128
$S:(NSiClMe_2)_2$	1250	1154	127
$S:(NSiMe_3)_2$	1242	1140	127
"	1240	1135	124
$S:(NSiCl_2Et)_2$	1238	1176	127
$S(N:S:NSiMe_3)_2$	1200	1173	124

Compound	ν_{asym} cm^{-1}	ν_{sym} cm^{-1}	ref.
$MeAs(N{:}S{:}N)_2AsMe$	1190	1066	129*
$S{:}(NSnMe_3)_2$	1175	1060	130
$S{:}(NSCF_3)_2$	1171	1105	131
$HN{:}S{:}NCl$	1140	988	124
$HN{:}S{:}NBr$	1139	988	124*
$S{:}(NSPh)_2$	1138	1087	132
	1135	1020	133
7x $S{:}(NSO_2R)_2$	1135-1130	1055-1035	134
$S{:}(NBr)_2$	1127	1035	135*
$Me_3CN{:}S{:}NSiMe_3$	1105	1035	136
$S{:}(NI)_2$	1094	1047	135*
$(SN_2O_2)^{4-}$	1080	935	137
	1080	1000	133
	1075	1010	133
	1075	1000	133
S_2N_2AsMe	1050?	930?	138
$S(N{:}S{:}NSiMe_3)_2$	1020?	985	124
$Tos{-}N{:}S{:}NCH{:}CR_2$	1010	963	139
S_3N_2O	981	910	140*
$S(Et_2){:}(NH)_2$	980-960	922	141
$S(Me)(C_{12}H_{25}){:}(NH)_2$	980-960	925	141
$S(Me_2){:}(NH)_2$	962	918	141
$SO_2(NH_2)_2$	929	902	142, 143
$SO_2(ND_2)_2$	902	868	142, 143
$(S(Me)(NMe_2)_2)^+$	752	690	144
$S(O)(NMe_2)_2$	678	664	145

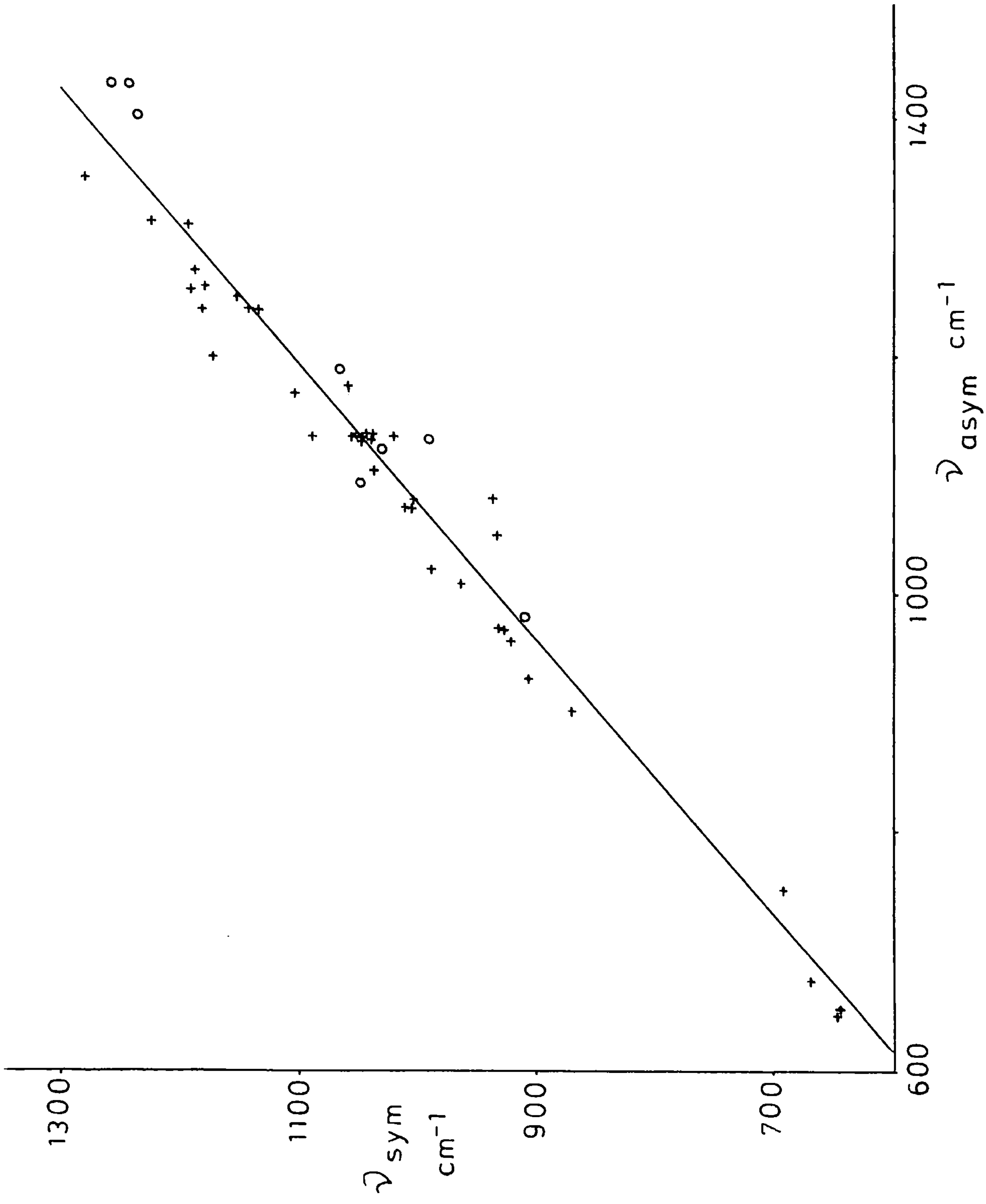


Figure 2.1

The graph of $\nu_{asym}(SN_2)$ versus $\nu_{sym}(SN_2)$:- "o" denotes assignments made by the present author.

Compound	ν_{asym} cm^{-1}	ν_{sym} cm^{-1}	ref.
$S(O)(NMe_2)_2$	654	642	145
$S(NMe_2)_2$	645	645	145

* denotes assignments made by the present author.

It is found that there is a linear relationship between $\nu_{asym}(SN_2)$ and $\nu_{sym}(SN_2)$ and that more symmetrical molecules generally lie close to the line. $\nu_{asym} = 1.151\ \nu_{sym} - 73.1$, correlation coefficient - 0.9752. As the frequencies decrease, the symmetric and asymmetric frequencies merge at about 650 cm^{-1} and so in compounds of the type $S(NR_2)_2$, only one SN absorption can be found in the infra-red spectrum as shown in the table. The above correlation can be used to characterise $\nu_{asym}(SN_2)$ and $\nu_{sym}(SN_2)$ from lists of unassigned spectra. Table 2.2 lists the published spectra[135] of $S:(NI)_2$ and $S:(NBr)_2$.

Table 2.2

Spectra of $S:(NI)_2$ and $S:(NBr)_2$[135].

$S:(NI)_2$	Infra-red	1094 s	1047 vs	950 s	631 s	465 m
$S:(NBr)_2$	Infra-red	1127 s	1035 vs	921 s	657 s	603 m
"	Raman	1133 w		926 vs	666 m	608 m

The highest frequency must be assigned to $\nu_{asym}(SN_2)$; $\nu_{sym}(SN_2)$ would therefore be expected in the region ~1030 cm^{-1} from Fig. 1. Bands at 1047 cm^{-1} and 1035 cm^{-1} are therefore assigned to $\nu_{sym}(SN_2)$ for $S:(NI)_2$ and $S:(NBr)_2$ respectively.

Sulphur-nitrogen Bond Distance - Stretching Wavelength Correlations.

The best deductions of bond-lengths from spectral data rely on force constant - bond length correlations. However, rigorous calculations of force constants have been made for very few S-N species and many force constant determinations appear to disagree either because the assignments of vibrational spectra differ or because the bond distances and angles have not been measured or estimated correctly. Glemser et al[146] produced the bond length - force constant relationship $f_{SN}.r_{SN}^{7.00} \doteq 1.45 \times 10^{16}$ — (1), where f_{SN} is in Nm^{-1} and r_{SN} is in pm., and used this to predict SN distances for a variety of compounds from their force constants. However, they obtained the relationship with just eight points from five compounds.

It is also possible to predict SN bond lengths from infra-red data since there are correlations between SN bond distance and stretching frequency or wavelength[28,29]. However, the accuracy of these correlations is limited by the small amount of data available at the time and the use of ring mode S-N frequencies.

There is now a wealth of infra-red data available but only data for acyclic species will be used. In order to have points with small SN bond orders it is necessary to consider species with groups attached to the sulphur and (or)nitrogen. This involves perturbation of the SN vibration. However, if the coupling between the attached groups and the SN vibration is small and there are no serious intermolecular interactions, the observed frequency should be close to the "pure" frequency.

An approximate value of the force constant may be obtained by treating the sulphur-nitrogen groups as simple diatomic molecules, provided the frequencies are averaged using Lehmann's rule[146] for SN_2 groups (Lehmann showed that for an AB_x group where the asymmetric stretch has a degeneracy (x - 1) then $\nu_{AB} \approx \frac{1}{x}[\nu_{sym} + (x - 1)\nu_{asym}]$). Thus the force constant:-

$$f_{SN} = \frac{5.889\,\nu_{SN}^{2} \times 10^{-6}}{1/m_S + 1/m_N} = 5.735\,\nu_{SN}^{2} \times 10^{-6} \qquad (2)$$

where f_{SN} is in Nm^{-1} and m_S and m_N are the atomic weights of sulphur and nitrogen respectively.

By combining (1) and (2)

$$\nu_{SN} = 5.028 \times 10^{10} r^{-3.5} \qquad (3)$$

and $$\lambda_{SN} = 1.989 \times 10^{-7} r^{3.5} \qquad (4)$$

It is therefore possible to predict the SN bond length purely from the stretching wavelength or frequency but this method introduces three inaccuracies; i) the force constant - bond length relationship, ii) the assumption that the SN stretching frequency is a pure vibration and iii) That the SN or SN_2 groups act as diatomic molecules.

It was therefore decided to collect the available bond length (d_{SN}) and stretching wavelength (λ_{SN}) data with a view to establishing a purely empirical relationship. It was found from a least squares fit that:-

$$d_{SN} = 4.672\,\lambda_{SN} + 110.12 \qquad \text{Correlation coefficient } +0.9894 \qquad (5)$$

where d_{SN} is in pm and λ is in microns. The existence of this relationship implies that the S-N bond vibration is remarkably unperturbed by the addition of groups to the sulphur or nitrogen for the compounds studied since the deviation from the straight line (5) is generally less than 2 pm.

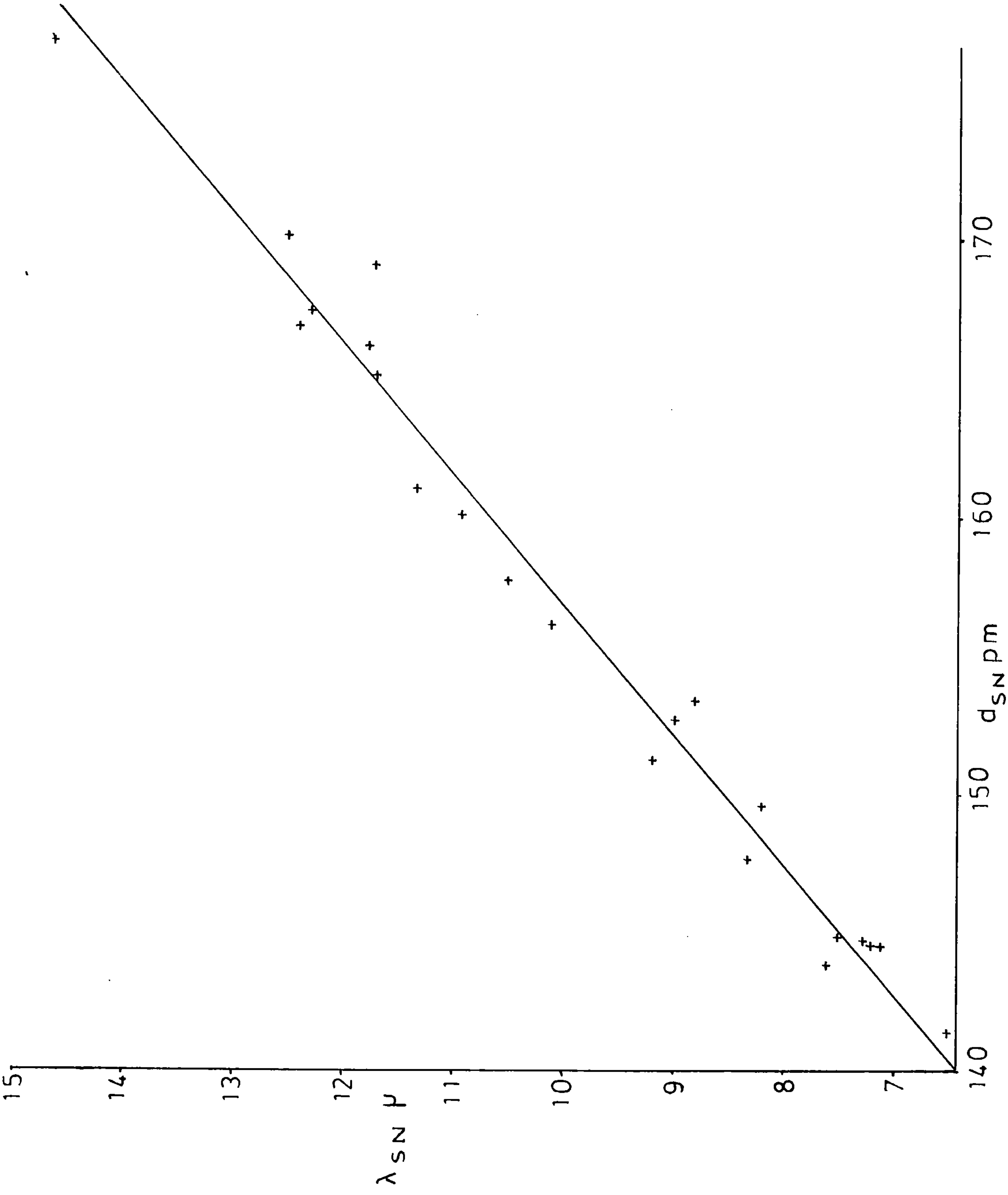


Figure 2.2

The graph of bond length (d_{SN}) pm against stretching wavelength (λ_{SN})μ for SN species.

Table 2.2.

Experimental and Deduced Parameters for Sulphur Nitrogen Compounds

Compound	λ_{SN} μ	f_{SN} Nm^{-1}		d_{SN} pm			
	exp.	exp.	ded.	** exp.	ded.A	ded.B	ded.C
NSF_3	6.56[147]	1268[147]	1332	141.6[148,149]	140.7	141.6	140.6
		1255[151]				141.8	
		1240[148]				142.1	
$(SN)^+$	6.96[152]	1185[152]	1184		142.6	143.0	143.0
$Hg(NSF_2)_2$	7.62[153]	990[154]	989	143.9[155]	145.7	146.7	146.7
CF_3NSF_2	7.13[156]		1128	144.7(6)[157]	143.4		144.0
$SN(C^{2\ +})$	7.14[158]	1127[159]	1126	144.7[158]	143.5	144.0	144.0
NSF	7.29[148]	1070[160]	1080	144.8[149,160]	144.2	145.1	144.9
		1071[149,161-2]				145.1	
		1072[151]				145.1	
		1094(6)[163]				144.7	
NSCl	7.54[164]	1003[162,165-6]	1010	145.0[165]	145.3	146.5	146.3
		1010[164]				146.3	
		1041(10)[163]				145.7	
NSBr	7.62[164]	988[164]	989		145.7	146.8	146.7
cis-HOSN	7.57[167]	990(1)[167]	1002		145.5	146.7	146.5
$ClNSF_2$	8.33[152]	820[168]	826	147.7(3)[169]	149.0	150.7	150.5
$INSF_2$	8.10[154]	870[154]	875		148.0	149.5	149.3
$SN(X^2II)$	8.20[158]	853[159]	852	149.6[158]	148.4	149.8	149.8
$BrNSF_2$	8.23[154]	848[154]	847		148.6	150.0	150.0
trans-HNSO	10.18[170]	530(4)[170]	553		157.7	160.4	159.4
cis-HNSO	9.21[171]	647(6)[171]	677	151.2(5)[91]	153.1	155,9	154.9
* $Me_2S(O)NH$	10.30[141]		541	152.1(3)[172]	156.8		159.9
$S(NSPh)_2$	8.99[132]		710	152.9(5)[44]	152.1		153.8
$(N(SCl)_2)^+$	8.85[72]		732	153.5(8)[72]	151.5		153.2
* $Me_2S(NH)_2$	10.64[141]		507	153.6(6)[96]	158.2		161.4
ClNSO	10.11[173]		561	156.1(4)[88]	157.4		159.1

Compound	λ_{SN} μ exp.	f_{SN} N m^{-1} exp.	ded.**	d_{SN} pm exp.	ded.A	ded.B	ded.C
$FNSF_2$	8.70[154]	760[154]	759		150.8	152.4	152.4
$SN(A^2{}_{3/2})$	10.52[158]	519[159]	519	157.7	159.3	160.9	160.9
$SO_2(NH_2)_2$	10.92[142-3]	366[142]	480	160.0(9)[174]	161.4	169.2	162.6
		542[143]				159.9	
$CH_3SO_2NH_2$	11.35[175]	374[175]	445	161.0[176]	163.2	168.6	164.4
$(PhCHN)_2S_4$	11.72[177]		418	165.1(6)[178]	164.9		165.9
$(PhCHN)_2S_3$	11.76[177]		415	166.1(3)[179]	165.1		166.1
$(NH_2SO_3)^-$	12.42[180]		385	166.6(6)[181]	168.2		168.7
$Et_2SNCOCH_2Cl_2$	12.28[182]		380	167.3[182]	167.5		168.2
* $S(NMe_2)_2$	15.50[145]		239	168.6(4)[183]	178.8		179.7
$(PhCHN)_2S_2$	11.75[177]		415	169.0(3)[184]	165.0		166.0
* $S(O)(NMe_2)_2$	15.36[145]		243	169.3(4)[183]	178.2		179.3
Me_2NSO_2F	13.91[185]	307[185]	297		175.1	173.5	174.3
* Me_2NSO_2Cl	13.93[185]	303[185]	296	169.0(2.0)[186]	175.2	173.8	174.3
Me_2NSO_2Br	14.12[185]	301[185]	288		176.1	173.9	175.0
$SN(B^2II)$	12.50[158]	367[159]	367	170.0[187]	168.5	169.1	169.0
trans-HSNO	18.39[171]	179[171]	170		196.1	187.3	188.7
Me_3NSO_3	16.08[188]	256[188]	222		185.2	178.1	181.6
		300[189]				174.0	
H_3NSO_3	14.66[190-1]	220[190]	267	177.2(1)[192]	178.6	181.9	176.9
		270[193]				176.7	
		310[189]				173.2	

*-compounds not used in calculation for equation (5)

**-deduced from equation (2)

A-deduced from equation (5)

B-deduced from equation (1)

C-deduced from equation (4)

In Table 2.3 the following data are listed:

1) experimental wavelengths,
2) experimental force constants,
3) force constants determined from equation (2),
4) experimental bond lengths,
5) bond lengths determined from equation (5),
6) bond lengths determined from equation (1), and
7) bond lengths determined from equation (4), for a large

variety of sulphur-nitrogen species. Points for species that have been starred (*), lie a long way from line (5) because they are either strongly hydrogen bonded e.g. $Me_2S(O){:}NH$ and $Me_2S(NH)_2$, and the stretching frequencies are thus reduced, or the compounds contain the $-S-NR_x$ group (R = Me, Et etc., x = 2,3) which give very low S-N stretching frequencies because the $-NR_x$ group acts like an increased mass.

The only other species that lies a long way from line (5) is trans-HSNO to which $\nu_{SN} = 542\ cm^{-1}$ and $f_{SN} = 179(2)\ Nm^{-1}$ have been assigned based on an expected r_{SN} of 170 pm[171]. Using equation (5) a stretching frequency around 780 cm^{-1} is required for this bond length. While no such band is observable in the parent a band at 789.7 cm^{-1} is observed in the radical SNO· and there are no bands in the 540 cm^{-1} region for this radical. The author suggests that the band at 789.7 cm^{-1} is the SN stretching absorption for trans-HSNO and not the SNO bend described by Tchir et al[171].

Sulphur-Oxygen Bond Length - Stretching Wavelength Correlations.

Gillespie and Robinson[109] plotted log f_{SO} versus log d_{SO} for various sulphur oxygen compounds and obtained the relationship

$$f_{SO}d_{SO}^{7.4} = 1.41 \times 10^7 \qquad (6)$$

Combining this equation with the relationship between SO stretching frequency (obtained using Lehmann's rule for SO_x groups) and the SO force constant,

$$f_{SO} = \frac{5.889\nu_{SO}^{2} \times 10^{-2}}{1/m_S + 1/m_O} = 0.6282\,\nu_{SO}^{2} \qquad (7)$$

they derived the relationship:-

$$\nu_{SO} = 1.203 \times 10^{11}\ d_{SO}^{-3.7} \qquad (8)$$

where d_{SO} is in pm and ν_{SO} is in cm^{-1}. This equation is subject to the same inaccuracies as equation (4) for sulphur-nitrogen compounds, so in Fig. 2.3 the wavelength $\lambda_{SO}(\mu)$ is plotted against the bond length d_{SO}(pm) for the compounds in Table 2.4. A least squares calculation for these points gives the empirical relationship:-

$$\lambda_{SO} = 0.251\ d_{SO} - 27.809 \qquad \text{Correlation coef. } 0.9776 \qquad (9)$$

The scatter of points is as expected for 1 e.s.d.(in d_{SO}). In Table 2.4, the following data are listed:-

1) the experimental wavelengths,

2) the bond lengths calculated from equation (8),

3) the bond lengths calculated from equation (9) and

4) the experimental bond lengths for a variety of sulphur-oxygen species and it can be seen that the empirical relationship (9) gives much better agreement with experiment than equation (8).

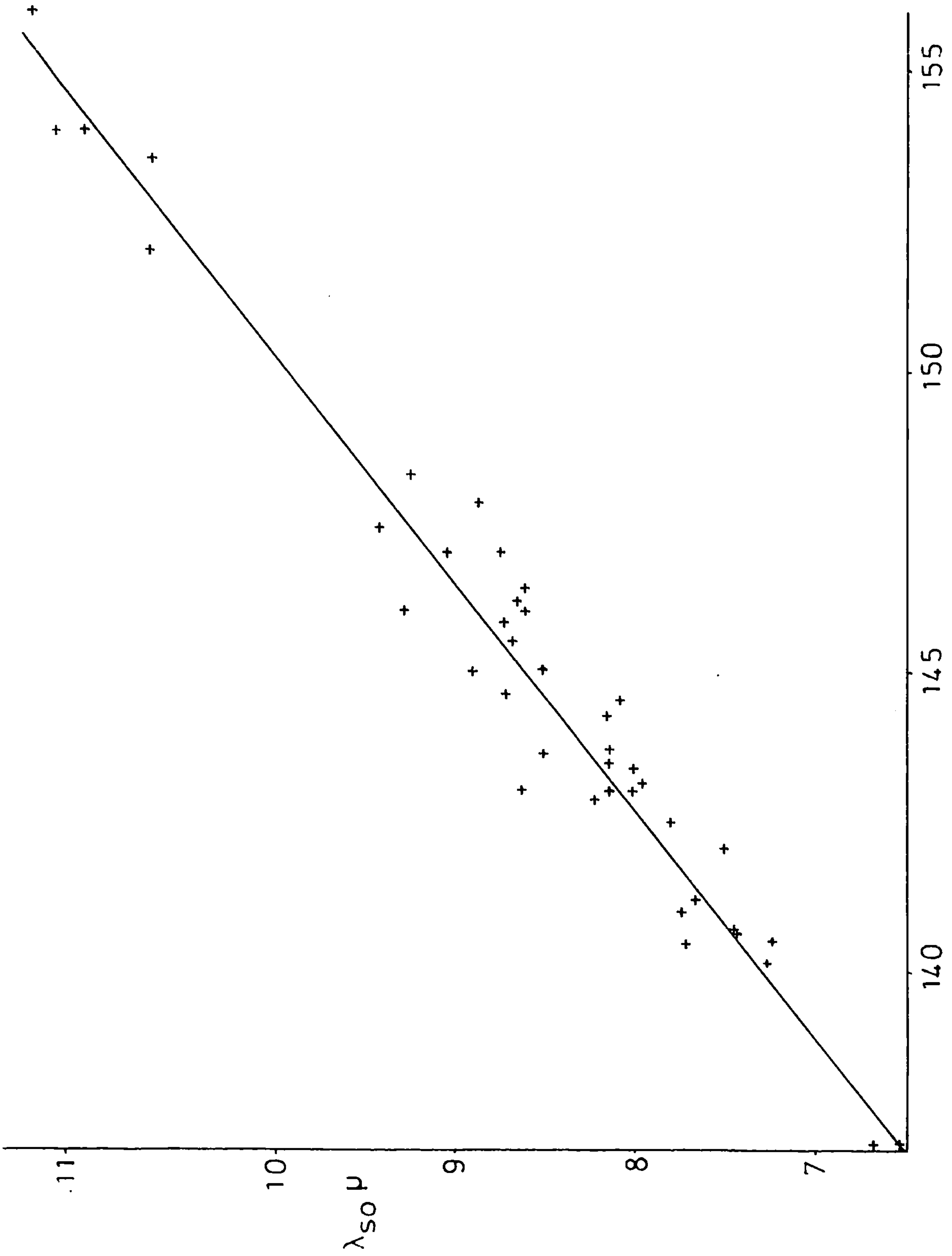


Figure 2.3

The graph of bond length (d_{SO}) pm against stretching wavelength (λ_{SO})μ for SO species.

Table 2.4

Experimental and Deduced Parameters for Sulphur-Oxygen compounds.

Compound	λ_{SO} μ	d_{SO} pm		
		exp.	deduced from equ.9	deduced from equ.8
$(SOF_3)^+$	6.51[194]	137.0(1.0)[195]	136.7	136.1
$S(NSO)_2$	8.45[196]	137.0[71]	144.5	146.0
$(SO_3)_3$ axial	6.66[197]	137.1(1.3)[86]	137.3	136.9
$SO_2(NH_2)_2$	7.97[143]	139.1(1.0)[174]	142.5	143.7
$(SO_3)_3$ average	7.27[197]	140.1(1.3)[86]	139.8	140.2
SO_2Cl_2	7.70[198]	140.4(4)[199]	141.5	142.4
SO_2F_2	7.22[198]	140.5(3)[200]	139.6	139.9
$(SNOCl)_3$	7.44[201]	140.7(7)[68]	140.4	141.1
$(MeNSO_2)_3$	7.45[202]	140.8(1)[203]	140.5	141.1
$(SNOF)_2(SNOPh)$	7.74[204]	141.0(2.0)[65]	141.6	142.6
SOF_2	7.65[198]	141.2(1)[87]	141.3	142.1
$(SNOCl)_2(PNCl_2)$	7.49[205]	142.1(1.3)[66]	140.6	141.3
$SO_2(OH)_2$	7.81[206]	142.5(1.0)[207]	141.9	142.9
$(S_3N_3O_4)^-$	8.20[208]	142.8(3)[52]	143.5	144.8
$(SO_3)_3$(equatorial)	8.00[197]	143.0(1.3)[86]	142.7	143.8
SO_3	8.13[197]	143.0(2.0)[209]	143.2	144.5
$(S_2O_6)^{2-}$	8.61[210]	143.0[211,212]	145.1	146.7
SO_2	7.94[30]	143.1(0)[213]	142.4	143.6
$(S_4N_5O)^-$	8.00[214]	143.3(4)[46]	142.7	143.9
$S(Me_2)O_2$	8.15[215]	143.5(3)[216]	143.3	144.6
SO_3NH_3	8.48[217]	143.6(1)[192]	144.6	146.1
$SOCl_2$	8.14[198]	144.3(6)[216]	143.2	144.5
$S_4N_4O_2$	8.07[208]	144.5(2.0)[62]	142.9	144.2
$(S_2O_7)^{2-}$	8.13[30]	143.7(4)[218]	144.0	145.3

Compound	λ_{SO} μ	r_{SO} pm		
		exp.	deduced from equ.9	deduced from equ.8
$(SNO_2)_3^{3-}$	8.70[219]	144.6(6)[69]	145.5	147.2
$(HN(SO_3)_2)^{2-}$	8.49[30]	145.0[220]	144.6	146.2
$SOBr_2$	8.92[221]	145.0(2.0)[222]	146.3	148.1
$(SO_3NH_2)^-$	8.67[30]	145.5(4)[181]	145.3	147.0
S_2O_2	8.70[223]	145.8(2)[223]	145.5	147.2
$(S_2O_3)^{2-}$	9.26[224]	146.0(2.0)[225]	147.7	149.7
$(EtO.SO_3)^-$	8.56[30]	146.0[226]	144.9	146.5
$(CH_2(SO_3)_2)^{2-}$	8.63[30]	146.1(5)[218]	145.2	146.6
S_2O	8.58[227]	146.4(1)[228]	145.0	146.6
$(SO_3OH)^-$	8.72[206]	147.0(1.5)[229]	145.5	147.2
$S(Me_2)O$	9.02[230]	147.0(3.0)[231]	146.7	148.6
$(SO_4)^{2-}$	9.42[232]	147.4(8)[233]	148.3	150.3
$R_2C_2N_2SO$	8.85[234]	147.8(5)[100]	146.1	147.8
S_8O	9.22[235]	148.3(9)[236]	147.5	149.5
$Me_2SO.BF_3$	10.66[237]	152.0[238]	153.3	155.5
$SO_2(OH)_2$*	10.65[206]	153.5(1.5)[207]	153.2	155.5
$Me_2SO.SnCl_4$	10.87[237]	154.0[238]	154.1	156.3
	11.05[237]	154.0[238]	154.8	157.0
$(SO_3OH)^-$	11.17[206]	156.0[229]	155.3	157.4

* refers to S-OH stretching wavelength and bond distance.

Only two points lie more than 3 pm. from the line viz. $S(NSO)_2$ and $SO_2(NH_2)_2$. $S(NSO)_2$ has already been described in Chapter 1 as probably having an inaccurate crystal structure.

Robinson found that as the effective electronegativity of the X group in SO_2X_2 molecules increased, there was a corresponding decrease in the SO bond length and stretching frequency. He compiled an order of effective electronegativity of groups attached to SO_2 moieties:-

$$F > OF > CF_3 > OR \simeq OH > Cl \simeq CCl_3 > SR \simeq NH_2 > Ar > R$$

The SO bond length and ν_{SO} frequencies of $SO_2(NH_2)_2$ (d_{SO} = 139.1(1.0) pm, ν_{SO} 1350, 1163 cm^{-1}) should therefore lie between those of SO_2Cl_2 (d_{SO} = 140.4(4) pm, ν_{SO} 1414, 1182 cm^{-1}) and $S(Me_2)O_2$ (d_{SO} = 143.5(3) pm, ν_{SO} 1310, 1143 cm^{-1}). It appears that in sulphamide either hydrogen bonding is reducing the SO frequencies even though there appears to be no reduction in the S-N frequency, or the crystal structure is at fault.

Structure Deduction

The equations (5) and (9) allow the prediction of S-N and S-O distances with an accuracy generally greater than ± 2 pm. (66% of SN predictions within 1.4 pm and 66% of SO predictions within 1.0 pm.). Using the equations (10) - (12) relating the $S\hat{N}S$ and $N\hat{S}N$ angles with S-N distance[239,240].

$d_{SN} = 176.2 - 0.128\hat{N}$ (10) unstrained $\hat{N}$ angles $< 130°$

$d_{SN} = 179.8 - 0.158\hat{N}$ (11) $S\text{-}N\text{-}S^{(IV)}$ angles $> 130°$

$d_{SN} = 219.2 - 0.531\hat{S}$ (12) unstrained S angles

It is possible to deduce the $S\hat{N}S$ and $N\hat{S}N$ angles purely from the stretching frequency.

Table 2.5 lists predictions made from these equations.

Table 2.5

Predicted Parameters for Some Acyclic S-N and S-O Compounds.

Compound	λ_{SN} μ	Predicted r_{SN}	λ_{SO} μ	Predicted r_{SO}	Pred. $S\hat{N}S$	Pred. $N\hat{S}N$	Ref.
$(SOClF_2)^+$			6.82	138.0(1.0)			241
SO_2ClF			7.46	140.5(1.0)			206
FNSO	9.93	156.5(1.4)	8.03	142.8(1.0)			242
$AsF_5.NSF_3$	6.06	138.4(1.4)					243
F_5SNSF_2	7.58	171.6(1.4)			132(6)		244
	13.16	145.5(1.4)					244
$((Ph_2S)_2N)^+$	10.75	160.4(1.4)			125(8)		245
$(SN_2O_2)^{4-}$	9.26	156.5(1.4)	11.24	158.4(1.0)		117(2)	246
	10.70		12.74				246
$F_2S(NSF_5)_2$	7.41	145.7(1.4)				138(2)	123
	7.81						123
$S(NI)_2$	9.14	153.7(1.4)				123(2)	135
	9.55						135

These predictions are based on purely empirical correlations but by comparing the deduced parameters with those of known structure, the strength of this method may be appreciated.

The crystal structure of $(SOClF_2)(AsF_6)$ has been studied[247] but the positions of the fluorine and oxygen atoms could not be determined uniquely due to rotational disorder about the S-Cl axis. The average S-X (X = F or O) distance was 143 pm, thus the predicted S-O distance (138(1)pm) (Table 2.5) requires an S-F distance of 145 pm. These two distances are very close to the S-O (137 pm) and S-F (145 pm) bond lengths found in the related compound $(SOF_3)(AsF_6)$[195].

The S-O bond length in SO_2ClF of 140.5(1.0) pm appears to be a good prediction when it is compared with the S-O bond lengths of related compounds (Table 2.6)

Table 2.6

S-O Bond Distances for SO_2X_2 Species

	Me	Cl	F
Me	143.5(3)[216]	142.4(3)[248]	141.0(3)[249]
Cl		140.4(4)[199]	140.5(1.0)*
F			140.5(3)[200]

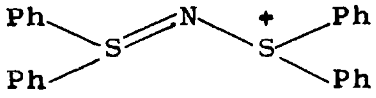
* prediction

The predicted bond lengths for FNSO (d_{SN} = 156.4(1.4), d_{SO} = 142.8(1.0) pm) are very similar to those of the related thionyl imide ClNSO (d_{SN} = 156.1(4), d_{SO} = 144.5 (4) pm)[90].

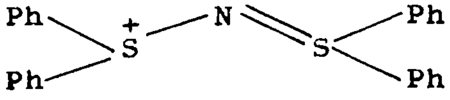
Lewis acids form many adducts with NSF_3 by coordinating through the nitrogen and there is a subsequent change in ν_{SN} ($\Delta\nu$= 135 cm^{-1}) and ν_{SF} ($\Delta\nu$= 139,114 cm^{-1}). This effect also occurs in nitriles[250] and the increase in force constant can be attributed to an increase in nitrogen lone pair "p" character and the "s" character of the S≡N bond leading to strengthening of the S-N σ-bond[251]. A shorter S-N bond length is therefore expected in $AsF_5.NSF_3$(138.4(1.4) pm) than in NSF_3 (141.6 pm)[148,149].

If the predicted parameters for $F_5SN:SF_2$ (d_{S-N}= 171.6(1.4) pm, $d_{S=N}$ = 145.5(1.4) pm, $S\hat{N}S$ = 132(6)°) are compared with those published for $CF_3N:SF_2$ ($d_{S=N}$ = 144.7(6) pm, $C\hat{N}S$ = 130.4(7)°)[157] and F_5S-NF_2 (d_{S-N} = 170.0(5) pm)[252], then the proposed bond lengths and angles are almost within experimental error. The slightly larger bond lengths and angles could be due to flourine-flourine repulsions.

The species $(Ph_2SNSPh_2)^+$ can be described by two canonical forms, I and II.



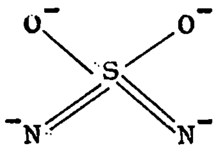
I



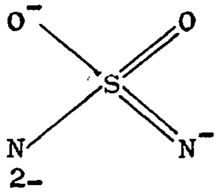
II

A similar compound $(Me_2SNSMe_2)(Br).H_2O$ was found to have d_{SN} = 163.5(4.0) pm and $S\hat{N}S$ = 110.8(2.0)° [35]. The discrepancy between the predicted $S\hat{N}S$ (125(8)°) and this published structure may be due to steric hinderance of the phenyl groups which would open out the $S\hat{N}S$ angle.

The anion $(SN_2O_2)^{4-}$ is isoelectronic with the sulphate ion. It can be described adequately by canonical III with small contributions from IV and equivalent resonance canonicals.



III



IV

The predicted parameters (d_{SN} = 156.5(1.4), d_{SO} = 158.4(1.0) pm and $N\hat{S}N$ = 117(2)°) are consistent with these canonicals although the actual SN species may well be polymeric as in $(Ag)_2(SO_2(NH)_2)$[253].

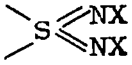
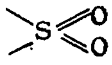
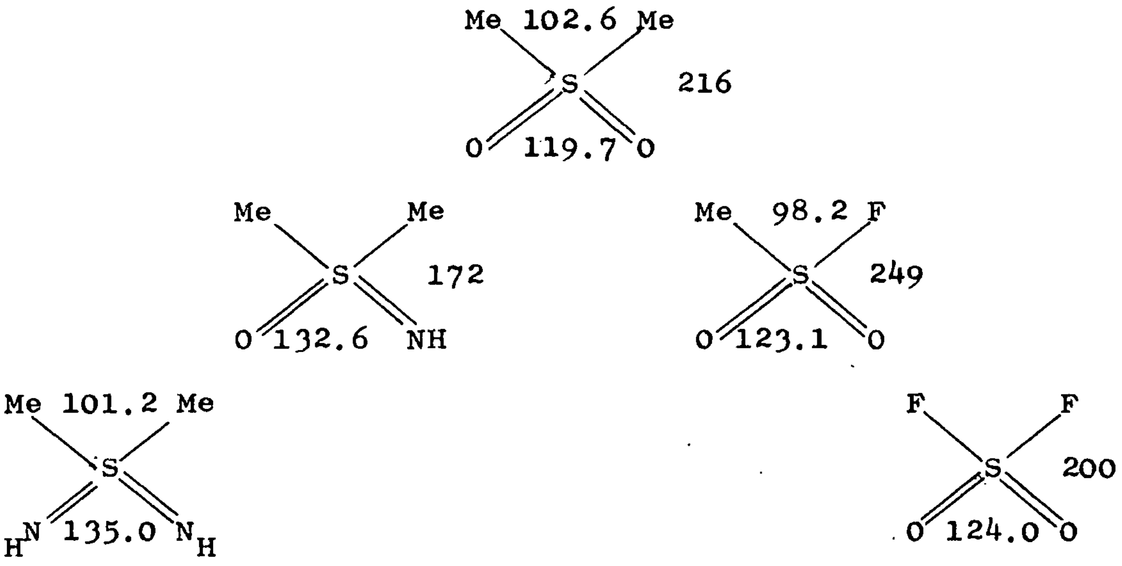
No structures of the type $F_2S{:}(NX)$ have ever been published so it is not possible to compare the predicted structure of $F_2S{:}(NSF_5)_2$ (d_{SN} = 145.7(1.4) pm, $N\hat{S}N$ = 138(2)°) with similar sulphur VI diimides. Electron diffraction studies (Table 2.7) show that as S=O is replaced by S=NH the $X\hat{S}X$ (X = O, NH) angle opens out and as S-Me is replaced by S-F the angle X$\hat{S}$X opens out also. This is because the lower electronegativity of the nitrogen σ and π orbitals causes the centre of gravity of the bonding electron cloud to lie nearer the sulphur atom in  than  as long as the electronegativity of X is less than oxygen. There is thus greater repulsion between the bonding electrons and a wider angle in the former case. Any electron withdrawing groups (e.g. -F) on the sulphur will draw this electron cloud closer to the sulphur atom and further increase the N$\hat{S}$N angle.

Table 2.7

Electron Diffraction Studies on Tetrahedrally Coordinated S-Compounds



There are many published structures of sulphur (IV) diimides e.g. S:$(NSC_6H_4Cl)_2$ (d_{SN} = 155.0(1.7) pm, N$\hat{S}$N = 124.0(1.0)^o). The predicted structure for S:$(NI)_2$ (d_{SN} = 153.7(1.4), N$\hat{S}$N = 123(2)^o) lies within one standard deviation of the known structure.

CHAPTER 3

Experimental

(A) Handling Techniques

1) Nitrogen Supply

Most of the compounds studied were air and moisture sensitive and to prevent decomposition all work was done in an atmosphere of dry nitrogen. The nitrogen was obtained as it evaporated from a tank of liquid nitrogen and dried by bubbling it through concentrated sulphuric acid and then passing it through a P_2O_5 tower. No attempt to remove oxygen was necessary as no compounds were found to be oxygen sensitive.

2) Glove Box

The atmosphere of nitrogen in the glove box was continuously recycled through a P_2O_5 tower, by means of a small pump inside the box. A dish of P_2O_5 was kept at all times inside the box to indicate how efficiently the purification system was working. A port, which was purged for thirty minutes with dry nitrogen before introduction of materials, provided a means of access. All samples for infra-red, ultraviolet, mass spectra and analysis were prepared inside the box.

3) Spectra

Infra-red spectra (250 - 4000 cm^{-1}) were recorded using Nujol mulls between KBr or AgCl plates or as potassium bromide discs on a Perkin-Elmer 457 prism grating spectrophotometer. Ultraviolet and visible spectra were obtained with a Unican SP. 800 spectrophotometer in a solution of dry acetonitrile using quartz cells of 1 and 2 cm. path length.

Mass spectra were obtained on an A.E.I MS9 mass spectrometer at 70 eV with an accelerating potential of 8 KeV. Samples were directly inserted into the ion source.

4) Analyses

Analyses of Cl, N, P,S and Sn were carried out by Mr. R. Coult and those of C,H, and N by Mrs. M. Cocks.

5) Melting Points

These were determined using thin-walled glass tubes sealed with silicone grease.

(B) Preparation and Purification of Starting Materials.

1. Solvents

Thionyl Chloride

Thionyl chloride was refluxed with flowers of sulphur for three hours and then distilled under nitrogen. The fraction boiling between 75° and 76°C was collected[245].

Sulphuryl Chloride

Analar sulphuryl chloride was distilled under nitrogen. The fraction boiling between 69° and 70°C was collected.

Sulphur Dichloride

Sulphur dichloride was purified by fractional distillation; the middle fraction (b.p. 50-62°C) was retained and refractioned (collected at 60°C)[256].

Disulphur Dichloride

Disulphur dichloride was distilled from sulphur and decolourising charcoal at atmospheric pressure and the fraction boiling at 137°C was collected. This was then redistilled from sulphur and charcoal under vacuum to give a clear yellow liquid[257].

Sulphur Dioxide

Sulphur dioxide was distilled from a cylinder into a flask, cooled to -78°C with acetone/dry ice, containing P_2O_5. The sulphur dioxide could then be vacuum distilled into a reaction vessel.

Phosphoryl Chloride

Phosphoryl chloride was distilled from P_2O_5 and the fraction boiling between 105° and 106°C was collected.

Ether, Hexane, Toluene, and Benzene

These were all dried over sodium wire[258].

Carbon Tetrachloride and Dichloromethane

These were distilled from P_2O_5 and kept over 4A molecular sieves.[258]

Pyridine

Pyridine was dried over sodium hydroxide[258].

Nitrobenzene

Nitrobenzene was distilled under reduced pressure and stored over calcium chloride.

Trichloroacetonitrile and Benzonitrile

These were dried over magnesium sulphate, fractionally distilled and stored over 4A molecular sieves.

Acetonitrile

Acetonitrile was stirred with calcium hydride until hydrogen evolution ceased. It was then decanted and distilled from phosphorus pentoxide (<5g./litre of solvent) under nitrogen. The first 5% of distillate was discarded and the rest was stored over 4A molocular sieves[259].

Carbon Disulphide

Carbon disulphide was dried with calcium chloride and fractionally distilled twice[260].

Tetrahydrofuran

Tetrahydrofuran was refluxed for eight hours with sodium/ potassium alloy and then fractionally distilled[261].

Liquid Ammonia

Ammonia was distilled from a cylinder into a flask containing sodium at -78°C (Acetone/CO_2). More sodium was added until the blue colouration became permanent. The liquid could then be distilled into the appropriate reaction vessel.

Acetic Anhydride

Acetic anhydride was fractionally distilled through a 1.5 metre column packed with glass helices[262].

Tetrahydrofurfuryl Alcohol and Cyclohexene

These were distilled under reduced pressure onto 4A molecular sieves.

Hexamethylphosphoramide ($OP(NMe_2)_3$)

Hexamethylphosphoramide was dried with sodium hydride then potassium metal was added to turn the batch completely blue. This was then distilled under vacuum onto 4A molecular sieves[263].

Nitric Acid, Ethanol (Absolute), Iodobenzene, Benzoyl Chloride, Di-N-Methyl Sulphamoyl Chloride and Hexafluoracetic Anhydride (Analar).

These were used without purification.

(C) Preparation and Purification of Reagents

Triphenylcarbonium Tetrafluoroborate

Triphenyl carbinol (4.5g, 0.017 mol.) was dissolved in propionic anhydride (45 ml.) by warming the mixture on a water bath. The solution was then cooled to 20°C and aqueous tetrafluoroboric acid (48%, 4.5 ml.) was added carefully making sure the temperature never rose above 25°C. The solution was cooled to 0°C for 30 minutes and deposited a white solid. The liquid was removed by syringe and the solid washed rapidly with three ~2.5 ml. portions of cold, dry ether, removing each portion with a syringe. The remaining ether was removed under vacuum. Yield 1.9g.

Tin(IV) Tetrachloride

Tin(IV) tetrachloride was freshly distilled at reduced pressure under nitrogen.

Tin(IV) Tetrachloride - Phosphoryl Chloride Adduct

Tin(IV) tetrachloride (1.2 ml., 0.01 mol.) and phosphoryl chloride (1.9 ml., 0.02 mol.) were mixed together and a considerable quantity of heat evolved. On cooling, large clear crystals formed mp. 52°-53°C, lit. 54.5°C[264].

Octachlorocyclopentene

Impure octachlorocyclopentene was recrystallised twice from absolute ethanol mp. 40°-41°C, lit. 39° - 40°C[265].

Boron Trichloride

Boron trichloride was distilled at 19°C.

Ferric Chloride

Ferric chloride was refluxed with thionyl chloride for one hour, filtered and then pumped to dryness. The solid was then sublimed onto a cold finger at reduced pressure.

Sodium Iodide, Ammonium Chloride and Lithium Bromide

These were dried in an oven at 110°C for two days.

Ethyldimethylsulphonium Iodide

Ethyl iodide (5.0 ml., 0.062 mol.) was added to dimethyl sulphide (4.2 ml., 0.060 mol.) in water (60 ml.) to form a 1.03 M solution of ethyldimethylsulphonium iodide.

Thiourea, Diphenyl Acetylene, Sodium Azide and Lithium Azide

These were used without purification.

(D) Preparation of Sulphur-Nitrogen Starting Materials

Chlorocyclotrithiadiazenium Chloride $(S_3N_2Cl)(Cl)$

$(S_3N_2Cl)(Cl)$ was prepared by a modification of Jolly's Method[132,267-8]. Dry ammonium chloride (200g.), sulphur(40g.) and S_2Cl_2 (200 ml.) were placed in a one litre flange head flask fitted with an air condenser (diameter 5 cm., length 1 m.) topped by a calcium chloride drying tube. The flask was heated until the refluxing S_2Cl_2 had risen to two-thirds of the way up the air condenser. Crystals of $(S_3N_2Cl)(Cl)$ slowly formed above this and the whole condenser could be filled with crystals by gradually lowering the reflux point. Once filled, the condenser was removed and the crystals scraped into a flask against a counter-current of dry nitrogen and pumped to dryness. The air condenser was replaced on the flange head flask and further crops of crystals were collected.

Cyclotetrathiatetrazene S_4N_4

S_4N_4 was prepared by the method due to Jolly[268] in which chlorine gas was passed through a solution of S_2Cl_2 in CCl_4 followed by the passage of ammonia gas for two hours. The precipitate was washed with water and then ether and extracted and recrystallised from benzene.

Trichlorocyclotrithiatriazene $(SNCl)_3$

i) From Cyclotetrathiatetrazene[269]

Excess sulphuryl chloride was added to crystals of S_4N_4 and the mixture stirred for 24 hours. The resulting yellow needles were filtered off and recrystallised from CCl_4 (10 ml/g.). A further crop of needles was obtained by pumping the filtrate to dryness and recrystallising the yellow solid from CCl_4.

ii) From Chlorocyclotrithiadiazenium Chloride $(S_3N_2Cl)(Cl)$[269].

Excess sulphuryl chloride was added to crystals of $(S_3N_2Cl)(Cl)$ and the resulting yellow suspension was evaporated to dryness leaving a yellow solid. This was recrystallised slowly from CCl_4 producing long yellow needles mp. 90-91°C, lit. 91°C[269].

Cycloazaheptasulphurane S_7NH[270]

Sodium azide (19.0g., 0.292 mol.) and sulphur (20.0g., 0.078 mol.) were added to hexamethylphosphoramide (400 ml.) and stirred at room temperature for three days during which the solution turned dark blue. The reaction mixture was then added to (400 ml.) of ice-cold 10% hydrochloric acid and a yellow precipitate slowly formed. This was filtered, washed with water and dried under vacuum(19.8g.). Extraction with ether (8 x 50 ml.) gave yellow crystals (6.8g. after evaporation of ether) which were dissolved in the minimum of CS_2 and chromatographed on silica gel to give S_8

(2.3g) and sulphur imides (4.4g.).

Each 20 ml. of elutant was evaporated to dryness and the residues weighed and the infra-red spectrum taken(table 3.1).

Table 3.1

Results

Number	Weight of Residue*	Infra-red Spectrum
1 - 5	0	
6 - 11	2.3136	sulphur
12	0.8973	3277 m, 793 m
13	0.9041	3240vs, 812 vs
14	0.9453	3240 vs, 813 vs
15	0.6579	3240 vs, 812 vs
16	0.3717	3240 vs, 812 vs
17	0.2052	3280 m, 3260 m, 797 s
18	0.1817	3258 vs, 812 s, 797 (sh)
19	0.1204	3259 s, 815 s, 797 s
20	0.0685	3259 s, 813 s, 797 (sh)
21	0.0397	3261 s, 813 s, 799s
22	0.0157	3280 m, 3263 m, 799s
23	0.0132	3285 m 797 m
24	0.0096	3285 m 797 m

Lit. S_7NH[16] 3265 m, 816 ms. * in g.

CHAPTER 4

Reactions of Diphenylmethyleneamino-Lithium with Sulphur-Chlorine Bonds

Introduction

Methyleneamino groups $R_2C{:}N$ have been attached to sulphur by three main methods:

1. by reaction of the imine, or its metallo derivative, with a sulphur halide, e.g.

   (a) $2Ph_2C{:}NH + S_2Cl_2 + 2Et_3N \longrightarrow (Ph_2C{:}N)_2S_2 + 2Et_3NHCl$[272,273]

   (b) $PhC{:}N \xrightarrow{PhMgBr} Ph_2C{:}NMgBr \xrightarrow{S_2Cl_2} (Ph_2C{:}N)_2S_2$[274,275]

   (c) $2(CF_3)_2C{:}NLi + S_2Cl_2 \longrightarrow ((CF_3)_2C{:}N)_2S_2 + 2LiCl$[276-279]

2. by reaction of a primary amine with sulphur or a sulphur source e.g.

   (a) $2PhCH_2NH_2 + (x + 3)S \xrightarrow{PbO} (PhCH{:}N)_2S_x + 3H_2S$[280,281]

   (b) $8PhCH_2NH_2 + S_4N_4 \longrightarrow (PhCH{:}N)_2S_x + 7NH_3 + 3PhCH{:}NCH_2Ph$
   $+ (4 - x)S$[177]

3. by condensation reactions of sulphamides, e.g.

   (a) $SO_2(NH_2)_2 + RR'CO \longrightarrow SO_2(N{:}CRR')_2 + 2H_2O$[282,283]

   (b) $SO_2(NH_2)_2 + \xrightarrow[\text{ii) } RR'CO\ -\ 2SO_2]{\text{i) } 2SOCl_2\ -\ 4HCl} SO_2(N{:}CRR')_2$[282]

   (c) $SO_2(N{:}PCl_3)_2 + RR'CO \longrightarrow SO_2(N{:}CRR')_2 + 2POCl_3$[282]

   (d) $SO_2(NH_2)_2 + 2RR'C{:}NH \longrightarrow SO_2(N{:}CRR')_2 + 2NH_3$[282,284]

Other methods have been used to attach chloromethyleneamino groups $RCCl{:}N$ or $Cl_2C{:}N$ to sulphur, e.g. the reaction of $RCCl{:}NCl$ with S[285], $(SCN)_2$ with Cl_2[286], ClCN with SCl_2[286] or $S(CN)_2$, with S_2Cl_2[287].

For the preparation of methyleneamino ($R_2C{:}N$) derivatives, the use of iminolithium reagents $R_2C{:}NLi$ (route 1(c) above) reportedly gives the highest yields.

In this chapter reactions between diphenylmethyleneamino-lithium, Ph_2CNLi, and the chlorides SCl_2, S_2Cl_2, $SOCl_2$ and SO_2Cl_2 have been used to prepare the compounds $(Ph_2CN)_2S$, $(Ph_2CN)_2S_2$, $Ph_2CNC(NSO)Ph_2$ and $(Ph_2CN)_2SO_2$ respectively. The disulphide $(Ph_2CN)_2S_2$ also results from the reaction between Ph_2CNLi and trichlorocyclotrithiatriazene $(SNCl)_3$. Features of the infra-red and mass spectra of the prepared diphenylmethyleneamino sulphur compounds are discussed, with particular reference to their sulphur-nitrogen bond orders.

Experimental

Diphenylmethyleneamino-lithium was prepared by adding equimolar amounts of n-butyl lithium in hexane to diphenylmethyleneamine at -196°C in ether and warming to room temperature.

Syntheses

1. Bis(diphenylmethyleneamino)disulphide, $(Ph_2C{=}N)_2S_2$

Addition of sulphur monochloride (0.7g, 0.005 mol.) to diphenylmethyleneamino-lithium (1.8g, 0.01 mol.) in hexane/ether (20 ml.) at -78°C produced a white precipitate. The mixture was filtered at room temperature, washed several times in hexane and recrystallised from ether to give yellow crystals, m.p. 177° - 178°C, (lit. 176°C)[272] yield 1.6 g (76%). I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 3056m, 3018m, 1597m, 1550w, 1449m, 1404m, 1377m, 1316m, 1297m, 1180m, 1155w, 1018w, 999w, 950m, 914w, 784m, 777m, 741w, 704s, 693s, 671w,667sh, 629w, 459w. Calcd. for $((C_6H_5)_2CN)_2S_2$: C,73.60; H, 4.71; N, 6.60; S, 15.09. Found : C, 74.51; H, 5.01; N, 6.93; S, 14.95%.

2. Bis(diphenylmethyleneamino)monosulphide, $(Ph_2C{=}N)_2S$

Addition of freshly distilled sulphur dichloride (1.2 ml, 0.015 mol) to diphenylmethyleneamino-lithium (5.4 g, 0.03 mol.) in hexane/ether (50 ml.) at -78°C gave an orange solution, which was stirred for 4 h. at 20°C, and deposited an orange-yellow precipitate. This was filtered and recrystallised from benzene to give an orange-yellow microcrystalline solid, m.p. 148-9°C, yield 4.9g.(84%). I.r. (Nujol mull) absorptions occurred (cm^{-1}) at: 3058m, 3015m, 1597w, 1545w, 1487m 1444vs, 1315w, 1296w, 1285w, 1262m, 1190m, 1155m, 1112s, 1090m, 1038m, 1008m, 960m, 926m, 860w, 815m, 787s, 764m, 728m, 712s, 700s, 675m, 648w, 627s, 565w, 440w. Major mass spectral peaks were found at m/e (relative intensities and assignments are given) : 392(48)$(Ph_2CN)_2S^+$, 360(3)$(Ph_2CN)_2^+$, 283(4)$Ph_2CNNCPh^+$, 269(3)Ph_2CNCPh^+, 212(37)Ph_2CNS^+, 180(100)Ph_2CN^+, 165(6)$C_6H_5CC_6H_4^+$, 154(17)Ph_2^+, 109(23)PhS^+, 104(30)$PhCNH^+$, 78(26)$C_6H_6^+$, 77(72)$C_6H_5^+$, 65(6)$C_5H_5^+$, 51(26)$C_4H_3^+$, 32(89)S^+. Calcd. for $((C_6H_5)_2CN)_2S$: C, 79.50; H, 5.10; N, 7.14; S, 8.16. Found: C, 79.26; H, 4.90; N, 7.11; S, 8.42%.

3. Diphenylmethyleneaminodiphenylmethylthionylimine, $Ph_2C{=}NC(NSO)Ph_2$.

Addition of thionyl chloride (1.3 ml., 0.015 mol.) to diphenylmethyleneamino-lithium (5.4 g, 0.03 mol.) in hexane/ether (50ml.) at -78°C gave a green solution which turned yellow on warming to room temperature and deposited a yellow precipitate. This was filtered and extracted with dry benzene and recrystallised from toluene to give yellow crystals m.p. 181 - 183°C, yield 5.3 g. (87%). I.r. (Nujol mull) absorptions occurred (cm^{-1}) at: 3050m, 3030w, 1598m, 1580m, 1560m, 1545vs, 1487w, 1444vs, 1377m, 1315s, 1287s, 1273sh, 1179w, 1160w, 1149w, 1130vs, 1072m, 1025m, 998w, 950m, 917m, 846w, 808w, 789m, 772s, 741w, 721s, 696vs, 638m, 615m, 568m, 427m. Major mass spectral peaks were found at m/e (relative intensities and assignments are given) : 408(2)$Ph_2CNC(Ph)_2NSO^+$, 392(4) $Ph_2CNC(Ph)_2NS^+$, 360(2)$(Ph_2CN)_2^+$, 346(6)$Ph_2CNCPh_2^+$, 283(2)$Ph_2CNNCPh^+$, 228(25)Ph_2CNSO^+, 194(5)$Ph_2CN_2^+$, 180(100)Ph_2CN^+, 165(5)$C_6H_4CC_6H_5^+$, 152(4)$PhCHNSO^+$, 104(25)$PhCHN^+$, 77(34)$C_6H_5^+$, 51(10)$C_4H_3^+$, 32(90) $S^+(O_2^+)$. Calcd. for $(C_6H_5)_2CNC(C_6H_5)_2NSO$: C, 76.47; H, 4.90; N, 6.86; S, 7.84. Found: C, 76.50; H, 4.77; N. 6.82; S, 7.96%.

4. Bis(diphenylmethyleneamino)sulphone, $(Ph_2CN)_2SO_2$.

Addition of sulphuryl chloride (1.2 ml, 0.015 mol.) to diphenylmethyleneamino-lithium (5.4 g, 0.03 mol.) in hexane/ether (50 ml.) at -78°C gave a clear solution which rapidly deposited a white precipitate on warming to room temperature. This was filtered and the clear solution evaporated leaving clear white crystals which were recrystallised from toluene m.p. 150 - 151°C (lit. 147° - 147.5°C, 143° - 145°C^{285}), yield 4.1 g (65%). I.r. (Nujol mull) absorptions occurred (cm^{-1}) at : 3051w, 3020w, 1585m, 1552m, 1477m, 1447vs, 1328s, 1290w, 1271w, 1150vs, 1065w, 1038w, 1010w, 957m, 932m, 839vs, 817m, 799m, 726s, 710vs, 699vs, 618m, 585m, 550w, 450w. Major mass spectral peaks were found at m/e (relative intensities and assignments are given) : 424(3)$(Ph_2CN)_2SO_2^+$, 408(2)$(Ph_2CN)_2SO^+$, 392(10)$(Ph_2CN)S^+$, 360(1)$(Ph_2CN)_2^+$, 346(17)$Ph_2CNCPh_2^+$, 269(3)Ph_2CNCPh^+, 228(31)Ph_2CNSO^+, 212(10)Ph_2CNS^+, 180(34)Ph_2CN^+, 164(17)$C_6H_4CC_6H_4^+$, 151(9)$PhCNSO^+$, 109(12)PhS^+, 104(100)$PhCHN^+$, 91(9)$PhCH_2^+$, 77(95)$C_6H_5^+$, 51(12)$C_4H_3^+$, 32(85)$S^+(O_2)^+$. Calcd. for $((C_6H_5)_2CN)_2SO_2$: C, 73.58; H, 4.72; N, 6.60; S, 7.54. Found : C, 73.44; H, 4.91; N, 6.25; S, 7.80%.

5. Reaction of Thionyl Chloride with Diphenylmethyleneamino-lithium 1:1.

Addition of thionyl chloride (2.6 ml, 0.030 mol.) to diphenylmethyleneamino-lithium (5.4 g, 0.030 mol.) in hexane/ether (50 ml.) at -196°C gave a yellow solution on warming to room temperature and deposited a white precipitate. This was filtered and the clear solution left to stand in the freezer. Yellow crystals were formed which were filtered, washed with ether and pumped dry. The infrared and mass spectra and the analyses were consistent with $Ph_2C{:}NC(NSO)Ph$.

6. Reaction of Trichlorocyclotrithiatriazene with diphenylmethyleneamino-Lithium.

Addition of trichlorocyclotrithiatriazene (2.4 g, 0.01 mol.) in benzene (20 ml.) to diphenylmethyleneamino-lithium (5.8 g, 0.03 mol.) in hexane/ether (50 ml.) at -78°C produced firstly a green then a red solution which deposited a brown precipitate. This was filtered and washed with ice cold ether and recrystallised from toluene to give large yellow crystals of $((C_6H_5)_2CN)_2S_2$, yield 1.6 g (26%). Major mass spectral peaks were found at m/e (relative intensities and assignments are given): 424(15)$(Ph_2CN)_2S_2^+$, 392(50)$(Ph_2CN)_2S^+$, 360(3) $(Ph_2CN)_2^+$, 283(5)$Ph_2CNNCPh^+$, 269(3)Ph_2CNCPh^+, 212(57)Ph_2CNS^+, 180(100) Ph_2CN^+, 154(20)Ph_2^+, 109(24)PhS^+, 104(15)$PhCNH^+$, 77(60)$C_6H_5^+$, 51(12) $C_4H_3^+$. Calcd. for $((C_6H_5)_2CN)_2S_2$: C, 73.60; H, 4.71; N, 6.60; S, 15.10. Found : C, 74.07; H, 5.07; N, 6.21; S, 14.87%.

Discussion

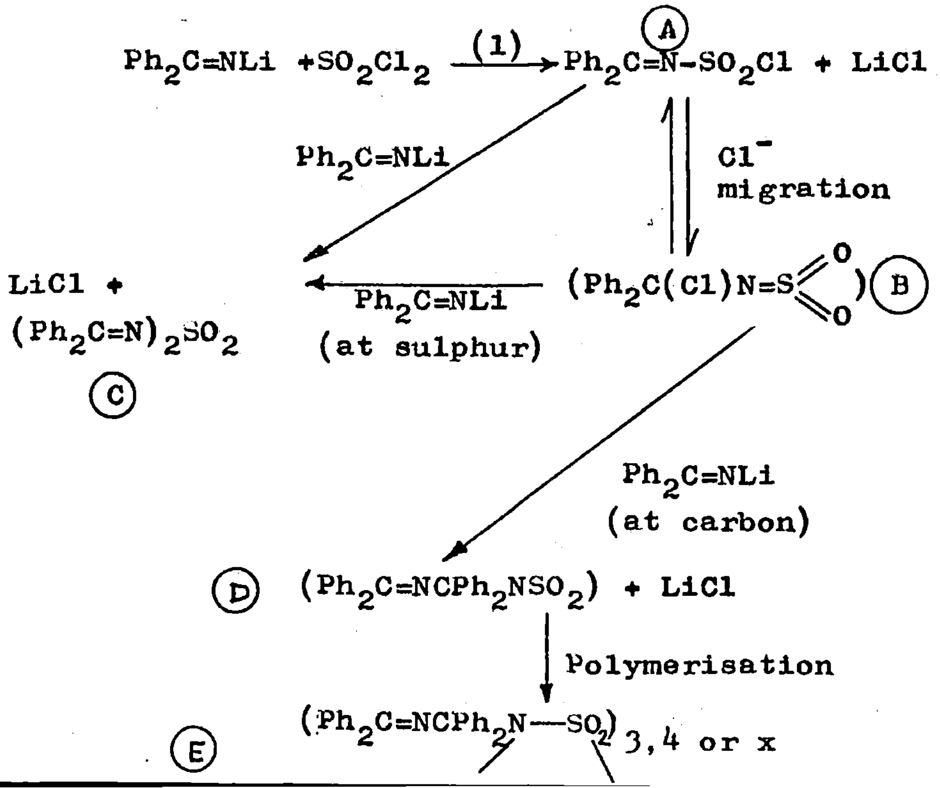
Diphenylmethyleneamino-lithium ($Ph_2C{:}NLi$) reacts with the chlorides S_2Cl_2 and SCl_2 to give good yields of $(Ph_2C{:}N)_2S_n$, (n=1,2). The corresponding reaction with $SOCl_2$ gives the N-sulphinylamine $Ph_2C{:}NC(Ph_2)NSO$ (IV) rather than the sulphoxide $(Ph_2C{:}N)_2SO$; an attempt to isolate the intermediates $Ph_2C(Cl)NSO$ or $Ph_2C{:}NS(O)Cl$ using 1:1 $Ph_2C{:}NLi$ and $SOCl_2$ gave the same product (IV). The N-sulphinylamine is probably formed by a halide ion migration reaction of the type described by Swindell et al[278] (cf. step (2) below). They found that $(CF_3)_2C{:}NLi$ and SOX_2 (X=Cl,F) react to form the N-sulphinylamine $(CF_3)_2C;N(CF_3)_2NSO$ rather than the sulphoxide $((CF_3)_2C{:}N)_2SO$, apparently because the carbon is more susceptible than the sulphur to nucleophilic attack.

$$\begin{tikzcd}
(CF_3)_2C{=}NLi + SOX_2 \arrow[r, "(1)"'] & ((CF_3)_2C{=}NS(O)X) \arrow[r, "(2)"'] & (CF_3)_2C(X)NSO \arrow[d, "LiN{=}C(CF_3)_2"] \\
 & & (CF_3)_2C{=}N{-}C(CF_3)_2NSO
\end{tikzcd}$$

The intermediate $(CF_3)_2C(F)NSO$ in this reaction has been isolated by von Halasz and Glemser[288].

The N-sulphinylamine structure of the product from the reaction of $Ph_2C{=}NLi$ with $SOCl_2$, is assigned on the basis of infra-red and mass spectra. The two strong absorptions at 1273 cm^{-1} and 1130 cm^{-1} (Table 4.1)are typical of $\nu_{as}(NSO)$ and $\nu_{sym}(NSO)$ for alkyl and aryl N-sulphinylamines RNSO ($\nu_{as}(NSO)$ 1300-1238 cm^{-1} and $\nu_{sym}(NSO)$ 1179-1120 cm^{-1} [289-291]) and the frequencies fit the linear correlation[28] between $\nu_{as}(NSO)$ and $\nu_{sym}(NSO)$. The infra-red spectrum is much more complex than for the more symmetrical diphenylmethyleneamino mono- and di-sulphides. The mass spectrum also indicates an N-sulphinylamine. The strong peak at m/e 346 $(Ph_2C{=}NCPh_2)^+$, indicating loss of -NSO is not found in the mono-and di-sulphide spectra.

The reaction between sulphuryl chloride and diphenylmethyleneamino-lithium is believed to involve the following stages:-



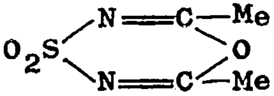
The initial stage of the reaction is postulated as nucleophilic attack by diphenylmethyleneamino-lithium an sulphuryl chloride with elimination of lithium chloride to form (A). This compound should be stable since stable analogues are known e.g. $Cl_2C{:}NSO_2Cl$[292].

The second stage can proceed by two routes. i) Diphenylmethyleneamino-lithium can attack the sulphur atom of (A), to form (C), with elimination of lithium chloride. This seems a likely product because this same compound (C) has been prepared by a different method[282] and it is known to be a stable compound with a similar melting point to the product from this reaction. ii) The chloride ion can migrate from the sulphur atom to the carbon atom in compound (A) to form the intermediate (B). Compounds like (B), of the type $RNSO_2$, have been postulated as intermediates in many reactions e.g. the Curtis and Lossen rearrangement of benzene sulphonyl azide[293],

$$C_6H_5SO_2N_3 \xrightarrow[-30^oC]{h\nu} C_6H_5SO_2\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}\cdot \xrightarrow{CH_3OH} (C_6H_5N{=}SO_2) \longrightarrow C_6H_5NHSO_2OCH_3$$

and they readily undergo nucleophilic attack at sulphur. Nucleophilic attack by diphenylmethyleneamino-lithium on the sulphur atom of (B) would again produce (C) with elimination of lithium chloride.

The alternative reaction mechanism for (B) would be nucleophilic attack by diphenylmethyleneamino-lithium on the carbon α-to the nitrogen in (B) to form (D) since chlorine atoms α-to nitrogen are readily ionised[294]. Atkins and Burgess succeeded in preparing a compound analagous to (D), $C_2H_5N{=}SO_2$, in solution at -78°C[295] but this underwent exothermic polymerisation upon warming (oligomers $(RNSO_2)_{3,4}$, $R = CH_3$ and C_2H_5 have been described[203, 296-301]). N-sulphuryl amines with larger R groups have also been prepared at low temperatures e.g. $PhC(O)NSO_2$[295] but on warming this rearranges to phenyl isocyanate and SO_2, even though the trimer has been characterised[297]. These highly electrophilic compounds can only be stabilised as monomers (cf. isoelectronic SO_3), by forming adducts with nucleophiles e.g. $MeOOCNSO_2.THF^{302}$ or $PhC(O)NSO_2.N(C_2H_5)_3^{295}$ which are stable at room temperature. No such solvent adducts would be formed under the conditions of the reaction so the author suggests that any (D) formed would quickly polymerise to form (E). The mass spectrum provides evidence for the formation of (E); the strong peak at m/e 346 assigned to $(Ph_2C{=}NCPh_2)^+$, would result from depolymerisation of (E) and loss of $-NSO_2$. However, the alternative product (C) could also produce this mass spectral peak by loss of $-NSO_2$ as occurs in the reactions of



with alkenes[303].

The product shows only two strong infra-red absorptions above 1000 cm^{-1} which differ from the mono- and di-sulphide derivatives. The spectrum is simple and it is possible to assign the two infra-red bands 1328 cm^{-1} and 1150 cm^{-1} to $\nu_{as}(SO_2)$ and $\nu_{sym}(SO_2)$ respectively, because they occur in the region of $-SO_2-$ vibrations of the $N{-}SO_2{-}N$ grouping[30]. These facts point to compound (C) as the product rather than (E).

The reaction of $(SNCl)_3$ with $Ph_2C{:}NLi$ led to an interesting ring breakdown and loss of nitrogen.

$$\begin{tikzcd}
(SNCl)_3 + LiN{=}CPh_2 \arrow[r] & 2((NSN{=}CPh_2)_3) \arrow[d, "-3N_2"] \\
3(Ph_2C{=}N)_2S_2 & 6(^{\bullet}SN{=}CPh_2) \arrow[l]
\end{tikzcd}$$

Most reactions of $(SNCl)_3$ with nucleophiles lead to ring breakdown and only two other cyclotrithiatriazenes are known (viz. $(SNF)_3$[304] and $(SNOR)_3$[305, 306]).

The structures of the N-S-O section of the products can be deduced from the infra-red spectra (Chapter 2). However, it has only been possible to assign the average S-N stretching frequency for three of the compounds (not the disulphide) because of the complexity of the spectra. In Table 4.1 are listed the predicted d_{SN} and $S\hat{N}S$ structures, and for comparison, the published structures of similar data for related compounds.

Table 4.1

Predictions of Structures and Comparisons with Related Compounds for $(Ph_2C{:}N)_2S$, $(Ph_2C{:}N)_2SO_2$ and $Ph_2C{:}NC(Ph_2)NSO$.

Compound	$\lambda_{SN},\lambda_{SO}$ μ	d_{SN} pm	d_{SO} pm	$N\hat{S}N^o$	ref.
$(Ph_2C{:}N)_2S$	λ_{SN}=12.30	167.6(1.4)		96.6(2.0)	Predn.
$(Ph_2C{:}N{\cdot}S_1{\cdot}N_1{:})_2S$		$167.9(5)_{S_1N_1}$		96.8(3)	43
$(PhCH{:}N)_2S_2$		169.1(4)			184
$(PhCH{:}N)_2S_3$		166.1(3)			178
$(PhCH{:}N)_2S_4$		165.5(6)			177
$(Ph_2C{:}N)_2SO_2$	λ_{SN}=11.92	165.8(1.4)		100.6(2.0)	Predn.
	λ_{SO}=8.07		142.9(1.0)		Predn.
$S(N{:}S{:}N)_2SO_2$		164.0	144.5	94.6	62
$Ph_2C{:}NC(Ph_2)NSO$	λ_{SN}=8.85	151.5(1.4)			Predn.
	λ_{SO}=7.77		141.7(1.0)		Predn.
cis-MeNSO		152.5(4)	146.6(4)		307
cis-H_3SiNSO		151.7(7)	144.2(5)		308

The predicted SN bond lengths in $(Ph_2C{:}N)_2S$ and $(Ph_2C{:}N)SO_2$ are less than the sum of the Pauling covalent radii (~174 pm) - a very rough guide to an SN single bond distance[309]. Bond contraction is often attributed to $d_\pi - p_\pi$ bonding or an increase in electrostatic contribution to the S-N covalent bond. The >C=N- stretching frequency provides some indication of which effect is dominant (Table 4.2).

Table 4.2

$\nu_{(C=N)}$ and $\nu_{(S-N)}$ for bis(diphenylmethyleneamino) sulphide, disulphide and sulphone.

Compound	$\nu_{(C=N)}$ cm^{-1}	$\nu_{(S-N)}$ cm^{-1}
$(Ph_2C{:}N)_2S_2$	1597	
$(Ph_2C{:}N)_2S$	1597	815
$(Ph_2C{:}N)_2SO_2$	1595	839

The absorption frequency $\nu_{(C=N)}$ will be affected by the rigidity of both the $^{C}_{C}\!\!>\!C$ and N-S units. No significant difference between the rigidity of the $^{C}_{C}\!\!>\!C$ skeleton is to be expected for the S^{II} and S^{VI} compounds but the N-S force constant should increase from S^{II} to S^{VI} [310]. This strengthened mechanical coupling normally increases $\nu_{(C=N)}$ [311] and should lead to higher frequencies in the S^{VI}compounds. The observed decrease in $\nu_{(C=N)}$ is not consistent with this interpretation.

Sulphur-nitrogen d_{π}- p_{π} bonding would reduce the non-bonding electron density in the $>$C=N- system and increase $\nu_{(C=N)}$. Also, the hybridisation at nitrogen would tend towards sp from sp^2, further increasing $\nu_{(C=N)}$. One would expect S^{VI} attached to four electronegative groups to participate better in d_{π}- p_{π} bonding than S^{II} and yet $\nu_{(C=N)}$ shows a decrease $S^{II} \rightarrow S^{VI}$ showing that d_{π}- p_{π} bonding is not dominant in these compounds.

The electronegativity of sulphur increases from S^{II} to S^{VI} and increasing the electronegativity of the atom attached to the $>$C=N- group will withdraw electron density from this region and increase $\nu_{(C=N)}$. This is indeed the case and therefore only the electronegativity of the sulphur seems to have a significant effect on $\nu_{(C=N)}$ and $\nu_{(S-N)}$ and consequently d_{SN}. The ease and rapidity of the reactions with $S_{1,2}Cl_2$ and $SO_{1,2}Cl_2$ and the high yields, open the way for more derivatives of S^{II}, S^{IV} and S^{VI} compounds to be prepared by this method. There are relatively few side reactions and the progress of a reaction can be monitored by the shift in $\nu_{(C=N)}$.

CHAPTER 5

Reactions of Trichlorocyclotrithiatriazene and Derivatives

In this chapter the chemistry of $(SNCl)_3$ is reviewed. This is followed by the experimental section which describes reactions of $(SNCl)_3$ and $(RCN_2S_2)^+$ salts, the results of which are discussed with regard to the possible reaction mechanisms involved.

Preparations of Trichlorocyclotrithiatriazene.

The reactions of S_4N_4 with chlorine or sulphuryl chloride probably proceed via the intermediate $(SNCl)_4$ to form $(SNCl)_3$[269,311]. Alternatively $(S_3N_2Cl)(Cl)$ may be used in place of S_4N_4.

$$3S_4N_4 + 6Cl_2 \xrightarrow{} 4(SNCl)_3{}^{311}$$
$$3S_4N_4 + 6SO_2Cl_2 \xrightarrow{20^\circ C} 4(SNCl)_3 + 6SO_2{}^{269}$$
$$3(S_3N_2Cl)(Cl) + 3Cl_2 \xrightarrow{} 2(SNCl)_3 + 3SCl_2{}^{267}$$
$$3(S_3N_2Cl)(Cl) + 3SO_2Cl_2 \xrightarrow{20^\circ C} 2(SNCl)_3 + 3SCl_2 + 3SO_2{}^{269}$$

The reaction of NH_4Cl with S_2Cl_2 in a 1:2 ratio leads to high yields of $(SNCl)_3$ but with excess NH_4Cl, $(S_3N_2Cl)(Cl)$ is produced.

$$3NH_4Cl + 6S_2Cl_2 \xrightarrow{reflux} (SNCl)_3 + 12HCl + 9S^{266,312}$$

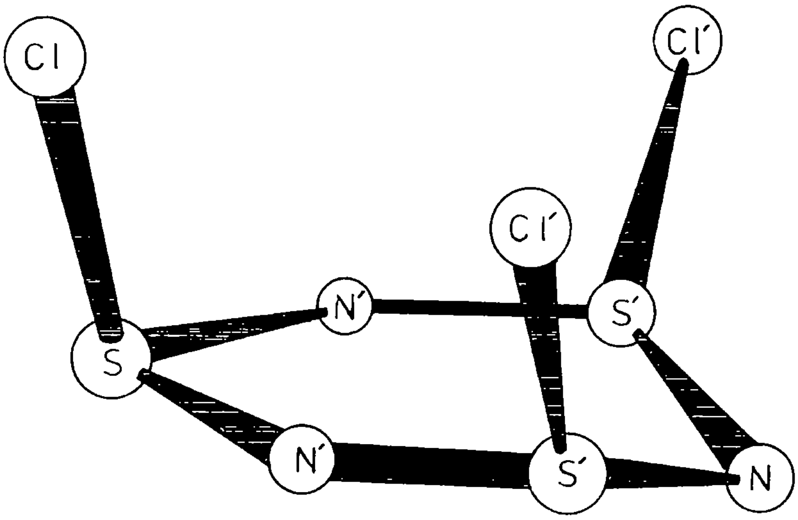
By passing S_2Cl_2 through a stream of active nitrogen, small quantities of NSCl and SCl_2 are produced and the monomer slowly trimerises[313].

The trimer has also been prepared in small quantities from thionyl chloride and two isomers of thionyl imide.

$$3HNSO \text{ or } 3HONS + 3SOCl_2 \xrightarrow{} (SNCl)_3 + 3SO_2 + 3HCl^{314,315}$$

Attempted halogen exchange of $(SNF)_4$ with $SiCl_4$, PCl_5 or Me_3SiCl produces $(SNCl)_3$, not the tetramer[316]. Trimeric products $(SNCl)_3$ and $(SNF)_3$ are the only compounds that can be recovered from the reaction of $(S_3N_3F_2)(AsF_6)$ with NOCl[1].

Figure 5.1



The structure of $(SNCl)_3$[53].

Structure

The S_3N_3 ring of trichlorocyclotrithiatriazene adopts the chair conformation with the three chlorine atoms in axial positions (Fig 5.1)[53]. Similar chair conformation are observed in many other six-membered sulphur ring systems e.g. α(SNOCl)$_3$[68], (SNO$_2^-$)$_3$[69], (MeNSO$_2$)$_3$[203], (SNF)$_3$[55] and (SO$_3$)$_3$[86]. The π-bonds in the ring are very similar since the system is of approximate $\underset{\sim}{3m}$ symmetry. All the S-N bond lengths are equal (160.5 pm) within experimental error but the SCl bonds are unequal (215.0, 215.0 and 208.4 pm), possibly because of their different molecular environments. The fact that all the SN bond lengths are equal implies the presence of delocalised p_π-d_π bonds[53,150]. The short SS distances (283 pm), considerably shorter than the sum of the van der Waals radii for sulphur (370 pm)[317], indicate the existence of some degree of SS bonding across the ring. SCF MO calculations with and without "d" orbitals for (SNCl)$_3$ have been reported (Table 5.1) which support this theory[78,81,318].

Table 5.1

CNDO/2 Calculations for (SNCl)$_3$

With "d" Orbitals

	Charges			Valencies	Bond Indices		
	ref.318	ref.81	ref.78	ref.78		ref.81	ref.78
Sulphur	+0.35	+0.33	+0.38	4.40	S-N	1.57	1.28
Nitrogen	-0.25	-0.23	-0.20	2.83	S-Cl	1.22, 1.30	1.29
Chlorine	-0.10	-0.10	-0.18	1.64	S-S		0.23
					N-N		0.04

Without "d" Orbitals

	Charges		Bond Indices
	ref.318		ref.78
Sulphur	+0.50	S-N	0.97
Nitrogen	-0.35	S-Cl	0.86
Chlorine	-0.18	S-S	0.03
		N-N	0.02

Inclusion of "d" orbitals in the calculations lifts the SN bond indices from virtual single bonds to partial double bonds. It is well established that CNDO/2 calculations overestimate the "d" orbital contributions to these systems[110], so the true picture lies somewhere between these two extremes. Comparisons of the calculated valencies with the maximum covalency for each atom has been used as a measure of the reactivity of atoms[319]. Thus sulphur and nitrogen atoms in $(SNCl)_3$ would be expected to increase their valencies in a reaction. The sulphur atom should be susceptible to nucleophilic attack and the nitrogen to electrophilic attack by virtue of the charges on these atoms.

Properties

Trichlorocyclotrithiatriazene is a pale yellow crystalline solid (density 2.09 g cm^{-3}) which is stable in a dry atmosphere but is decomposed by water to SO_2 and NH_4Cl. It has a melting point of 91°C[267] or 162.5°C (decomp.)[150,304,320]. This higher melting point has been disputed by Patton [321], who has suggested that as $(SNCl)_3$ melts, other unspecified yellow solids are formed, which themselves decompose to $(S_4N_3)(Cl)$; the latter melts with decomposition at 180-200°C, when pure. $(SNCl)_3$ is soluble in benzene, carbon disulphide, carbon tetrachloride, phosphoryl chloride, liquid sulphur dioxide, sulphuryl chloride and thionyl chloride.

The trimer undergoes reversible decomposition to the monomer

$$(SNCl)_3(s) \rightleftharpoons 3SNCl\ (g)^{322-324}$$

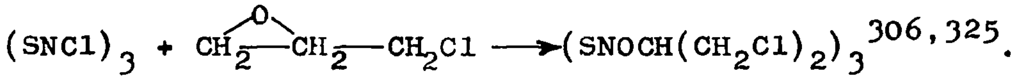
the trimeric form being predominant below 55°C[324]; chlorine inhibits the depolymerisation above this temperature.

The Chemistry of Trichlorocyclotrithiatriazene

Most reactions of $(SNCl)_3$ fall into four categories: i) substitution, ii) adduct formation, iii) ring cleavage, and iv) formation of other sulphur-nitrogen rings.

i) Substitution

$(SNCl)_3$ reacts with AgF_2 in CCl_4 to form $(SNF)_3$[304] and with $(CF_3)_2CNO$ and epoxides to form compounds of the type $(SNOR)_3$, e.g.



$$(SNCl)_3 + \overset{O}{CH_2—CH_2}—CH_2Cl \longrightarrow (SNOCH(CH_2Cl)_2)_3{}^{306,325}.$$

ii) Adduct Formation

The adduct $(SNCl)_3.6SO_3$ can be prepared from SO_3 and $(SNCl)_3$[326] and Armstrong *et al*[78] have suggested from their calculated charges (Table 5.1) that there is one SO_3 group associated with each nitrogen and each chlorine atom. The SO_3 groups attached to the chlorine atoms are more weakly bound and can be removed by heating to form $(SNCl)_3.3SO_3$[326]. Further heating, in vacuo, produces trichlorotrioxocyclotrithiatriazene $(SNOCl)_3$ (yield 4%) in which oxygen atoms have replaced the sulphur lone pairs in $(SNCl)_3$[327]. Trichlorocyclotrithiatriazene also forms adducts with Lewis acids in thionyl chloride which are of unknown structure and extremely moisture sensitive.

$(SNCl)_3.a\ AlCl_3$ (a = 1,2)[328]
$(SNCl)_3.b\ FeCl_3$ (b = 1,2)[328]
$(SNCl)_3.c\ SbCl_5$ (c = 1,2,3)[92,329,330]
$2(SNCl)_3.d\ SnCl_4$ (d = 1)[330]

$(SNCl)_3 . e\ TiCl_4\ (e = 1)$[330]

These undergo further reaction with S_4N_4 to yield $(S_5N_5)^+$[328,329] or with SCl_2 to form $(S_2NCl_2)^+$ salts[72,92,154,329]. In CCl_4, $(SNCl)_3$ reacts with $SbCl_5$ in a 1:1 ratio to form $(S_3N_3Cl_2)(SbCl_6)$[331]. Using the same reactants but in SO_2 with an $(SNCl)_3$:$SbCl_5$ ratio of 1:2 Gillespie <u>et al</u> produced $(S_4N_4)(SbCl_6)_2$ although the reaction was complex and there was at least one unidentified product[120].

iii) Ring Cleavage

Reaction of $(SNCl)_3$ with strong nucleophiles, electrophiles or oxidising agents generally leads to breakdown of the S_3N_3 ring.

Oxygen Nucleophiles

Hydrolysis of $(SNCl)_3$ in alkaline conditions produces ammonia, sulphite and thiosulphate but in hot concentrated hydrochloric acid only ammonium chloride and sulphur dioxide are formed. The main products in cold, moderate acid conditions are sulphur dioxide, ammonium sulphate and it is claimed, $H_4N_2S_2O$[332]. Ethanolysis results in ring breakdown and formation of diethyl ether[332].

$$(SNCl)_3 + 12C_2H_5OH \longrightarrow 3NH_4Cl + 3SO_2 + 6(C_2H_5)_2O$$

but with cholestan-3β- ol only cholestan-3β-yl sulphite is formed[333].

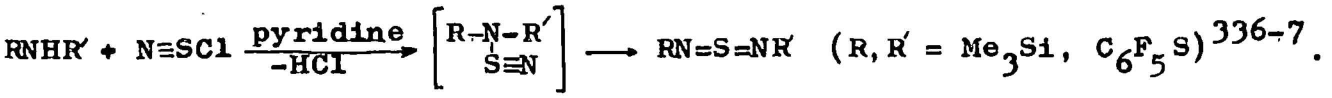
$$R\text{-}O\text{-}H + (SNCl)_3 \longrightarrow R\text{-}O\text{-}SO_2H$$

The reaction with dimethylsulphoxide leads to the formation of the bis(dimethylthio) nitrogen cation [334].

$$Me_2S{=}O + (SNCl)_3 \longrightarrow (Me_2SNSMe_2)(Cl) + SO_2$$

Nitrogen Nucleophiles

Sulphur diimide, $S(NH)_2$, can be isolated as the mercury or silver salts from the reaction of $(SNCl)_3$ with ammonia[335]. In this reaction and in the reactions with secondary amines, $(SNCl)_3$ generally acts as if it were in its monomeric form



$$RNHR' + N{\equiv}SCl \xrightarrow[-HCl]{pyridine} \left[\begin{matrix} R-N-R' \\ S{\equiv}N \end{matrix}\right] \longrightarrow RN{=}S{=}NR' \quad (R,R' = Me_3Si,\ C_6F_5S)^{336-7}.$$

However, the reaction with benzophenone p-nitrophenylhydrazone produces two products by a series of rearrangements

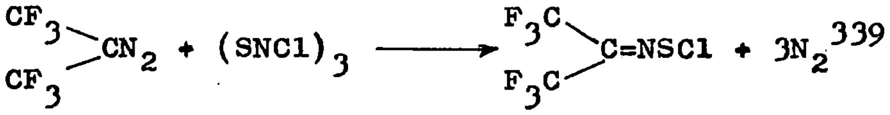
$$Ph_2C{=}N{-}NHC_6H_4NO_2 + (SNCl)_3 \xrightarrow[-HCl]{pyridine} (Ph_2C{=}N)_2S + Ph_2C{=}NSC_6H_4NO_2{}^{333},$$

with organometallic substituents on the nitrogen substituted di-imides are formed[331].

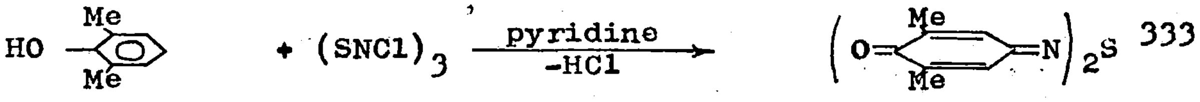
$$P_3N_3F_5N(SnMe_3)_2 + (SNCl)_3 \longrightarrow P_3N_3F_5N{=}S{=}N{-}SMe$$

Electrophiles

Strong electrophiles attack the nitrogen atoms of trichlorocyclotrithiatriazene and lead to ring breakdown, e.g.



$$(CF_3)_2CN_2 + (SNCl)_3 \longrightarrow (F_3C)_2C{=}NSCl + 3N_2{}^{339}$$



Oxidising Agents

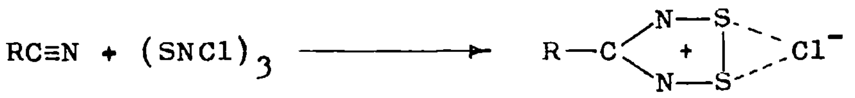
$(SO_3)^{2-}$ anions are reduced to $(S_2O_3)^{2-}$ by $(SNCl)_3{}^{340}$ and NO_2 oxidises $(SNCl)_3$ to $(NO)_2S_2O_7{}^{332}$.

iv) Formation of Other Rings or Cages

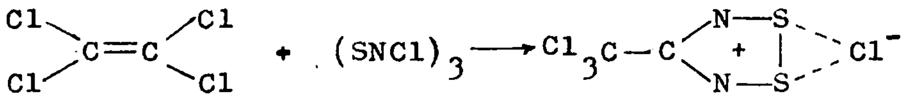
The formation of various sizes of rings and cages from trichlorocyclotrithiatriazene represents the most versatile preparative use of this compound.

Five-membered Rings

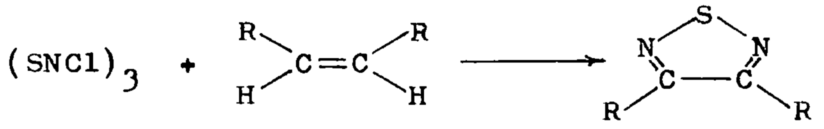
Dithiadiazolium salts can be prepared by reaction with nitriles[341-3 or alkenes[341,342].



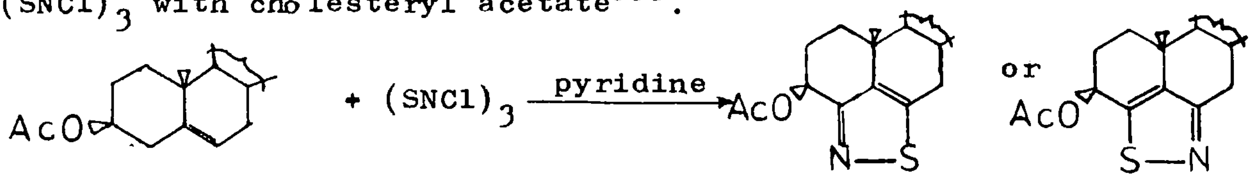
(R =Ph, CCl_3 or tBu)



1,2,5-thiadiazoles have been prepared in small yields from alkenes,



and isothiazoles have been isolated from reaction products of $(SNCl)_3$ with cholesteryl acetate[333].



Derivatives of the S_3N_2 ring can be isolated by reaction with NO[21], S_2Cl_2[3,312,344] or HBr[345]

$$24NO + (SNCl)_3 \longrightarrow 6S_3N_2Cl + 12NOCl + 3S_2Cl_2 + 12N_2O$$

$$3S_2Cl_2 + 2(SNCl)_3 \longrightarrow 3S_3N_2Cl_2 + 3SCl_2$$

$$6HBr + 2(SNCl)_3 \xrightarrow{-6HCl} 2(SNBr)_3 \longrightarrow 2S_3N_2Br_2 + N_2 + Br_2$$

Six-membered Rings

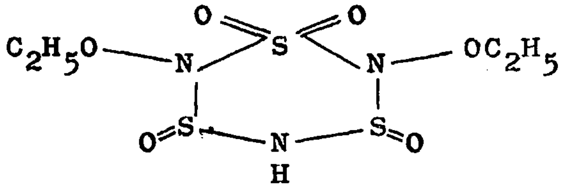
Three different types of six-membered ring have been prepared. The monochloride S_3N_3Cl has been known since 1932[344], but only recently has a repeat preparation been reported from $(SNCl)_3$ and S_4N_4[101].

$$3S_4N_4 + 2(SNCl)_3 \longrightarrow 6S_3N_3Cl$$

With cycloazaheptasulphane (S_7NH) the intermediate S_8N_2 is postulated and some of the S_4N_2 decomposes to form S_4N_4 and sulphur[338].

$$\begin{tikzcd}(SNCl)_3 + 3S_7NH \arrow[r, "pyridine"] & 3(S_8N_2) \arrow[d] & + 3Py.HCl \\ & S_4N_2 + 12S & \end{tikzcd}$$

The reaction of ethyl hypochlorite (C_2H_5OCl) with $(SNCl)_3$ produces the unusual and improbable cyclic compound with the sulphur atoms in different oxidation states and only single bonds in the ring[332].



Seven-membered Rings

$(SNCl)_3$ reacts with S_7NH or $S_4N_4H_4$ in the absence of pyridine to form $(S_4N_3)(Cl)$[150].

$$\begin{array}{l}(SNCl)_3 + S_7NH \longrightarrow S_4N_4.4HCl \xrightarrow[\text{trace}]{H_2O} S_4N_3Cl \\ \qquad\quad \text{or } S_4N_4H_4\end{array}$$

Eight-membered Rings and Cages

$(SNCl)_3$ reacts with $ON(CF_3)_2$ to form the tetrameric $(NSON(CF_3)_2)_4$[306]. With the Lewis acid, $SbCl_5$, trichlorocyclotrithiatriazene undergoes a complex rearrangement to form $(S_4N_4)(SbCl_6)_2$[120], and neutral cyclotetrathiatetrazene (S_4N_4) is produced by the reaction of $S_4N_4H_4$ with pyridine and $(SNCl)_3$ in boiling carbon tetrachloride[325].

Ten-membered Rings

$(SNCl)_3$ reacts with S_4N_4 and Lewis acids to form $(S_5N_5)^+$ salts[328,329].

Other Reactions

The reaction of $(SNCl)_3$ with metal carbonyls appears to leave the S_3N_3 ring intact e.g.

$$\begin{tikzcd}\mathrm{Mo(CO)_6} + \mathrm{(SNCl)_3} \arrow[r] & \mathrm{MoS_3N_3Cl_3} + 6\mathrm{CO} \arrow[d, "\Delta"] \\ & \mathrm{Mo_2S_9N_3Cl_6}\end{tikzcd}$$

The compound $MoS_3N_3Cl_3$ reacts with moist air to form SO_2 suggesting the presence of S-Cl bonds and it can only be dissolved in polar solvents, implying that the compound is polymeric[347].

Experimental

Reactions of Trichlorocyclotrithiatriazene

1. Reactions with Lewis Bases

a) With n-butyl lithium

A suspension of trichlorocyclotrithiatriazene (1.4 g, 0.0057 mol) in dry hexane (20 ml) was frozen to -196°C and n-butyl lithium in hexane (10 ml, 1.51 M, 0.0151 mol) was added. The reaction mixture was stirred and allowed to warm to room temperature. The brown solution slowly deposited a green precipitate over two hours at room temperature and this was filtered and found to be mainly LiCl. The brown solution was evaporated slowly depositing a yellow brown precipitate which was filtered and pumped to dryness under vacuum. As nitrogen was admitted to bring the pressure in the flask back to atmospheric, the precipitate suddenly changed colour from brown to red and a foul smelling red gas was evolved. The red precipitate was extracted with carbon tetrachloride (20 ml). Yellow crystals (1) formed slowly in the red solution and they were filtered and pumped to dryness. The solution was pumped dry in vacuo and a red solid remained (2). The yellow crystals (1) had mp. 85 - 89°C. Calcd. for $Cl_3N_3S_3$: Cl, 43.56; N, 17.18; S, 39.26. Found: Cl, 35.42; N, 19.00; S, 42.09%. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1330m, 1268w, 1245w, 1080sh, 1018vs, 967s, 710m, 671w, 630w, 587m, 560m, 526s, 500w, 474m, 456m, 399s.

The red solid (2) showed i.r. (Nujol mull) absorptions (cm^{-1}) at 3145s, 3055s, 1411vs, 1268w, 1200w, 1162w, 933s, 805w(broad), 733m, 706s, 557s, which is the spectrum of S_4N_4 contaminated with N-H groups.

b) With pyridine

Pyridine (1.55 ml, 0.0190 mol) was added to trichlorocyclotrithiatriazene (1.6 g, 0.0065 mol) suspended in carbon tetrachloride (30 ml) at room temperature. The suspended $(SNCl)_3$ dissolved, producing a yellow solution which slowly turned green and deposited a yellow precipitate (1). This was filtered and the green solution left standing for a week, deposited black crystals(2). Yellow crystals (1):- Calcd. for $C_{10}H_{10}N_2S_2Cl_2$: C, 40.96; H, 3.41; Cl, 24.23; N, 9.56; S, 21.84. Found: C, 41.08; H, 3.63; Cl, 25.35; N, 10.16; S, 19.84%. I.r. (Nujol mull) absorptions occurred at (cm^{-1}): 3140s, 3060vs, 2950s, 2105m, 1638m, 1614s, 1539s, 1489vs, 1388m, 1364m,1340w, 1286m, 1256m, 1199m, 1170w, 1142w, 1047m, 1004m, 925w(br), 790m, 754vs, 681vs, 611m. Major mass spectral peaks at 150°C (relative intensities and assignments are given) were found at m/e: 184(3) $S_4N_4^+$, 138(10) $S_3N_3^+$, 120(9) $C_5H_4NS^+$, 119(25) $C_5H_3NS^+$, 118(13) $C_5H_2NS^+$, 92(31) $S_2N_2^+$, 79(100) $C_5H_5N^+$, 78(28) $C_5H_4N^+$, 64(55) S_2^+, 52(100) $C_4H_4N^+$, 51(62) $C_4H_3N^+$, 50(37) $C_4H_2N^+$, 46(35) SN^+. The black crystals (2) were very difficult to mull but had essentially the same infra-red spectrum as (1).

2. Reactions with Alkenes and Alkynes

a) With cyclohexene

Cyclohexene (30 ml, 0.296 mol) was added to a suspension of trichlorocyclotrithiatriazene (1.5 g, 0.0057 mol) in hexane (20 ml) and stirred at room temperature. The initial yellow suspension turned brown overnight and deposited a brown precipitate. This was filtered leaving a red solution which was pumped under vacuum to give a red brown oil. The brown precipitate was washed with hexane (10 ml), filtered and pumped to dryness. An attempt to sublime this residue resulted in the collection of a red oil (1) from the brown solid (2).

The red oil (1) showed i.r. (Nujol mull) absorptions (cm^{-1}) at: 2940vs, 2860s, 1450vs, 1340m, 1270m, 1204s, 1195s, 1007s, 987s, 911s, 868m, 848m, 835s, 820s, 735s, 695s, 615s.

The brown solid (2) showed i.r. (Nujol mull) absorptions (cm^{-1}) at: 3140vs(broad), 3045vs, 2940s, 2860s, 1445s(sh), 1410vs, 1340w, 1202w(sh), 1192m, 1026w, 1007w, 987w, 932vs, 870w, 848w, 833w, 820w, 772w, 732s, 705vs, 621m, 557vs, 536m, 420w, 353s. Analysis found: C, 16.67; H, 4.06; Cl, 24.27; N, 21.21; S, 33.79%.

b) With octachlorocyclopentene

Trichlorocyclotrithiatriazene (3.5 g, 0.0143 mol) was added to octachlorocyclopentene (14.0 g, 0.0407 mol) in carbon tetrachloride (50 ml) and stirred at 42°C for two days. The initial yellow solution turned green on warming to 42°C but became yellow when cooled, forming large yellow crystals. These were filtered and pumped to dryness. The infra-red spectrum showed that these were unreacted starting materials. The experiment was repeated by heating trichlorocyclotrithiatriazene (2.0 g, 0.0082 mol) with octachlorocyclopentene (8.5 g, 0.0247 mol) for two days at 70°C. The octachlorocyclopentene melted at 40°C forming a green solution and an orange sublimate (1) formed at the top of the flask. On cooling the solution solidified as yellow crystals(2).

The orange sublimate (1) showed i.r. (Nujol mull) absorptions (cm^{-1}) at: 1018 m, 942vs, 728s, 720s, 587m. Calcd. for $Cl_2N_2S_3$: Cl, 36.41; N, 14.36; S, 49.23. Found: C, 0.85; H, 0.00; Cl, 38.21;

N, 12.92; S, 47.97%

The yellow crystals (2), analysis found: C, 13.98; H, 0.00; Cl, 74.76; N, 3.50; S, 7.82% corresponding to $C_{4.77}Cl_{8.60}N_{1.02}S_1$. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at: 1614s, 1588w, 1268w, 1193vs, 1159m, 1038m sh, 1020s, 948w, 909m, 892m, 821m, 761vs, 712m, 688s, 660s, 652s, 600m, 523m, 399m.

c) With diphenyl acetylene

Trichlorocyclotrithiatriazene (1.0 g, 0.0041 mol) was added to diphenyl acetylene (2.1 g, 0.0118 mol) in ether (20 ml.) and stirred at room temperature. The yellow suspension turned green and deposited an orange solid after four hours and after twenty four hours the solution had turned red and the orange solid had become green/yellow. This was filtered and pumped to dryness. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at: 1175s, 998vs, 962m, 940m, 893w, 846w, 762w, 724w, 701m, 688m, 589w, 572m, 476s, 460m. Corresponding to the spectrum of $(S_4N_3)(Cl)$ with some $(S_3N_2Cl)(Cl)$ and "$(S_3N_2)(Cl)$" as impurities.

3. Substitution Reactions

a) With hexafluoroacetic anhydride

Trichlorocyclotrithiatriazene (1.3 g, 0.0052 mol) was added to hexafluoroacetic anhydride (5ml, 0.016 mol) in carbon tetrachloride (30 ml) and stirred at room temperature. The yellow solution slowly turned red over three hours. The solution was pumped gently under vacuum until yellow crystals precipitated. These were filtered and found to be $(SNCl)_3$ from their infra-red spectrum. The reaction mixture was taken up to reflux temperature for two hours. A red solid formed in the reflux condenser and a yellow solid was deposited from the solution. These were found to be $(S_3N_2Cl)(Cl)$ and $(S_4N_3)(Cl)$ respectively from their infra-red spectra.

b) With lithium bromide

Trichlorocyclotrithiatriazene (4.0 g, 0.0164 mol) was added to excess of lithium bromide (7.0 g, 0.0806 mol) in phosphoryl chloride (40 ml). The yellow solution turned green and deposited a white precipitate immediately. On heating to 40°C for half an hour the solution became red and deposited an orange precipitate. This was filtered and pumped to dryness. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1065vs, 1010 vs, 678m(sh), 568m, 475vs.

Reaction of $(SNCl)_3$ with Sulphur Dichloride and Boron Trichloride

Trichlorocyclotrithiatriazene (2.2 g, 0.0090 mol) was dissolved in thionyl chloride (20 ml) and boron trichloride (4.5 ml, 0.027 mol) added by a vacuum transfer process. Immediately a yellow precipitate formed in the red solution . Sulphur dichloride (5.0 ml, 0.030 mol) was added and the mixture stirred for two hours. The yellow precipitate became thicker and the solution changed from red to yellow. This precipitate (1) was filtered, pumped carefully to dryness and then sublimed at room temperature onto a cold finger where it collected as a red solid. This eliminated a volatile liquid (BCl_3) and turned yellow on warming to room temperature(2). The compound had a considerable vapour pressure even at room temperature. Analysis of (1) found: Cl, 63.75; N, 3.26; S, 25.03; B (by difference 7.96). Calcd. for $B_2Cl_8N_2S_3$: B,5.2; Cl, 66.0; N, 5.2; S, 22.3%. Calcd. for $BCl_5N_2S_3$: B, 3.5; Cl, 57.2; N, 9.0%. S, 30.9%. Calcd. for BCl_6NS_2: B, 3.6; Cl, 70.3; N, 4.7; S, 21.4%. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at: 1120w, 989s, 950vs, 719s, 702m, 670m, 523m, 496s, 453vs. Analysis of yellow sublimate (2) found: Cl, 68.24; N, 5.16; S, 22.53; B (by difference 4.07). I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1123m, 991w, 952m, 740m(sh), 720s, 704vs, 696vs, 668vs, 655vs, 523s, 516s, 500s(sh).

Reaction of $(SNCl)_3$ with Nitriles

a) With trichloroacetonitrile.

Trichlorocyclotrithiatriazene (2.4 g, 0.0098 mol) was dissolved in trichloroacetonitrile (20 ml, 0.096 mol) and refluxed for 24 hours. The initial green solution turned brown and then red after three hours and deposited orange crystals. The product (3.1 g) was filtered from the cold solution and recrystallised twice from thionyl chloride (40 ml/g) to give 1.7 g of product, m.p. 221-2°C (42% based on $(SNCl)_3$). I.r. absorptions occurred (cm^{-1}) at 1280w, 1075w, 1055s, 1024w(sh), 911w, 861s, 827s(sh), 818vs, 796vs, 765m, 678vs, 673w(sh), 548s, 542w(sh), 520w. Solutions in CH_3CN (dried spectroscopic grade) absorbed between the cut-out at ~210nm and 700nm, at 228 nm (ϵ = 7550) and 262 nm (shoulder, ϵ = 2315). Solutions decompose quite quickly. Mass spectral peaks at 200°C (with relative intensities) were: $C_2Cl_3N_2S_2$, 225(5), 223(14), 221(13); $C_2Cl_2N_2S_2$, 190(16), 188(73), 186(100); C_2Cl_2NS, 142(14), 140(21); CCl_3, 121(4), 119(11), 117(11); C_2Cl_2N, 110(8), 108(13); CCl_2, 84(13), 82(9); NS_2, 78(39); CS_2, 76(55); S_2, 64(88); C_2N_2, 52(44); SN, 46(50). Analysis found: C, 9.27; Cl, 55.23; N, 10.71; S, 25.12. Calcd. for $C_2Cl_4N_2S_2$: C, 9.31; Cl, 55.00; N, 10.86; S, 24.82%.

b) With benzonitrile

Trichlorocyclotrithiatriazene (13 g, 0.0532 mol) was added to benzonitrile (6.2 ml, 0.0602 mol) in carbon tetrachloride (20 ml) and stirred at 60°C for two days. The initial orange/yellow solution turned green and then red, depositing an orange precipitate after one and a half hours. Stirring at 60°C was continued for two days and then the solution was allowed to cool, depositing orange needles, which were filtered and recrystallised from nitrobenzene (50 ml/g) m.p 201-203°C, (yield 6.5 g, 50% based on benzonitrile). Analysis found: C, 38.65; H, 2.06; Cl, 15.85; N, 12.45; S, 30.29.

Calcd. for $C_7H_5ClN_2S_2$: C, 38.80; H, 2.31; Cl, 16.38; N, 12.94; S, 29.57%. I.r. absorptions occurred (cm^{-1}) at 3020w, 1598w, 1584w, 1451vs, 1370vs, 1346s, 1299m, 1213m, 1176w, 1153m, 1074w, 1045w, 1029m, 1006w, 947w, 926m, 898vs, 847s, 789vs, 761m, 699vs, 670m(sh), 553s. Major mass spectral peaks at 200°C (relative intensities are given) occurred (m/e) at: $PhCN_2S_2$, 181(9); $PhCN_2S$, 149(3); PhCNS, 135(6); $PhCNH_2$, 105(3); PhCNH, 104(10); PhCN, 103(100); C_6H_4CN, 102(2); NS_2, 78(9); C_6H_5, 77(9); C_6H_4, 76(31); C_6H_3, 75(31); $S_2(SO_2)$, 64(70); CNS, 58(15); C_4H_4, 52(18); C_4H_3, 51(13); C_4H_2, 50(16); $SNH_2(SO)$, 48(42); SN, 46(10); CS, 44(9).

Reactions of 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride

a) With sodium azide

Sodium azide (0.1 g, 0.0015 mol) was added to $(CCl_3CN_2S_2)(Cl)$ (0.4 g, 0.0016 mol) in tetrohydrofuran (20 ml) and stirred at 0°C. The initial orange solution turned yellow, then yellow/green over 20 hours and deposited a white precipitate which was found to be unreacted sodium azide from its infra-red spectrum. The yellow/green solution was filtered and pumped under vacuum until a red oil remained which was found to be unreacted starting material in tetrahydrofuran from its infra-red spectrum.

b) With lithium azide in tetrahydrofuran

Lithium azide (0.2 g, 0.0041 mol) was added to $(CCl_3CN_2S_2)(Cl)$ (1.0 g, 0.0039 mol) in tetrahydrofuran (50 ml) and stirred at room temperature. The initial orange solution slowly changed to yellow and a creamy white solid precipitated after five hours. This was filtered and found to be unreacted lithium azide. The filtrate was pumped under vacuum until a red oil remained which was mainly unreacted starting material in tetrahydrofuran.

c) With lithium azide in acetonitrile

Lithium azide (0.2 g, 0.0041 mol) was added to $(CCl_3CN_2S_2)(Cl)$ (1.0 g, 0.0039 mol) in acetonitrile (50 ml) and stirred at room temperature. The initial orange solution became red and deposited a white precipitate. This was filtered and found to be lithium azide. The filtrate was pumped to dryness leaving a red/brown solid. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 2315w, 2285m, 2140m, 1268s, 1175m, 1068m(sh), 1022s, 990m sh, 939m, 870m, 849m, 812m(sh), 779s, 729s, 640m, 558m.

d) With liquid ammonia.

4-Trichloromethyl-1,2,3,5-dithiadiazolium chloride (2.0 g, 0.0078 mol) was added, with stirring, to ammonia (25 ml) dried over sodium at -78°C. A vigorous reaction occurred immediately and the original orange solution became purple/brown and deposited a purple/brown solid. This was filtered and pumped to dryness but was found to be impossible to mull. Ether (25 ml) was added to solid forming a red solution which was filtered and pumped slowly. No crystals formed, so the ether was removed completely, in vacuo, leaving a red brown solid. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 3125vs (broad), 3040vs(broad), 1405vs, 1270s, 1237m, 1105m(broad), 1026s, 867m, 860m(sh), 795s, 780s, 732s, 707w, 630m, 550m, 519w.

Reactions of 4-phenyl-1,2,3,5-dithiadiazolium chloride

a) With damp atmosphere

4-Phenyl-1,2,3,5-dithiadiazolium chloride was left standing in air for 10 minutes. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 3420w(broad), 2060vs, 1269vs, 1056s, 1020m, 976m, 960m, 808m, 754s, 730m(sh), 681w, 620w, 492s, 478m.

b) With nitric acid

4-Phenyl-1,2,3,5-dithiadiazolium chloride (0.7 g, 0.0032 mol) was added to concentrated nitric acid (5 ml) and stirred at room temperature. There was an immediate, vigorous reaction evolving NO_2 and the solution deposited a white precipitate. This was filtered and pumped under vacuum but not all the liquid could be removed. The crystals were washed with carbon tetrachloride (20 ml) and ether (20 ml) and pumped to dryness. Found : C, 29.89; H, 3.67; Cl, 0.00; N, 11.37; S, 19.85; O (by difference) 35.22. Calcd. for $C_7H_8N_2O_6S_2$: C, 29.89; H, 2.84; N, 9.96; S, 22.78; O, 34.16%. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 3385m, 3160s, 1680s, 1612w, 1598w, 1525w, 1291m, 1228vs, 1173vs, 1068m, 1037vs, 979w, 942w, 875s, 791m, 724m, 700m, 663m, 604m, 579s, 446m.

c) With acetic anhydride

4-Phenyl-1,2,3,5-dithiadiazolium chloride (0.5 g, 0.0023 mol) was dissolved in acetonitrile (30 ml) and acetic anhydride (1 ml, 0.009 mol) added. On refluxing for three hours the orange solution turned red. This deposited orange crystals of unreacted starting material on cooling.

d) With ferric chloride

Ferric chloride (2.25 g, 0.0139 mol) was added to 4-phenyl-1,2,3,5-dithiadiazolium chloride (3.0 g, 0.0139 mol) in thionyl chloride (40 ml) and the mixture stirred for 6 hours at room temperature. Orange platelets which formed slowly over this time were filtered and recrystallised from thionyl chloride (20 ml/g). Yield 4.7 g (89.4%), m.p.146-148°C, found: C, 21.95; H, 1.52; Cl, 37.03; N, 7.58; S, 16.99. Calcd. for $C_7H_5Cl_4FeN_2S_2$: C, 22.18; H, 1.32; Cl, 37.44; N, 7.39; S, 16.89%. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1608w, 1600w, 1588w, 1507m, 1409vs, 1402vs, 1347s, 1300m, 1266w, 1201s, 1188w, 1169s, 1100w, 1076w, 1050w, 1035m, 998w, 980w, 935s, 920vs, 848m, 780vs, 729m, 702vs, 688s, 672m, 623w, 566s, 495w, 412s, 392s, 369s, 340s.

e) With sodium iodide in liquid sulphur dioxide

Sodium iodide (1.5 g, 0.01 mol) was added, with stirring, to 4-phenyl-1,2,3,5-dithiadiazolium chloride (2.0 g, 0.0092 mol) in liquid SO_2 (25 ml) at $-78^{o}C$. The yellow solution became green and deposited a yellow precipitate. The solution was filtered at low temperature and the solvent was removed leaving yellow platelets of $(PhCN_2S_2)(Cl)$. The residue was pumped to dryness and washed with carbon tetrachloride (30 ml) which extracted iodine leaving a multicoloured solid. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1664vs, 1583w, 1510w, 1288m, 1223s, 1172vs, 1075m, 1037s, 1005w, 980w, 874s, 788m, 723w, 699m, 598s, 582s, 445m. The same spectrum as the product from the reaction with concentrated nitric acid.

f) With sodium iodide in dichloromethane

Sodium iodide (1.0 g, 0.0067 mol) was added to 4-phenyl-1,2,3,5-dithiadiazolium chloride in dichloromethane (150 ml) and stirred at room temperature for three hours. The orange solution slowly turned red and deposited a white precipitate (1) which was filtered and pumped to dryness. A brown solid (2) remained after removing the solvent from the filtrate in vacuo. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1600w, 1460s, 1378s, 1358m, 1181w, 1028m, 972m, 860m, 832vs, 782vs, 694s, 676s, 520m. Found: C, 30.02; H, 2.21; N, 9.76; S, 22.41. Calcd. for $C_7H_5IN_2S_2$: C, 27.27; H, 1.62; N, 9.09; S, 20.78%.

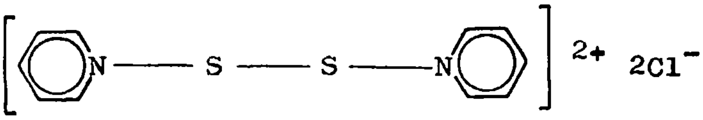
Reactions of $(SNCl)_3$ and Derivatives

The reactions of $(SNCl)_3$ have rarely been the subject of mechanistic study, so, it is often necessary to look at related systems in order to suggest reaction paths and products.

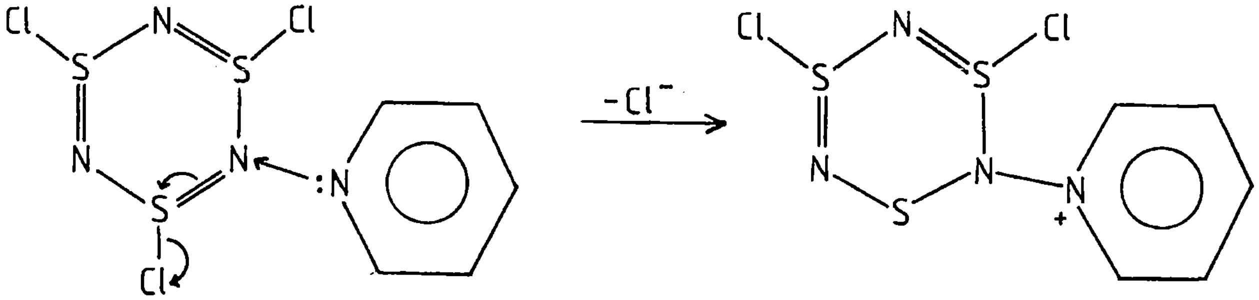
Reactions of Trichlorocyclotrithiatriazene with Nucleophiles

The reaction of trichlorocyclotrithiatriazene with diphenylmethyleneamino-lithium resulted in the formation of bis-diphenylmethyleneamino disulphide by elimination of nitrogen (Chapter 4). To further understand the mechanism, the reaction of $(SNCl)_3$ with n-butyl lithium was attempted. The main product was S_4N_4 but the foul smelling product removed during filtration (suspected to be bis-n-butyl disulphide) was quickly discarded. No attempt was made to repeat this reaction due to the antisocial nature of the reaction products.

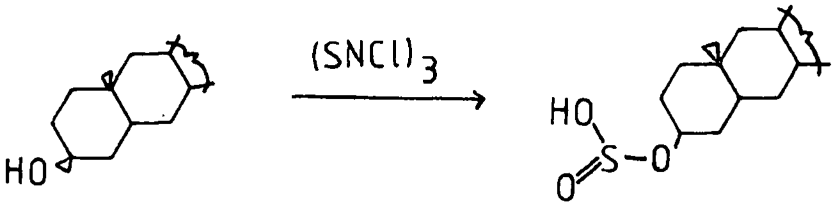
It was suspected that the ring breakdown in these two cases could have been due to using too strong a nucleophile so the reaction of $(SNCl)_3$ with pyridine was studied. The main product from this reaction was the compound $(C_5H_5N)_2S_2Cl_2$. This same compound has also been made by the reaction of pyridine with disulphurdichloride and was shown to ionise in acetonitrile[348]. The probable structure is therefore:



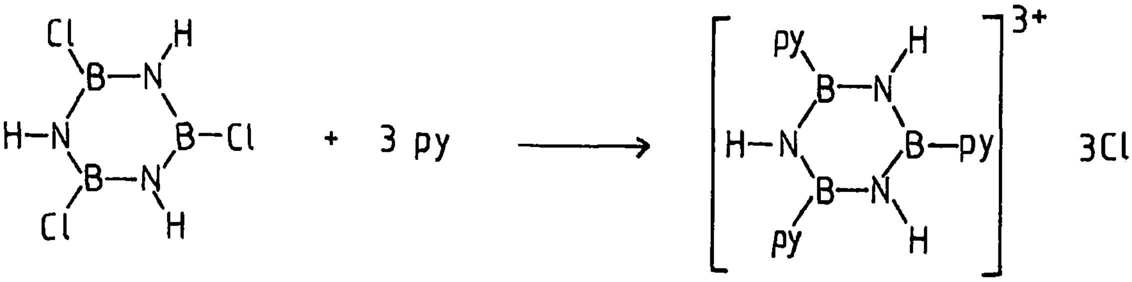
The mass spectrum indicated that small quantities of S_4N_4 were also formed in this reaction. Although Barton and Bubb describe nucleophilic attack by pyridine on the nitrogens of trichlorocyclotrithiatriazene[333], the initial attack of a nucleophile is likely to



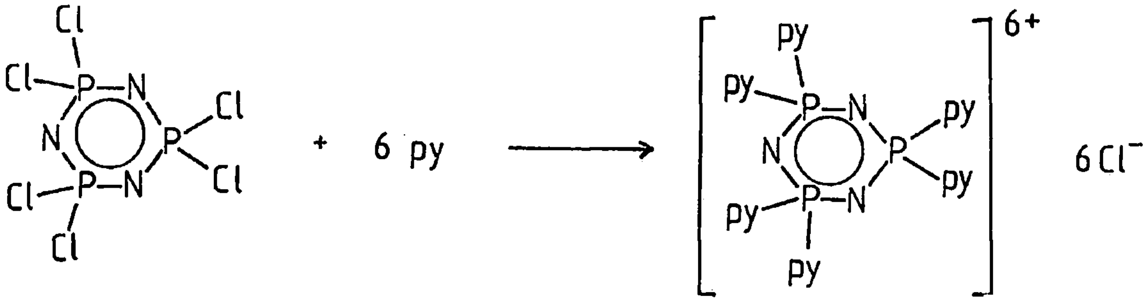
be on the sulphur due to the high positive charge on this atom.[78,81,318] The referee to Barton and Bubb's paper commented that the formation of cholestanol sulphite from cholestanol and $(SNCl)_3$ demonstrated this[333].



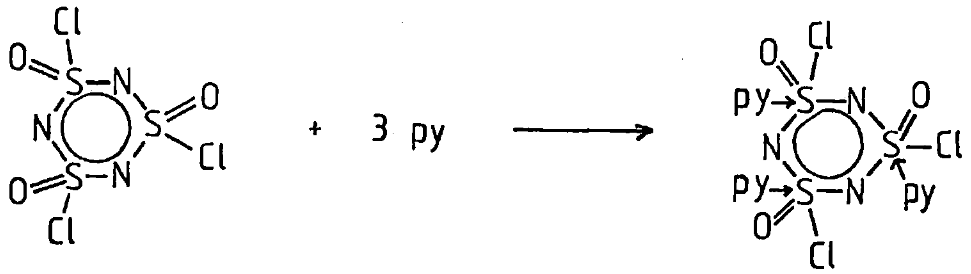
Related compounds also react with nucleophiles by nucleophilic attack at the positively charged site, e.g.



349

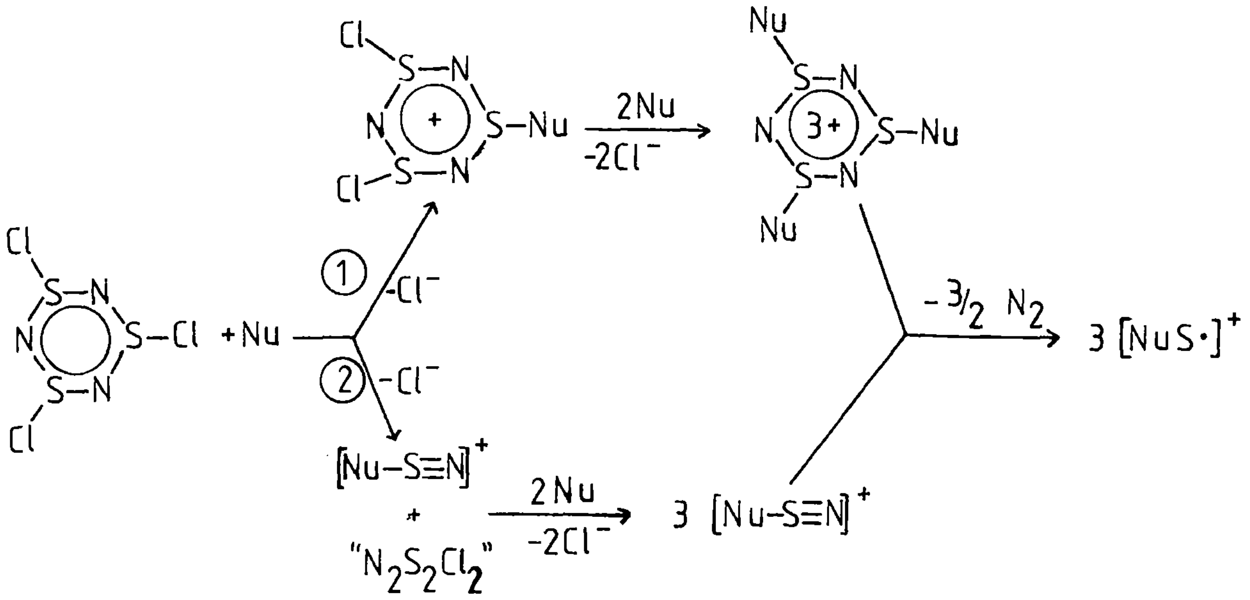


350,351



352

The nucleophilic attack would probably proceed by one of two routes:-



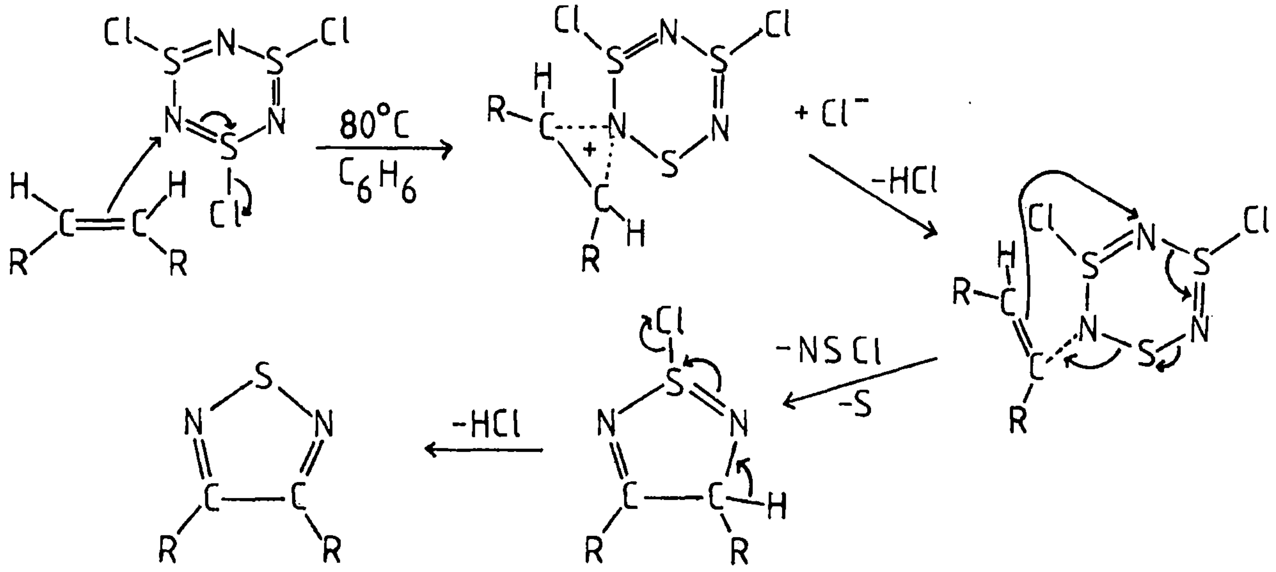
The radicals combine to form $(NuSSNu)^{2+}$ if the nucleophile is neutral or NuSSNu if the nucleophile is negatively charged.

These reaction paths account for the main products of nucleophilic attack on $(SNCl)_3$ but with both n-BuLi and pyridine the production of S_4N_4 was noted. Barton and Bubb noticed the formation of S_4N_4 in small quantities from solutions of $(SNCl)_3$ with small amounts of pyridine[333]. This could be due to hydrogen abstraction from the nucleophile or possibly contamination of the reactions by traces of water.

Reactions with Alkenes and Alkynes

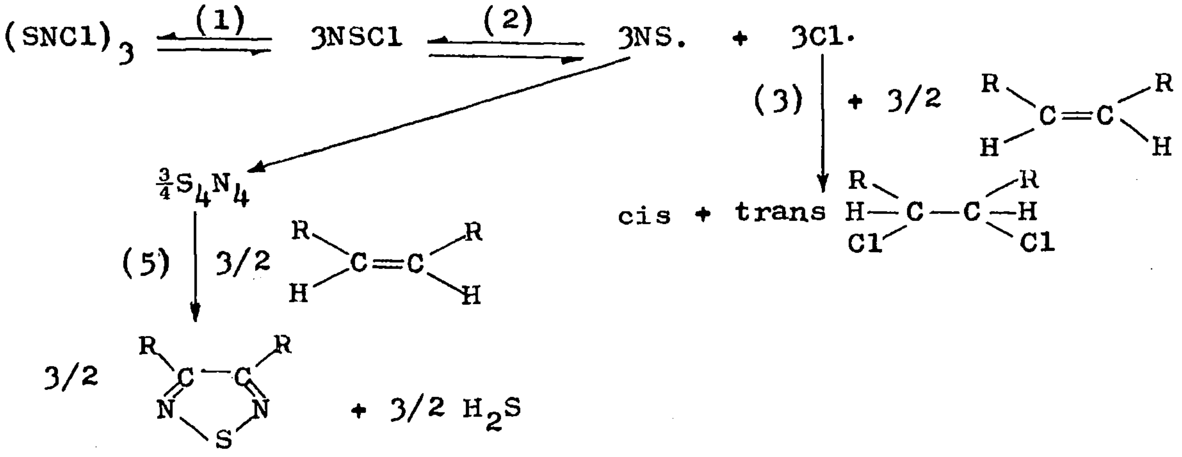
Trichlorocyclotrithiatriazene reacts with alkenes to produce three different types of product; isothiazoles[333], thiadiazoles[333] and dithiadiazolium salts[341,342]. The type of product depends on the substituents on the alkenes and the conditions used. It was therefore decided to study the mechanism through reaction with other alkenes.

The reaction of $(SNCl)_3$ with cyclohexene produced S_4N_4 and 1,2-dichlorocyclohexane as the main products. With octachlorocyclopentene the carbon-carbon double bond remained untouched, the products being chlorocyclotrithiadiazenium chloride, $(S_3N_2Cl)(Cl)$, and an intimate mixture of starting materials. The reaction of trichlorocyclotrithiatriazene with diphenyl acetylene produced one major product, cyclotetrathiatriazenium chloride $(S_4N_3)(Cl)$, slightly contaminated by chlorocyclotrithiadiazenium chloride $(S_3N_2Cl)(Cl)$ and cyclotrithiadiazenium chloride $(S_3N_2)(Cl)$. Burton and Bubb described a mechanism of electrophilic addition by the nitrogens of $(SNCl)_3$ on alkenes, to form 1,2,5-thiadiazoles[333].



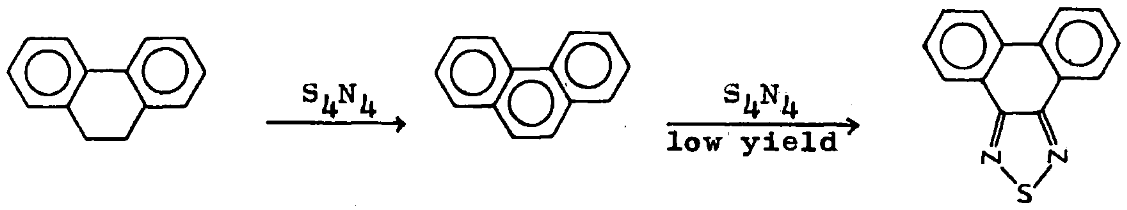
Not only is the initial electrophilic attack on the negative centre unlikely but at 80°C the reactive species in solution will probably be the monomer N≡SCl and not the trimer.

The following alternative mechanism is proposed (from discussions of the author with Dr. A. J. Banister).

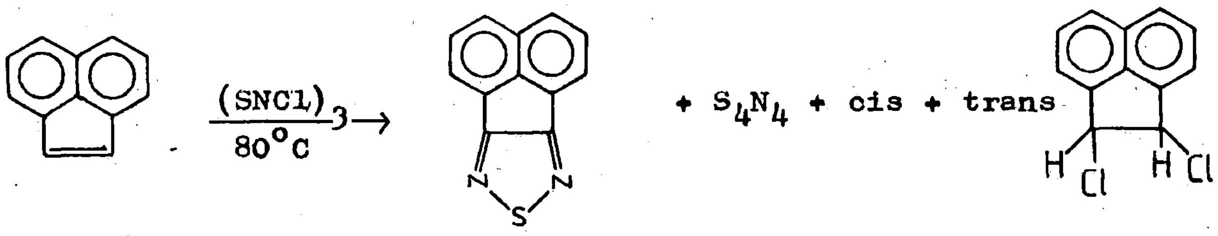


The reversible process (1) has been well studied and the equilibrium lies well over to the right at 80°C[324]. The justification for the reversible process (2) is that chlorine was found to inhibit the depolymerisation of $(SNCl)_3$[324]. Also in hot solutions and in the early stages of solution reactions of $(SNCl)_3$ there is a vivid green colour which could be due to $NS^{\cdot}$ rather than NSCl because the latter is only a pale green gas.

Route (3) is the simple addition of chlorine across a double bond which is well documented and route (4) is the oligomerisation of $SN^{\cdot}$ radicals to form S_4N_4. There are good grounds for proposing route (5), (i) because S_4N_4 reacts easily with ethylene displaying strong dehydrogenating power[353] and (ii) S_4N_4 reacts with 9,10-dihydrophenanthrene to form a 1,2,5-thiadiazole[354].

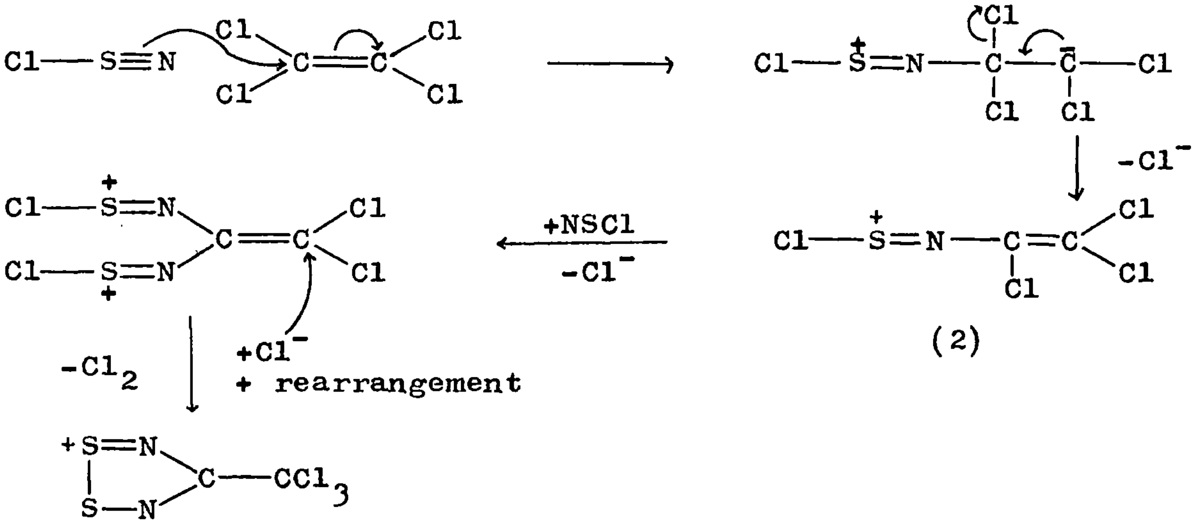


The overall reaction mechanism seems justified because when $(SNCl)_3$ reacts with acenapthylene, all three products of the scheme can be isolated[333].

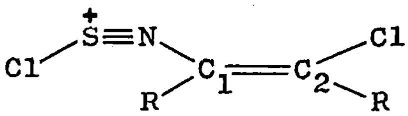


In the reaction of cyclohexene with $(SNCl)_3$ no thiadiazole was recovered. This is probably due to the fact that the temperature was too low. However, 1,2-dichlorocyclohexane and S_4N_4 were formed which suggests that stages 1-4 can occur at room temperature.

Tetrachloroethylene reacts with $(SNCl)_3$ at 121°C to form 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride[342]. This reaction is complex and the driving force for the formation of the ionic product is probably its insolubility in the solvent used (C_2Cl_4). At the temperatures employed, $(SNCl)_3$ would exist largely in its monomeric form and there would possibly be an appreciable concentration of NS· and Cl· radicals. There are many routes that would lead to the product, involving attack by NSCl, NS· or Cl· on the C=C bond. Attack by NSCl would probably be followed by elimination of a Cl^- ion to the nitrogen as this is very susceptible to ionisation[294].



Alternatively, attack by the SN· radical could follow much the same path. With octachlorocyclopentene however, once stage (2) has been reached, attack by further NSCl or SN· units appears unlikely because the C-R bond is unlikely to be broken. The most favourable step appears to be chloride ion or radical attack on C_1 with



elimination of NSCl to produce the original perchlorocycloalkene as observed. In both these reactions $(S_3N_2Cl)(Cl)$ was formed in cooler parts of the apparatus[342,343]. This is probably due to further decomposition of NSCl to nitrogen and ·SCl radicals. Two of these combine to form disulphur dichloride, which is known to react with

NSCl to form $(S_3N_2Cl)(Cl)$[344].

In the reaction between diphenyl acetylene and trichlorocyclotrithiatriazene the temperature was kept low so the reactive species was probably the trimer. The fact that $(S_4N_3)(Cl)$, $(S_3N_2Cl)(Cl)$ and "$(S_3N_2)(Cl)$" were formed implies that breakdown of the $(SNCl)_3$ ring to form disulphur dichloride and nitrogen is one of the major reaction paths.

$$2(SNCl)_3 \longrightarrow 3S_2Cl_2 + N_2$$

Disulphur dichloride reacts with trichlorocyclotrithiatriazene to form $(S_3N_2)(Cl)$[355] in small quantities and $(S_3N_2Cl)(Cl)$[344]. These can be further converted to $(S_4N_3)(Cl)$with disulphur dichloride[267].

$$\begin{tikzcd}
 & 2(SNCl)_3 + 2S_2Cl_2 \arrow[dl, "355"'] \arrow[dr, "344"] \arrow[d, "344"] & \\
 & & 2(S_4N_3)(Cl) + 2SCl_2 + 2Cl_2 \\
3(S_3N_2)(Cl) + SCl_2 + 5/2Cl_2 \arrow[r] & (S_3N_2Cl)(Cl) + SCl_2 + Cl_2 \arrow[ur, "267"'] &
\end{tikzcd}$$

Substitution Reactions

The reaction of trichlorocyclotrithiatriazene with trifluoroacetic anhydride was an attempt to replace chlorine atoms with -OR groups in which R has no active hydrogens to complicate the reaction.

$$(SNCl)_3 + 3CF_3\overset{O}{C}\text{-}O\text{-}\overset{O}{C}CF_3 \longrightarrow (SNO\overset{O}{C}CF_3)_3 + CF_3\overset{O}{C}Cl$$

It was hoped that the $(SNOR)_3$ ring would be stable since other derivatives have been made, ($R = CH_2CH_2Cl$, $CH(CH_2Cl)_2$, $CH(CH_2Cl)CH_2Br$, $CH(CH_3)CHClCH_3$ and $N(CF_3)_2$)[306, 325].

However, the only products isolated were $(S_3N_2Cl)(Cl)$ and $(S_4N_3)(Cl)$, since the reaction temperature was quite high in this reaction (80°C) these products can be accounted for by the breakdown of NSCl (see page 108).

With lithium bromide in phosphoryl chloride there was an immediate reaction producing impure $S_3N_2Br_2$ contaminated with S_4N_3Br. The substituted cyclotrithiatriazene was probably unstable and decomposed (cf. $(SNCl)_3 + 3HBr \longrightarrow S_3N_2Br_2$[345]).

$$\begin{tikzcd}
(SNCl)_3 + 3LiBr \arrow[r, "-3LiCl"] & \begin{array}{c}(SNBr)_3\\ \text{unstable}\end{array} \arrow[d] \\
S_4N_3Br & S_3N_2Br_2 + \tfrac{1}{2}N_2 + \tfrac{1}{2}Br_2 \arrow[l, "(SNBr)", "-Br_2"']
\end{tikzcd}$$

The structure of $S_3N_2Br_2$ probably resembles that of $(S_3N_2Cl)(Cl)$ because it forms conducting solutions in nitromethane[7].

Reaction of $(SNCl)_3$ with BCl_3 and SCl_2

There were three reasons for carrying out this experiment. First, the crystal structure of $(N(SCl)_2)(BCl_4)$ had been determined and the nitrogen angle was found to lie off the d_{SN} vs. $S\hat{N}S$ line (Chapter 1). Second, the infrared spectrum quoted[72] differs from that of related compounds[329] and the S-N absorptions do not fit the λ_{SN}-d_{SN} correlation (Chapter 2). Thirdly, Clarke[329] was unable to prepare this compound from the $(SNCl)_3.BCl_3$ adduct, which meant that his proposed reaction mechanisms were suspect.

The cation has been prepared by three routes and the following mechanisms have been proposed[154],

1)

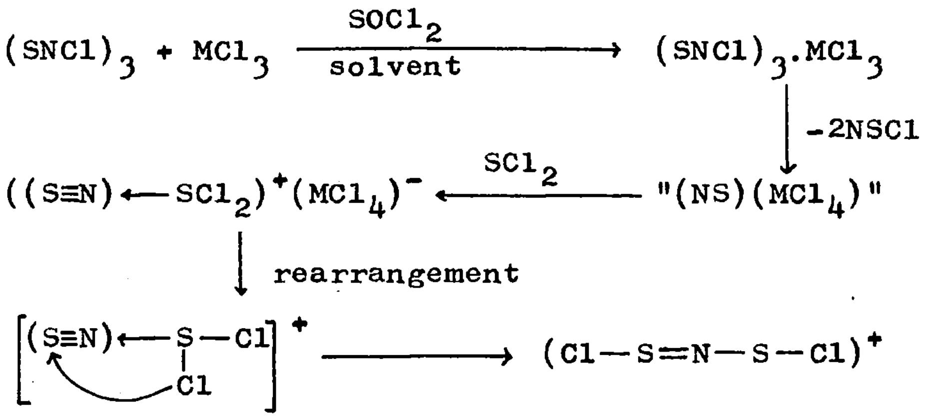
$$\begin{tikzcd}
BCl_3 + NSF_3 \arrow[r] & Cl_3B.NSF_3 \arrow[r, "BCl_3"] & (NSCl_3) + BCl_3 + BF_3 \arrow[dr] & \\
(SCl)^+(BCl_4)^- \arrow[d, "NSCl"] & SCl_2 \arrow[l, "BCl_3"'] & S_2Cl_2 + N_2 \arrow[l, "Cl_2"'] & NSCl + Cl_2 \arrow[l, "+NSCl"'] \\
(N(SCl)_2)(BCl_4) & & &
\end{tikzcd}$$

2) $BCl_3 + SCl_2 \longrightarrow (SCl)^+(BCl_4)^- \xrightarrow{1/3\ (SNCl)_3} (N(SCl)_2)(BCl_4)$

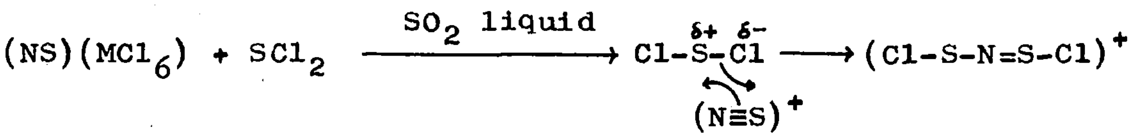
3)
$$\begin{tikzcd}
(SNCl)_3 \arrow[r] & NSCl \arrow[r] & S_2Cl_2 + N_2 \arrow[d, "Cl_2"] \\
(N(SCl)_2)(BCl_4) & (SCl)(BCl_4) \arrow[l, "NSCl"'] & SCl_2 \arrow[l, "BCl_3"']
\end{tikzcd}$$

all involving the electrophilic attack of the $(SCl)^+$ ion on NSCl. Nabi and Khaleque[356] have isolated 1:1 complexes of SCl_2 with $AlCl_3$, $FeCl_3$ and $SbCl_5$ and consider them to be chlorosulphenium salts of the type $(SCl)(MCl_{3\text{ or }5})$. However, it is difficult to envisage the presence of a positive charge on monocoordinate sulphur (S^+ normally 3 covalent).

Clarke[329] prepared many derivatives of the $(N(SCl)_2)^+$ cation by reaction of sulphur dichloride with Lewis acid adducts of $(SNCl)_3$ and he favoured the following mechanism in which the $(SNCl)_3$. Lewis acid adducts act as sources of $(NS)^+$.



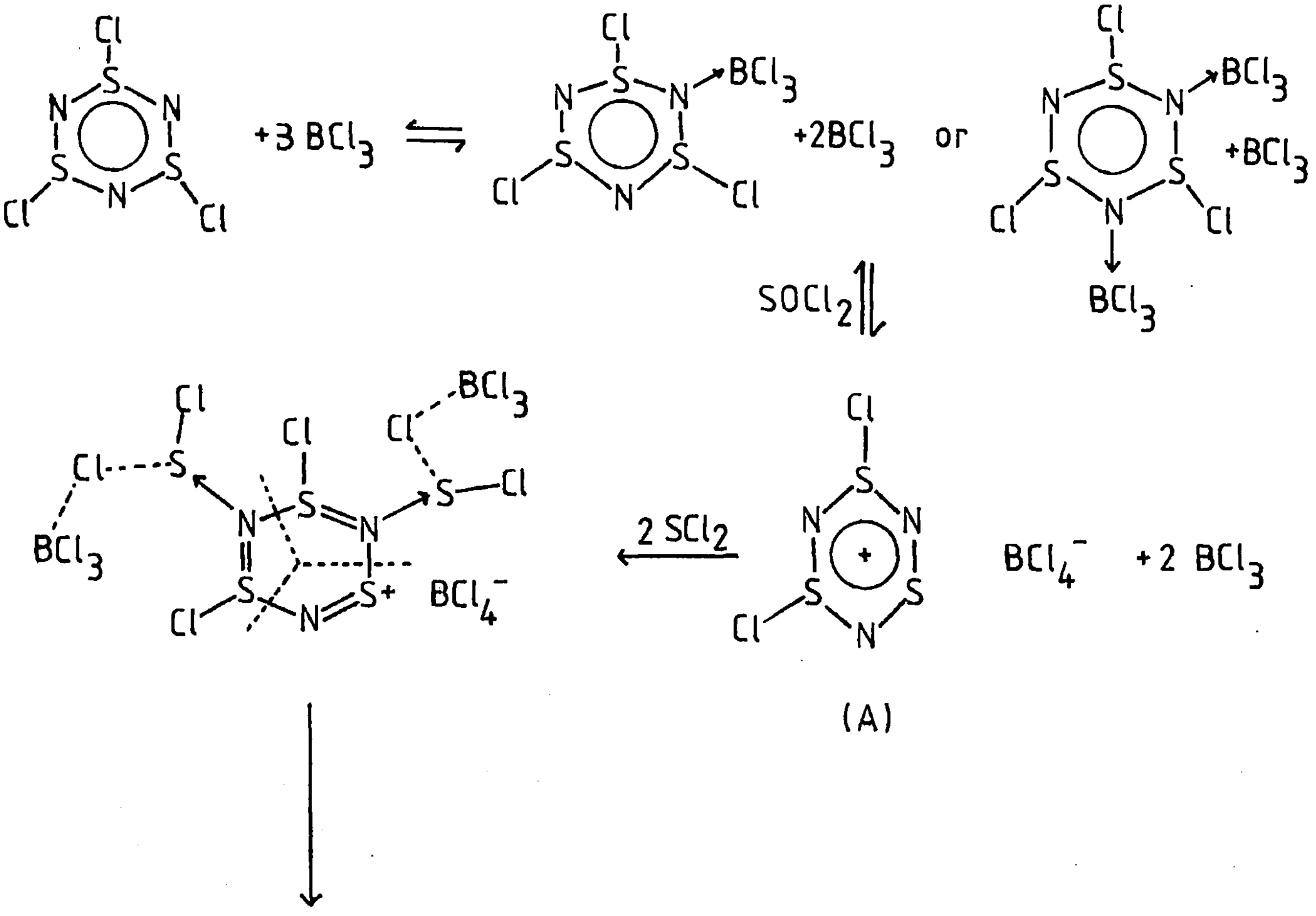
This kind of mechanism is supported by Mews[357] who, using thionitrosyl cations $(NS)^+$, isolated as the hexafluoro-arsenate or hexafluoro-stibate derivatives, inserted them into the polar S-Cl bonds of sulphur dichloride.



This mechanism is general for sulphenyl chlorides as the salts

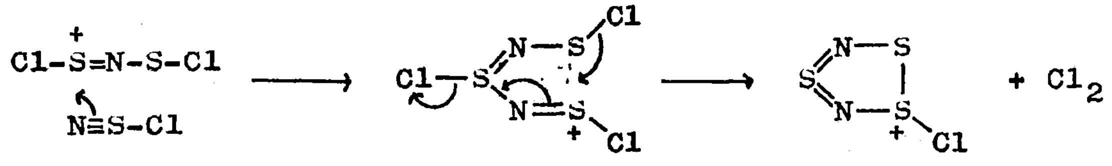
$(CF_3SNSCl)(MF_6)$ and $((CF_3)_2C{=}N{-}SNSCl)(MF_6)$ have been prepared from CF_3SCl and $(CF_3)_2C{=}N{-}SCl$, respectively, with $(NS)(MF_6)$[357].

In the reaction of trichlorocyclotrithiatriazene with boron trichloride in thionyl chloride solution a yellow adduct precipitated which was probably $(SNCl)_3.(BCl_3)_{1\text{ or }2}$. In the poor donor, polar solvent this probably exists as (A).



$$2\,[Cl{-}S{=}N{-}S{-}Cl][BCl_4] + [NS][BCl_4] \xrightarrow{SCl_2} [Cl{-}S{=}N{-}S{-}Cl][BCl_4]$$

The impurity $(S_3N_2Cl)(BCl_4)$ is presumably caused by attack of $N{\equiv}S{-}Cl$ on $(ClSNSCl)^+$.



The infra-red spectra of all the bis(chlorothio) nitrogen cations are listed in Table 5.2.

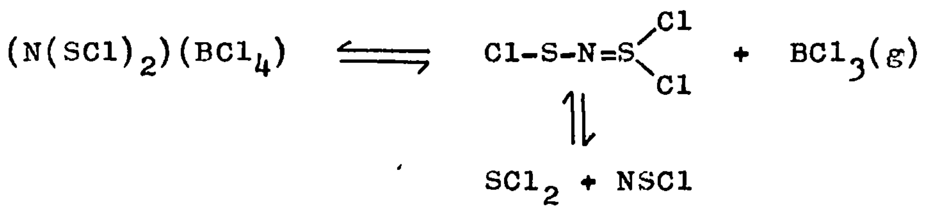
Table 5.2.

Infra-red spectra of bis(chlorothio)nitrogen cations.

Ref. 72 $(N(SCl)_2)^+$ $(BCl_4)^-$		Ref. 343 $(N(SCl)_2)^+$ $(BCl_4)^-$	Ref. 92 $(N(SCl)_2)^+$ $(AlCl_4)^-$		Ref. 329 $(N(SCl)_2)^+$ $(AlCl_4)^-$	Ref. 92,329 $(N(SCl)_2)^+$ $(SbCl_5)^-$		Ref. 329 $(N(SCl)_2)^+$ $(FeCl_4)^-$
I.r.	Raman	I.r.	I.r.	Raman	I.r.	I.r.	Raman	I.r.
1380s			1410w					
1340s								
1325s								
1265m								
			1220w					
		1123m	1130vs		1136m	1130m		1130m
		991w?						
		952m?						
			800w					
		740m(sh)			738(sh)	735(sh)		735m(sh)
	720s	720s		718	721m	721m	720	721m
705w	706w	704vs	695s					704(sh)
		696,668vs	655vs	657	654s	654s	657	654s
	652w	655vs			649(sh)			645(sh)
525s		523s			524s	521s	518	
	516s	516s		516	510s		511	517s
	499m	500s(sh)					500	505s
			490s	496	496s	494s		494s
423s	452s	445m		448			450	
408s	408m							

It must be noted that the infrared spectrum of $(N(SCl)_2)(BCl_4)^{72}$ is completely different from the other $(N(SCl)_2)^+$ salts, so that it appears to be a spectrum of decomposition products rather than a pure compound. It further proves that the d_{SN} versus λ_{SN} graph can be used to point out either suspect crystal structures or incorrect infra-red spectra. The infra-red spectrum of $(N(SCl)_2)(AlCl_4)^{92}$, taken at 80°C between AgCl plates, differs slightly in the high frequency region from the spectra of the other salts. The high temperature could accelerate atmospheric decomposition and give rise to N-H (1410 cm^{-1}) and S=O (1220 cm^{-1}) absorptions.

It is possible to make a few tentative assignments of the spectrum of $(N(SCl)_2)(BCl_4)$. Waddington and Klanberg[358], in a study of $(BCl_4)^-$ salts, noted strong bands at around 692 and 664 cm^{-1} which they attributed to ν_3 and $(\nu_1 + \nu_4)$ respectively. Two strong bands at 696 and 668 cm^{-1} are found in $(N(SCl)_2)(BCl_4)$ but are surprisingly missing from the spectrum of Glemser et al[72]. Could it be that there is an equilibrium in the plates such that the $(BCl_4)^-$ ion breaks down?



Compounds of the type $R\text{-}N{=}S{<}^{Cl}_{Cl}$ have ν_{SN} in the region 1323 - 1461 cm^{-1} [288, 359, 360] and NSCl absorbs at 1327 cm^{-1} [164], so the bands found in this region could be these breakdown products. Using character tables for the $(N(SCl)_2)^+$ ion assuming C_{2v} symmetry

	E	C_2	σ_v	σ_v'
n_R	5	1	5	1
χ_R	3	-1	1	1
χ_0	15	-1	5	1
χ_t	3	-1	1	1
χ_r	3	-1	-1	-1
χ_{t+r}	6	-2	0	0
$\chi_0 - \chi_{t+r} = \chi_{vib}$	9	1	5	1

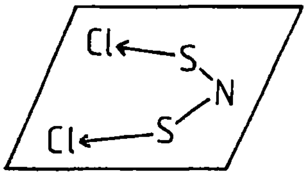
$$g = 4, \qquad a_\mu = 1/g \sum g_i \chi_i{}^{*\mu} \chi_i{}^{(\Gamma)}$$

$$\Rightarrow a_1 = 4,\ a_2 = 1,\ b_1 = 3, \text{ and } b_2 = 1$$

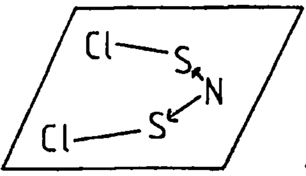
$$\Gamma_{vib} = 4A_1 + A_2 + 3B_1 + B_2$$

All are Raman active and all but A_2 are infra-red active.

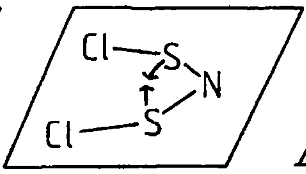
Approximate vibrational characters.



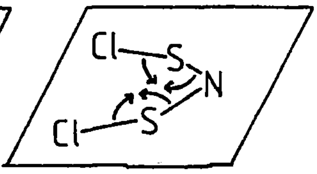
A_1 (S-Cl stretch)



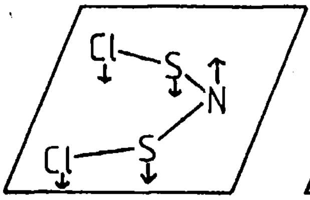
A_1 (SNS sym. stretch)



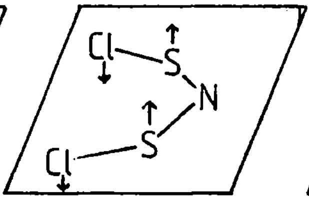
A_1 (SNS angle deformation)



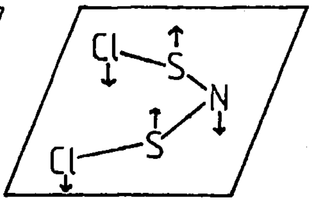
A_1 (ClSN angle deformation in plane)



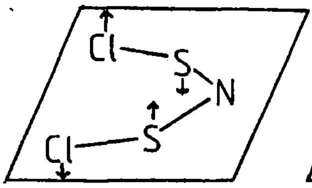
B_1 (out of plane deformation)



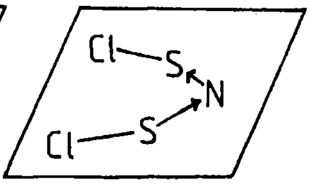
B_1 (out of plane deformation)



B_1 (out of plane deformation)



A_2 (S-Cl bend)



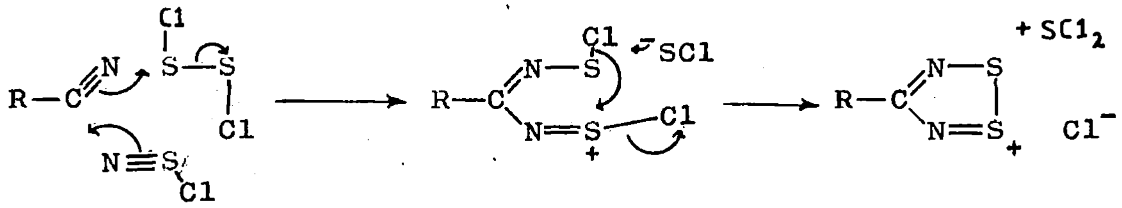
B_2 (SNS asym. stretch)

It appears from the spectra that there is quite a lot of splitting of the absorption bands, which makes assignment difficult but the band at ≈1130 cm^{-1} being the highest frequency must be assigned to B_2 (SNS asym. stretch), although no Raman band has been observed. The band at ≈720 cm^{-1} must therefore be A_1 (SNS sym. stretch). S^{II}-Cl stretching vibrations generally occur in the region 514 - 542 cm^{-1} [85], so the bands in the region 520 cm^{-1} are assigned to these (A_1, S-Cl stretch). The A_1 ($S\hat{N}S$ angle deformation) is the only other vibration that could reasonably occur above 500 cm^{-1} and it is assigned to ≈655 cm^{-1}.

Dithiadiazolium Salts

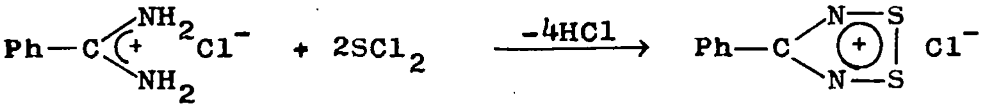
Trichlorocyclotrithiatriazene was known to react with nitriles RC≡N (R = CCl_3, Bu^t and Ph) to give 1,2,3,5-cyclodithiadiazolium chlorides $(RCN_2S_2)(Cl)$[342] but as found for the related Herz compounds[361], the dithiadiazolium chlorides were not easily purified. However, the products $(CCl_3CN_2S_2)(Cl)$ and $(PhCN_2S_2)(Cl)$ were found to be of high purity by infra-red and ultraviolet spectroscopy, analysis and mass spectroscopy due to improvements in purification techniques. The same compounds prepared by other routes e.g. $Cl_2C{=}CCl_2$ and $(SNCl)_3$, were contaminated with closely related compounds and could not be easily purified [342]. The impurities had infra-red peaks at: 1116s, 1100s, 1000m, 878m, 781s, 708w and 620w. The mechanism of the reaction probably involves the breakdown of monomeric NSCl to disulphur dichloride and nitrogen.

$$(SNCl)_3 \rightleftharpoons 3NSCl \rightleftharpoons (3/2)N_2 + (3/2)S_2Cl_2$$



This structure is confirmed by the formation of 4-phenyl -1,2,3,5-

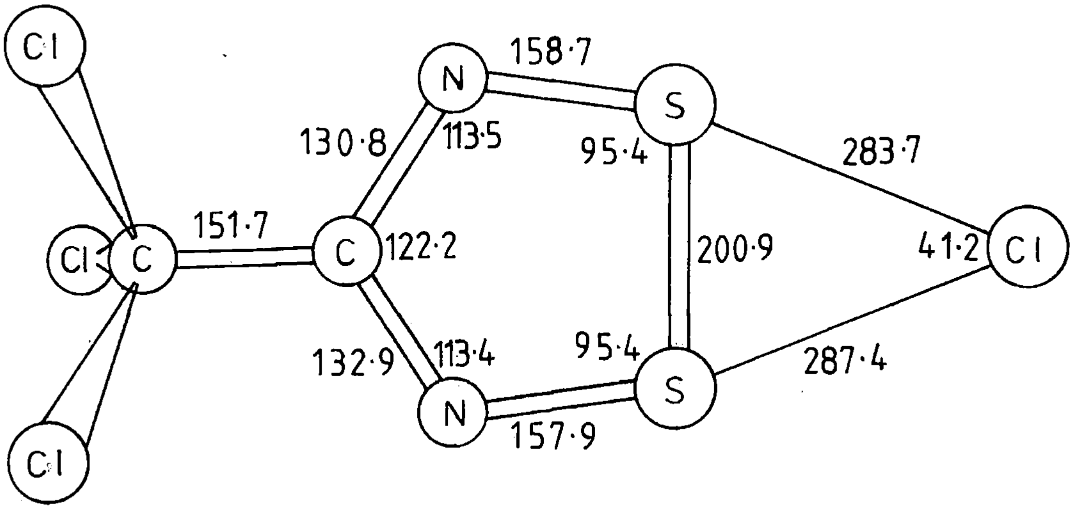
dithiadiazolium chloride from benzamidinium chloride and sulphur dichloride[342].



The X-ray crystal structure of $(CCl_3CN_2S_2)(Cl)$[362] shows that the five membered ring and the C atom attached to it are coplanar and the bond lengths in the ring indicate a large degree of double bond character. There is also a very short S-S distance (200.9(5) pm) indicating considerable π-bonding (Figure 5.2).

Figure 5.2

The X-ray crystal structure of $(CCl_3CN_2S_2)(Cl)$[362]



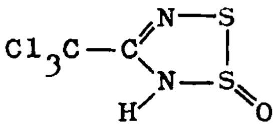
The structure can probably be regarded as a delocalised aromatic 6π system. A notable feature is the proximity of the Cl^- anion to the S-S bond (S-Cl = 283.7(6) and 287.4(6) pm). Using Pauling's formula[309] for calculating atomic radii, assuming a +½ charge on each sulphur atom and a -1 charge on the chloride anion an S-Cl distance of 360 pm. is calculated; since the distance is 75 pm shorter than this there must be some covalent bonding, or at least a three centre $\overset{Cl}{S\cdots\cdots S}$ bond.

These cyclodithiadiazolium salts are insoluble in most organic solvents but have low solubility in acetonitrile, nitrobenzene, dichloromethane, nitromethane or thionyl chloride. They decompose in air or in solvents that are not scrupulously dry by slowly turning white, the trichloro derivative being the least stable. They sublime at high temperatures in vacuo (e.g. $(PhCN_2S_2)(Cl)$ at 140°C and 0.1 mm). The mass spectra showed that breakdown was different for the two compounds but in both cases the parent peak was $(RCN_2S_2)^+$ with no sign of the chlorine atom being covalently attached.

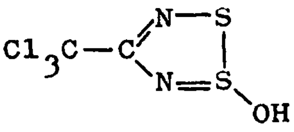
Reactions of Cyclodithiadiazolium Salts

Reaction of $(CCl_3CN_2S_2)(Cl)$ with Air

In the mass spectrum of $(CCl_3CN_2S_2)(Cl)$ exposed to air there were peaks (m/e) from 237 to 242 which implied that slight hydrolysis had taken place and that compounds A or B were formed.



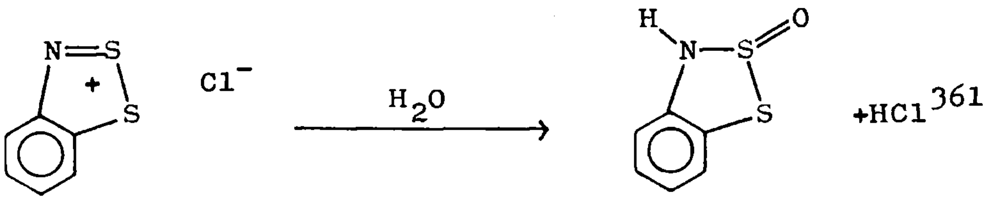
or



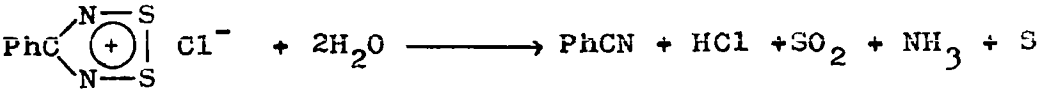
A

B

Structure A is favoured because the compound is white i.e. the aromaticity of the ring has been lost and also because of the similarity of dithiadiazolium chlorides with 1,3,2-benzothiazolium chlorides (Hertz compounds).

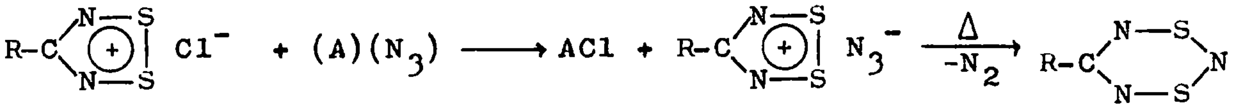


4-Phenyl-1,2,3,5-cyclodithiadiazolium chloride underwent further hydrolysis in the air and the peak at 2060 cm^{-1} in the product indicated the formation of PhC≡N.



Reaction of Cyclodithiadiazolium Salts with Sodium and Lithium Azides

The reaction of cyclodithiadiazolium salts with azides was attempted in order to prepare a new C-N-S ring:-



Although both the cyclodithiadiazolium salts and the azides dissolved slightly in tetrahydrofuran there was no sign of the formation of products from these reactions. In acetonitrile a red/brown solid was recovered which did not mull very well but had characteristic absorptions of the azide anion and the 4-trichloromethyl-1,2,3,5-cyclodithiadiazolium cation (Table 5.3).

Table 5.3

Infra-red Spectra of Products and Reactants (cm^{-1})

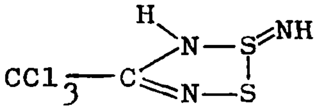
LiN_3 + $(CCl_3CN_2S_2)(Cl)$	LiN_3	$(CCl_3CN_2S_2)(Cl)$	$(CCl_3CN_2S_2)(Cl)$ + NH_3
2315w			3125vs, 3040vs, 1405vs (N-H)
2285m			
2140m	2090vs		
1268s		1280w	1270s, 1237m
1175m			1105m
1068m(sh)		1075w	
1022s		1055s, 1024w(sh)	1026s
990m(sh)			
939m		911w	
870m		861s	867m, 860m(sh)

LiN_3 + ($CCl_3CN_2S_2$)(Cl)	LiN_3	($CCl_3CN_2S_2$)(Cl)	($CCl_3CN_2S_2$)(Cl) + NH_3
849m		827s(sh)	
812m(sh)		818vs	795s
779s		796vs	780s
729s		765vs, 678vs	732s, 707w
640m	640vs		630m
558m		548s	550m

The correlation is not exact, implying that some reaction has occurred. The $(N_3)^-$ asymmetric stretching frequency has moved 50 wavenumbers to higher frequency, which suggests there is some interaction between the anion and cation. The compound resisted attempts at purification and analysis results were inconsistent, so the reaction was not proceeded with.

Reaction of ($CCl_3CN_2S_2$)(Cl) with Liquid Ammonia

The red brown product from this reaction had a similar spectrum to the pure dithiadiazolium salt but with N-H stretching and bending frequencies. Although purification was not successful structure (A) seems a likely product from the infra-red spectrum, because this is

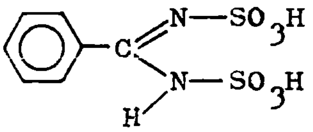


(A)

isoelectronic with the proposed hydrolysis product.

Reaction of ($PhCN_2S_2$)(Cl) with Concentrated Nitric Acid

The attempt to make the cyclodithiadiazolium nitrate was not successful because the ring broke up inder the highly oxidising conditions. The analysis figures correspond to $C_7H_8N_2O_6S_2$.



(B)

Structure (B) is proposed because there are O-H and N-H stretching frequencies and the compound dissolved in water. The infra-red spectrum also has a peak at 1680(s) (cm^{-1}) which can be assigned to a C=N stretching frequency.

Reaction of $(PhCN_2S_2)(Cl)$ with $FeCl_3$

This reaction produced the tetrachloroferrate salt in high yields. The infra-red spectrum shows a few new bands and most of the peaks are shifted compared with the parent (Table 5.4). The product can be left in air for long periods without noticeable signs of decomposition and can be recrystallised easily from thionyl chloride.

The facile formation of an easily handled salt should make the purification of cyclodithiadiazolium salts an easy matter in the future.

Reaction of $(PhCN_2S_2)(Cl)$ with NaI

The attempt to produce the iodide in SO_2 only succeeded in producing a compound with an almost identical infra-red spectrum to the product from the reaction with nitric acid (Table 5.4) which implies that the solvent was not scrupulously dry. In dichloromethane however, a brown solid was formed which analysed closely to $(PhCN_2S_2)(I)$. The infra-red spectrum shows many similarities to the chloride but there are definite shifts in frequency for many of the absorptions (Table 5.4).

The success in preparing different salts of the cyclodithiadiazolium cation depends on the choice of solvent and of those tried , dichloromethane and thionyl chloride appear to be the best.

Table 5.4

Infra-red spectrum of $(PhCN_2S_2)(Cl)$ and products of reactions.

$(PhCN_2S_2)(Cl)$	$(PhCN_2S_2)(Cl)+HNO_3$	$(PhCN_2S_2)(FeCl_4)$	$(PhCN_2S_2)(Cl)+NaI$	
			in SO_2	in CH_2Cl_2
	3385m, 3160s			
3020w				
	1680s		1664vs	
1598w	1612w, 1598w	1608w, 1600w		1600w
1584w		1588w	1583w	
	1525w	1507m	1510w	
1451vs				1460vs
		1409vs		
1370vs		1402vs		1378s
1346s		1347s		1358m
1299m	1291m	1300m	1288m	
		1266w		
1213m	1228vs	1201s	1223s	
		1188w		
1176w	1173vs	1169s	1172vs	1181w
1153m				
		1100w		
1074w	1068m	1076w	1075m	
1045w		1050w		
1029m	1037vs	1035m	1037s	1028m
1006w		998w	1005w	
	979w	980w	980w	972m
947w	942w			
926m		935s		
898vs		920vs		
	875s		874s	

$(PhCN_2S_2)(Cl)$	$(PhCN_2S_2)(Cl)+HNO_3$	$(PhCN_2S_2)(FeCl_4)$	$(PhCN_2S_2)(Cl)+NaI$	
			in SO_2	in CH_2Cl_2
847s		848m		860m
				832vs
789vs	791m	780vs	788m	782vs
761m				
	724m	729m	723w	
699vs	700m	702vs	699m	694s
		688s		
670m(sh)	663m	672m		676s
	604m	623w	598s	
553s	579s	566s	582s	520m

CHAPTER 6.

Sulphur - Nitrogen - Oxygen Compounds.

Introduction.

The study of sulphur - nitrogen - oxygen species has been one of the most neglected areas of sulphur - nitrogen chemistry. This is surprising since the compounds have been known for many years and some S-N-O rings are among the most stable systems in S-N chemistry.

In this chapter the chemistry of the compounds used in the experimental section, viz: $S_3N_2O_2$, $S_3N_2O_5$ and 'cyclosulphimides' are introduced and the experimental and discussion sections describe the preparative routes used and the reactions of these species.

Preparation and Chemistry.

Sulphur bis(sulphinylimide), $S(NSO)_2$

$S(NSO)_2$ can be prepared by a variety of routes. By reacting S_4N_4 with thionyl chloride at room temperature[122], or with SO_2 and thionyl chloride in nitromethane[363] a 25% yield of $S(NSO)_2$ results. The main impurities are said to be $(S_4N_3)(Cl)$, S_4N_2 and chlorosulphanes. Moderate yields are produced if SO_2 is bubbled into $(S_4N_3)(Cl)$, in thionyl chloride[364],

$$2\ (S_4N_3)\ (Cl) + 6SOCl_2 \xrightarrow{SO_2} 3\ S(NSO)_2 + 7Cl_2 + 5S$$

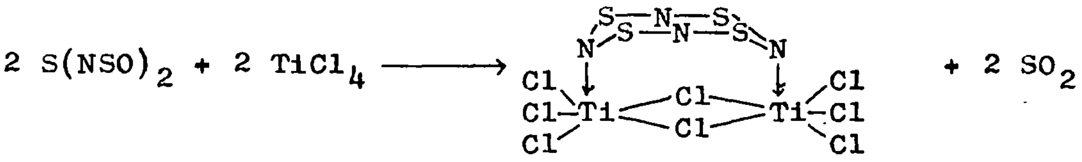
or if $(SNF)_4$ is heated with an NO_2/O_2 mixture at 120°C.[8] Yields are higher in the reactions between NH_3 and $SOCl_2$ or between NH_4Cl, $SOCl_2$ and sulphur[365]. However, the best preparative route is the reaction of Me_3SiNSO with SCl_2[196] or $SOCl_2$[366].

Sulphur bis(sulphinylimide) is a pale yellow crystalline solid (mp. 100.7°C) which is soluble in benzene or alcohol but undergoes hydrolysis with moist air or water[367, 368].

$$S(NSO)_2 + 4\ H_2O \longrightarrow (NH_4)_2(S_3O_6)$$

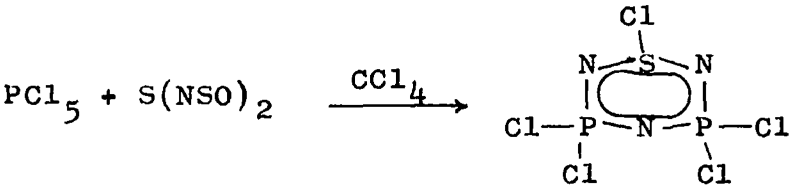
$$S(NSO)_2 + \text{trace } H_2O \longrightarrow S_4N_4 + SO_2$$

The formation of S_4N_4 with traces of water could explain the production of S_4N_4 - Lewis acid adducts in the reaction of $S(NSO)_2$ with Lewis acids,[369] e.g. -



Sulphur bis(sulphinylimide) is oxidised by sulphur trioxide to $S_3N_2O_5$[370] and reacts with liquid chlorine to form $S_3N_3OCl_3$[371].

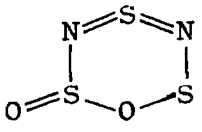
With phosphorus pentachloride in carbon tetrachloride, $S(NSO)_2$ undergoes a complicated rearrangement to form a clear oil[372]



and with silated amines in refluxing dichloromethane, amine exchange takes place[373].

$$S(NSO)_2 + Me_3SiNR_2 \xrightarrow[\text{Reflux}]{CH_2Cl_2} Me_3SiNSO + (OSN)S(NR_2)$$

Three structures for $S(NSO)_2$ were proposed as a result of hydrolysis reactions,[363] labelling of sulphur[364] and the study of the oxidation of $S(NSO)_2$ by SO_3[370, 374],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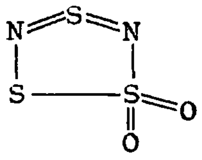
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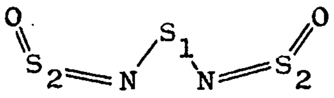

III

but an X-ray diffraction study found structure III to be the correct one[71]. The bond lengths and angles are listed in Table 6.1.

Table 6.1

Distances (pm)		Angles	
S_1-N	169	NS_1N	95.3°
S_2-N	158	NS_2O	115.3°
S_2-O	137	S_1NS_2	120.0°
S_2-S_1	283		

The molecule was found to be planar with an essentially single SN bond. (A fuller discussion of this structure appears in Chapters 1 and 2).

$S_3N_2O_5$

Goehring and Heinke[364] proposed that the oxidation of S_4N_4 by SO_3 at 70 - 80°C first produces the adducts $S_4N_4.2SO_3$ and $S_4N_4.4SO_3$ and thermal decomposition of the latter produces $S_3N_2O_5$. If labelled sulphur trioxide is used, 67% of the radioactive sulphur is found in the solid product[364].

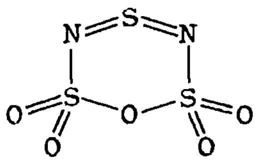
$$S_4N_4 \xrightarrow{4\overset{*}{S}O_3} S_4N_4\cdot 4\overset{*}{S}O_3 \xrightarrow{2\overset{*}{S}O_3} \overset{*}{S}_3N_2O_5 + 2\overset{*}{S}O_2 + 2SO_2.$$

However, Roesky could only isolate the 1:1 adduct $S_4N_4.SO_3$ in this reaction[208]. Both $S(NSO)_2$ and $(SNF)_4$ can also be oxidised to $S_3N_2O_5$[8,370].

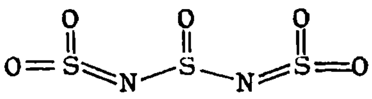
$S_3N_2O_5$ dissolves in benzene, toluene, xylene and nitrobenzene[370] but reacts with diethyl ether[355,375], ethanol, pyridine, nitromethane and water[370].

$$\overset{*}{S}_3N_2O_5 \xrightarrow{H_2O} SO_2 + \overset{*}{S}O_2(OH)NH_2 + H_2\overset{*}{S}O_4 + NH_3.$$

Although the compound is well-crystallised and sublimable no crystal structure has been attempted to date. Goehring et al[326,370,376-378], suggested structure lV but structure V has also been proposed by analogy with $S(NSO)_2$[355].



IV



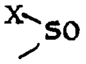
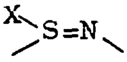
V

Tri - and Tetrameric Sulphur-Nitrogen-Oxygen Ring Systems.

These rings can be considered to be formed by the condensation of unstable monomers (A-E) derived from sulphur oxygen compounds by replacing one oxygen atom by (=NR) or ($=N^-$) groups (Table 6.2).

Table 6.2

SO Compound	Derived NSO Monomer	
SO_3	$(O_2SN)^-$	A
SO_2	$(OSN)^-$	B
$X{>}SO_2$	$X{>}OS{=}N\diagdown$	C

SO Compound	Derived NSO Monomer
	 D
$(SO)^{2+}$ (unknown)	$(SN)^{+}$ E

In Table 6.3, the trimers and tetramers prepared to date are presented.

Table 6.3

	(O_2SN^-)	(OSN^-)	$(OS(X)N)$	(XSN)	(SN^+)
$2(O_2SN^-)$	$(S_3N_3O_6)^{3-}$				$(S_3N_3O_4)^-$
$3(O_2SN^-)$	$(S_4N_4O_8)^{4-}$				
$2(OSN^-)$		$S_3N_3(OR)_3$			$(S_3N_3O_2)^-$
$3(OSN^-)$		$S_3N_3O_3H_3$			
$2(OS(X)N)$	$(S_3N_3O_4F_2)^-$	$(S_3N_3O_3F_2)^-$	$S_3N_3O_3Cl_3$	$S_3N_3O_2F_3$	
$3(OS(X)N)$			$S_4N_4O_4F_4$		
$2(XSN)$			$S_3N_3OCl_3$	$S_3N_3Cl_3$	$(S_3N_3F_2)^+$
$3(XSN)$				$S_4N_4F_4$	

In this chapter only the group of species commonly known as cyclosulphimides $(O_2SNH)_n$ will be discussed. At present all attempts to isolate the free acids $(O_2SNH)_n$ have been unsuccessful. Only salts containing the unions $(O_2SN)_n^{n-}$ (n=3 or 4) and covalent derivatives $(O_2SNR)_n$ (n=2 - 4) have been prepared.

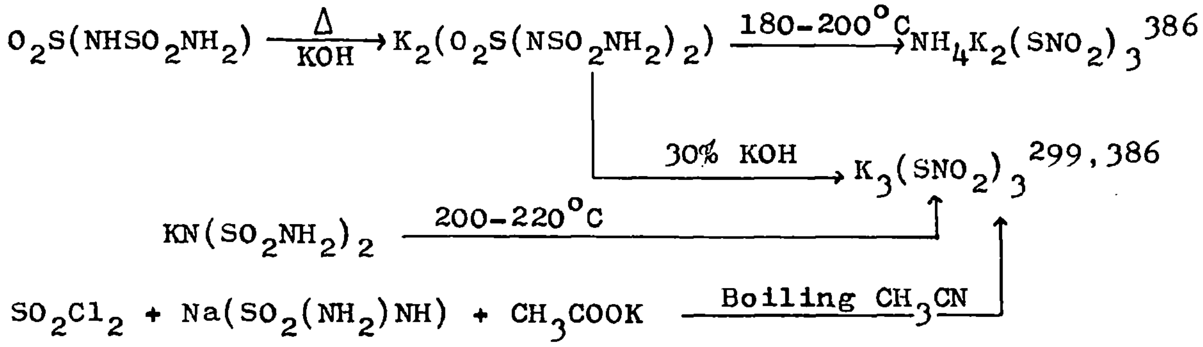
Preparations.

A) Trimers.

Triammonium hexaoxocyclotrithiatriazenide, $(NH_4)_3(SNO_2)_3$, is readily prepared by the thermal decomposition of sulphamide $SO_2(NH_2)_2$, at 180° - 200° for 6 hours. The reaction proceeds through many intermediates, many of which can be isolated by chromatography e.g. $(NH_4)(N(SO_2NH_2)_2)$[380].

$$3\ SO_2(NH_2)_2 \xrightarrow{\Delta} \text{intermediates} \xrightarrow{\Delta} (NH_4)_3(SNO_2)_3$$

The ammonium salt can also be prepared as a biproduct from the reactions of sulphuryl chloride[297,381,382], or sulphur trioxide[381,383,384] with ammonia or sodium amide. Other salt derivatives may be prepared from this salt by metathetical reactions[11,385]. There are a variety of ways of forming potassium salts:-



The silver salt can be precipitated by hydrolysing $(SNOCl)_3$ with dilute silver nitrate,

$$(SNOCl)_3 + 6\ AgNO_3 \xrightarrow{H_2O} Ag_3(SNO_2)_3.5H_2O + AgCl$$ [387].

Pyridine reacts with sulphamoyl chloride $SO_2(NH_2)Cl$ to form the dipyridinium salt, $(pyH)_2(H)(SNO_2)_3$, but attempts to form $(O_2SNH)_3$ by ion exchange in SO_2 or D.M.F. resulted in ring breakdown.[388] Barium[299], cobalthexammine[298], lead[298], lithium[385], mercury (I) and (II)[298], sodium[385] and thallium[298] salts have been prepared by metathetical reactions, usually of the silver salt.

N-Methyl and N-ethyl derivatives have been prepared from the silver salt and the corresponding iodide,[296-299]

$$3\ RI + Ag_3(SNO_2)_3 \longrightarrow AgI + (O_2SNR)_3 \qquad (R= Me,\ Et)$$

whereas the benzoyl derivative was prepared from benzoyl chloride and the silver salt[297].

B) Tetramers

The reaction of SO_3 with NH_3 in nitromethane at 0°C leads to small quantities of tetra-ammonium octaoxocyclotetrathiatetrazenide (ref. 381,383), which can be isolated as the silver salt.

$$8\ NH_3 + 4\ SO_3 \longrightarrow (NH_4)_4(SNO_2)_4 + 4\ H_2O$$

Small yields of the ammonium salt (≈15%) are formed from the reaction of $Na(SO_2(NH)_2NH)$ with SO_2Cl_2 but it must be converted to the barium or silver salt in order to obtain the pure tetramer[386].

The pyridinium salt $(pyH)_2H_2(SNO_2)_4$ is formed in the reaction of sulphamoyl chloride with pyridine[301,388], but the best route to tetrameric derivatives is the condensation of $SO_2(NH_2)_2$ with SO_2Cl_2 in boiling acetonitrile[301].

$$SO_2(NH_2)_2 + SO_2Cl_2 \longrightarrow (NH_4)_4(SNO_2)_4 + 4\ HCl$$

Simple metathetical reactions with the ammonium salt lead to the barium[301,386], N-butylammonium[301], potassium and silver salts[301,381,386]. N-methyl and N-ethyl derivatives have been prepared from the silver salt with the respective iodide[300,301,381].

Physical and chemical properties

Lithium, sodium and potassium hexaoxocyclotrithiatriazenides decompose above 306°C, $2\ M_3(SNO_2)_3 \xrightarrow{\Delta} 3\ M_2SO_4 + 3N_2 + 3S$ (M= Li,Na,K) but the silver salt decomposes differently at 292°C,

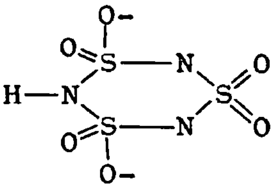
$Ag_3(SNO_2) \xrightarrow{\Delta} 3\ Ag + 1\tfrac{1}{2}\ N_2 + SO_2$ [385].

The ammonium salt breaks down at even lower temperatures (225°C),

$(NH_4)_3(SNO_2)_3 \xrightarrow{\Delta} N_2, S_8, NH_3, (HNSO)_4, SO_2(NH_2)_2$ and $(NH_4)_2(HN(SO_3)_2)$, and above 300°C the ammonium imidodisulphonate undergoes further decomposition,

$$3\ (NH_4)_2(HN(SO_3)_2) \xrightarrow{\Delta} 3\ (NH_4)_2SO_4 + 3\ SO_2 + NH_3 + N_2$$
$$\hookrightarrow 6\ NH_3 + 3\ SO_3 + 3\ H_2O$$ [385]

$(O_2SNH)_3$ can be formed in solution by treating the silver salt with aqueous HCl [298]. By titrating this solution, it is found that two protons are highly acidic but the third is strongly bonded, probably due to the formation of



in solution[298]. On standing in solution the ring is hydrolytically cleaved and after three days a 1:1:1 mixture of sulphuric acid, sulphamide and sulphamic acid remains[298,370,389]. The ring breakdown appears to be auto-acid catalysed because in neutral or weakly acid solutions the ring is relatively stable.

The tetramer is less hydrolytically stable than the trimer, needing 20 minutes in 2M HCl at room temperature to undergo ring breakdown, whereas the trimer requires 2 hours of boiling 2M HCl [301].

Structures.

X-ray structure determinations of $(Ag)_3(SNO_2)_3.3H_2O$[69] and $(SO_2NMe)_3$[203] have shown that the S_3N_3 ring adopts a chair conformation of approximate C_{3v} symmetry. In the silver salt the S-N bond distances are equal within experimental error (163.6(4)pm) but the S-O axial bond (145.1(6)pm) is longer than the S-O equatorial bond (142.7(6)pm) probably because of weak interactions between the oxygen and silver atoms [69], or because the equatorial sites are less sterically hindered. The methyl derivative, however, has S-N bond distances approximately the same (166.2(1)-167.3(2)pm) and all S-O bond lengths equal within experimental error (140.8(1)pm) [203].

Table 6.4 lists the geometries of molecules isolectronic with $(SNO_2)_3^{3-}$ together with those of $(O_2SNMe)_3$. Comparing the three SN compounds, it can be seen that the S-N bond length increases in the series $(SNOCl)_3$, $(SNO_2)_3^{3-}$, $(O_2SNMe)_3$. This can be attributed to the fact that the π-electrons are shared between 6 SN and 3 SO bonds in $(SNOCl)_3$ but 6 SN and 6 SO bonds in $(SNO_2)_3^{3-}$ and the attachment of methyl groups to the nitrogen atoms in $(O_2SNMe)_3$ reduces the π-bonding in the ring still further.

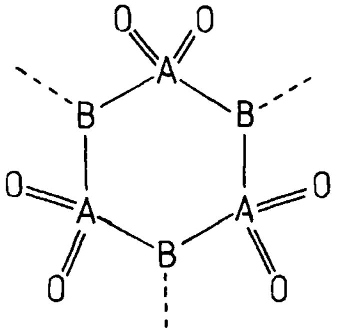
Table 6.4

Molecular Geometry for Six Membered $(AB)_3$ rings with Two Exocyclic Groups (C,D).

(A = S,P. B = O,N,NMe. C = O,Cl. D = O,Cl).

	Exocyclic Bond Lengths	Ring Bond Lengths	$B\hat{A}B$°	$A\hat{B}A$°	$C\hat{A}D$°	A-A Distance
$(SO_3)_3$ [86]	143.0(13) 137.1(13)	162.6(7)	98.7(8)	121.5(8)	126.1(8)	282.4
$(SNO_2)_3^{3-}$ [69]	145.1(6) 142.7(6)	163.6(4)	106.1(4)	115.1(3)	117.4(4)	276.1
$(PO_3)_3^{3-}$ [390]	148.9(3) 148.0(3)	161.5(2)	101.3(1)	126.9(1)	120.2(1)	289.0(2)
α-$(SNOCl)_3$ [68]	140.7(7)	157.1(4)	112.8(4)	122.0(4)	107.9(4)	274.8
$(O_2SNMe)_3$ [203]	140.9(1) 140.7(1)	166.9(1)	104.5(1)	117.1(1)	121.9(1)	284.7

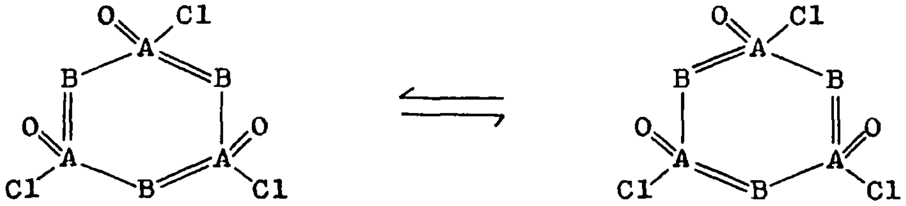
One canonical (I) describes $(O_2SNMe)_3$ and $(SO_3)_3$ reasonably accurately and accounts for the long AB and short SO bonds



(I)

Canonicals (II) and (III) describe the short SO bonds in $(SNOCl)_3$.

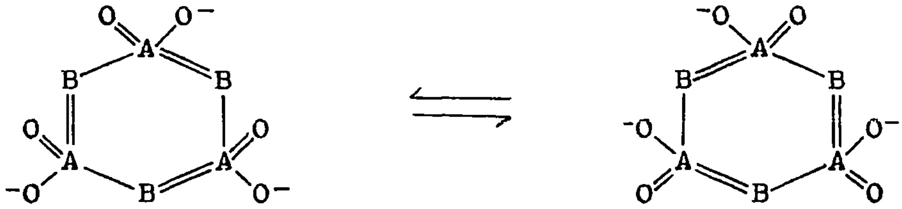
(II)



(III)

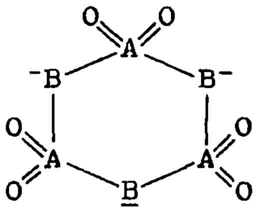
For $(SNO_2)_3^{3-}$ and $(PO_3)_3^{3-}$ the exocyclic bonds are much longer implying the involvement of (IV) and (V),

(IV)



(V)

but the ring bond lengths are longer in $(SNO_2)_3^{3-}$ than in $(SNOCl)_3$ so canonical (VI) must be invoked for the former.



(VI)

The contribution of canonicals (IV) - (VI) in the structure of the hexaoxocyclotrithiatriazenide (3-) anion is exemplified by the SCF MO calculations of Armstrong et al[78] (Table 6.5).

Table 6.5

CNDO/2 Calculations for $(SNO_2)_3^{3-}$ [78]

Charges.				Bond Indices			
S	N	O eq	O ax	S-N	S-O eq	S-O ax	S-S
+0.57	-0.46	-0.59	-0.51	1.20	1.50	1.48	0.16

with equal negative charges on both nitrogen and oxygen and larger S-O bond indices than S-N bond indices.

Experimental.

Reaction of Sulphur Trioxide with cyclotetrathiazene (S_4N_4).

Oleum (150 ml, 20%) was heated to 120°C at a pressure of 15 torr and SO_3 was distilled from this on to cyclotetrathiazene (5g, 0.027 mol). The orange crystals of cyclotetrathiazene turned dark brown and a vigorous reaction took place evolving yellow/brown fumes. The flask was kept cool with iced water and the reaction slowly subsided. Sulphur trioxide was distilled over for a further two hours to ensure complete reaction. A brown solid remained. The flask was heated to 30°C at 1 torr and the excess SO_3 was distilled off. Finally the flask was heated briefly to 60°C at 1 torr to remove the last traces of SO_3. The temperature was raised to 78°C at 1 torr pressure and yellow/white crystals sublimed on to the cold finger. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 3150m, 1565w (broad), 1300-1250m (broad), 1160m (broad), 1060s, 1000w, 870m, 720m, 700s, 600w, 550m. The mass spectrum showed no peaks above 80m/e.

The product appeared to be mainly SO_3 contaminated by grease. The experiment was repeated using 'Voltalef Graise 90' to discourage the attack by SO_3 upon the greased joints. Only 0.3g of product was recovered. Found: N, 10.21; S, 45.97. Calcd. for $N_2O_5S_3$: N, 13.7; S, 47.1%. I.r.(Nujol mull) absorptions occurred (cm^{-1}) at 3170w, 1434vs, 1290m (broad), 1230s, 1212s, 1198m (sh), 1133s, 1108s, 1070s, 976w, 855w, 780msh, 758s, 732s, 699m, 647s, 547s, 493m, 450s, 431msh. Major mass spectral peaks at 150°C occurred at m/e: 213; $S_3N_2O_5$, 204; 149; $S_2N_2O_2$ (S_3N_2), 124; 122; 105; NH_2SO_3H, 97; S_2N_2, 92; SO_3, 80; SO_2, 64; SO, 48.

Since there was a large brown mass of material that would not sublime, an attempt was made to take it up into dichloromethane. Immediately a yellow-orange powder was deposited, i.r.(Nujol mull) absorptions occurred (cm^{-1}) at 1320s, 1288vs, 1267vs, 1191s, 1140s, 1120s, 1071s(sh), 1052vs, 990m, 878w, 821s, 695w, 646s, 629m, 567s, 552m, 529m, 509w, 458w.

Reaction of thionyl chloride with cyclotetrathiazene.

Thionyl chloride (150ml) was added to cyclotetrathiazene (5g,0.027 mol) and the solution warmed to 40°C for 24 hours, with stirring. On cooling, red-orange crystals were deposited together with a green powder from the red solution. The solution was filtered and the infra-red spectrum of the red crystals and the green powder showed that they were $(S_4N_3)(Cl)$ and impure $(S_4N_3)(Cl)$ respectively. The red solution was pumped to dryness leaving a red-brown solid. Dry benzene (50ml) was added and the resulting red suspension was filtered and pumped to dryness leaving a greenish black residue. This was sublimed at 40°C and 1 torr pressure to form shining yellow platelets. Yield 42%. Analysis found: N, 17.9; S, 62.1; $N_2O_2S_3$ requires N, 17.9; S, 61.5%.

I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1180vs, 1038s, 680s, 656w, 550m, 503m, 365s.

The major mass spectral peaks at 150°C (relative intensities in brackets) occurred (m/e) at $S_3N_2O_2$, 158(5); $S_3N_2O_2$, 156(42); S_2NO, 110(6); SNSO, 94(13); S_2N_2, 92(35); $S_2O(SO_3)$, 80(2); S_2N, 78(5); N_2OS, 76(13); SO_2, 64(14); HNSO, 63(10); SO, 48(28); SN, 46(100); S, 32(47).

Reaction of sulphur bis(sulphinylimide) with sulphur trioxide.

A large quantity of solid sulphur trioxide was heated to 100°C and passed by vacuum transfer on to $S(NSO)_2$ (3g,0.019 mol) which was kept at -196°C. The vessel was then allowed to warm to room temperature and kept at this temperature for three hours. The temperature was raised to 60°C to pump off the excess SO_3 and the product sublimed at 70-80°C and 1 torr pressure producing white needles. I.r.(Nujol mull) absorptions occurred (cm^{-1}) at 3165w, 1434vs, 1288m, 1234vs, 1217s, 1198m, 1136vs, 1100vs, 1077s, 935w, 772vs, 762vs, 740m, 712w, 691w, 643s, 546vs, 494m, 458vs, 431w.

Reaction of liquid ammonia with sulphuryl chloride.

Liquid ammonia (400ml) was collected in a cooled (-78°C acetone/CO_2) 2 litre flask and sodium metal added until a permanent blue colour persisted (indicating $NaNH_2$ was being formed and all the moisture had reacted with the sodium). The flask was allowed to warm to room temperature and the dry ammonia was distilled to another cooled 2 litre flask. Sulphuryl chloride (50 ml) in hexane (500 ml) was added with stirring over a period of six hours, taking care not to let the dropping funnel become blocked with ammonium chloride.

The resulting green/yellow solution was allowed to stand exposed to the air overnight so that the excess ammonia could evaporate. The residue was a creamy solid in hexane. This was filtered and pumped to dryness at 70°C. The chain-type sulphur-nitrogen-oxygen compounds formed as side products were hydrolysed to sulphomide by dissolving in 10% hydrochloric acid (250 ml) and warming to 80°C for ten minutes. The solid was then filtered and pumped to dryness at 80°C.

The off-white solid was then shaken with analar acetone (5 x 30 ml), to remove ammonium chloride and the resulting solutions were collected together and pumped to dryness leaving a light brown solid. This was recrystallised twice from absolute alcohol. Yield, 15.2g. (26% based on SO_2Cl_2). Mp. 91-92°C lit. 92.1°C [394].

Found: H, 4.62; N, 28.94; S, 32.92. Calcd. for $H_4O_2N_2S$ H, 4.16; N, 29.16; S, 33.33%. I.r.(KBr disc) absorptions occurred (cm^{-1}) at 3335 - 3170 broad, 2720w, 2670w, 1616w, 1552m, 1545m, 1357vs, 1330s(sh), 1165vs, 1142sh, 930m(sh), 913m, 722s, 562m, 535s.

Action of heat on sulphamide, $SO_2(NH_2)_2$ [380].

Sulphamide (15g , 0.156 mole) was heated slowly in a flask connected to a reflux condenser. After melting at 92°C the temperature was raised to 180°C over the period of one hour and further raised to 200°C over the next hour. This temperature was maintained for five hours during which a red compound formed in the air condenser. I.r.(Nujol mull) absorptions occurred (cm^{-1}) at 3170s (broad), 1430vs, 1262vs, 1239vs, 1210vs, 1175s, 1162vs, 1090s, 1048vs, 1013vs, 980s, 930vs, 812m, 730s, 668m, 595s, 568s, 462m.

This decomposed to an orange compound over two days. At the bottom of the flask a hard brown mass formed on cooling. This was dissolved in 0.88 ammonia and the dark dolution boiled with decolourising charcoal, filtered and pumped slowly to dryness, leaving white crystals (2). Yield 81%.

Found: H, 5.12; N, 24.61; S, 28.24. Calcd. for $(NH_4)_3(SNO_2)_3$ H, 4.16; N, 29.16; S, 33.33%.

The infra-red spectrum showed large -OH absorptions so the crystals were warmed to 60°C and pumped for three hours.

Found: H, 4.49; N, 25.26; S, 28.98%. I.r.(KBr disc) absorptions occurred (cm^{-1}) at 3170s (broad), 1430vs, 1250vs, 1233vs, 1150vs, 1080vs, 1050vs, 1019vs, 838vs, 767m, 671m, 600vs, 580vs, 560s, 540s, 468m.

Preparation of trisilver - hexaoxocyclotrithiatriazenide [385].

Triammonium-hexaoxocyclotrithiatriazenide (5g, 0.017 mol) was dissolved in the minimum of water and silver nitrate (8.5g, 0.050 mol) was added in the dark. Long white needles precipitated over a period of three days and these were filtered and pumped to dryness at 110°C in vacuo.

Found: Ag, 58.10; H, 0.71; N, 7.66; S, 16.07. Calcd. for $(Ag)_3(SNO_2)_3$: Ag, 58.04; H, 0.00; N, 7.53; S, 17.21%. I.r.(KBr disc) absorptions occurred (cm^{-1}) at 3420w (broad), 1630w (broad), 1242vs, 1217vs, 1204vs, 1150vs, 1110vs(sh), 1090vs, 1052vs, 842vs, 824vs, 745m, 677s, 577vs, 420m.

Preparation of trisodium - hexaoxocyclotrithiatriazenide [385].

Triammonium-hexaoxocyclotrithiatriazenide (2.88g, 0.01 mol) was added to sodium hydroxide (1.2g, 0.03 mol) in tetrahydrofuran (60 ml). The solution was slowly heated to 177°C during which the colour changed from clear to deep red/brown owing to the decomposition of the alcohol. The solution was allowed to cool, depositing a white precipitate which was filtered, washed with methanol and recrystallised from a 50:50 methanol-water mixture and dried in vacuo. Yield 76%.

Found: N, 14.23. Calcd. for $(Na)_3(SNO_2)_3$: N, 13.87%.
I.r.(KBr disc) absorptions occurred (cm^{-1}) at:
1238vs, 1210vs, 1150vs, 1115vs, 1066vs, 1035vs,
1009s, 991s, 840vs, 821vs, 782m, 755m, 678s, 620vs,
571vs, 529w, 420m.

Reaction of iodobenzene with trisilver - hexaoxocyclotrithiatriazenide.

Trisilver-hexaoxocyclotrithiatriazenide (2.9g, 0.005 mol) was added to iodobenzene (20 ml) in benzene (30 ml) and the mixture refluxed, with one spatula of calcium carbonate, for three hours. On cooling, a greyish solid (1) was deposited which was filtered off. The solution was pumped to dryness at 60°C under vacuum but no solid remained. The greyish solid (1) was found to be unreacted starting materials.

Reaction of benzoylchloride with trisodium - hexaoxocyclotrithiatriazenide.

Trisodium-hexaoxocyclotrithiatriazenide (3g, 0.01 mol) was added to benzoyl chloride (20 ml) in benzene (40 ml) and stirred for three days with occasional heating. There was no sign of reaction so the reaction mixture was refluxed for eight hours. On cooling, a grey powder was deposited which was filtered and pumped to dryness. The infra-red spectrum showed this to be unreacted starting materials.

Reaction of di-N-methyl sulphamoyl chloride with trisodium-hexaoxocyclotrithiatriazenide.

Trisodium-hexaoxocyclotrithiatriazenide (1g, 0.003 mol) was heated with di-N-methyl sulphamoyl chloride to 180°C for six hours. The initial clear solution turned red after a short time and a sticky red/brown solid was deposited. This was found impossible to mull so the reaction was not continued.

Reaction of sulphuryl chloride with trisodium - hexaoxocyclotrithiatriazenide.

Trisodium-hexaoxocyclotrithiatriazenide (2.0g, 0.007 mol) was added to sulphuryl chloride (20 ml) and the mixture refluxed for six hours. A white solid was filtered from the cooled solution but the infra-red spectrum showed some -OH stretching frequencies, so the solid was then refluxed with thionyl chloride, filtered and pumped to dryness.

Found: Cl, 7.34; N, 5.83; S, 25.74. I.r.(Nujol mull) absorptions occurred (cm^{-1}) at 3400w, 3300w, 3170m, 1540w, 1305vs, 1260vs, 1215s, 1158vs, 1069vs, 1017s, 970s, 918s, 890vs, 856s, 760m, 690m, 617s, 600vs 585vs, 555s, 543s, 525m, 472m, 434m.

Reaction of dimethylethylsulphonium iodide with trisodium - hexaoxocyclotrithiatriazenide.

Trisodium-hexaoxocyclotrithiatriazenide (3g, 0.01 mol) was added to dimethylethylsulphonium iodide (6g, 0.03 mol) in water (30 ml) and stirred at room temperature. White crystals formed slowly from the orange/yellow solution. These were filtered and found to contain iodine. Methanol (30 ml) was added to the orange/ yellow solution and a creamy white precipitate formed which was filtered, pumped to dryness and washed with ether.

I.r.(Nujol mull) absorptions occurred (cm^{-1}) at 3500m (broad), 3000vs, 2985vs, 2910m, 1650w (broad), 1432s, 1422s, 1367w, 1338m, 1242vs, 1215vs, 1170vs, 1152vs, 1118vs, 1075vs, 1066vs, 1045vs, 1000vs, 942m, 838vs, 781m, 728w, 685w, 620vs, 585vs, 534m, 510m, 418w.

Discussion of results.

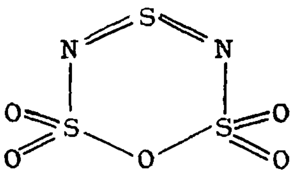
The preparation of $S_3N_2O_5$ was attempted by two routes, neither was successful in producing crystals suitable for X-ray crystallographic studies. However some light can be shed on the structure of this compound from the infra-red and mass spectra.

Table 6.6

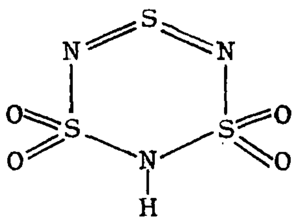
Infra-red spectra of $S_3N_2O_5$ and related compounds.

$S_3N_2O_5$	$(S_5N_5)(S_3N_3O_4)^{392}$	$S_3N_3O_4H^{393}$	$S_4N_4O_4{}^{394}$
3170w		3130m(N-H)	
1434vs	1310vs $\nu_{as}(SO_2)$	1420vs	1420s $\}\nu_{as}(SO_2)$
		1400vs	1400s
1290m	1290vs	1295s	1328vs
			1280w
1230s		1210s	1218s
1212s		1205s	1202m
1198m	1180m		1175s
1133s	1130vs $\nu_s(SO_2)$	1175vs	1137vs
1108s		1110s	1115vs
1070s	1060s	1080vs	1072w

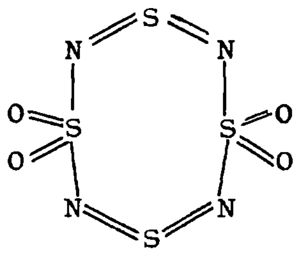
It can be seen from Table 6.6 that there is a striking similarity between the infra-red spectra of $S_3N_3O_4H$, $S_4N_4O_4$ and $S_3N_2O_5$ but less between $(S_5N_5)(S_3N_3O_4)$ and the others.



(A)

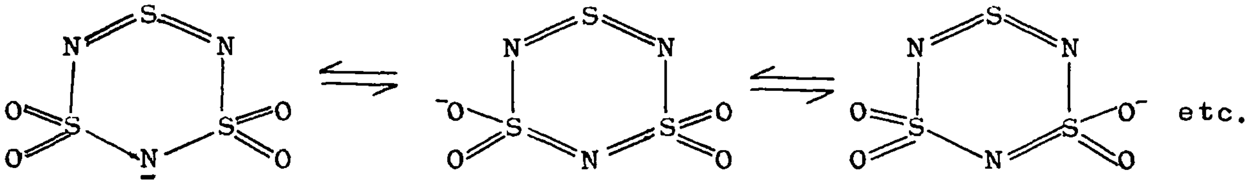


(B)



(C)

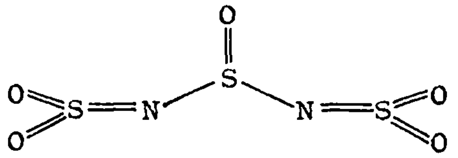
This implies that the structure of $S_3N_2O_5$ is related to $S_4N_4O_4$ and $S_3N_3O_4H$. In fact structure (A) is isoelectronic with (B) and very similar to (C).



(D) (E)

The $(S_3N_3O_4)^-$ anion (D), although isoelectronic with (A), must have a contribution to its structure from canonicals like (E), which explains the lower asymmetric SO_2 frequency found in this compound[392].

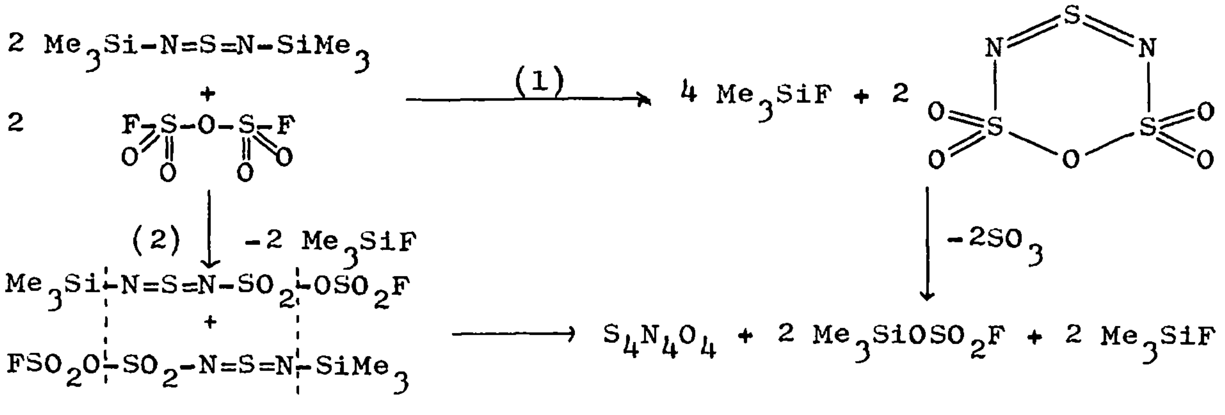
The presence of SO_3 in the mass spectrum of $S_3N_2O_5$ is also evidence in favour of structure (A) over structure (F).



(F)

This structure contains two highly electrophilic N-sulphuryl imide groups (see chapter 4), none of which have been isolated at room temperature in the free state.

An attempt to prove structure (A) by reaction of $(Me_3SiN=)_2S$ with $S_2O_5F_2$ in a 1:1 ratio via route (1), only resulted in the formation of $S_4N_4O_4$.[394]



This may have been because the reaction proceeded by a different route (2) or any $S_3N_2O_5$ formed reacted with Me_3SiF with loss of SO_3.

One other product was isolated in the reaction of S_4N_4 with SO_3 which had many absorptions in the S=O region of the infra-red spectrum and was probably the $S_4N_4.SO_3$ adduct prepared by Roesky[208].

Action of heat on sulphamide.

Sulphamide is a white crystalline solid and the expected product of pyrolysis, $(NH_4)_3(SNO_2)_3$, is also white. The discovery of a red compound in the reflux condenser was therefore unexpected. The infra-red spectrum of this red product when compared with sulphamide and $(NH_4)_3(SNO_2)_3$ shows extra peaks which correspond largely with those of $(HNSO)_4$, a red crystalline solid (Table 6.7). Since the temperature never rose above 200°C, $(NH_4)_3(SNO_2)_3$ may have decomposed below this temperature which is lower than the 225°C recorded by Nachbaur et al [385].

Table 6.7

Infra-red spectra of:-(i) red product from pyrolysis of $SO_2(NH_2)_2$, (ii) $SO_2(NH_2)_2$, (iii) $(NH_4)_3(SNO_2)_3$ and (iv) $(HNSO)_4$ [395].

(i) cm^{-1}	(ii) cm^{-1}	(iii) cm^{-1}	(iv) cm^{-1}
	3335-3170vs		
3170s		3170s	3250vs
	1552m		
	1545m		
1430vs		1430vs	1415vs
	1357vs		
	1330s		
1262vs		1250vs	
1239vs		1233vs	1234s
1210vs			1215s

(i) cm^{-1}	(ii) cm^{-1}	(iii) cm^{-1}	(iv) cm^{-1}
1175s			
1162vs	1165vs 1142s	1150vs	
1090s		1080vs	
1048s			1055s
1013vs		1019vs	1018vs
980s			
930vs	930m 913m		940m
812m		838vs 767m	
730s	722s		
668m		671m	
595s		600vs	
568s	562m	580vs 560s	
	535s	540s	
462m		468m	

Reactions of the hexaoxocyclotrithiatriazenide (3-) anion.

The reaction of the silver salt with iodobenzene and the sodium salt with benzoyl chloride and di-N-methyl sulphamoyl chloride were unsuccessful possibly because of the low solubility of the salts in the solvents used (benzene and $SO_2(Cl)NMe_2$). The sodium salt was used thereafter because of its high stability (the silver salt is unstable in the light), and it was possible to effect reaction in polar solvents such as SO_2Cl_2 or H_2O.

The aim of the reaction with SO_2Cl_2 was to prepare $(ClO_2SNSO_2)_3$ analogous to $(FO_2SNSO_2)_2$ which had been prepared by a different route [396]. The product had sulphur : nitrogen : chlorine ratios of 4 : 2 : 1 but these atoms only account for 40% of the total weight. The rest must be due to sodium or oxygen.

The infra-red spectrum of the product (Table 6.8) shows SO stretching frequencies higher than those of the $(SNO_2)_3^{3-}$ system. This implies the presence of either substituents on the ring which leads to higher SO frequencies or ring breakdown to form different SNO compounds. The low chlorine analysis tends to rule out $(ClO_2SNSO_2)_3$ unless it is present in small quantities and the low nitrogen analysis implies ring breakdown and loss of nitrogen. Any further analysis of the results would be purely speculative. However, reactions of this type deserve further investigation.

Table 6.8

Infra-red spectra of products and starting materials from reactions of $(Na)_3(SNO_2)_3$ with SO_2Cl_2(1) and $(EtMe_2S)(I)$(2).

Product I	$(Na)_3(SNO_2)_3$	$(EtMe_2S)(I)$	Product (2)
3400w, 3300m			3500m
3170m			2995vs
		2982vs	2985vs
		2908m	2908m
		1430s	1432m
		1421s	1421m
		1337m	1337m
1305vs			
1260vs			
	1238vs		1244vs
1215vs	1210vs		1216vs
1158vs	1150vs		1153vs
	1115vs		1118vs

Product I	$(Na)_3(SNO_2)_3$	$(EtMe_2S)(I)$	Product (2)
1069vs	1066vs		1075vs
	1035vs	1038vs	1045vs
1017s	1009s		1000vs
970s	991s		
			948m(sh)
918s		941m	941m
890vs			
856s	840vs		838s
	821vs		
	782m		782m
760m	755m		
690m	678s		
617vs	620vs		620s
585vs	571vs		586s
555s			

The infra-red spectrum of the product (2) from the reaction of $(EtMe_2S)(I)$ and $(Na)_3(SNO_2)_3$ shows many similarities with the starting materials but the region below 800 cm^{-1} is much simpler implying that the infra-red spectrum is not just the summation of the starting materials. Unfortunately, analyses were not very consistent which implies the presence of a mixture. From the infra-red spectrum this mixture appears to be $(EtMe_2S)_3(SNO_2)_3$ and NaI.

CHAPTER 7

Electron Rich Aromatic Sulphur Nitrogen Species

Introduction

In this chapter the idea of aromaticity in sulphur-nitrogen compounds is introduced and extended to include compounds not generally described in this category. The experimental section describes attempts to prepare new compounds with $(4n + 2)\pi$-electrons which although not entirely successful in their original aim, produced some interesting new compounds e.g. S_7NCOCF_3, $(S_5N_5)(SnCl_5OPCl_3)$ and $S_4N_4.POCl_3.SnCl_4$. The crystal structure of $(S_5N_5)(SnCl_5OPCl_3)$ is described in some detail.

Aromaticity

There are many compounds in sulphur-nitrogen chemistry that cannot adequately be represented by canonical structures. Consider the cyclotetrathiatriazenium ion$(S_4N_3)^+$, Johnson <u>et al</u>[397] concluded from the electronic spectra that the system involved 10 π-electrons. This was supported by the SCF MO calculations of Friedman who concluded that each sulphur atom donates two electrons and each nitrogen atom one electron to the π-system . This tetracovalency of sulphur prevents representation by usual canonical forms, instead it is necessary to invoke canonicals of type ($=S=\overset{+}{N}=S=$) and cross ring S-S bonds. These species are said to be "electron rich"[31] and if the sum of the π-electrons is $(4n + 2)$ where n is an integer, then these species are termed electron rich aromatics[31]. The characteristic planarity of aromatics is exhibited by $S_2N_2(6\pi)$, $(S_4N_3)^+$ (10π) and $(S_5N_5)^+$ (14π).

It is a characteristic feature of these compounds that each sulphur atom carries a positive charge due to the greater electronegativity of the nitrogen and in some cases the charge of the cation. This charge probably assists in stabilising the sulphur d orbital contribution to the bonding[399]. In S_4N_2, Friedman's electron count shows that the system has 10 π-electrons[398], however, the compound is unstable and readily disproportionates to S_4N_4 and sulphur. This suggests that each sulphur atom in a stable aromatic sulphur-nitrogen system needs an appreciable positive charge and it is therefore doubtful if anionic sulphur-nitrogen species will be aromatic. The infra-red spectrum of $(S_3N_3)^-$, an unstable anion[400], lends evidence to the non-planarity of the ion which should be a 10 π system using Friedman's π-electron counting rules[398]. SN Hückel species with N-N bonds will tend to be highly unstable due to the fact that lone pair delocalisation cannot occur along the nitrogen-nitrogen bond and there is the possibliity of elimination of nitrogen on thermodynamic and kinetic grounds. $(S_4N_5)^-$ (14π) has been prepared; it is not planar and there are no N-N bonds but nevertheless it is highly unstable.

In consultation with Dr. A.J. Banister the following rules for stable aromatic electron rich SN compounds have been drawn up. There must be:-

i) a high positive charge on each sulphur;

ii) no N-N bonds;

iii) no anions;

iv) $(4n + 2)\pi$-electrons (n is an integer).

In Table 7.1 are listed the π-electron counts for SN and S species. Ringed species are known, planar aromatics. Underlined Hückel species have been prepared but their structures have not been determined and starred species are those aromatics that have yet to be prepared.

Table 7.1

π-Electron Count for Neutral S_xN_y Species

No. of N atoms, (y)	No. of S atoms (x) 2	3	4	5	6
1	5	7	d-orbitals too		
2	⑥	8	10	weakly con-	
3	Unstable	9	11	13	tracted
4	due to N-N bonds		12	14*	16
5				15	17
6					18*

π-Electron Count for Unipositive $(S_xN_y)^+$ species

No. of N atoms, (y)	No. of S atoms (x) 2	3	4	5	6
1	4	6*	d-orbitals too		
2	5	7	9	weakly contra-	
3	Unstable	8	⑩	12	cted
4	due to N-N bonds		11	13	15
5				⑭	16
6					17

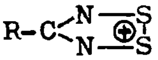
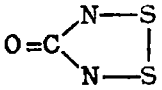
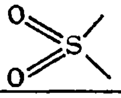
π-Electron Count for Dipositive $(S_xN_y)^{2+}$ species

No, of N atoms, (y)	2	3	No. of S atoms (x) 4	5	6	7
0		4	6	d-orbitals too		
1	3	5	7	9	weakly contra-	
2	4	6	8	10*	12	cted
3		7	9	11	13	15
4	Unstable due		⑩+	12	14*	16
5	to N-N bonds			13	15	17
6					16	18*

"+" indicates that the compound was prepared elsewhere[120] after this experimental work was completed.

Many more sulphur-nitrogen Hückel structures can be prepared by inserting groups which provide no further π-electrons e.g. putting Cl-S<+ into S_2N_2, produces $(S_3N_2Cl)^+$ which is not strictly aromatic (since the Cl-S< group is out of plane of the remaining portion of the ring), there is still considerable π delocalisation, other groups can be inserted which provide no π-electrons (Table 7.2)

Table 7.2

Inserted group	"Original Huckel Species"	New Pseudo Aromatic Species
Cl-S<+	S_2N_2	$(S_3N_2Cl)^+$
O=S<	S_2N_2	S_3N_2O
Me-As<	S_2N_2	$MeAsS_2N_2$
R-C<+	S_2N_2	
O=C<	S_2N_2	
X-N=S<	S_2N_2	XNS_3N_2
	"S_3N_4"	$S_4N_4O_2$

In crystal structures of the new "pseudo aromatic species" it is found that the section of the ring containing the "original Hückel species" is always planar.

In all these structures it is accepted that sulphur contributes two π-electrons to the π-system thus an X-S< group will only contribute one π-electron to the π-system. In this way species such as $(SNF)_3$ and $(SNCl)_3$ can be considered to be 6π aromatics and the ring structures are close to planar with equal ring bond lengths, whereas compounds of the type $(SNX)_4$(8π) are non-planar and have alternating ring bond lengths. Species such as $(SNX)_3$ will be referred to as "quasi-aromatics".

The experimental section gives details of attempts to produce new examples of these Hückel species.

Experimental

Reaction of Thiourea with Sulphur Dichloride

Thiourea (5 g. 0.066 mol)was added to excess sulphur dichloride (30 ml) and the mixture heated to 55°C for three hours. There was some reaction at this temperature and the red suspension deposited an orange red solid which was filtered and pumped to dryness. Attempts to recrystallise from ether and toluene resulted in decomposition, so analyses were carried out on the unpurified material. Found: Cl, 51.75; N, 14.76; S, 25.18. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 3460vs, 3370vs, 3270vs, 3180vs, 2690m, 2360w, 1680vs, 1618vs, 1415vs, 1331m, 1293s, 1276m, 1082s, 879m, 836m, 720s, 663s, 633s, 535m(sh), 472vs, 454vs, 414m. Major mass spectral peaks with assignments (relative intensities in parentheses) occurred (m/e) at: S_8, 256(3); S_6, 192(1); S_5, 160(1); S_4, 128(3); CHN_3S_2, 119(3); CHN_2S_2, 105(4); CHNSCl, 94(5); CH_2NS_2, 92(5); $CHNS_2$, 91(6); CH_4N_2S, 76(7); CHN_2S, 73(7); 71(6); S_2, 64(25); CNS, 58(100).

Reaction of Cycloazaheptasulphane with Triphenyl Carbonium Tetrafluoroborate.

Cycloazaheptasulphane (1.4 g, 0.006 mol) was added to triphenylcarbonium tetrafluoroborate (1.9 g, 0.006 mol) in dichloromethane (50 ml) and the solution was stirred for six hours. There was no obvious sign of reaction and the infra-red spectrum showed that the N-H group was still present. The reaction was repeated in liquid SO_2 at -20°C, again there appeared to be no reaction.

Reaction of Trifluoroperacetic Acid with Cycloazaheptasulphane

Hexafluoroacetic anhydride (5.6 ml) and 40% hydrogen peroxide (0.5 ml) were added to cycloazaheptasulphane (0.9 g, 0.004 mol) in dichloromethane (50 ml). The original pale yellow solution became deep yellow and deposited a yellow solid (1) which was filtered and pumped to dryness. On contact with potassium bromide plates the compound turned red. The yellow solution was left to stand overnight in the fridge and it deposited long yellow needles of sulphur. The i.r. (Nujol mull) absorptions of the yellow solid (1) occurred (cm^{-1}) at 1675m, 1212s, 1150s, 849w, 798s, 730m, 717m, 621m. Major mass spectral peaks at 200°C (relative intensities in brackets) occurred (m/e) at; S_8, 256(12); S_7N 238(2); S_7, 224(4); S_6, 192(5); 182(4); S_5, 160(20); 150(2); S_4, 128(22); CF_3COOH, 114(8); CF_3CO, 97(13); S_3, 96(15); CF_3CN, 95(27); CF_3OH, 86(5); CF_3CH, 82(8); CF_3, 69(100); S_2, 64(58); CF_2H, 51(98); CF_2, 50(52).

Reaction of Trichlorocyclotrithiatriazene with Tin(IV) Tetrachloride

Trichlorocyclotrithiatriazene (2 g, 0.008 mol) was dissolved in phosphoryl chloride (20 ml) and tin(IV) tetrachloride (0.83 ml, 0.008 mol) was added with stirring. A scarlet solution formed immediately which was refluxed for one hour and allowed to cool. A very air sensitive orange powder (1) and yellow crystals (2) were deposited. These were filtered and pumped to dryness. The major mass spectral peaks from (2) at 200°C occurred (m/e) at: $SnClOPCl_3$, 309 -299(1); $SnCl_4$, 271 -256(15); $SnCl_3$, 233 - 221(100); $SnCl_2$, 194 - 186(2); S_4N_4, 184(1); $POCl_3$, 158 -152(4); SnCl, 159 - 151(5); S_3N_3, 140 - 138(2); $POCl_2$, 121 -117(6); S_3N_2, 124(2); Sn, 120 -116(6); SCl_2, 104 - 102(4); S_2N_2, 92(7); S_2N, 78(2); SCl, 69 -67(6); $S_2(SO_2)$, 64(5); SO, 48(4); SN, 46(14), (relative intensities in brackets). The orange powder was too air sensitive for mass spectral analysis.

Reaction of Cyclotetrathiazene with Phosphoryl Chloride.

Cyclotetrathiazene, S_4N_4, (0.1 g, 0.0005 mol) was added to phosphoryl chloride (20 ml) and the mixture heated slowly. At 80°C the mixture began to change colour from red to yellow and the reaction appeared to be complete after ten minutes. The yellow solid was filtered and pumped to dryness. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1163vs, 998vs, 681s, 566s, 470vs, 455s which corresponds to the infra-red spectrum of $(S_4N_3)(Cl)^{267}$.

Reaction of Chlorocyclotrithiadiazenium Chloride with Phosphoryl Chloride.

Chlorocyclotrithiadiazenium chloride, $(S_3N_2Cl)(Cl)$, (4.0 g) 0.022 mol) was added to phosphoryl chloride (40 ml) and the mixture warmed slowly to 60°C. Reaction occurred at this temperature and a green precipitate was deposited from the red solution. A sample of this was withdrawn and pumped to dryness. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1014w, 960s, 943s, 709s, 697s, 670(sh), 586s. This is the infra-red spectrum of "$(S_3N_2)(Cl)$"^{267}. On further heating and refluxing at 105°C for three hours the solution became orange and deposited a bright yellow precipitate. I.r. (Nujol mull) absorptions occurred (cm^{-1}) at 1159vs, 998vs, 682s, 565vs, 470vs, 456s, which corresponds with the infra-red spectrum of $(S_4N_3)(Cl)^{267}$.

Reaction of Bis-cyclotetrathiazene-tin(IV)tetrachloride with Phosphoryl Chloride.

Bis-cyclotetrathiazene-tin(IV)tetrachloride (1.3 g, 0.002 mol) was added to phosphoryl chloride (20 ml) and the mixture heated to reflux for one hour. There appeared to be no reaction. The purple precipitate was filtered and pumped to dryness and was found to be unchanged $(S_4N_4)_2.SnCl_4$.

Reaction of Trichlorocyclotrithiatriazene with Phosphoryl Chloride.

Trichlorocyclotrithiatriazene (1.0 g, 0.004 mol) was dissolved in phosphoryl chloride (20 ml) and heated to 60°C for two hours. No reaction was observed. A sample of the solution was evaporated to dryness and an infra-red spectrum of the yellow residue corresponded to $(SNCl)_3$. The solution was then heated at 80°C for two hours and a yellow solid slowly precipitated. This was filtered and found to be $(S_4N_3)(Cl)$ from its infra-red spectrum.

Reaction of Cyclotetrathiazene with Sulphuryl Chloride, Phosphoryl Chloride and Tin(IV)tetrachloride.

A mixture of Tin(IV)tetrachloride (0.9 ml, 0.0076 mol) and sulphuryl chloride (0.62 ml, 0.0076 mol) was poured into a flask containing a slurry of cyclotetrathiazene (1.40 g, 0.0076 mol) in phosphoryl chloride (20 ml). Transparent crystals of (I) formed on the lower part of the filter stick. The solution, on stirring at room temperature, quickly turned red and purple brown $(S_4N_4)_2SnCl_4$ (II) precipitated. A small amount of the adduct was withdrawn and characterised by its i.r. spectrum (Table 7.3). Both the solution and the solid turned brown as the temperature was raised to the boiling point. During refluxing for two hours (oil bath at 105°C) the solution and precipitate lightened to red. A brown powder (III) adhered to the upper part of the flask above the liquid level. Yellow crystals of the $S_5N_5^+$ salt (IV) separated out on cooling.

The mixture was filtered and after pumping dry the yellow platelets were separated by hand in a glove box from the brown powder (III) to give 1.5 g. of the $S_5N_5^+$ salt (IV) (30% yield based on S_4N_4). Found: Cl, 41.55; N, 10.4; S, 23.7; Sn, 17.75. Calcd. for $Cl_8N_5OPS_5Sn$: Cl, 41.75; N, 10.3; S, 23.6; Sn, 17.45%. Major mass spectral peaks were found at m/e (relative intensities and assignments are given): $SnClOPCl_3$, 307-301(3); $SnOPCl_3$, 270-268(2); $SnCl_4$, 266-256(16); $SnCl_3$, 233-217(100); $SnCl_2$, 192-186(3); S_4N_4, 184(2); SnCl, 157-151(3); $POCl_3$, 156-152(3); S_3N_3, 138(2); S_3N_2, 124(2); Sn, 122-116(6); $POCl_2$, 119-117(6); S_2N_2, 92(8); S_2N, 78(5); S_2, 64(2); SN, 46(15).

The colourless crystals (I) taken from the filter stick were found to have an i.r. spectrum (Table 7.3) identical to that of $(POCl_3)_2SnCl_4$ prepared by the method due to Garner and Sugden[264].

The brown powder (III) was recrystallised from $POCl_3$ to give 1.1 g small orange-brown crystals (Found; Cl, 41.25; N, 9.7; S, 21.9; Sn, 18.9. Calcd. for $Cl_7N_4POS_4Sn$: Cl, 41.5; N, 9.35; S, 21.45; Sn, 19.85%). I.r. spectrum (Table 7.3)

Table 7.3

I.R. Spectra of Starting Materials and Products

S_4N_4 ref.401	$(S_4N_4)_2SnCl_4$ ref.401	$S_4N_4.POCl_3.SnCl_4$ this work	(S_5N_5)-$(SnCl_5OPCl_3)$ this work	$(POCl_3)_2SnCl_4$ this work
		1285vs		1300vs
				1268vs
			1210vs	1204m
		1166s		
			1112s	
1062w			1050w	
1040w(sh)	1040s			
1000w	1025m(sh)	1022m	1020s	
	960s	970w(sh)	980w(sh)	
920s				
	805s	800m	804m	
795vw	795s(sh)			

S_4N_4 ref. 401	$(S_4N_4)_2SnCl_4$ ref.401	$S_4N_4.POCl_3.SnCl_4$ this work	(S_5N_5)- $(SnCl_5OPCl_3)$ this work	$(POCl_3)_2SnCl_4$ this work
	785s(sh)			
757m				
720s(sh)	715w(sh)	722s	731m	720s
690s				
	675m	672w		670w
619w(sh)	619m		619vs	
		585vs		
545s	556w	536s	542m	
521m				515w
510m	506s			
		470w	476w	481m
408vw				404m

Results and Discussion

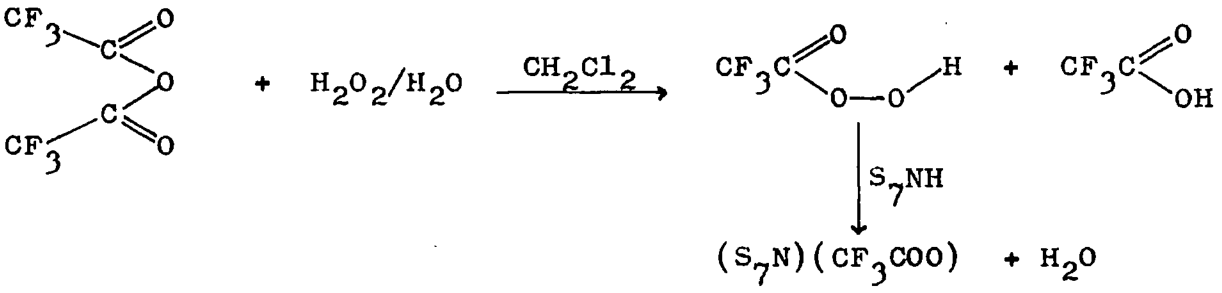
a) The reaction of thiourea with sulphur dichloride

The aim of this reaction was to eliminate four moles of HCl and form a five-membered 6π ring,

which is similar to the cyclodithiadiazolium salts. The product mix was complex and the analysis figures approximate to an empirical formulae of $C_2S_2N_3Cl_4H_2$. The presence of N-H stretching frequencies in the infra-red spectrum shows that not all the hydrogen atoms have been removed. The new peaks in the spectrum (compared with thiourea) occur at cm^{-1}: 1680vs, 1332s, 1293vs, 1276s, 878m, 835m, 664s. The peak at 1680 cm^{-1} can probably be assigned to a $>$C=N stretch. The mass spectrum does not succeed in clarifying the situation, since only one fragment with chlorine atoms can be distinguished.

b) The reactions of cycloazaheptasulphane with hydride ion abstractors.

These reactions were attempts to extract the hydride ion from S_7NH to form the 14π system $(S_7N)^+$ which would have a similar structure to $(S_8)^{2+}$. The first reaction with triphenyl carbonium tetrafluoroborate produced no new products. With trifluoroperacetic acid however, reaction took place. A slight excess of perfluoroacetic anhydride was present to remove any water formed in the reaction and move the equilibrium to the right.



However, the product did not give the correct infra-red spectrum required for the $CF_3C{<}^{O}_{O}{}^{-}$ group and the S_7N^+ ion was not very prominent in the mass spectrum.

Colchester <u>et al</u>[402] reported that when cycloazaheptasulphane reacted with carboxylic acids in the presence of a dehydrating agent, then N-acylimides could be isolated.

In the reaction studied carboxylic acids are formed and the presence of excess perfluoroacetic anhydride serves to act as the dehydrating agent. The following mechanism is thus proposed.

$$\begin{tikzcd} 2CF_3COOOCF_3 + H_2O \arrow[r] & 2CF_3COOH + CF_3COOOCCF_3 \arrow[d, "S_7NH"] \\ & S_7NCOCF_3 + 3CF_3COOH \end{tikzcd}$$

The infra-red spectrum of the product can be assigned by comparison with related compounds S_7NH[403], $(S_7NCO)_2$[403], and $P(O_2CCF_3)_3$[404] (Table 7.4).

Table 7.4

Product	S_7NH[403]	$(S_7NCO)_2$[403]	$P(O_2CCF_3)_3$[404]
1675		1695 C=O	
1212			1210 C-F
1150		1095 C-N	1155 C-F
849			854 C-C
798	820 (S-N)		
730			726 C-F
717			
621			

The mass spectrum is also consistent with S_7NCOCF_3 even though the parent peak cannot be distinguished.

c) The reaction of trichlorocyclotrithiatriazene with tin(IV) tetrachloride.

This was an attempt to pluck off one or two chlorine atoms from the S_3N_3 ring to produce either $(S_3N_3Cl_2)^+$ or $(S_3N_3Cl)^{2+}$, which would be a positively charged quasi-aromatic system. Clarke[329] had tried a similar reaction in thionyl chloride but found the product too air sensitive to handle whereas Fild had prepared the adduct $2(SNCl)_3.SnCl_4$ by mixing the two materials together[330]. It was therefore necessary to try another solvent, phosphoryl chloride. Crystals were formed which were analysed in the mass spectrometer for signs of the cations described above. The peaks occur in the same region and with the same intensity as $(S_5N_5)(SnCl_5OPCl_3)$, and the conclusion is that this is the main product of this reaction. It appears that at the $POCl_3$ reflux temperature (~105°C), NSCl loses chlorine:-

$$\begin{tikzcd}
5(SNCl)_3 \arrow[r, shift left, harpoon] & 15NSCl \arrow[l, shift left, harpoon] \arrow[r, shift left, harpoon] \arrow[d, "3SnCl_4"] & 12NS\cdot + 12Cl\cdot \arrow[l, shift left, harpoon] \arrow[r] \arrow[d, bend right] & 6Cl_2\uparrow \\
 & 3\text{"}(NS)(SnCl_5)\text{"} \arrow[r] & 3(S_5N_5)(SnCl_5) \arrow[d, "POCl_3"] & \\
 & & (S_5N_5)(SnCl_5OPCl_3) &
\end{tikzcd}$$

d) Further reactions in phosphoryl chloride

Reactions in phosphoryl chloride have the advantage over those carried out in thionyl chloride because the latter participates in side reactions with S_4N_4. The discovery that S_4N_4 was unaffected by phosphoryl chloride up to 80°C meant that reactions such as

$$S_4N_4 + SO_2Cl_2 + SnCl_4 \xrightarrow{POCl_3} (S_4N_4)^{2+}(SnCl_6)^{2-} + SO_2$$

could be tried in an attempt to produce the new 10π $(S_4N_4)^{2+}$ cation. Four products were characterised from this reaction :- $(POCl_3)_2.SnCl_4$, $(S_4N_4)_2.SnCl_4$, $(S_5N_5)(SnCl_5.OPCl_3)$ and $S_4N_4.POCl_3.SnCl_4$.

The adduct $(S_4N_4)_2.SnCl_4$ was the first to be precipitated from the solution together with the transparent crystals of $(POCl_3)_2.SnCl_4$ which removed the rest of the $SnCl_4$ from solution. The adduct $(S_4N_4)_2.SnCl_4$ was found to be unaffected by boiling $POCl_3$ in a separate experiment. Since sulphuryl chloride is known to react with S_4N_4 to give $(SNCl)_3$[269], the coordinated S_4N_4 was probably chlorinated by the SO_2Cl_2 to form an oligomer of NSCl or perhaps $S_4N_4Cl_2$ (as yet unknown), which remains coordinated to $SnCl_4$. Rearrangement then takes place involving solvent $POCl_3$ which enters the anion. The overall reaction is:

$$2\tfrac{1}{2}S_4N_4 + SO_2Cl_2 + 2SnCl_4 + 2POCl_3 \longrightarrow 2(S_5N_5)(SnCl_5OPCl_3) + SO_2\uparrow$$

Since this product was also isolated from $(SNCl)_3$, $SnCl_4$ and $POCl_3$

it seems that any ratio of $SN\cdot$ and SNCl with $SnCl_4$ in $POCl_3$ will yield the most insoluble salt, $(S_5N_5)(SnCl_5.OPCl_3)$.

The reaction also yielded $S_4N_4.POCl_3.SnCl_4$ which is a new adduct which has similarities in its infra-red spectrum to both $(S_4N_4)_2.SnCl_4$ and $(POCl_3)_2.SnCl_4$ (table 7.3). Other possible side reactions involve the formation of the $(SNCl)_3.POCl_3.SnCl_4$ adduct or $(S_4N_4)(SnCl_6)$ but these were either not formed or consumed during the reaction.

Table 7.5 shows all possible 2:1 adducts of $(Cl)^-$, $POCl_3$ and S_4N_4 with $SnCl_4$. With the formation of the two new species $S_4N_4.POCl_3.SnCl_4$ and $(SnCl_5.OPCl_3)^-$, only one species, $(S_4N_4.SnCl_5)^-$, remains to be synthesised to complete the table.

Table 7.5

Possible 2:1 adducts of $(Cl)^-$, $POCl_3$ and S_4N_4 with $SnCl_4$.

	$(Cl)^-$	$POCl_3$	S_4N_4
$(Cl)^-$	$(SnCl_6)^{2-}$		
$POCl_3$	$(POCl_3.SnCl_5)^-$ (a)	$(POCl_3)_2.SnCl_4$ (b)	
S_4N_4	$(S_4N_4.SnCl_5)^-$ (c)	$S_4N_4.POCl_3.SnCl_4$ (a)	$(S_4N_4)_2.SnCl_4$ (d)

(a) This work.

(b) Ref.401 and this work.

(c) Compound unknown.

(d) Ref.264 and this work.

e) The structure and bonding in $(S_5N_5)(SnCl_5.OPCl_3)$.

The X-ray crystal structure was carried out by Rayment and Shearer[61] and was found to consist of discrete $(S_5N_5)^+$ cations and $(SnCl_5.OPCl_3)^-$ anions and these will be discussed separately. Bond distances and angles are given in tables 7.6 and 7.7.

The $(S_5N_5)^+$ cation.

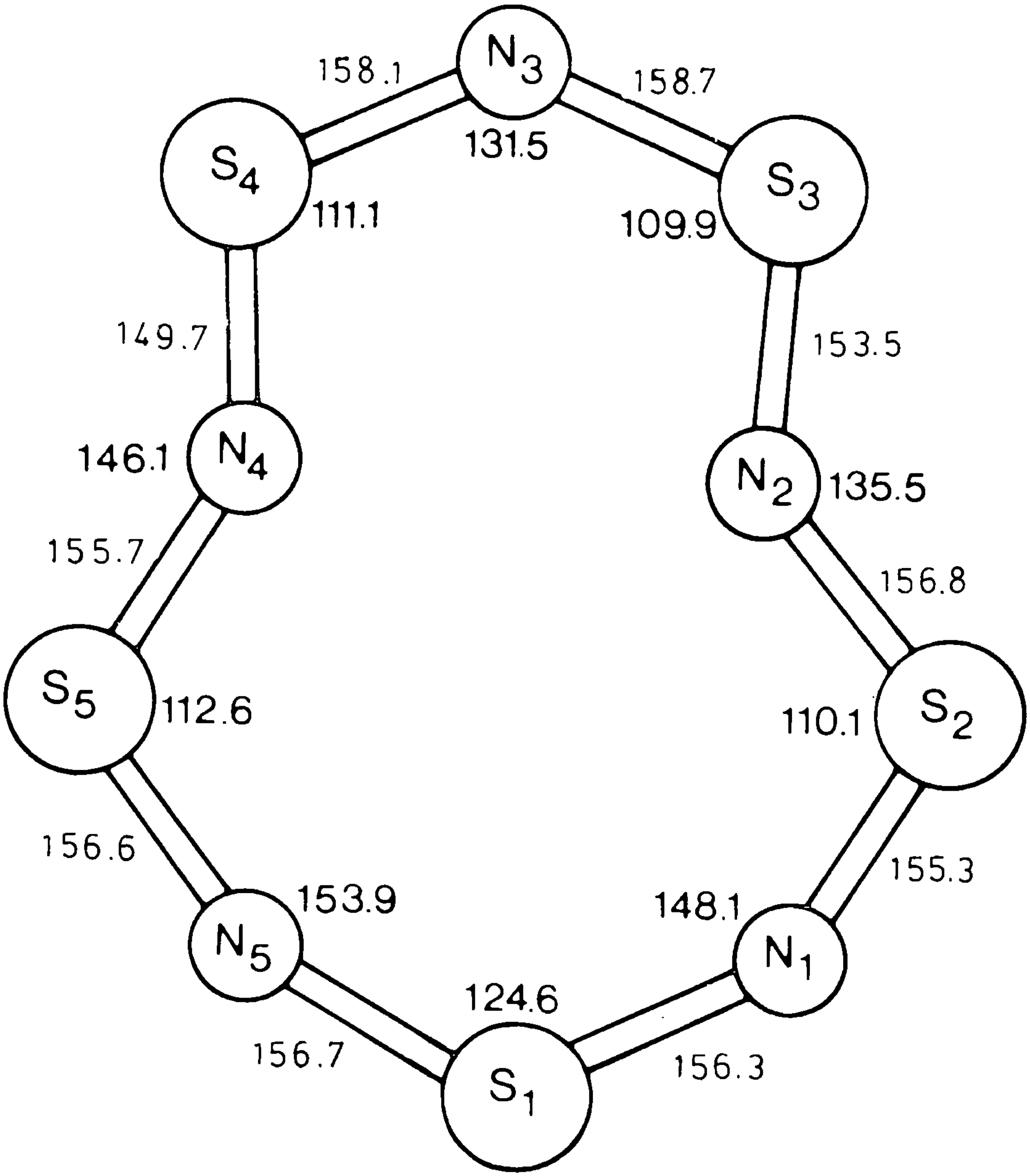
The cation which consists of a ten-membered ring of alternating sulphur and nitrogen atoms (Figure 7.1), is a 14π-electron member of the series of aromatic thiazenes[83]. The bond distances and angles are very similar to those of the cation in $(S_5N_5)(S_3N_3O_4)$[52]. In both $(S_5N_5)(S_3N_3O_4)$ and $(S_5N_5)(SnCl_5.OPCl_3)$ there is less variation in S-N bond distances and in nitrogen angles than in $(S_5N_5)(AlCl_4)$; the mean values also differ significantly (table 7.8).

Table 7.8

Some bond distances(pm) and bond angles(°) in $(S_5N_5)^+$ salts.

	$(S_5N_5)(AlCl_4)$ Ref.111	$(S_5N_5)(S_3N_3O_4)$ Ref.52	$(S_5N_5)(SnCl_5.OPCl_3)$ Ref.61
SN bond lengths	146.5-159.0	154.3-158.0	149.7-158.7
(av. value)	153.9	156.0	155.8
N angle	129-177	133-151	132-153
(av. value)	151.9	142.4	142.6

The difference between a or a′ and b (Figure 7.2) cannot be explained by intermolecular forces since these are insignificant because there are no short contacts between cation and anion[112]. The second explanation of disorder in the crystal structure of $(S_5N_5)(AlCl_4)$ is discussed fully in Chapter 1.



$S_5N_5^+$

Figure 7.1

The $(S_5N_5)^+$ cation found in $(S_5N_5)(SnCl_5POCl_3)$[112]

Table 7.6

Bond distances (pm) and their estimated standard deviations (pm x 10) for $(S_5N_5)(SnCl_5OPCl_3)$[112]

Sn	-	Cl(1)	237.0(4)
Sn	-	Cl(2)	237.8(4)
Sn	-	Cl(3)	238.8(4)
Sn	-	Cl(4)	240.4(4)
Sn	-	Cl(5)	240.6(4)
Sn	-	O	227.1(1.0)
P	-	Cl(6)	191.3(7)
P	-	Cl(7)	193.2(7)
P	-	Cl(8)	195.3(6)
P	-	O	146.2(1.1)
S(1)	-	N(1)	156.3(1.5)
S(1)	-	N(5)	156.7(1.4)
S(2)	-	N(1)	155.3(1.5)
S(2)	-	N(2)	156.8(1.2)
S(3)	-	N(2)	153.5(1.3)
S(3)	-	N(3)	158.7(1.3)
S(4)	-	N(3)	158.1(1.4)
S(4)	-	N(4)	149.7(1.4)
S(5)	-	N(4)	155.7(1.3)
S(5)	-	N(5)	156.6(1.4)

Table 7.7

Bond Angles (degrees) with their estimated standard deviations (deg x 10^2) for $(S_5N_5)(SnCl_5OPCl_3)$[112]

Cl(1) - Sn - Cl(2)	96.00(14)
Cl(1) - Sn - Cl(3)	96.85(14)
Cl(1) - Sn - Cl(4)	92.63(14)
Cl(1) - Sn - Cl(5)	95.94(14)
Cl(1) - Sn - O	176.06(28)
Cl(2) - Sn - Cl(3)	89.39(14)
Cl(2) - Sn - Cl(4)	171.30(14)
Cl(2) - Sn - Cl(5)	88.97(14)
Cl(2) - Sn - O	87.85(27)
Cl(3) - Sn - Cl(4)	90.66(13)
Cl(3) - Sn - Cl(5)	167.21(14)
Cl(3) - Sn - O	84.02(27)
Cl(4) - Sn - Cl(5)	89.06(13)
Cl(4) - Sn - O	83.51(27)
Cl(5) - Sn - O	83.25(27)
Cl(6) - P - Cl(7)	106.16(36)
Cl(6) - P - Cl(8)	106.04(32)
Cl(6) - P - O	115.67(50)
Cl(7) - P - Cl(8)	104.59(33)
Cl(7) - P - O	112.31(50)
Cl(8) - P - O	111.27(48)
N(1) - S(1) - N(5)	124.64(76)
N(1) - S(2) - N(2)	110.09(72)
N(2) - S(3) - N(3)	109.92(71)
N(3) - S(4) - N(4)	111.09(74)
N(4) - S(5) - N(5)	112.63(70)
Sn - O - P	147.29(64)
S(1) - N(1) - S(2)	148.08(1.02)
S(2) - N(2) - S(3)	135.50(83)
S(3) - N(3) - S(4)	131.46(93)
S(4) - N(4) - S(5)	146.10(91)
S(1) - N(5) - S(5)	153.96(94)

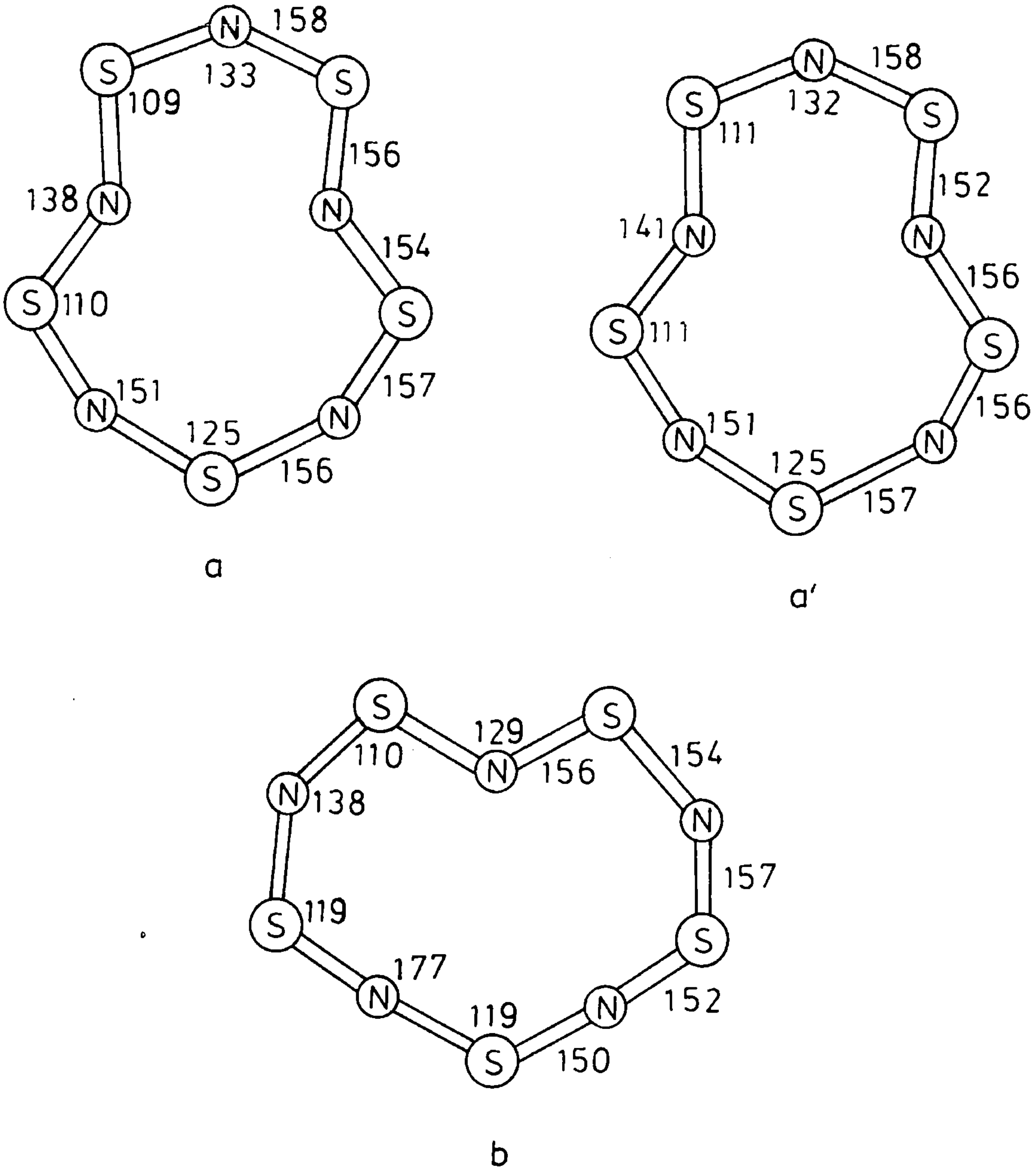
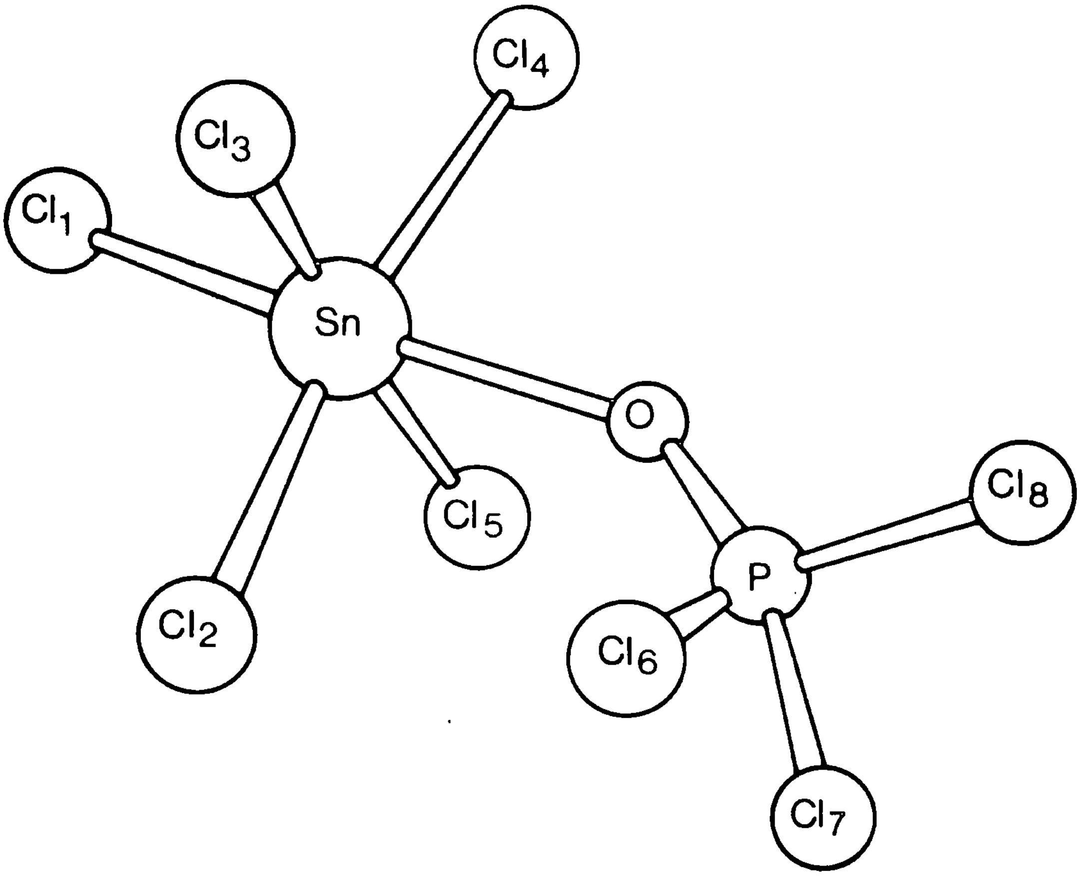


Figure 7.2

The $S_5N_5^+$ cations in (a)$(S_5N_5)(S_3N_3O_4)$[52]

(a′)$(S_5N_5)(SnCl_5OPCl_3)$[61]

(b)$(S_5N_5)(AlCl_4)$[111]



$[SnCl_5POCl_3]^-$

Figure 7.3

The $(SnCl_5POCl_3)^-$ anion found in $(S_5N_5)(SnCl_5POCl_3)$[112]

The $(SnCl_5.OPCl_3)^-$ anion.

The anion consists of a central tin atom coordinated to five chlorine atoms and a $POCl_3$ molecule, as shown in Figure 7.3. The most interesting features in the ion concern the coordination of the $POCl_3$ ligand and its effect on the rest of the anion. The Sn-O distance of 227(1)pm is longer than the single bond distance of 211pm calculated from Paulings covalent radii[309] but is the same, within experimental error, as the mean value found in $(POCl_3)_2.SnCl_4$ (228(3)pm)[405]. The Sn-O-P angle (147.3(6)°) also does not differ significantly from the angle at oxygen in $(POCl_3)_2.SnCl_4$ (148.2(2.7)°)[405] or the Sb-O-P angle in the isoelectronic $POCl_3.SbCl_5$ (145.0(1.6)°)[406]. The P-O distance of 146(1)pm, does not differ significantly from that found in free $POCl_3$ (144.8(5)pm)[407] and is the same within experimental error as that in $(POCl_3)_2.SnCl_4$ (145(5)pm)[405] and $POCl_3.SbCl_5$ (147(2)pm)[406].

CHAPTER 8

Theoretical Considerations of Structure and Bonding in Some Cyclic Sulphur-Nitrogen Species

Introduction

In the last chapter, the planar species, $(S_4N_3)^+$, $(S_4N_4)^{2+}$ and $(S_5N_5)^+$ were described as aromatic Hückel species obeying the $(4n + 2)$ π-electron rule. The concept of expanding the aromatic area to include "pseudoaromatic" $(S_3N_2Cl)^+$ and "quasiaromatic" $(SNCl)_3$ and $(SNOCl)_3$ was introduced. In this chapter the structure and bonding of these molecules have been investigated theoretically in an all valence electron SCF MO CNDO/2 treatment.[416]

Theoretical

Most theoretical investigations of sulphur compounds up to 1969, concentrated on the π-bonding between divalent sulphur and carbon but there was little agreement between various workers as to the importance of d-orbital participation. This disagreement is not surprising since the procedures used (mainly Hückel and PPP-π-SCF-MO) are unsuitable for establishing the extent to which d-orbitals are involved because the large number of parameters whose values must be estimated, are crucial to deriving orbital occupation numbers. The problem can only be solved by non-empirical quantum mechanical treatments[408].

"Ab initio" treatments of molecules of this size have only been carried out for S_2N_2 by Collins and Duke[409] who found that the presence of d-orbitals on sulphur was crucially important for predicting good geometries and Jafri *et al*[410] who employed d-orbitals on sulphur and found that S_2N_2 was a 6π system.

For larger molecules the best approximation to date is the semi-empirical all valence electron SCF MO treatment. Where comparisons with non-empirical treatments are available, it has been shown that this method tends to overestimate the extent of d-orbital involvement because it uses them as polarising functions[408], due to the limitations of the basis set. It is for this reason that the calculations have been carried out, where possible, both with and without the use of d-orbitals.

Charge Distributions

Knowledge of the charge distribution in these species is important not only as a guide to the reactivity of the rings but also to see whether Dewar's island model[411] can be applied to these systems. Table 8.1 gives the geometrical parameters and the calculated charges both with and without d-orbitals on sulphur.

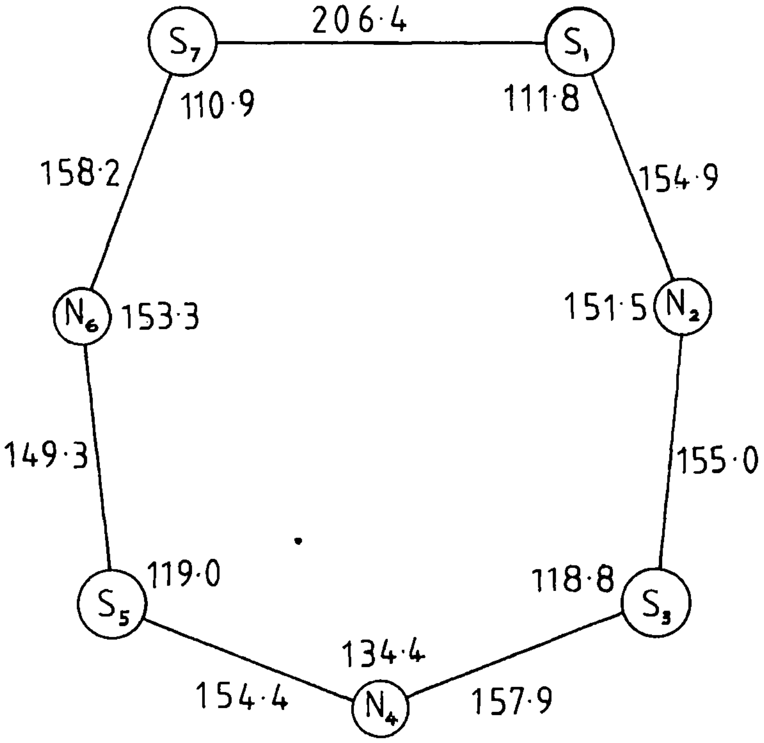
Table 8.1

Geometrical parameters and charges for sulphur-nitrogen species.

$(S_4N_3)^+$, with d-orbitals[110] (parameters from $(S_4N_3)(NO_3)$[412])

Charge distribution

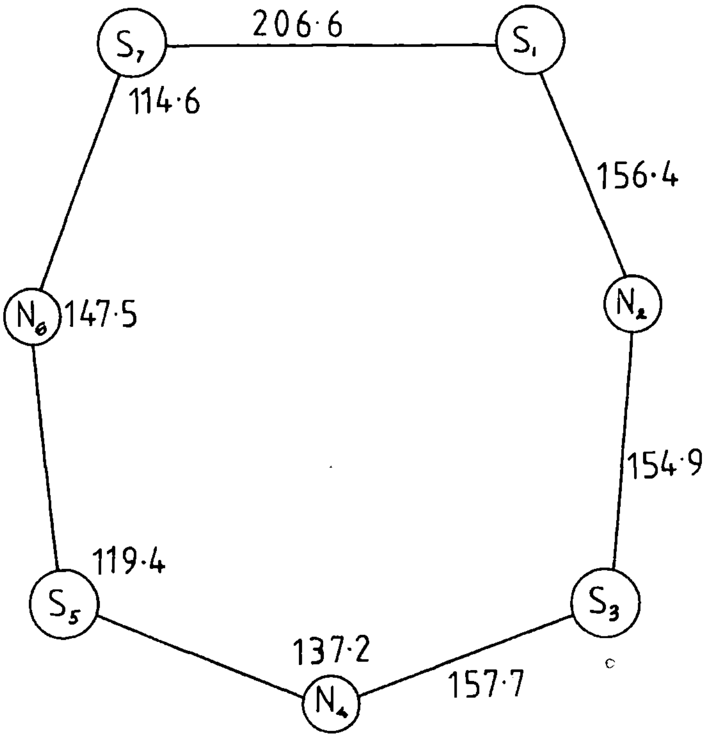
S_1 +0.05	S_7 +0.03
N_2 -0.04	N_6 +0.01
S_3 +0.53	S_5 +0.55
N_4 -0.11	



$(S_4N_3)^+$ without d-orbitals (averaged parameters from $(S_4N_3)_2(SbCl_5)^{60}$)

Charge distribution

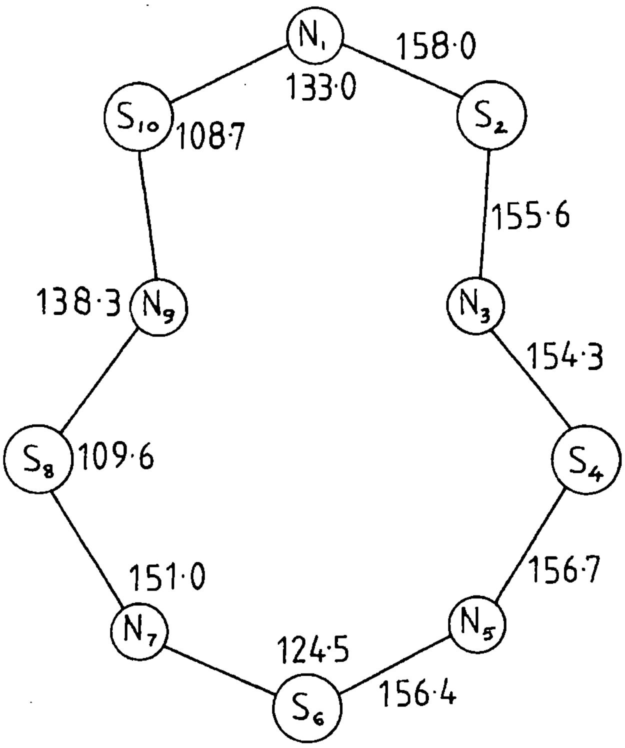
S_1,S_7	+0.29
N_2,N_6	-0.03
S_3,S_5	+0.51
N_4	-0.53



$(S_5N_5)^+$ (averaged parameters from $(S_5N_5)(S_3N_3O_4)^{52}$)

Charge distribution

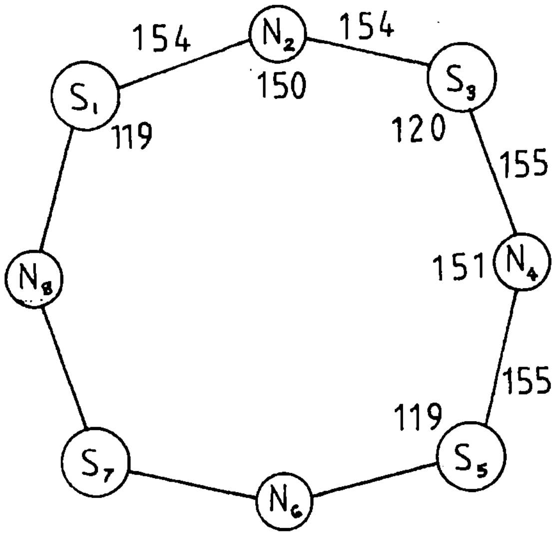
With d-orbitals		Without d-orbitals
-0.21	N_1	-0.28
+0.30	S_2,S_{10}	+0.40
-0.02	N_3,N_9	-0.07
+0.38	S_4,S_8	+0.43
-0.16	N_5,N_7	-0.37
+0.19	S_6	+0.49



$(S_4N_4)^{2+}$ (A) (parameters from $(S_4N_4)(SbF_6)(Sb_3F_{14})$[120])

Charge distribution

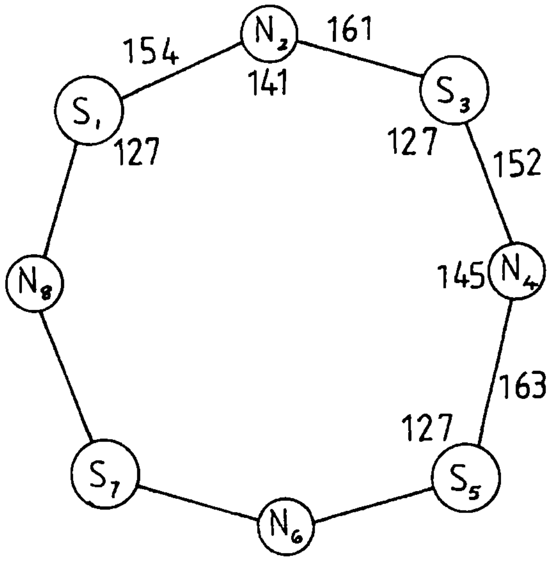
With d-orbitals		Without d-orbitals
+0.64	S_1, S_5	+0.72
-0.12	N_2, N_6	-0.29
+0.63	S_3, S_7	+0.72
-0.14	N_4, N_8	-0.15



$(S_4N_4)^{2+}$ (B) (parameters from $(S_4N_4)(SbF_6)(Sb_3F_{14})$[120])

Charge distribution

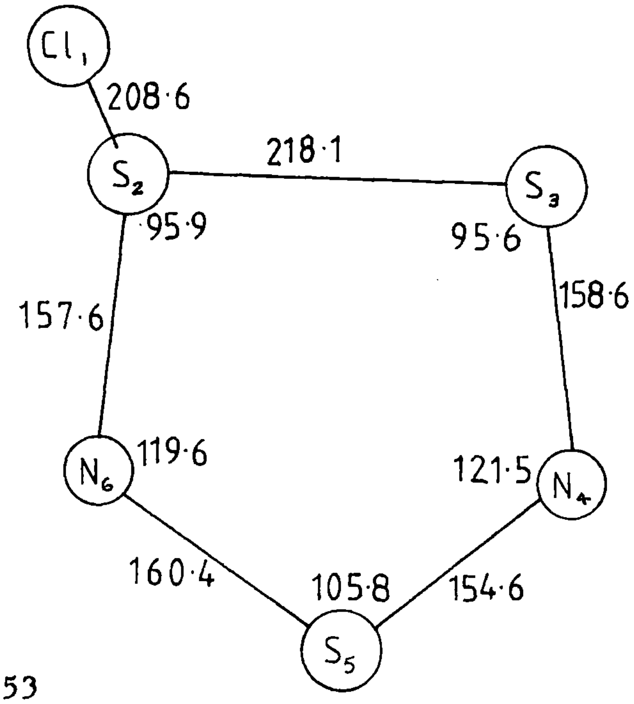
With d-orbitals		Without d-orbitals
+0.63	S_1, S_5	+0.65
-0.11	N_2, N_6	-0.14
+0.60	S_3, S_7	+0.67
-0.11	N_4, N_8	-0.18



$(S_3N_2Cl)^+$ (parameters from $(S_3N_2Cl)(FeCl_4)^{64}$)

Charge distribution

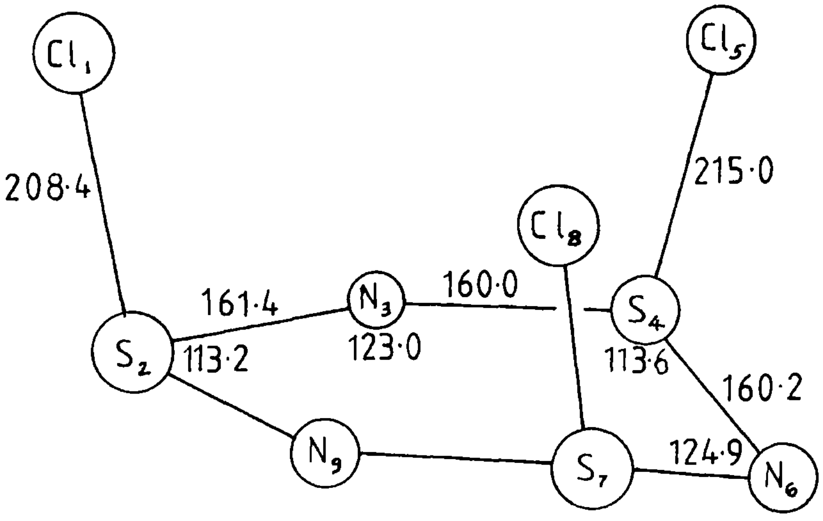
With d-orbitals			Without d-orbitals
Ref 110	This thesis		This thesis
+0.18	-0.01	Cl_1	+0.01
+0.12	+0.58	S_2	+0.51
+0.24	+0.25	S_3	+0.29
+0.02	-0.22	N_4	+0.01
+0.76	+0.43	S_5	+0.51
-0.32	-0.03	N_6	-0.33



$(SNCl)_3^{53}$

Charge distribution

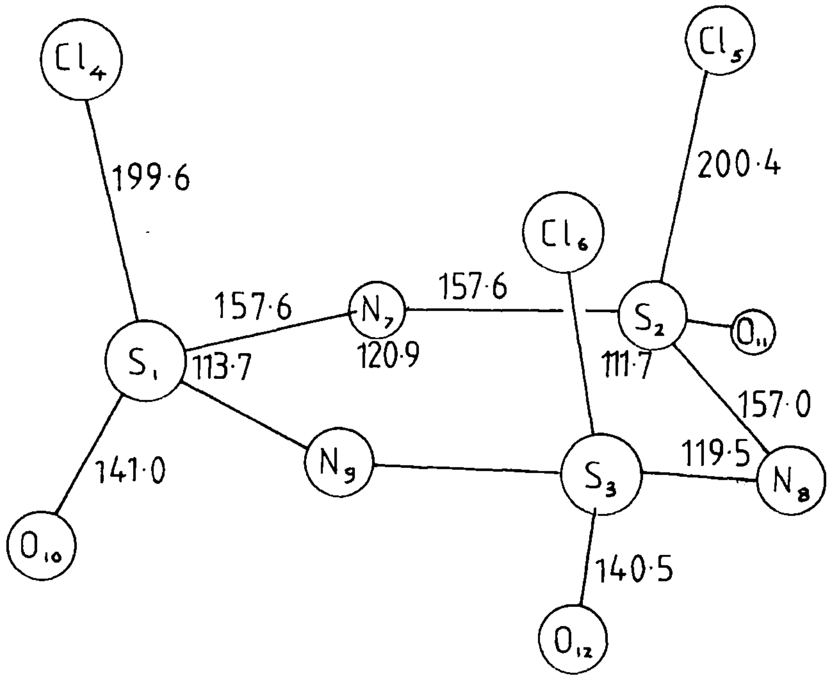
With d-orbitals				Without d-orbitals
This thesis	Ref 81	Ref 78		This thesis
-0.09	-0.10	-0.18	Cl_1	-0.16
+0.36	+0.33	+0.38	S_2	+0.52
-0.24	-0.23	-0.20	N_3,N_9	-0.35
+0.35	+0.33	+0.38	S_4,S_7	+0.47
-0.12	-0.10	-0.18	Cl_5,Cl_8	-0.19
-0.26	-0.23	-0.20	N_6	-0.35



$(\mathrm{SNOCl})_3$[68]

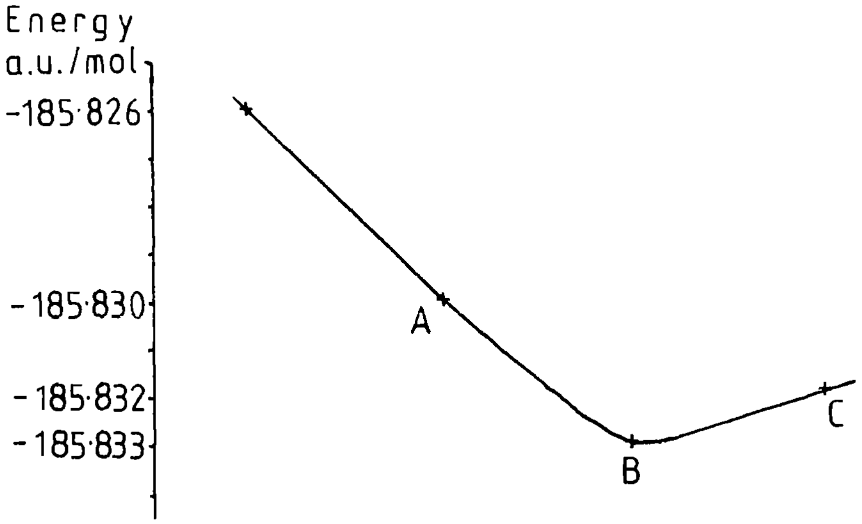
Charge distribution

With d-orbitals				Without d-orbitals	
This thesis	Ref 81	Ref 78	Ref 80	This thesis	
+0.43	+0.42	+0.68	+0.42	+1.05	$S_{1,2,3}$
-0.19	-0.20	-0.25	-0.20	-0.46	$N_{7,8,9}$
-0.03	-0.03	-0.16	-0.03	-0.17	$Cl_{4,5,6}$
-0.20	-0.19	-0.27	-0.19	-0.42	$O_{10,11,12}$



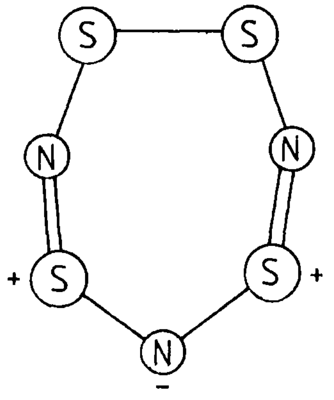
The net atomic charges on the ring atoms in all cases are quite different from zero, the nitrogen atoms are generally negative whereas the sulphur atoms are positive.

The results are in excellent agreement with those of the other workers except in the case of $(S_3N_2Cl)^+$ where Adams *et al*[110] found a high positive charge (+0.76) on S_5 but not S_2. The computer carries out an iterative process which terminates when the difference in electronic energy between each process is less than the convergence limit. By setting a convergence limit of 0.001 a. u./mol (divergence problems occurred below this value) we were able to repeat the results of Adams <u>et al</u>[110] and found that the energy had passed the minimum (B) and stopped at (C). By using a convergence limit of 0.003 a. u./mol we were able to stop the process at (B), the point of minimum electronic energy. (Fig. 8.1).



The charge distribution thus obtained was more consistent with the addition of an $(Cl-S\langle)^+$ group to the S_2N_2 ring (Chapter 7) and had the positive charge situated on the three coordinate sulphur (S_2) as expected.

The calculations with d-orbitals for $(S_4N_3)^+$ show that the positive charge is located essentially on S_3 and S_5 whereas the nitrogen atoms are approximately neutral. However the calculations without d-orbitals point to a considerable negative charge on N_4 which suggest that canonical forms such as (I) must be important if d-orbitals are excluded.



(I)

The result that one nitrogen atom is more negatively charged than the other two is compatible with the ^{15}N nmr data[413]. In $(S_5N_5)^+$ the positive charge is extensively delocalised over all sulphur atoms in both calculations and all the nitrogen atoms except the reentrant atoms carry negative charges. The two structures of $(S_4N_4)^{2+}$ bear similar charges:- large positive charges on the sulphur atoms and small negative charges on the nitrogens. Structure (A) has a more negative electronic energy by 0.3 a. u./mol, indicating a more stable structure than structure (B).

The charge distributions in $(SNCl)_3$ and $(SNOCl)_3$ are very similar to those in cyclophosphazenes[414] and support the validity of Dewar's model for cyclothiazenes since the charges are so large that they cancel any possibility for the π-electrons to give rise to a ring current[81].

Eigenvalues and Eigenvectors.

The eigenvalues and eigenvectors confirm the 10π electron nature of $(S_4N_3)^+$, $(S_4N_4)^{2+}$(A and B) and the 14π electron nature of $(S_5N_5)^+$. The pseudo 6π electron character of $(S_3N_2Cl)^+$ is also confirmed. With $(SNCl)_3$ and $(SNOCl)_3$ however, there is a great deal of overlap between both the chlorine and oxygen atoms and the sulphur P_z orbitals in the S_3N_3 rings. Taking the case of $(SNCl)_3$ as an example, the three chlorine P_z orbitals overlap with the sulphur P_z orbitals and so the concept of a 6π electron P_z system becomes meaningless, since partition of the P_z charge between S and Cl is impossible.

Table 8.2

Compound	Ionisation potential eV.		Electron Affinity eV.	
	no d-orbitals	d-orbitals	no d-orbitals	d-orbitals
$(S_4N_4)^{2+}$(B)	21.34	21.69	12.66	14.76
$(S_4N_4)^{2+}$(A)	21.15	21.59	12.27	14.44
$(S_3N_2Cl)^+$	17.24	18.21	6.81	9.55
$(S_4N_3)^+$	15.37	15.7 *	5.97	8.16
$(SNOCl)_3$	13.49	14.41	1.03	1.95
$(S_5N_5)^+$	12.48	14.42	5.33	7.08
$(SNCl)_3$	11.55	13.10	- 0.26	0.34

* ref. 110

The calculated ionisation potentials are listed in order in Table 8.2. It is interesting that the positively charged species $(S_5N_5)^+$ has a comparable ionisation potential with $(SNOCl)_3$ and $(SNCl)_3$ of which the latter can be ionised with $SbCl_5$ [331]. It should therefore be possible to ionise $(S_5N_5)^+$ to the radical $(S_5N_5)^{2+}$ with sufficiently strong Lewis acids.

The electron affinities are in a similar order except $(S_5N_5)^+$ has a higher electron affinity than $(SNOCl)_3$ because of its positive charge. The negative electron affinity of $(SNCl)_3$ (-0.26 eV) would explain why no Lewis base adducts of $(SNCl)_3$ are known, whereas those of $(SNOCl)_3$ with an electron affinity of + 1.03 eV have been isolated [352].

Bond Overlap Populations.

In a zero differential overlap treatment, the bond overlap populations are misleading as measures of interactions between pairs of atoms. A more reliable parameter is the partitioned bond overlap population (PBOP) defined as the product of the electron density matrix with the bond overlap matrix [415]. This parameter is similar to bond order but is much more clearly defined.

Directly Bonded Atoms.

a) Sulphur - Sulphur.

Unfortunately the calculations for $(S_4N_3)^+$ with d-orbitals did not converge but previous calculations by Adams et al [110] have shown considerable π-bonding between the adjacent sulphur atoms. In $(S_3N_2Cl)^+$ which has a longer S - S bond length (218.1 pm compared with 206.6 pm in $(S_4N_3)^+$), the calculations (d-orbitals included) demonstrated that there is still appreciable S - S π-bonding at this distance (π PBOP = 0.1035, total PBOP = 0.7306). Calculations without d-orbital involvement for $(S_4N_3)^+$ give the π-component of the PBOP as ~10% of the total. This π-component is of the same order as cross ring S - S bonding in $(S_3N_2Cl)^+$, $(SNCl)_3$ and $(SNOCl)_3$ and hence makes a significant contribution to S - S bond strength.

b) Sulphur - Nitrogen Bonds.

The correlations between SN bond length and PBOP both with and without d-orbitals, are shown in figure 8.2 and listed in Table 8.3. These correlations indicate that partitioned bond overlap is a reasonable indication of the extent of bonding interaction in these systems.

Table 8.3

Partitioned Bond Overlap Populations.

$(S_4N_3)^+$

Bonds.	SN Bond length pm.	PBOP without d-orbitals.	SN Bond length pm.	PBOP with d-orbitals.*
S_1-N_2	156.4	0.70	154.9	1.07
N_2-S_3	154.9	0.73	155.0	1.06
S_3-N_4	157.7	0.64	157.9	1.05
N_4-S_5	157.7	0.64	154.4	1.09
S_5-N_6	154.9	0.73	149.3	1.18
N_6-S_7	156.4	0.70	158.2	1.03

$(S_5N_5)^+$

Bonds.	SN Bond length pm.	PBOP	
		Without d-orbitals.	With d-orbitals.
N_1-S_2, S_{10}-N_1	158.0	0.66	1.03
S_2-N_3, N_9-S_{10}	155.6	0.70	1.07
N_3-S_4, S_8-N_9	154.3	0.69	1.08
S_4-N_5, N_7-S_8	156.7	0.69	0.99
N_5-S_6, S_6-N_7	156.4	0.69	1.11
	$(S_4N_4)^{2+}$ (A)		
S_1-N_2, S_5-N_6	154.0	0.72	1.11
N_2-S_3, N_6-S_7	154.0	0.72	1.10
S_3-N_4, S_7-N_8	155.0	0.72	1.10
N_4-S_5, N_8-S_1	155.0	0.72	1.10

* Ref. 110

Bonds.	SN Bond length pm.	PBOP	
		Without d-orbitals.	With d-orbitals.
		$(S_4N_4)^{2+}$ (B)	
S_1-N_2, S_5-N_6	154.0	0.73	1.13
N_2-S_3, N_6-S_7	161.0	0.65	1.00
S_3-N_4, S_7-N_8	152.0	0.75	1.18
N_4-S_5, N_8-S_1	163.0	0.63	0.96
		$(S_3N_2Cl)^+$	
S_2-N_6	157.6	-	0.99
N_6-S_5	160.4	-	1.03
S_5-N_4	154.6	-	1.13
N_4-S_3	158.6	-	0.92
		$(SNCl)_3$	
S_2-N_3, S_2-N_9	161.4	0.56	0.97
S_4-N_6, S_7-N_6	160.2	0.57	1.00
S_7-N_9, S_4-N_3	160.0	0.57	1.00
		$(SNOCl)_3$	
S_1-N_7, S_1-N_9	157.6	0.58	1.04
S_2-N_8, S_3-N_8	157.0	0.58	0.98
S_3-N_9, S_2-N_7	157.6	0.61	1.08

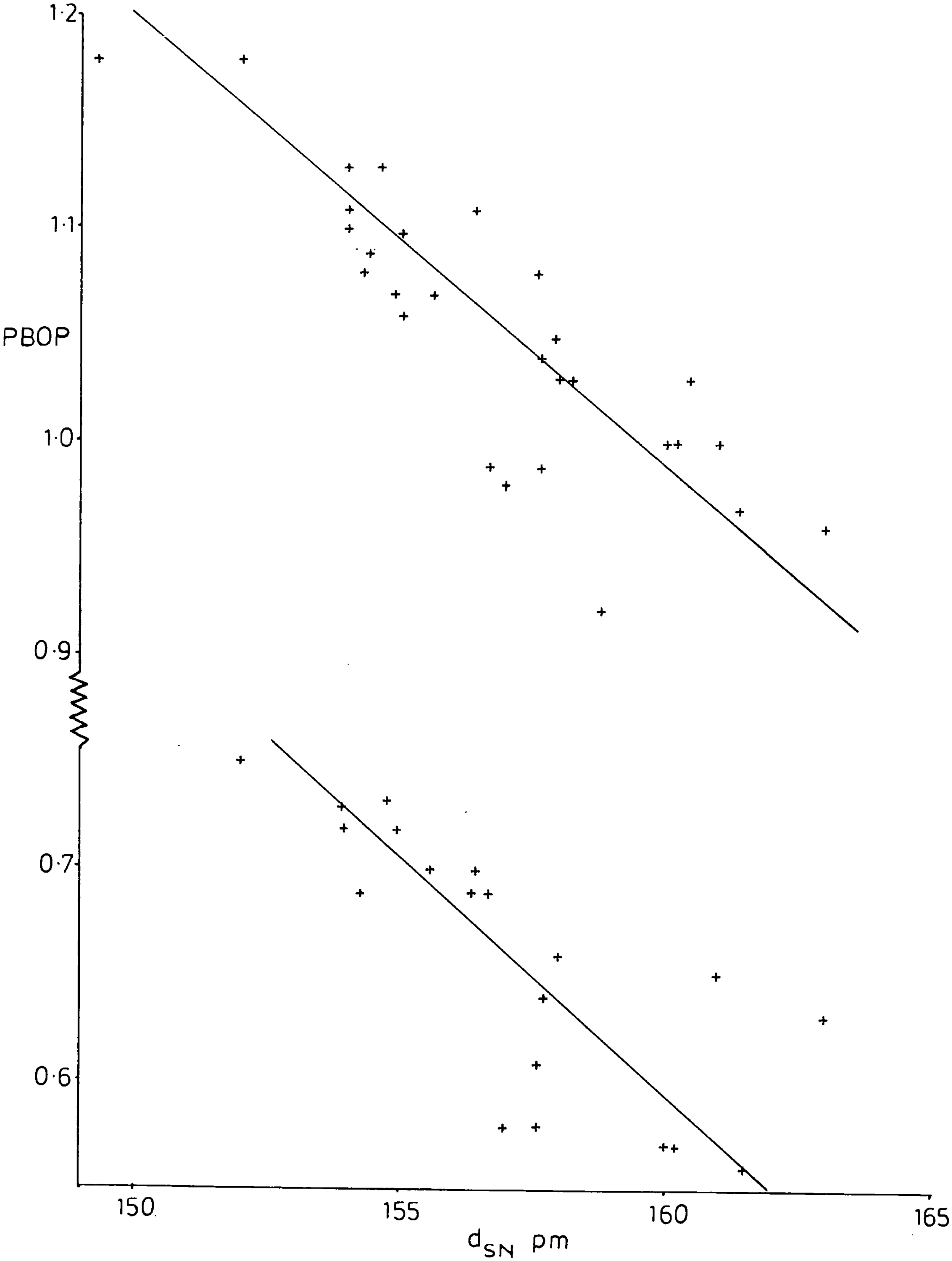


Figure 8.2

The graphs of PBOPs versus d_{SN} pm :- top line (with d-orbitals) and bottom line (without d-orbitals).

Overlap with the Nitrogen 2s Orbital.

The partitioned bond overlap population (PBOP) of the nitrogen 2s orbital affords indirect information about the hybridisation of the relevant lone pair orbitals as follows:-

(1) Without d-orbitals, if the nitrogen atom employed sp orbitals to two sulphur atoms the bond angle would be 180° and the PBOP involving the 2s orbital on nitrogen would be large and the lone pair pure p in character. With the bond angle at 120°, the nitrogen atom would employ sp^2 orbitals and the PBOP involving the 2s orbital on nitrogen would be smaller and the lone pair would also be sp^2. There is no overlap of the sulphur p orbitals with the lone pair on nitrogen and there should be a relationship between $\hat{N}$ and the PBOP of the 2s orbital on nitrogen; this is in fact the case (Table 8.4, fig. 8.3).

(2) With inclusion of d-orbitals the situation becomes complicated since there will not only be additional $N(sp^x) - S(d)$ bond overlap in both cases but also $N(sp^2)$ lone pair - $S(d)$ bond overlap in the 120° case (π' bonding). The fact that the relationship between $\hat{N}$ and the PBOP still holds with the inclusion of d-orbitals (fig. 8.4) serves to strengthen the assumptions made in Chapter 1 to explain the $S\hat{N}S - d_{SN}$ relationship.

In Chapter 1 the term 'strained' was used for the nitrogen atoms in $(SNOCl)_3$ and $(S_3N_2Cl)^+$ and the re-entrant nitrogen atoms of $(S_5N_5)^+$. Here, in both calculations for these species, we find that the PBOPs are too large for the observed angle, i.e. these nitrogen angles have been reduced by ring strain.

Table 8.4

Partitioned Bond Overlap Populations for the 2s Orbital on N.

Compound	Atom	$S\hat{N}S^o$	PBOPs for 2s orbital on N.	
			Without d-orbitals	with d-orbitals.
$(S_4N_3)^+$	N_2,N_6	147.5	0.48	-
	N_4	137.2	0.42	-
$(S_5N_5)^+$	N_1	133.0	0.40	0.67
	N_3,N_9	138.3	0.49	0.72
	N_5,N_7	151.0	0.47	0.70
$(S_4N_4)^{2+}$(A)	N_2,N_8	150.0	0.49	0.75
	N_4,N_6	151.0	0.49	0.74
$(S_4N_4)^{2+}$(B)	N_2,N_6	141.0	0.42	0.69
	N_4,N_8	145.0	0.43	0.70
$(S_3N_2Cl)^+$	N_4	121.5	-	0.65
	N_6	119.6	-	0.63
$(SNCl)_3$	N_3,N_9	123.0	0.28	0.60
	N_6	124.9	0.30	0.61
$(SNOCl)_3$	N_7,N_9	120.9	0.33	0.65
	N_8	119.5	0.34	0.66

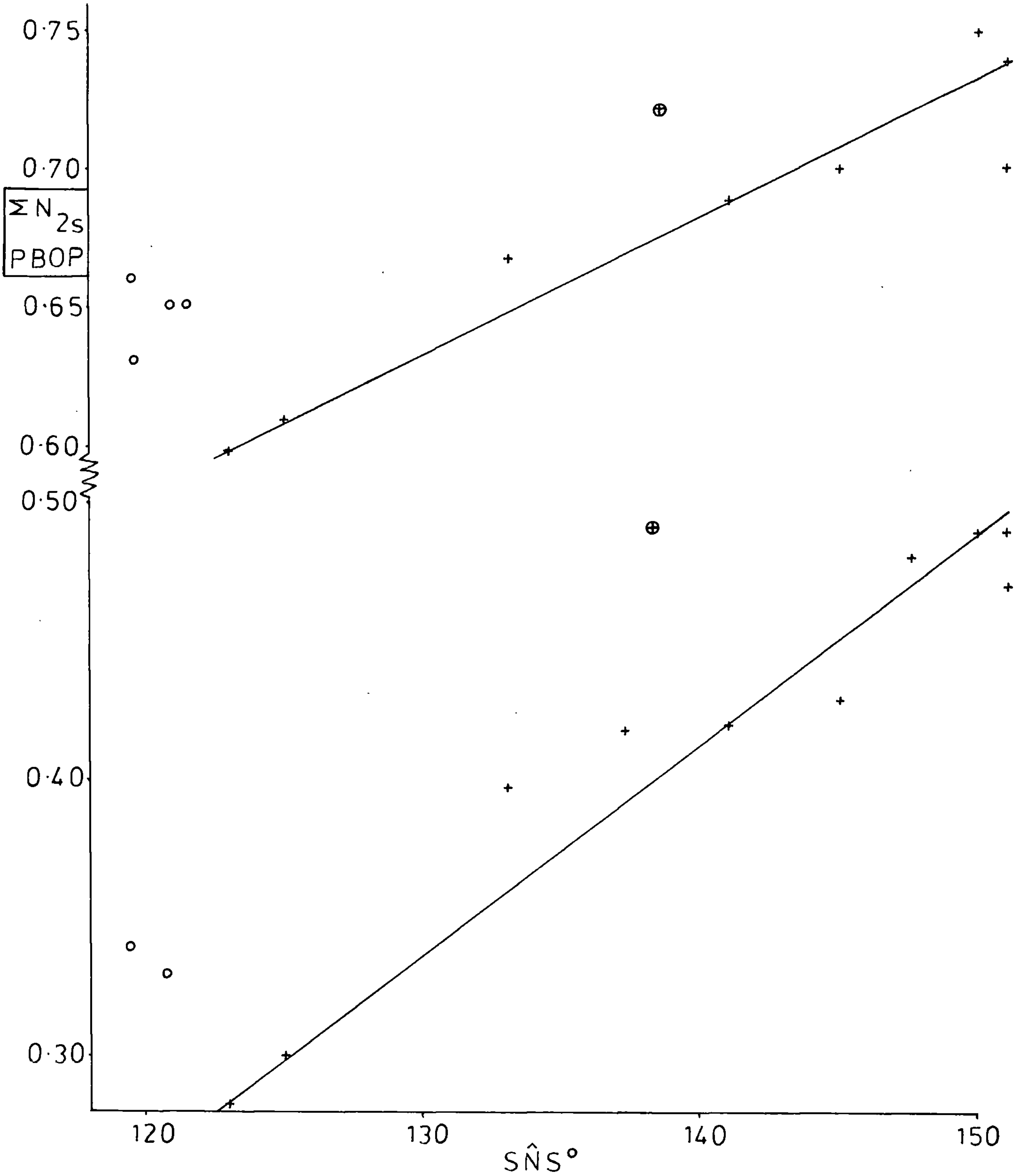


Figure 8.3

The graphs of the sum of the PBOP on the N_{2s} orbital versus the $\hat{N}$ angle. Top line (with d-orbitals) and bottom line (without d-orbitals).

"+" denotes compounds described as "virtually unstrained" in Chapter 1,

"o" denotes compounds described as "strained" in Chapter 1 and

"⊕" refers to the re-entrant N atoms in $S_5N_5^+$ also described as strained.

Table 8.5

Partitioned Bond Overlap Populations for S - S Bonds

Molecule	Interaction	$S\hat{N}S^{o}$	Distance (pm)	PBOP	
				With d-orbitals	Without d-orbitals
$(S_3N_2Cl)^+$	S_3-S_5	121.5	273	0.059	-
	S_5-S_2	119.6	275	0.054	-
$(S_4N_3)^+$	S_5-S_7	153.3	299	0.028*	-
	S_1-S_3	151.5	300	0.028*	-
	S_3-S_5	134.4	288	0.037*	-
	S_3-S_5,S_1-S_3	147.5	299	-	-0.006
	S_5-S_7	137.2	294	-	-0.001
$(S_5N_5)^+$	S_2-S_4	138.3	290	0.031	-0.009
	S_4-S_6	151.0	303	0.018	-0.005
	S_2-S_{10}	133.0	286	0.035	-0.001
$(SNCl)_3$	S_2-S_4,S_2-S_7	123.0	282	0.058	+0.006
	S_4-S_7	124.9	285	0.059	+0.005
$(SNOCl)_3$	S_2-S_3	119.5	271	0.058	+0.005
	S_1-S_3,S_1-S_2	120.9	274	0.059	+0.005
$(S_4N_4)^{2+}$(A)	S_1-S_3	151.0	298	0.023	-0.005
	S_3-S_5	150.0	299	0.022	-0.005
$(S_4N_4)^{2+}$(B)	S_1-S_3	141.0	297	0.032	-0.002
	S_3-S_5	145.0	300	0.027	-0.002

* Ref. 110.

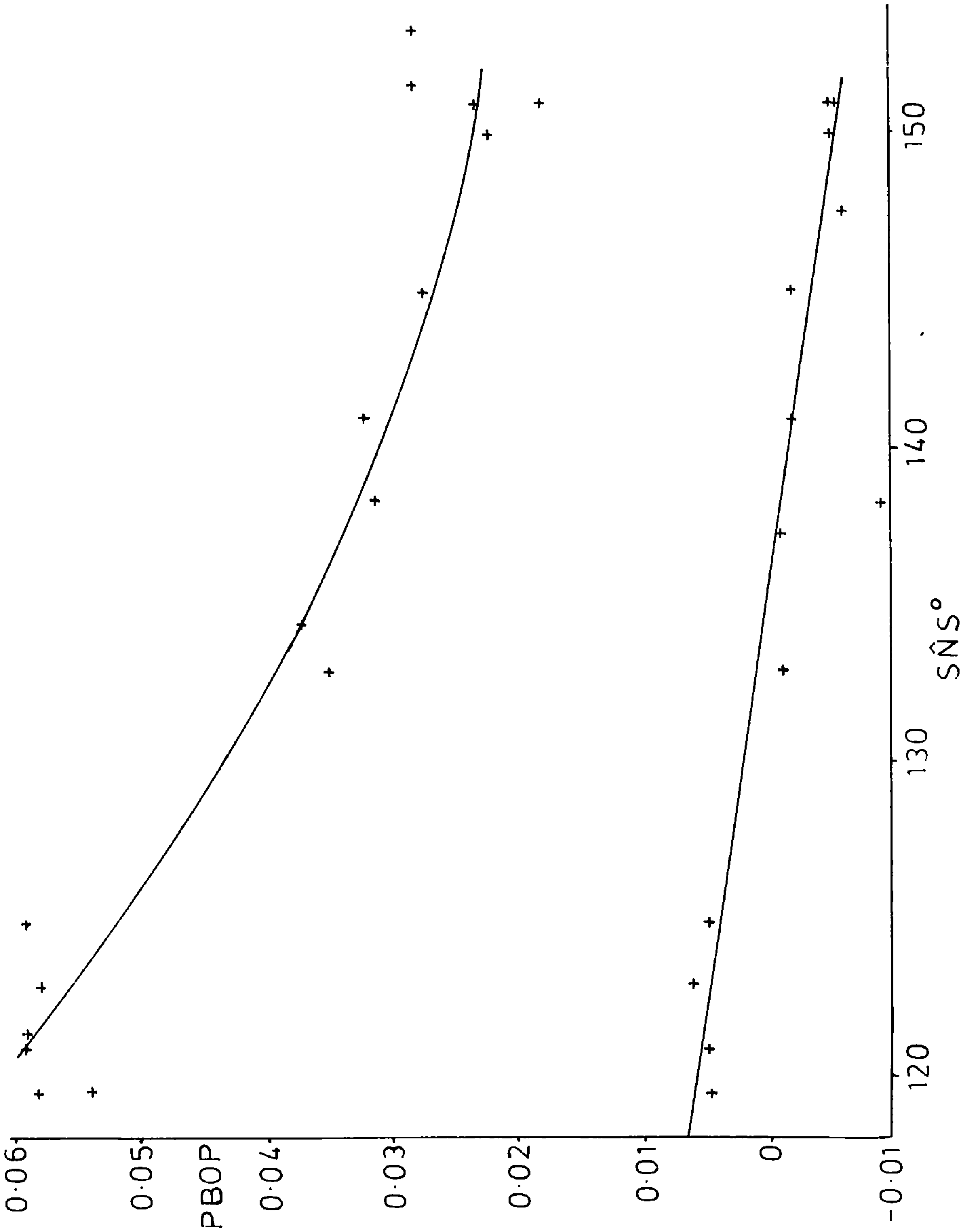


Figure 8.4

The graphs of S - S PBOP against N̂ angle:- top line (with d-orbitals) and bottom line (without d-orbitals).

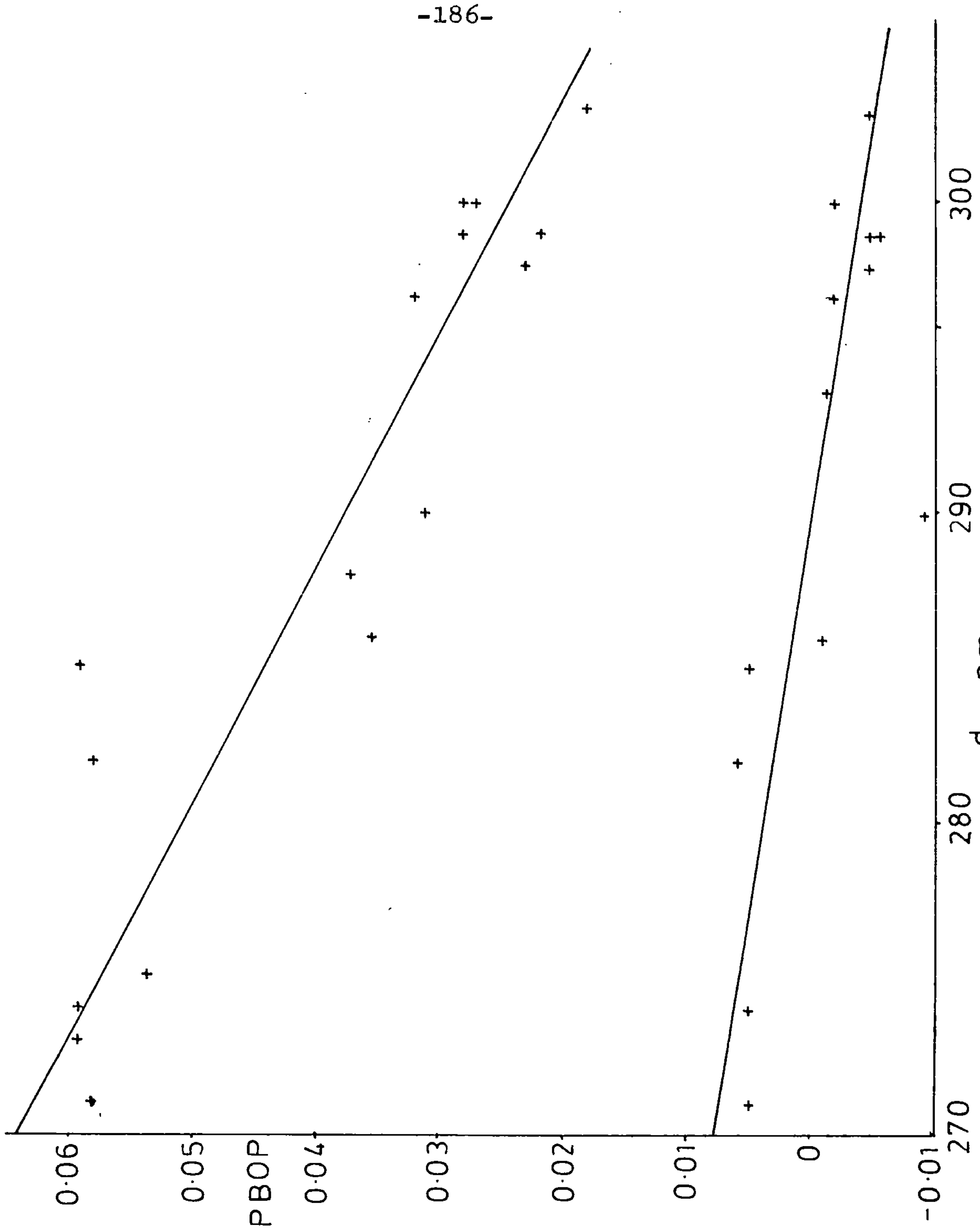


Figure 8.5

The graphs of S - S PBOP against S - S distance (pm).

Top line (with d-orbitals) and bottom line (without d-orbitals).

2. Long Range Interactions.

Many S - S distances in these species are considerably shorter than the sum of the van de Waals' radii and the presence of transannular S - S bonding may determine the preferred conformation of these structures. In the calculations with d-orbitals excluded the PBOPs are small and negative for aromatic species and small and positive for 'quasiaromatics'. When d-orbitals are introduced the PBOPs are much larger and positive. (Table 8.5). The S - S bonding is dominated by the contributions of the σ-bonds, the π-bonding being overall antibonding and there appears to be a relationship between the nitrogen angle or S - S distance and the degree of S - S bonding (Figures 8.4 and 8.5).

References

The abbreviations used are in accordance with the recommendations of the Journal of the Chemical Society. Reference citations in American Chemical Abstracts (abbreviation CA) are given where necessary.

1. R. Mews, Advan. Inorg. Chem. Radiochem., 1976, 19, 185.
2. H.W. Roesky, Z. Naturforsch., 1976, 31b, 680.
3. A.J. Banister in "International Review of Science, Inorganic Chemistry," Ser. 2, Vol. 3, ed. V. Gutmann, Butterworths University Park Press, Baltimore, 1975, p.41.
4. H.J. Emeléus, Endeavour, 1973, 32, 76.
5. H.-G. Horn, Flourine Chemistry Reviews, 1973, 6, 135.
6. D.A. Armitage,"Inorganic Rings and Cages," Edward Arnold Ltd., London, 1972, p.343.
7. H.G. Heal, Advan. Inorg. Chem. Radiochem., 1972, 15, 375.
8. O. Glemser and R. Mews, Advan. Inorg. Chem. Radiochem., 1972, 14, 333.
9. H. Garcia-Fernandez, H.G. Heal and G. Teste de Sagey, Compt. Rend., 1972, 275C, 323.
10. M. Becke-Goehring, Inorg. Macromol. Rev., 1970, 1, 17.
11. I. Haiduc,"The Chemistry of Inorganic Ring Systems," Vol. 2, Wiley Interscience, New York, 1970.
12. O. Glemser, Endeavour, 1969, 28, 86.
13. K.W.C. Burton and G. Nickless in "Inorganic Sulphur Chemistry," ed. G. Nickless, Elsevier, Amsterdam-London-New York, 1968, p.607.

14. H.G Heal in "Inorganic Sulphur Chemistry", ed. G. Nickless, Elsevier, Amsterdam-London-New York, 1968, p.459.

15. H.R. Allcock, "Heteroatomic Ring Systems and Polymers", Academic Press, New York, 1967.

16. C.W. Allen, J. Chem. Ed., 1967, 44, 38.

17. O. Glemser and M. Fild in "Halogen Chemistry", Vol. 2, ed. V. Gutmann, Academic Press, London-New York, 1967, p.1.

18. M. Becke-Goehring, Sulfur Inst. J., 1966, 2, 2.

19. M. Becke-Goehring and E. Fluck in "Developments in Inorganic Nitrogen Chemistry" Vol. 1, ed. C.B. Colburn, Elsevi r, Amsterdam-London-New York, 1966, P.150.

20. "Gmelins Handbuch der anorganischen Chemie", Verlag Chemie - G.M.B.H.- Weinham 1 Bergstrasse, 1963, 9, p.1531.

21. M. Becke-Goehring, Prog. Inorg. Chem., 1959, 1, 207.

22. M. Goehring, Quart. Rev. Chem. Soc., 1956, 10, 437.

23. A.V. Kirsanov, J. Gen. Chem. (U.S.S.R.), 1952, 22, 93.

24. I.U.P.A.C., "Nomenclature of Inorganic Chemistry", 2nd edn., "Definitive Rules 1970", Butterworths, London, 1971.

25. S.C. Nyburg, J. Cryst. Mol. Struct., 1973, 3, 331.

26. D. Chapman and T.C. Waddington, Trans. Faraday. Soc., 1962, 58, 1679.

27. O. Glemser, A. Müller and B. Krebs, Z. anorg. Chem., 1968, 357, 184.

28. A.J. Banister, L.F. Moore and J.S. Padley, Spec. Acta, 1967, 23A, 2705.

29. H. Garcia-Fernandez, Bull. Soc. Chim., 1968, 5, 1879.

30. E.A. Robinson, Canad. J. Chem., 1961, 39, 247.

31. A.J. Banister, Nature Phys. Sci., 1972, 239, 69.

32. H. -J. Hecht, R. Reinhardt, R. Steudel and H. Bradaczek, Z. anorg. Chem., 1976, 426, 43.

33. A. Barrie, H. Garcia-Fernandez, H.G. Heal and R.J. Ramsay, J. Inorg. Nuclear Chem., 1975, 37, 311.

34. R. Hoffmann "Advances in Chemistry", Vol.42, American Chemical Society, Washington D.C., 1964, p.80.

35. A.M. Griffin and G.M. Sheldrick, Acta Cryst., 1975, B31, 893.

36. A.F. Cameron, N.J. Hair and D.G. Morris, J.C.S. Perkin II, 1973, 1951.

37. A. Kálmán, B. Duffin and Á. Kucsman, Acta Cryst., 1971, B27, 586.

38. A. Kálmán and K. Sasvári, Cryst. Struct. Comm., 1972, 1, 243.

39. A. Kálmán, Acta Cryst., 1967, 22, 501.

40. A.F. Cameron, I.R. Cameron, M.M. Campbell and G. Johnson, Acta Cryst., 1976, B32, 1377.

41. C.M. Mikulski, P.J. Russo, M.S. Saran, A.G. Macdiarmid, A.F. Garito and A.J. Heeger, J. Amer. Chem. Soc., 1975, 6358.

42. H.W. Roesky, G. Holtschneider, H. Wiezer and B. Krebs, Chem. Ber., 1976, 109, 1358.

43. E. M. Holt, S. L. Holt and K. J. Watson, J.C.S. Dalton, 1974, 1357.

44. J. Leitch, S.C. Nyburg, D.A. Armitage and M.J. Clark, J. Cryst. Mol. Struct., 1973, 3, 337.

45. F.B. Olsen and J.C. Barrick, Inorg. Chem., 1973, 12, 1353.

46. R. Steudel, P. Luger and H. Bradaczek, Angew. Chem. Internat. Edn., 1973, 12, 316.

47. B.D. Sharma and J. Donohue, Acta Cryst., 1963, 16, 891.

48. U. Thewalt, Angew. Chem. Internat. Edn., 1976, 15, 765.

49. W. Flues, O.J. Scherer, J. Weiss and G. Wolmeshäuser, Angew. Chem. Internat. Edn., 1976, 15, 379.

50. J. Weiss, I. Ruppert and R. Appel, Z. anorg. Chem., 1974, 406, 329.

51. A.M. Griffin and G.M. Sheldrick, Acta Cryst., 1975, B31, 895.

52. H.W. Roesky, W. Grosse-Böwing, I. Rayment and H.M.M. Shearer, J.C.S. Chem. Comm., 1975, 735.

53. G.A. Wiegers and A. Vos, Acta Cryst., 1966, 20, 192.

54. H.J. Emeléus, R.A. Forder, R.J. Poulet and G.M. Sheldrick, J. Chem. Soc.(D), 1970, 1483.

55. B. Krebs and S. Pohl, Chem. Ber., 1973, 106, 1069.

56. G.A. Wiegers and A.Vos, Acta Cryst., 1963, 16, 152.

57. E.M. Holt, S.L. Holt and K.J. Watson, J.C.S. Dalton, 1977, 514.

58. E.M. Holt and S.L. Holt, J.C.S. Dalton, 1974, 1990.

59. M.G.B. Drew, D.H. Templeton and A. Zalkin, Inorg. Chem., 1967, 6, 1906.

60. B. Kruss and M.L. Ziegler, Z. anorg. Chem., 1972, 388, 158.

61. A.J. Banister, J.A. Durrant, I. Rayment and H.M.M. Shearer, J.C.S. Dalton, 1976, 928.

62. I. Rayment and H.M.M. Shearer, personal communication.

63. R.J. Gillespie, P.R. Ireland and J.E. Vekris, Canad. J. Chem., 1975, 53, 3147.

64. H.M.M. Shearer, personal communication.

65. D.A. Arrington, T. Moeller and I.C. Paul, J. Chem. Soc.(A), 1970, 2627.

66. J.C. van de Grampel and A. Vos, Acta Cryst., 1969, B25, 651.

67. P.A. Tucker and J.C. van de Grampel, Acta Cryst., 1974, B30, 2795.

68. A.C. Hazell, G.A. Wiegers and A. Vos, Acta Cryst., 1966, 20, 186.

69. G.A.P. Dalgaard, A.C. Hazell and R.G. Hazell, Acta Cryst., 1974, B30, 2721.

70. M. Boudeulle, Cryst. Struct. Comm., 1975, 4, 9.

71. J. Weiss, Z. Naturforsch., 1961, B16, 477.

72. O. Glemser, B. Krebs, J. Wegener and E. Kindler, Angew. Chem. Internat. Edn., 1969, 8, 598.

73. G. Ertl and J. Weiss, Z. Naturforsch., 1974, B29, 803.

74. D.P. Craig and N.L. Paddock in "Nonbenzenoid Aromatics", Academic Press, New York-London, 1971, Vol.2, p.273.

75. A.W. Schleuter and R.A. Jacobson, J. Chem. Soc.(A), 1968, 2317.

76. J.-P. Faucher, J.-F. Labarre and R.A. Shaw, Z. Naturforsch., 1976, B31, 677.

77. D.R. Armstrong, G.H. Lonmuir and P.G. Perkins, J.C.S. Chem. Comm., 1972, 464.

78. D.R. Armstrong, R.C.W. King and P.G. Perkins, Rev. Roumaine de Chem.,1973, 18, 2011.

79. J.-P. Faucher and J.-F. Labarre, Phosphorus, 1974, 3, 265.

80. J.-P. Faucher, J.C. van de Grampel, J.-F. Labarre, S.N. Nabi, B. de Ruiter and R.A. Shaw, J. Chem. Research (S), 1977, 112.

81. P. Cassoux, O. Glemser and J.-P. Labarre, Z. Naturforsch., 1977, B32, 41.

82. J.A. Durrant, Ph.D. Thesis, 1977, p. 183.

83. A.J. Banister, Nature Phys. Sci., 1972, 237, 92.

84. D.E. Parry and J.M. Thomas, J. Phys. C. Solid State Phys., 1975, 8, 145.

85. A.J. Banister, L.F. Moore and J.S. Padley in "Inorganic Sulphur Chemistry", ed. G. Nickless, Elsevier, Amsterdam-London-New York, 1968, p.138.

86. W.S. McDonald and D.W.J. Cruickshank, Acta Cryst., 1967, 22, 48.

87. R.C. Ferguson, J. Amer. Chem. Soc., 1954, 76, 850.

88. H. Eysel, J. Mol. Structure, 1970, 5, 275.

89. J.A. Durrant, Ph.D. Thesis, 1977, p. 55.

90. H. Oberhammer, Z. Naturforsch., 1970, A25, 1497.

91. W. Kirchoff, J. Amer. Chem. Soc., 1969, 91, 2437.

92. O. Glemser and J. Wegener, Inorg. Nuclear Chem. Letters, 1971, 7, 623.

93. J.A. Durrant, Ph.D. Thesis, 1977, p. 50.

94. W.L. Jolly, Sulfur Research Trends, Adv. Chem. Ser., 1972, 110, 92.

95. G. Leandri, V. Busetti, G. Valle and M. Mammi, J.C.S. Chem. Comm., 1970, 413.

96. E. Prince, Acta Cryst., 1975, B31, 2536.

97. A. Gieren and F. Pertlik, Angew. Chem. Internat. Edn., 1976, 15, 782.

98. A. Gieren, B. Dederer, H.W. Roesky and E. Janssen, Angew. Chem. Internat. Edn., 1976, 15, 783.

99. T. Debaerdemaecker and R. Allmann, Chem. Ber., 1973, 106, 2807.

100. S.K. Arora, Acta Cryst., 1974, B30, 2923.

101. J. Weiss, Acta Cryst., 1974, B30, 2888.

102. F.A. Momany and R.A. Bonham, J. Amer. Chem. Soc., 1964, 86, 162.

103. R.R. McDonald, Ph.D. Dissertation Indiana Univ. (Diss. Abs., 1962, 23, 1897).

104. J.P. Schaefer and S.K. Arora, J.C.S. Chem. Comm., 1971, 1623.

105. M. Mellini and S. Merlino, Acta Cryst., 1976, B32, 1077.

106. F.A. Momany and R.A. Bonham, J. Amer. Chem. Soc., 1961, 83, 4475.

107. S.V. Dobyns and L. Pierce, J. Amer. Chem. Soc., 1963, 85, 3553.

108. A.J. Banister, H.G. Clarke, I. Rayment and H.M.M. Shearer, Inorg. Nuclear Chem. Letters, 1974, 10, 647.

109. R.J. Gillespie and E.A. Robinson, Canad. J. Chem., 1963, 41, 2074.

110. D.B. Adams, A.J. Banister, D.T. Clark and D. Kilcast, Int. J. Sulfur Chem., 1971, 1, 143.

111. A.C. Hazell and R.G. Hazell, Acta Chem. Scand., 1972, 26, 1987.

112. I. Rayment, Ph.D. Thesis, Durham Univ., 1975.

113. A.C. Hazell and R.G. Hazell, personal communication.

114. A.J. Banister, plenary lecture at Amer. Chem. Soc., Centenary Symposium, "Chemistry of Sulphur and Its Binary Inorganic Compounds", New York, 7-9 April 1976.

115. R. Steudel, Spectrochim. Acta., 1975, A31, 1065.

116. D. Neubauer and J. Weiss, Z. anorg. Chem., 1960, 303, 28.

117. I. Csöregh, P. Kierkegaard and R. Norrestam, Acta Cryst., 1975, B31, 314.

118. H. Binas, Z. anorg. Chem., 1967, 352, 271.

119. S. Geller and J.L. Hoard, Acta Cryst., 1951, 4, 399.

120. R.J. Gillespie, D.R. Slim and J.D. Tyrer, J.C.S. Chem. Comm., 1977, 253.

121. O. Glemser and J. Wegener, Angew. Chem. Internat. Edn., 1970, 9, 309.

122. M. Lustig and J.K. Ruff, Inorg. Chem., 1965, 4, 1444.

123. A. Clifford, Inorg. Chem., 1969, 8, 1789.

124. W. Lidy, W. Sundermeyer and W. Verbeck, Z. anorg. Chem., 1974, 406, 228.

125. H.W. Roesky and H. Wiezer, Angew. Chem. Internat. Edn., 1974, 13, 146.

126. E. Niecke, O. Glemser and H. Thamm, Chem. Ber., 1970, 103, 2864.

127. W. Wolfsberger and H.H. Pickel, Z. anorg. Chem., 1971, 384, 131.

128. H.W. Roesky and M. Diet, Angew. Chem. Internat. Edn., 1973, 12, 424.

129. O.J. Scherer and R. Wies, Angew. Chem. Internat. Edn., 1971, 10, 812.

130. D. Hänssgen and W. Roelle, J. Organometallic Chem., 1973, 56, C14.

131. A. Haas and P. Schott, Angew. Chem. Internat. Edn., 1967, 6, 370.

132. A.J. Banister and J.R. House, J. Inorg. Nuclear Chem., 1971, 33, 4057.

133. G. Kresze and H. Grill, Tetrahedron Letters, 1969, 4117.

134. W. Wurcherpfennig and G. Kresze, Tetrahedron Letters, 1966, 1671.

135. K. Seppelt and W. Sundermeyer, Angew. Chem. Internat. Edn., 1969, 8, 771.

136. O.J. Scherer and G. Wolmershauser, Angew. Chem. Internat. Edn., 1975, 14, 485.

137. E. Nachbaur and A. Popitsch, Angew. Chem. Internat. Edn., 1973, 12, 339.

138. O.J. Scherer and R. Wies, Angew. Chem. Internat. Edn., 1972, 11, 529.

139. G. Kresze and C. Seyfried, Angew. Chem. Internat. Edn., 1966, 5, 1042.

140. H.W. Roesky and H. Wiezer, Angew. Chem. Internat. Edn., 1975, 14, 258.

141. R.G. Laughlin and W. Yellin, J. Amer. Chem. Soc., 1967, 89, 2435.

142. T. Uno, K. Machida and K. Hanai, Spectrochim. Acta, 1966, 22, 2063.

143. I.W. Herrick and E.L. Wagner, Spectrochim. Acta, 1965, 21, 1569.

144. W. Warthman and A. Schmidt, Z. anorg. Chem., 1975, 418, 57.

145. R. Paetzold and E. Rönsch, Spectrochim. Acta, 1970, 26A, 569.

146. W.J. Lehmann, J. Mol. Spectroscopy, 1961, 7, 261.

147. A. Müller, A. Ruoff, B. Krebs, O. Glemser and W. Koch, Spectrochim. Acta, 1969, 25A, 199.

148. H. Richert and O. Glemser, Z. anorg. Chem., 1961, 307, 328.

149. W.H. Kirchoff and E.B. Wilson Jnr., J. Amer. Chem. Soc., 1963, 85, 1726.

150. O. Glemser, Angew. Chem. Internat. Edn., 1963, 2, 530.

151. W. Sawodny, A. Fadini and R. Ballein, Spectrochim. Acta, 1965, 21, 995.

152. O. Glemser and W. Koch, Angew. Chem. Internat. Edn., 1971, 10, 127.

153. O. Glemser, R. Mews and H.W. Roesky, Chem. Ber., 1969, 102, 1523.

154. O. Glemser, Int. J. Sulfur Chem., 1971, 6, 35.

155. B. Krebs, E. Meyer-Hussein, O. Glemser and W. Koch, J.C.S. Chem. Comm., 1968, 1579.

156. J.E. Griffiths, Spectrochim. Acta, 1969, 25A, 1355.

157. R.R. Karl Jnr. and S.H. Bauer, Inorg. Chem., 1975, 14, 1860.

158. J.J. Smith and B. Meyer, J. Mol. Spectroscopy, 1964, 14, 160.

159. O. Glemser, A. Müller, D. Böhler and B. Krebs, Z. anorg. Chem., 1968, 357, 184.

160. R.L. Cook and W.H. Kirchoff, J. Chem. Phys., 1967, 47, 4521.

161. A.M. Mirri and A. Guarnieri, Spectrochim. Acta, 1967, 23A, 2159.

162. A. Müller, G. Nagarajan, O. Glemser and S.J. Cyvin, Spectrochim. Acta, 1967, 23A, 2683.

163. A. Müller, N. Mohan, S.J. Cyvin, N. Weinstock and O. Glemser, J. Mol. Spectroscopy, 1976, 59, 161.

164. S.C. Peake and A.J. Downs, J.C.S. Dalton, 1974, 859.

165. T. Beppu, E. Hirota and Y. Morino, J. Mol. Spectroscopy, 1970, 36, 386.

166. S. Mizumoto, J. Izumi, T. Beppu and E. Hirota, Bull. Chem. Soc. Japan, 1972, 45, 786.

167. P.O. Tchir and R.D. Spratley, Canad. J. Chem., 1975, 53, 2311.

168. R. Kebabcioglu, R. Mews and O. Glemser, Spectrochim. Acta, 1972, 28A, 1593.

169. J. Haase, H. Oberhammer, W. Zeil, O. Glemser and R. Mews, Z. Naturforsch., 1970, A25, 153.

170. P.O. Tchir and R.D. Spratley, Canad. J. Chem., 1975, 53, 2331.

171. P.O. Tchir and R.D. Spratley, Canad. J. Chem., 1975, 53, 2318.

172. H. Oberhammer and W. Zeil, Z. Naturforsch., 1970, A25, 845.

173. J. Haase, H. Oberhammer, W. Zeil, O. Glemser and R. Mews, Z. Naturforsch., 1971, A26, 1333.

174. K.N. Trueblood and S.W. Mayer, Acta Cryst., 1956, 9, 628.

175. L.G. Vorontsova, Zh. Struct. Khim., 1966, 7, 280.

176. K. Hanai, T. Okudu, T. Uno and K. Machida, Spectrochim. Acta, 1975, 31A, 1217.

177. Y. Sasaki and F.P. Olsen, Canad. J. Chem., 1971, 49, 271.

178. J.C. Barrick, C. Calvo and F.P. Olsen, Canad. J. Chem., 1973, 51, 3691.

179. J.C. Barrick, C. Calvo and F.P. Olsen, Canad. J. Chem., 1973, 51, 3697.

180. A.M. Vuagnat and E.L. Wagner, J. Chem. Phys., 1957, 26, 77.

181. G.W. Cox, T.M. Sabine, V.M. Padmanabhan, N.T. Ban, M.K. Chung and A.J. Surjadi, Acta Cryst., 1967, 23, 578.

182. A. Kálmán, K. Sasvári and Á. Kucsman, J. Chem. Soc.(D), 1971, 1447.

183. I. Hargittai and M. Hargittai, Acta Cryst., 1969, A25, S165.

184. J.C. Barrick, C. Calvo and F.P. Olsen, Canad. J. Chem., 1974, 52, 2985.

185. A. Buerger, K. Burczyk, A. Blaschette and H. Safari, Spectrochim. Acta, 1971, 27A, 1073.

186. L.V. Vilkov and I. Hargittai, Acta Chim. Hung., 1967, 52, 423.

187. P. Goudmand and O. Dessaux, J. Chem. Phys., 1967, 63, 135.

188. F. Watari, Z. anorg. Chem., 1964, 332, 322.

189. J. Goubeau, Angew. Chem. Internat. Edn., 1966, 5, 567.

190. I. Nakagawa, S. Mizushima, A. Saracento, T.J. Lane and J.V. Quagliano, Spectrochim. Acta, 1958, 12, 239.

191. R.J. Philippe and H. Moore, Spectrochim. Acta, 1961, 17, 1004.

192. A.F. Cameron and F.D. Duncanson, Acta Cryst., 1976, B32, 1563.

193. H. Siebert, Z. anorg. Chem., 1957, 292, 167.

194. M. Brownstein, P.A.W. Dean and R.J. Gillespie, J.C.S. Chem. Comm., 1970, 9.

195. C. Lau, H. Lynton, J. Passmore and P.-Y. Siew, J.C.S. Dalton, 1973, 2535.

196. D.A. Armitage and A.W. Sinden, Inorg. Chem., 1972, 11, 1151.

197. R.J. Gillespie and E.A. Robinson, Canad. J. Chem., 1961, 39, 2189.

198. R.J. Gillespie and E.A. Robinson, Canad. J. Chem., 1961, 39, 2171.

199. I. Hargittai, Acta Chim. (Budapest), 1969, 60, 231. (C.A. 1969, 71, 54515f).

200. D.R. Lide, D.E. Mann and R.M. Fristom, J. Chem. Phys., 1957, 26, 734.

201. T. Moeller, T.-H. Chang, A. Ouchi, A. Vandi and F. Failli, Inorg. Syn., 1971, 13, 9.

202. A.J. Banister, personal communication.

203. A.C. Hazell, Acta Cryst., 1974, B30, 2724.

204. T. Moeller and A. Ouchi, J. Inorg. Nuclear Chem., 1966, 28, 2147.

205. R. Clipsham, R.M. Hart and M.A. Whitehead, Inorg. Chem., 1969, 8, 2431.

206. R.J. Gillespie and E.A. Robinson, Canad. J. Chem., 1962, 40, 644.

207. R. Pascard, Compt. Rend., 1955, 240, 2162.

208. H.W. Roesky, personal communication.

209. K.J. Palmer, J. Amer. Chem. Soc., 1938, 60, 2360.

210. W.G. Palmer, J. Chem. Soc., 1961, 1552.

211. S. Martinez, Acta Cryst., 1956, 9, 145.

212. E. Stanley, Acta Cryst., 1956, 9, 897.

213. S. Saito, J. Mol. Spectroscopy, 1963, 30, 1.

214. R. Steudel, Z. Naturforsch., 1969, B24, 934.

215. E.A. Robinson and S.K. Hall, unpublished results in ref. 109.

216. M. Hargittai and I. Hargittai, J. Mol. Structure, 1974, 20, 283.

217. V. Wannagat and R. Pfeiffenschneider, Z. anorg. Chem., 1958, 297, 151.

218. H.R. Lynton and M.R. Truter, J. Chem. Soc., 1960, 5112.

219. J.A. Durrant, Ph.D. Thesis, 1977, p. 138.

220. D.W.J. Cruickshank, J. Chem. Soc., 1954, 332.

221. D.A. Long and R.T. Bailey, Trans. Farad. Soc., 1963, 59, 792.

222. D.P. Stevenson and R.A. Cooley, J. Amer. Chem. Soc., 1940, 62, 2477.

223. F.J. Lovas, E. Tiemann and D.R. Johnson, J. Chem. Phys., 1974, 60, 5005.

224. U. Agawala, C.E. Rees and M.G. Thode, Canad. J. Chem., 1965, 43, 2082.

225. V.M. Padmanabhan, V.S. Yadava, Q.O. Navarro, A. Garcia, L. Karsono, I.-H. Suh and L.S. Chien, Acta Cryst., 1971, B27, 253.

226. J.A.J. Jarvis, Acta Cryst., 1953, 6, 327.

227. P.W. Schenk and R. Steudel, Angew. Chem. Internat. Edn., 1965, 4, 402.

228. E. Tiemann, J. Hoeft, F.J. Lovas and D.R. Johnson, J. Chem. Phys., 1974, 60, 5000.

229. L.H. Loopstra and C.H. Macgillary, Acta Cryst., 1958, 11, 349.

230. W.D. Horrocks and F.A. Cotton, Spectrochim. Acta, 1961, 17, 134.

231. O. Bastiansen and H. Viervoll, Acta Chem. Scand., 1948, 2, 702.

232. G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. 11, Van Nostrand, New York, 1944, p.167.

233. J.A. McGinnety, Acta Cryst., 1974, B30,. 1640.

234. K. Pilgrim, J. Org. Chem., 1970, 35, 1165.

235. R. Steudel and M. Rebsch, Angew. Chem. Internat. Edn., 1972, 11, 302.

236. R. Steudel, P. Luger, H. Bradaczek and M. Rebsch, Angew. Chem. Internat. Edn., 1973, 12, 423.

237. M.F. Lappert and J.K. Smith, J. Chem. Soc., 1961, 3224.

238. I. Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds", Academic Press, New York, 1963.

239. A.J. Banister and J.A. Durrant, J. Chem. Research. (In press 1).

240. A.J. Banister and J.A. Durrant, J. Chem. Research. (In press 2).

241. C. Lau and J. Passmore, J.C.S. Dalton, 1973, 2528.

242. W. Verbeek and W. Sundermeyer, Angew. Chem. Internat. Edn., 1969, 8, 376.

243. R. Mews and O. Glemser, Angew. Chem. Internat. Edn., 1975, 14, 186.

244. A.F. Clifford and J.W. Thompson, Inorg. Chem., 1966, 5, 1424.

245. N. Furukawa, T. Yoshimura and S. Oae, Tetrahedron Letters, 1973, 2113.

246. E. Nachbaur and A. Popitsch, Angew. Chem. Internat. Edn., 1973, 12, 339.

247. R.F. Dunphy, C. Lau, H. Lynton and J. Passmore, J.C.S. Dalton, 1973, 2533.

248. M. Hargittai and I. Hargittai, J. Chem. Phys., 1973, 59, 2513.

249. I. Hargittai and M. Hargittai, J. Mol. Structure, 1973, 15, 399.

250. T.L. Brown and M. Kubota, J. Amer. Chem. Soc., 1961, 83, 4175.

251. A. Müller, O. Glemser and K. Scherf, Chem. Ber., 1966, 99, 3568.

252. J. Haase, H. Oberhammer, W. Zeil, O. Glemser and R. Mews, Z. Naturforsch., 1971, A26, 1333.

253. H. Greschonig, E. Nachbaur and H. Krischner, personal communication.

254. H. Oberhammer and W. Zeil, Z. Naturforsch., 1969, A24, 1612.

255. D.L. Cottle, J. Amer. Chem. Soc., 1946, 68, 1380.

256. G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd Edn., Vol.1, Academic Press, New York, 1963, 370.

257. E.H. Harvey and H.A. Schnette, J. Amer. Chem. Soc., 1926, 48, 2065.

258. J.A. Riddick and W.B. Bunger, "Organic Solvents, Physical, Properties and Methods of Purification", 3rd Edn., Wiley Interscience, 1970.

259. J.F. Coetzee, Pure Appl. Chem., 1966, 13, 429.

260. O.L.I. Brown and G.G. Manov, J. Amer. Chem. Soc., 1937, 59, 500.

261. D.N. Bhattacharyya, C.L. Lee, J. Smid and M. Szwarc, J. Phys. Chem. 1965, 69, 608.

262. D.C. Jones and H.F. Betts, J. Chem. Soc., 1928, 1177.

263. T. Chivers and I. Drummond, J.C.S. Dalton, 1974, 631.

264. F.B. Garner and S. Sugden, J. Chem. Soc., 1929, 1298.

265. H.J. Prins, Rec. Trav. Chim., 1946, 65, 455.

266. W.L. Jolly, K.D. Maguire and D. Rabinovich, Inorg. Chem., 1963, 2, 1304.

267. W.L. Jolly and K.D. Maguire, Inorg. Syn., 1967, 9, 102.

268. W.L. Jolly and M. Villera-Blanco, Inorg. Syn., 1967, 9, 98.

269. G.G. Alange, A.J. Banister and B. Bell, J.C.S. Dalton, 1972, 2399.

270. J. Bojes and T. Chivers, J.C.S. Dalton, 1975, 1715.

271. J. Nelson, Spectrochim. Acta, 1971, 27A, 1105.

272. O. Exner, Coll. Czech. Chem. Comm., 1963, 28, 3150.

273. D.H.R. Barton, P.D. Magnus and S.I. Pennanen, J.C.S. Chem. Comm., 1974, 1007.

274. C. Brown, B.T. Grayson and R.F. Hudson, J.C.S. Chem. Comm., 1974, 1007.

275. L.N. Markovskii, V.G. Shermolovich and V.I. Shevenko, Zh. Org. Khim., 1975, 11, 2533.

276. R.F. Swindell, T.J. Ouellette, D.P. Babb and J.M. Shreeve, Inorg. Nuclear Chem. Letters, 1971, 7, 239.

277. S.G. Metcalf and J.M. Shreeve, Inorg. Chem., 1972, 11, 1631.

278. R.F. Swindell, D.P. Babb, T.J. Ouellette and J.M. Shreeve, Inorg. Chem., 1972, 11, 242.

279. R.F. Swindell and J.M. Shreeve, J. Amer. Chem. Soc., 1972, 94, 5713.

280. F.P. Olsen and Y. Sasaki, J. Amer. Chem. Soc., 1970, 92, 3812.

281. Y. Sasaki and F.P. Olsen, Canad. J. Chem., 1971, 49, 283.

282. M. Knollmueller and K.R. Reich, Monatsh. Chem., 1975, 106, 1095.

283. J.B. Wright, J. Org. Chem., 1964, 29, 1905.

284. E. Ziegler and W. Rüf, Z. Naturforsch., 1975, B30, 951.

285. J. Geevers and W.P. Trompen, Tetrahedron Letters, 1974, 18, 1687.

286. R.G.R. Bacon, R.S. Irwin, J. McC. Pollock and A.D.E. Pullin, J. Chem. Soc., 1958, 764.

287. A.E. Barnett, P. Piotis and B. Tittle, J. Inorg. Nuclear Chem., 1976, 38, 1575.

288. S.P. von Halasz and O. Glemser, Chem. Ber., 1970, 103, 553.

289. W.K. Glass and A.D.E. Pullin, Trans. Farad. Soc., 1961, 57, 546.

290. G. Kresze, A. Maschke, R. Albrecht, K. Bederke, P. Patzschke, H. Smalla and A. Trede, Angew. Chem. Internat. Edn., 1962, 1, 89.

291. G. Kresze and A. Maschke, Chem. Ber., 1961, 94, 450.

292. H.W. Roesky and U. Biermann, Angew. Chem. Internat. Edn., 1967, 6, 882.

293. W. Lwowski and E. Scheiffele, J. Amer. Chem. Soc., 1965, 87, 4359.

294. J.M. Williams, S.W. Peterson and G.M. Brown, Inorg. Chem., 1968, 7, 2577.

295. G.M. Atkins Jnr. and E.M. Burgess, J. Amer. Chem. Soc., 1972, 94, 6135.

296. K. Fischer and K.R. Andress, Z. anorg. Chem., 1955, 281, 169.

297. A. Hantzch and A. Holl, Chem. Ber., 1901, 34, 3430.

298. G. Heinze and A. Meuwsen, Z. anorg. Chem., 1954, 275, 49.

299. K. Nara, M. Nakagaki and H. Hiyama, Kogyo Kagaku Zasshi, 1965, 68, 606. (C.A. 1965, 63, 5222).

300. R. Appel and M. Goehring, Angew. Chem., 1952, 64, 616.

301. K. Bencker, G. Leiderer and A. Meuwsen, Z. anorg. Chem., 1963, 324, 202.

302. E.M. Burgess and W.M. Williams, J. Amer. Chem. Soc., 1972, 94, 4386.

303. E.M. Burgess and W.M. Williams, Org. Syn., 1973, 53, 1856.

304. H. Schröder and O. Glemser, Z. anorg. Chem., 1959, 298, 78.

305. A.J. Banister and B. Bell, unpublished results.

306. H.J. Emeléus and R.J. Poulet, J. Fluorine Chem., 1971, 1, 13.

307. B. Beagley, S.J. Chantrell, R.G. Kirby and D.G. Schmidling, J. Mol. Structure, 1975, 25, 319.

308. S. Cradock, E.A.V. Ebsworth, G.D. Meikle and D.W.H. Rankin, J.C.S. Dalton, 1975, 805.

309. L. Pauling, "The Nature of the Chemical Bond", 3rd Edn., Cornell University Press, 1960.

310. M.R. Truter, J. Chem. Soc., 1962, 3400.

311. H.G. Heal and J. Nelson, Inorg. Nuclear Chem. Letters, 1970, 6, 429.

312. K.D. Maguire, J.J. Smith and W.L. Jolly, Chem. Ind., 1963, 39, 1589.

313. J.J. Smith and W.L. Jolly, Inorg. Chem., 1965, 4, 1006.

314. R.L. Dekock and M.S. Haddad, Inorg. Chem., 1977, 16, 216.

315. M. Becke-Goehring, R. Schwarz and W. Spiess, Z. anorg. Chem., 1958, 293, 294.

316. O. Glemser and W. Koch, unpublished results, 1970, in Adv. Inorg. Chem. Radiochem., 1972, 14, 333.

317. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd Edn., Wiley Interscience, New York, 1973.

318. J.A. Durrant, Ph.D. Thesis, University of Durham, 1977, Chapter 8.

319. D.R. Armstrong, P.G. Perkins and J.J.P. Stewart, J.C.S. Dalton, 1973, 2273.

320. H.G. Heal, Inorg. Sulfur Chem., 1968, 459.

321. R.L. Patton, Ph.D. Thesis, University of California, 1969, 107.

322. O. Glemser and H. Perl, Naturwissenschaften, 1961, 48, 620.

323. A. Guarnieri, Z. Naturforsch., 1971, A26, 1246.

324. R.L. Patton and W.L. Jolly, Inorg. Chem., 1970, 9, 1079.

325. B. Bell, Ph.D. Thesis, University of Durham, 1970, 113.

326. M. Goehring, H. Hohenschutz and R. Appel, Z. Naturforsch., 1954, B9, 678.

327. M. Goehring and H. Malz, Z. Naturforsch., 1954, B9, 567.

328. A.J. Banister and H.G. Clarke, J.C.S. Dalton, 1972, 2661.

329. H.G. Clarke, Ph.D. Thesis, University of Durham, 1974, 137.

330. I. Fild, Thesis, University of Hollenberg, Gottingen, 1965.

331. R. Mews, D.-L. Wagner and O. Glemser, Z. anorg. Chem., 1975, 412, 148.

332. A. Meuwsen, Silicium, Schwefel, Phosphate, Colloq. Sek. anorg. Chem. Internat. Union reine u. Angew. Chem., Münster, 1954, 130 (Pub. 1955). (C.A. 1955, 52, 6048h).

333. D.H.R. Barton and W.A. B~~a~~ubb, J.C.S. Perkin I, 1977, 916.

334. M. Becke-Goehring and H.P. Latscha, Angew. Chem. Internat. Edn., 1962, 1, 551.

335. M. Goehring, W. Berg and H. Malz, Z. anorg. Chem., 1956, 283, 13.

336. A. Golloch and M. Kuss, Z. Naturforsch., 1974, B29, 320.

337. A. Golloch and M. Kuss, Z. Naturforsch., 1972, B27, 1280.

338. H.W. Roesky and E. Janssen, Chem. Ber., 1975, 108, 2531.

339. J. Varwig, H. Steinbeisser, R. Mews and O. Glemser, Z. Naturforsch., 1974, B29, 813.

340. O. Glemser, S. Austin and F. Gerhardt, Chem. Ber., 1964, 97, 1262.

341. G.G. Alange, A.J. Banister, B. Bell and P.W. Millen, Inorg. Nuclear Chem. Letters, 1977, 13, 143.

342. G.G. Alange, A.J. Banister, B. Bell and P.W. Millen, J. Inorg. Nuclear Chem., (In press).

343. J.A. Durrant, Ph.D. Thesis, University of Durham, 1977, Chapter 5.

344. A. Meuwsen, Ber., 1932, 65, 1724.

345. Y. Monteil and H. Vincent, Z. Naturforsch., 1976, B31, 673.

346. L. Zborilová, J. Touzin, D. Navatrilova and J. Mrksova, Z. Chem., 1972, 12, 27. (C.A. 1972, 76, 121045w).

347. W.L. Jolly and K.J. Wynne, J. Inorg. Nuclear Chem., 1968, 30, 2851.

348. H.G. Heal and J. Kane, J. Inorg. Nuclear Chem., 1967, 29, 1539.

349. J.J. Harris, U.S. Patent, 3052682 (1962), (C.A. 1963, 58, 3402).

350. G.I. Migachev and B.I. Stepanov, Zh. Neorg. Khim., 1966, 11, 1737.

351. S.M. Zhivukhin and V.V. Kireev, Zh. Neorg. Khim., 1964, 9, 2671.

352. L.F. Moore, Ph.D. Thesis, University of Durham, 1967, 147.

353. V. Bertini and A. De Munno, Gazz. Chim. Ital., 1967, 97, 1614. (C.A. 1968, 69, 2910v).

354. V. Bertini, A. De Munno and A. Marraccini, J. Org. Chem., 1972, 37, 2587.

355. M. Goehring, "Ergebnisse und Probleme der Chemie der Schwefelstickstoff-verbindungen", Akad. Verlag, Berlin, 1957.

356. S.N. Nabi and M.A. Khaleque, J. Chem. Soc., 1965, 3626.

357. R. Mews, Angew. Chem. Internat. Edn., 1976, 15, 691.

358. T.C. Waddington and F. Klanberg, J. Chem. Soc., 1960, 2339.

359. R. Mews and O. Glemser, Inorg. Chem., 1972, 11, 2521.

360. R. Mews and O. Glemser, Inorg. Nuclear Chem. Letters, 1971, 7, 823.

361. L.D. Huestis, M.L. Walsh and N. Hahn, J. Org. Chem., 1965, 30, 2763.

362. O. Andreasen, A.C. Hazell and R.G. Hazell, Acta Cryst., 1977, B33, 1109.

363. M. Goehring and J. Heincke, Z. anorg. Chem., 1953, 272, 297.

364. M. Goehring and J. Heincke, Z. anorg. Chem., 1955, 278, 53.

365. W.L. Jolly and M. Becke-Goehring, Inorg. Chem., 1962, 1, 76.

366. D.A. Armitage and A.W. Sinden, J. Inorg. Nuclear Chem., 1974, 36, 993.

367. M. Becke-Goehring and G. Magin, Z. anorg. Chem., 1965, 340, 126.

368. M. Goehring and D. Schuster, Angew. Chem., 1952, 64, 617.

369. A. Meuwsen and M. Losel, Z. anorg. Chem., 1953, 271, 221.

370. M. Goehring, H. Hohenschutz and J. Ebert, Z. anorg. Chem., 1954, 276, 47.

371. D. Schläfer and M. Becke-Goehring, Z. anorg. Chem., 1968, 362, 1.

372. H.W. Roesky, Angew. Chem. Internat. Edn., 1972, 11, 642.

373. H.W. Roesky and W. Schaper, Chem. Ber., 1974, 107, 3451.

374. M. Goehring, H. Hohenschutz and R. Appel, Z. Naturforsch., 1954, B9, 47.

375. G. Dehoust, Dissertation, Heidelberg, 1961. (Quoted in ref. 355).

376. M. Goehring, Inorg. Syn., 1960, 6, 123.

377. M. Goehring, Quart. Rev., 1956, 10, 437.

378. M. Goehring, Prog. Inorg. Chem., 1959, 1, 221.

379. Y. Monteil, Bull. Soc. Chim. France, 1971, 2474.

380. Y. Monteil, Bull. Soc. Chim. France, 1971, 2479.

381. R. Appel and M. Goehring, Z. anorg. Chem., 1953, 271, 171.

382. A. Perret and R. Perrot, Compt. Rend., 1934, 199, 955.

383. R. Appel and W. Huber, Z. anorg. Chem., 1954, 275, 338.

384. R. Appel and W. Huber, Chem. Ber., 1956, 89, 386.

385. E. Nachbaur and E. Baumgartner, Monatsh. Chem., 1973, 104, 1131.

386. A. Meuwsen and T. Papenfuss, Z. anorg. Chem., 1962, 318, 190.

387. A.C. Hazell, Acta Chem. Scand., 1972, 26, 2542.

388. R. Appel and G. Berger, Z. anorg. Chem., 1964, 327, 114.

389. A. Hantzch and B.C. Stuer, Chem. Ber., 1905, 38, 1022.

390. H.M. Ondik, Acta Cryst., 1965, 18, 226.

391. C.A. Anderson and C.E. Miller, J. Amer. Pharm. Assoc., Sci. Edn., 1948, 37, 204.

392. H.W. Roesky, communication to I. Rayment.

393. H.W. Roesky and B. Kuhtz, Chem. Ber., 1974, 107, 1.

394. H.W. Roesky and O. Petersen, Angew. Chem. Internat. Edn., 1972, 11, 918.

395. E. Fluck and M. Becke-Goehring, Z. anorg. Chem., 1957, 292, 229.

396. K.-D. Schmidt, R. Mews and O. Glemser, Angew. Chem. Internat.

Edn., 1976, 15, 614.

397. D.A. Johnson, G.D. Blyholder and A.W. Cordes, Inorg. Chem., 1965, 4, 1790.

398. P. Friedman, Inorg. Chem., 1969, 8, 692.

399. D.W.J. Cruickshank in "Inorganic Sulphur Chemistry", ed. G. Nickless, Elsevier, Amsterdam-London-New York, 1968, p.20.

400. J. Bojes and T. Chivers, J.C.S. Chem. Comm., 1977, 453.

401. P.J. Ashley and E.C. Torrible, Canad. J. Chem., 1969, 47, 2587.

402. J.E. Colchester, P. Tavs and H.J. Schulz-Steinen, J. Chem. Soc., 1963, 4918.

403. R.J. Ramsay, H.G. Heal and H. Garcia-Fernandez, J.C.S. Dalton, 1976, 237.

404. C.D. Garner and B. Hughes, Inorg. Chem., 1975, 14, 1722.

405. T. Moritani, K. Kuchitsu and Y. Morino, Inorg. Chem., 1971, 10, 344.

406. I. Lindqvist and C.I. Brandon, Acta Chem. Scand., 1963, 17, 353.

407. C.I. Brandon, Acta Chem. Scand., 1963, 17, 759.

408. D.T. Clark in "Organic Compounds of Sulphur, Selenium and Tellurium", Vol. 1, ed. The Chemical Society, London, 1970.

409. M.P.S. Collins and B.J. Duke, J.C.S. Chem. Comm., 1976, 701.

410. J.A. Jafri, M.D. Newton, T.A. Pakkanen and J.L. Whitten, J. Chem. Phys., 1977, 66, 5167.

411. M.J.S. Dewar, E.A.C. Lucken and M.A. Whitehead, J. Chem. Soc., 1960, 2423.

412. A.W. Cordes, R.F. Kruh and E.K. Gordon, Inorg. Chem., 1965, 4, 681.

413. W.L. Jolly and N. Logan, Inorg. Chem., 1965, 4, 1508.

414. J.-P. Faucher, J. Devanneaux, C. Leibovici and J.-F. Labarre, J. Mol. Structure, 1971, 10, 439.

415. R.L. Flurry, D. Breen and D.L. Havland, Theor. Chim. Acta, 1971, 20, 371.

416. J.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, 1970.