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Addition and some other reactions of sulphanuric chloride

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ADDITION AND SOME OTHER REACTIONS OF

SULPHANURIC CHLORIDE

by

L.F. MOORE. A.R.I.C.

A tnesis suomitted in canaidature ior the Degree of Doctor

of Philosophy in the University of

Durham.

September 1967

(i)

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Dr.A.J. Banister, under whose supervision this research was
carried out, for his constant encouragement and advice;
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during the tenure of which this research was completed; and
to the Science Research Council for financial support.

Memorandum

The work described in this thesis was carried out
in the University of Durham between October 1964 and August
1967.   This work has not been submitted for any other
degree and is the original work of the author except where
stated by reference.

Parts of the work described in this thesis have been
the subject of the following publications:

A.J.Banister, L.F.Moore and J.S.Padley, Chapter 5
Inorganic Sulphur Chemistry, (Ed.G.Nickless),
Elsevier, Amsterdam, (in press).

A.J.Banister, L.F.Moore and J.S.Padley, Spectrochim.
Acta, 1967, (in press).

Summary

This thesis can conveniently be divided into four parts:
(i) Attempted syntheses of sulphanuric compounds, (ii) Addition
reactions of sulphanuric chloride and other sulphur(VI) compounds,
(iii) Other reactions of sulphanuric chloride, (iv) Spectroscopic
studies on sulphur-oxygen and sulphur-nitrogen bonds.

(i) Attempted syntheses of sulphanuric compounds

The investigation of several routes is discussed.   None of
these routes lead to the formation of a sulphanuric derivative
and, in particular, it is shown that the reaction by which sulphanuric
chloride is prepared is not a general reaction for the preparation
of other sulphanuric compounds.

(ii) Addition reactions of sulphanuric chloride and other sulphur(VI)
   compounds.

The reactions between sulphanuric chloride and donor molecules
containing N,P, As and Sb are reported and discussed.   It is shown
that in general compounds of the type, $3L.(NSOCl)_3$, are formed,
where L = tertiary amine or triphenyl phosphine, arsine or stibine.
The possibility of strong C-H hydrogen bonding in the amine adducts
is discussed.   The acceptor properties of other compounds containing
sulphur(VI) are examined; only for sulphuryl chloride are similar
adducts formed, and these are less stable than are the compounds

derived from sulphanuric chloride. The reactions of sulphuryl chloride with triphenylarsine and triphenylstibine provide a new convenient synthesis of the triphenylarsine and triphenylstibine dichlorides. Sulphanuric chloride also forms as an adduct with the π-donor, hexamethylbenzene.

(iii) Other reactions of sulphanuric chloride.

Several attempted substitution reactions are reported. In general ring breakdown occurs though reaction with N,N diethylaminotrimethylsilane results in simple substitution. A brief investigation of the donor properties of sulphanuric chloride is reported.

(iv) Spectroscopic studies on sulphur-oxygen and sulphur-nitrogen bonds.

The literature data is thoroughly reviewed, particularly with respect to inorganic compounds. Previously reported correlations for sulphur-oxygen compounds are confirmed and for sulphur-nitrogen compounds several new correlations are discussed.

(v)

Erratum

EXPERIMENTAL : p.122, 'The reaction between ∝-sulphanuric

chloride and hexamethylbenzene' is

misplaced and should follow at the

end of section d, p.110.

INDEX

SPECTROSCOPIC STUDIES ON SULPHUR-OXYGEN AND SULPHUR-NITROGEN BONDS

(xii)

Appendix 2: Structural Studies on Sulphur Species, by

A.J.Banister, L.F.Moore and J.S.Padley.

(uncorrected, first proofs).

INTRODUCTION

The compounds considered in this introduction fall

conveniently into two classes. First, those compounds, e.g.

sulphamic acid and sulphamide, which can be regarded as aquo-

ammonosulphuric acids, and secondly, tetrasulphur tetranitride

and the cyclic and acyclic sulphur-nitrogen halides and oxohalides.

The cyclic trisulphimide, which is derived from sulphamide, is

included in the first class though structurally it has some

similarity to some of the compounds in the second class.

The aquo-ammonosulphuric acids and derivatives

Franklin[1] has suggested that the chemistry of a large

number of (particularly) acyclic sulphur-nitrogen compounds may

be rationalised if these are regarded as derivatives of a

relatively small number of the so-called aquo-ammonosulphuric

acids. These may be depicted diagrammatically as in Fig.1.

Successive replacement of the hydroxyl groups in sulphuric acid by

the isoelectronic NH_2 group leads to sulphamic acid (1) and

sulphamide (2), both of which are formally mixed aquo-ammonosulphuric

acids. Imidosulphonic (3) and nitrilosulphonic (4) acids may be

regarded as deammonation products of sulphamic acid. Imidodisul-

phamide (5), sulphimide (6) and trisulphimide (7) are similarly

related to sulphamide. The arrangement shown in Fig.1 is

reminiscent of the relationships which exist among the aquo-

ammonocarbonic acids, urea and cyanuric acid.   This similarity

is illustrated in Table 1 in which analogous compounds from the

two systems are compared.

<u>Fig.1.</u>

The aquo-ammonosulphuric acids and derivatives.
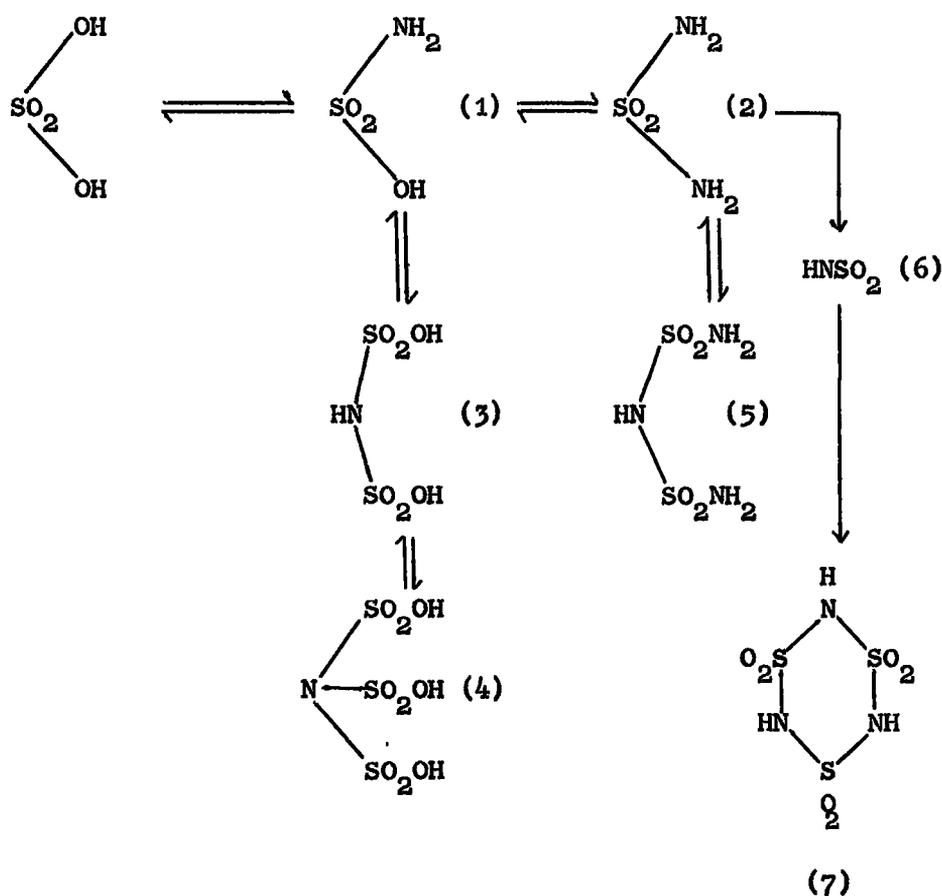
Audrieth <u>et al.</u>[2] have discussed the chemistry of these

compounds in some detail and have shown that this apparent similarity

between the aquo-ammonosulphuric and aquo-ammonocarbonic acid

system is not merely formal, but may be used to explain

much of the chemistry of the former class of compounds.

Table 1

Mixed aquoammono acids related to sulphuric and carbonic acids.

Related to $SO_2(OH)_2$		Related to $CO(OH)_2$	
$H_2N.SO_2.OH$	sulphamic acid	$H_2N.CO.OH$	carbamic acid
$H_2N.SO_2.NH_2$	sulphamide	$H_2N.CO.NH_2$	urea
$HN.(SO_2NH_2)_2$	imidodisulphamide	$HN.(CONH_2)_2$	biuret
$HN.(SO_2OH)_2$	imidosulphonic acid	$HN.(CO.OH)_2$	imidodicarbonic acid
$HN.SO_2$	sulphimide	$HN.CO$	cyanic acid
$(HN.SO_2)_3$	trisulphimide	$(HNCO)_3$	cyanuric acid

Sulphamic acid $H_2N.SO_2.OH$

Sulphamic acid was first isolated by Berglund[3] in 1878

and the first convenient synthesis was due to Raschig[4] in 1887.

It is a crystalline, non-hygroscopic solid, m.pt. $205°$(dec.)

Its solubility in oxygen containing compounds is slight[5], but

in nitrogenous solvents[5,6] it is freely soluble.

Becke-Goehring[7] considers the acid to have the structure (8),

the zwitterion form being unambiguously confirmed by both

X-ray[8] and neutron diffraction[9] studies. The experimentally

determined bond lengths are d_{SN} = 1.74Å and d_{SO} = 1.44Å. The

sulphamate ion[10] in which the sulphur-nitrogen distance is 1.60Å is
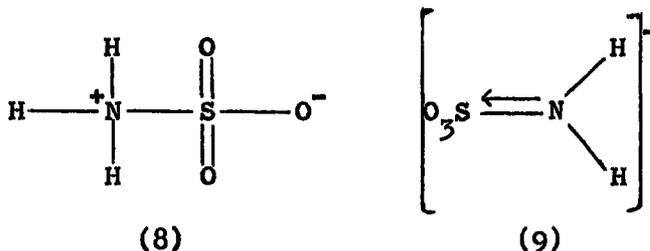
best represented by structure (9).

Four general methods[2, 11] may be used to prepare sulphamic

acid, and all are based upon reactions which emphasise the

nature of the acid as an aquo-ammonosulphuric acid.

(i) The ammonolysis of sulphuric acid and related compounds

(ii) The nitridation of sulphur dioxide, sulphurous acid,
      sulphites and hydrosulphites.

(iii) The hydrolysis of aquo-ammonosulphuric acids

(iv) The hydrolysis of N-acyl sulphamic acids.

Whilst the derivatives of sulphamic acid are numerous,

only the action of chlorinating agents is particularly relevant

to this thesis. Ephraim and Gurewitsch[12] studied the reaction

with thionyl chloride but were unable to obtain the desired

sulphamoyl chloride, $H_2N.SO_2.Cl$. These authors also reported[12]

the formation of the addition compound, $PCl_3.ClSO_2NH_2$ from the

reaction between sulphamic acid and phosphorus(V) chloride.

However, Kirsanov[13] has shown that this reaction gives

trichlorphosphazosulphuryl chloride, $Cl_3P=N.SO_2.Cl$. This

compound is very sensitive to moisture, hydrolysis giving a

quantitative yield of sulphamic and phosphoric acids. The

high stability of the sulphur-nitrogen bond, which is clearly

greater than that of the phosphorus-nitrogen bond, is shown

by this result. Thionyl chloride reacts in an analogous manner

with the mercury salt[14] though not with the free acid; the

products $OSN-SO_3M$ (M=Na,K) are stable polymeric compounds.

Sulphamoyl chloride, which cannot be prepared directly

from sulphamic acid, has recently been obtained by saponification[15,16]

of chlorsulphonyl isocyanate, $OCN.SO_2.Cl$, which is formed by

reaction between cyanogen chloride and sulphur trioxide.[17,18]

Sulphamoyl fluoride is obtained from the chloride by reaction

with potassium fluoride in acetonitrile[19].

Sulphamide, $SO_2.(NH_2)_2$

Sulphamide, the diamide of sulphuric acid, was first prepared[20]

as long ago as 1838. It is, however, a difficult compound to

prepare in any quantity. Virtually all of the methods which have

been investigated depend upon the ammonolysis of either sulphuryl

chloride or sulphuryl fluoride or chlorsulphonyl imides.

Theoretically the equation,

$$SO_2Cl_2 + 4NH_3 \longrightarrow SO_2(NH_2)_2 + 2NH_4Cl$$
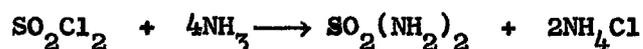
represents a possible reaction between sulphuryl chloride and
ammonia. However, only small amounts of sulphamide are formed
as a primary product.

Early investigators[20-22] reacted gaseous ammonia with
an excess of sulphuryl chloride in an inert solvent. None of
these workers isolated the pure compound. Ruff[23] reversed this
procedure and, keeping ammonia in excess, isolated pure sulphamide
(m.pt. 92°). This method of preparation is normally used in
preference to any other, [12,24-26] Ephraim and Michel[27] and Broja[28]
have studied the product formed when ammonia is in excess. It
seems that salts of sulphimide, imidodisulphamide or long chain
sulphuryl imido imides, $H_2N.SO_2(-NH.SO_2-)_nNH.SO_2.NH_2$, are formed
in addition to sulphamide. Chain compounds containing four
SO_2 groups are the most common, and the low yield of sulphamide is
largely due to the fact that hydrolysis of these compounds gives
only one mole of sulphamide to three of sulphamic acid. A
similar situation obtains in the reaction between sulphur trioxide
and ammonia[29,30] when only in the presence of an excess of ammonia
is an appreciable yield ($\sim 10\%$) of sulphamide obtained. Modern
theories[29, 31] on the formation of sulphamide suggest that in
each case a condensation reaction leads to the formation of
sulphamide. Thus in the case of the preparation from sulphuryl

chloride,

$$SO_2Cl_2 \rightleftharpoons SO_2Cl^+ \ Cl^-$$

$$SO_2Cl^+ + NH_3 \longrightarrow SO_2NH_2^+ + HCl$$

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$SO_2NH_2^+ + NH_2^- \longrightarrow H_2N.SO_2.NH_2$$
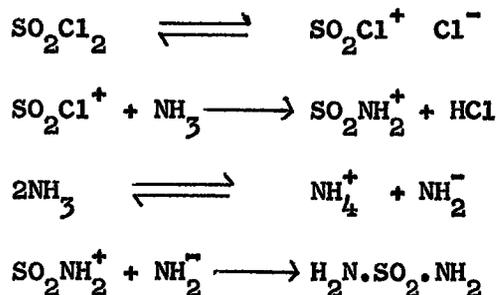
Both SO_3 and SO_2Cl^+, which is isoelectronic with SO_3, are not only capable of undergoing condensation reactions but, as Lewis acids, also have a strong tendency to undergo addition reactions. Hence, it is not surprising that products other than sulphamide result from these reactions.

Sulphuryl fluoride reacts smoothly with even aqueous ammonia to give sulphamide. Wood and Battye[26] have stated that this route cannot be recommended because of the difficulty of handling gaseous sulphuryl fluoride and of preparing it in the pure state.

Both inorganic and organic derivatives of sulphamide are numerous, but in the main are not relevant to this thesis. The number of organic derivatives is particularly large since all four hydrogen atoms can be replaced by alkyl, aryl and acyl groups, either singly or together. The tendency of sulphamide to stabilise itself by forming a six-membered ring, as in the case of trisulphimide, is also apparent in the formation of some cyclic organic derivatives.[32, 33]

Sulphimide, SO_2NH, and trisulphimide, $(SO_2NH)_3$

Various sulphur imides based on sulphur trioxide are possible, assuming that one or more oxygen atoms can be replaced by the isoelectronic NH group. Traube[21] examined the effect of heat on sulphamide and, though unable to obtain a free imide, prepared what he believed to be salts of sulphimide, SO_2NH. Hantæsch and Holl[34] concluded that these compounds were derived from the cyclic trisulphimide, $(SO_2NH)_3$. The free imide reported by these authors has been shown[35] to be imidodisulphamide. More recently several workers[36-38] have re-examined the action of heat on sulphamide. Ito[38] has studied the reaction in some detail. It appears that sulphamide is stable up to $120°C$, but at temperatures above this two reactions may occur,

$$2 \, SO_2(NH_2)_2 \longrightarrow NH_4N.(SO_2NH_2)_2 \qquad \cdots \; (1)$$

$$3 \, NH_4N(SO_2NH_2)_2 \longrightarrow NH_2(NH_4.N.SO_2)_2SO_2NH_2 + (NH_4.NSO_2)_3 \quad \cdots (2)$$
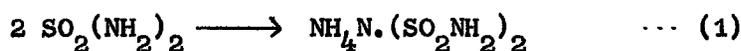
The main product at temperatures of $< 170°C$ is $NH_4N.(SO_2NH_2)_2$. Yields from reaction (2) increase at higher temperatures and prolonged heating at $200°C$ causes complete conversion to the ammonium salt. Metal salts of trisulphimide are readily prepared[36] from the ammonium compound. The silver salt with methyl iodide yields the trimethyl compound, $(SO_2N.CH_3)_3$, which molecular weight determinations show to be a trimer.

From an examination[39] of the silver salt it appears that the
anion is a planar six-membered ring of alternating sulphur
and nitrogen atoms.

Attempts to prepare the free trisulphimide have failed.
Heinze and Meuwsen[36] decomposed the silver salt with an equivalent
quantity of hydrochloric acid and showed that a tribasic acid
resulted.   This acid readily lost two protons, though the third
proton could be removed only with difficulty, hence the ion (10)
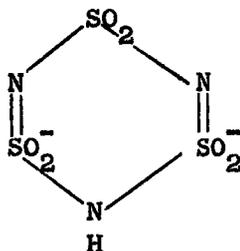
(10)

has a high stability.   The dipyridinium salt of trisulphimide,
which is derived from this ion, can also be obtained[40] by
reaction of sulphamoyl chloride with pyridine.

Appel and Becke-Goehring[41] have attempted a direct synthesis
of sulphimide by reacting ammonia with excess sulphur trioxide
in nitromethane.   The main product was $(NH_4)_2S_3O_{10}$; the small
amount of water soluble substance, $(HNSO_2)_n \cdot H_2SO_4$, also present
was shown to be a polysulphimide sulphonic acid[42].

Tetrasulphur tetranitride and the cyclic and acyclic sulphur-nitrogen halides and oxo-halides

These compounds are of considerable chemical interest. Not only do they exhibit some remarkable chemical properties but, from the theoretical standpoint, they raise some interesting questions as to chemical bonding. They also represent the first examples known so far in pure inorganic chemistry where single, double and triple bonds as well as localised and delocalised double bonds occur. Rings containing delocalised double bonds may be regarded as inorganic aromatic compounds, analogous to the better known phosphonitrilic compounds. Several reviews concerning some or all of these compounds have been published.[7, 43-45] The most important of these compounds and one which may be considered the parent of many of the others is tetrasulphur tetranitride.

Tetrasulphur tetranitride, S_4N_4

Tetrasulphur tetranitride was first prepared[46,47] in 1835 as one of the products of the reaction between sulphur monochloride and ammonia. However, it was not until 1850 that the composition of the compound was determined[48], and not until 1896 that molecular weight determinations[49, 50] gave the formula S_4N_4. Tetrasulphur tetranitride is a solid at room temperature. It forms orange-yellow crystals[51] of the class D_{2d} and space group C_{2h}^5. It is

diamagnetic and strongly exothermic.   The pure compound has

m.pt. 192°C, but impure specimens have been reported to explode

when heated at $>100^{\circ}$C.

Whilst tetrasulphur tetranitride can be prepared in low

yield by several methods[52-57], the only convenient preparation

is from the complex reaction between sulphur chlorides and ammonia.

Whilst sulphur monochloride alone may be used as the starting

material[53, 58, 59] better yields are obtained from the dichloride.

[48, 50, 60].   The accepted method of preparation[43, 61, 62] involves

the preparation of the dichloride in situ from the reaction

between the monochloride and chlorine,

$$S_2Cl_2 \ + \ Cl_2 \longrightarrow 2SCl_2$$
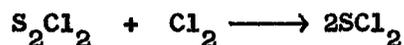
The subsequent reaction with ammonia may be represented as,

$$6SCl_2 \ + \ 16NH_3 \longrightarrow S_4N_4 \ + \ 2S \ + \ 12NH_4Cl$$

The actual course of the reaction is not yet understood, besides

tetrasulphur tetranitride, sulphimide, heptasulphur imide,

sulphur and ammonium chloride are formed.

The chemical and physical properties of tetrasulphur

tetranitride show it to contain delocalised p_π (nitrogen)-d_π(sulphur)

bonds, i.e. it is an inorganic, aromatic compound.   Chemical

investigations[53, 63-65] show all of the sulphur to be present in

the sulphur (III) state, e.g. in weakly alkaline solution[63]

hydrolysis occurs according to the equation,

$$2S_4N_4 + 6OH^- + 9H_2O \longrightarrow 2S_3O_6^{2-} + S_2O_3^{2-} + 8NH_3$$
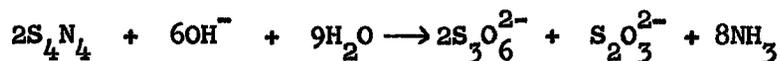
and in strongly alkaline solution,[65]

$$S_4N_4 + 6OH^- + 3H_2O \longrightarrow 2SO_3^{2-} + S_2O_3^{2-} + 4NH_3$$
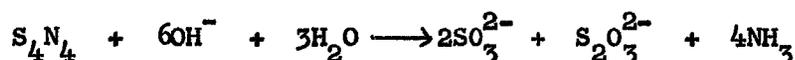
These results eliminate the possibility that tetrasulphur tetranitride is a nitrile of dithionous acid.[63] The equivalence of sulphur atoms in tetrasulphur tetranitride has also been shown by labelling techniques[66] and by a study of the K_α X-ray emission spectrum.[67] Reduction[65, 68, 69] leads to tetrasulphur tetraimide, $S_4(NH)_4$, which has been shown by chemical[70] and physical[71] methods to have structure (11).

H——N——S——N——H   N══S══N
    | | | |
    S   S   S   S
    | | | |
H·——N——S——N——H   N══S══N
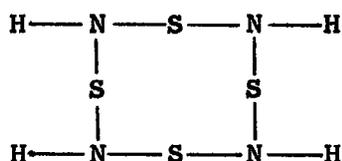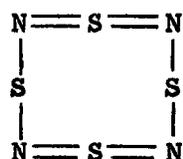
(11)   (12)

Since the tetraimide is readily reoxidised[69] to the tetranitride it is reasonable to postulate some such structure as (12) for the tetranitride. That is, a structure containing an eight-membered ring of alternating sulphur and nitrogen atoms. The equivalence of the sulphur atoms is explained[43, 44] by resonance

between such limiting forms as (13a-13d).
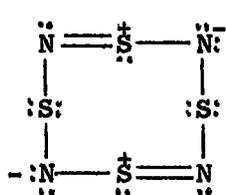
(13a)
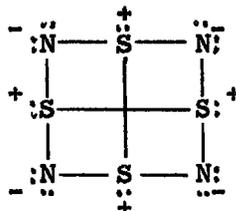
(13b)
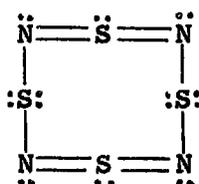
(13c)
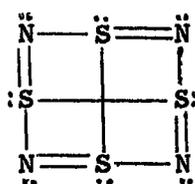
(13d)

Structural determinations[51, 72, 73] support these suggestions.

The molecule has the structure shown in Fig.2.   The sulphur-
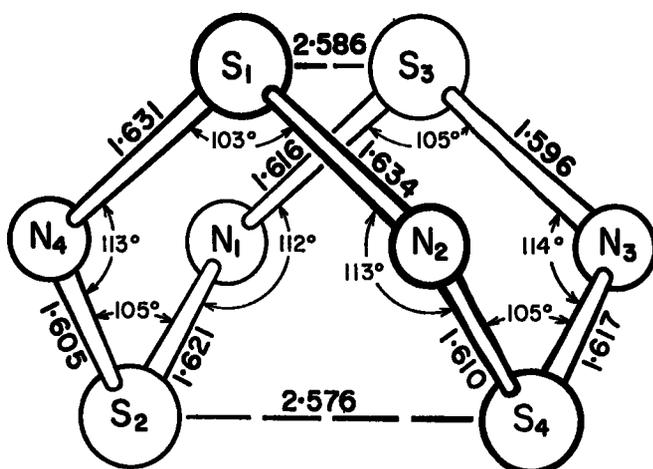
Fig.2.
The structure of tetrasulphur tetranitride[73]

nitrogen bond lengths are all equal, and the average value[73]

(1.616 ± 0.010Å) implies a considerable amount of double bond

character[44,73]. On the other hand,[73] the angles at sulphur

(N$\widehat{S}$N = 105°) and nitrogen (S$\widehat{N}$S = 113°) do not imply much, if any,

double bond character. This apparent paradox is not resolved

by a consideration of the most important resonance forms (13a-13d).

Donohue and Sharma[73] suggest that the geometrical restraints of

the molecular symmetry may result in some strain, which could

also account for the instability of the molecule. The distance

(2.58Å) between two sulphur atoms not linked by nitrogen is

shorter than the sum of the van der Waal's radii (3.3Å) and

rather longer than a sulphur-sulphur single bond (2.05Å).

Hence, there must be some interaction between the sulphur atoms,

and Lindquist[74] has postulated a p-bond. Donohue and Sharma[73]

consider that this suggestion leaves unexplained the short

sulphur-nitrogen bond length.

Several theoretical treatments of the bonding in tetrasulphur

tetranitride are reported. Craig et.al.[75] consider delocalised

π-bonds, resulting from p_π (nitrogen)-d$_\pi$ (sulphur) overlap, to be

of some importance. This suggestion is supported by measurements

of the electron spin resonance of sulphur nitride ions.[76] On

the other hand, Dewar et.al.[77] conceive the π-bonds as three-centre

bonds, each involving a central nitrogen atom and two adjacent

containing the metal in a higher oxidation state (Tl(III),

Ag(II), Cu(II)) may be obtained.   Metal thionitrosylates are

also readily obtained from tetrasulphur tetraimide.[86,87]

In these reactions, in contrast to those with the tetranitride,

the metal does not change its oxidation state.   Very stable

compounds are obtained by reaction of tetrasulphur tetranitride

with some transition metal derivatives;[88,89] compounds isolated

to date have M = Ni, Pt, Pd, Co and Fe.   These compounds were

initially formulated as $M(NS)_4$, but have since been shown[90,91]

to contain hydrogen, and should be written as $M(S_2N_2H)_2$.   The

magnetic properties are reported[92-94] and structural studies[95]

show that these compounds contain the S_2N_2H ligand.   Various

other metal derivatives are known, and the field has been recently

reviewed[96].   Tetrasulphur tetranitride also forms adducts with

metal salts in inert solvents.[96-101]   A series of novel metal

derivatives has recently been prepared by dissolution of these

adducts in thionyl chloride[102].

The cyclic sulphur-nitrogen halides and oxyhalides

Tetrathiazyl tetrafluoride. $S_4N_4F_4$

The ring system of tetrasulphur tetranitride remains intact

on cautious fluorination with silver fluoride[103], which gives

tetrathiazyl tetrafluoride.   Alkali hydrolysis of $S_4N_4F_4$ gives

ammonium fluoride and sulphurous acid, which suggests that the

sulphur has an average oxidation number of 4, and that the

fluorines are attached to sulphur.   The nuclear magnetic

resonance spectrum[104] shows that the molecule is symmetrical,

that all the fluorine atoms are structurally equivalent and

that the fluorine atoms are attached to sulphur.   Structural

investigations[103, 105] confirm these suggestions.   The

molecule consists of a puckered eight-membered ring (Fig.3)

the form of which is quite different from that of tetrasulphur
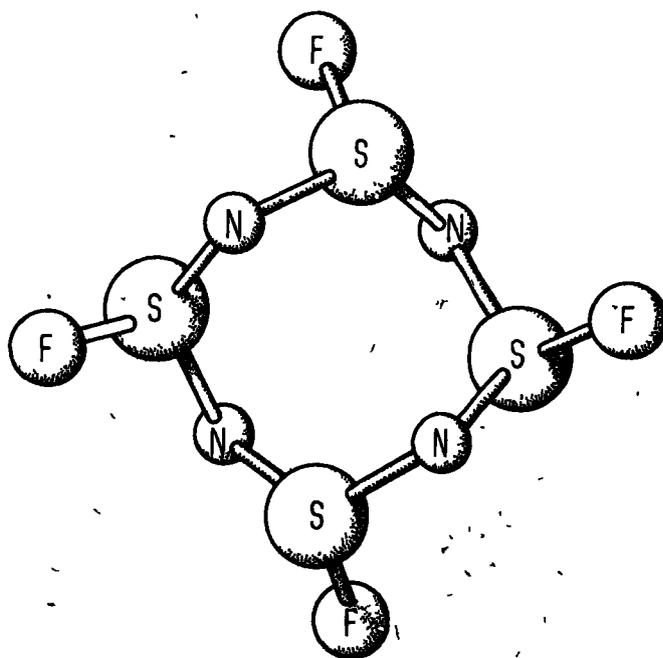
Fig.3.
The structure of $N_4S_4F_4$

18

tetranitride. Two sulphur-nitrogen bond lengths, 1.66 and
1.54Å are observed. These bond distances correspond[44] to
bond orders of 1.4 and 2.0 respectively, so that, in contrast
to S_4N_4, essentially localised bonds are present in the molecule.

Tetrathiazyl tetrafluoride functions as a Lewis base;
thus the unstable adduct, $N_4S_4F_4BF_3$ is reported[106]. Thermal
decomposition[107] of the tetrafluoride gives the unstable thiazyl
fluoride, NSF.

Trithiazyl trifluoride $N_3S_3F_3$

Trithiazyl trichloride, $N_3S_3Cl_3$, reacts[108] with silver
difluoride to give trithiazyl trifluoride. The compound
decomposes in moist air, and is quantitatively hydrolysed[108, 109]
by dilute alkali according to the equation,

$$N_3S_3F_3 + 9H_2O \longrightarrow 3NH_4F + 3H_2SO_3$$
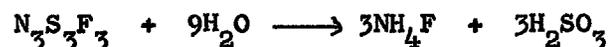
in which respect it behaves analogously to $N_3S_3Cl_3$. The
mechanism of the hydrolysis of these two compounds has been
studied in detail,[44, 107] and appears to proceed via nucleophilic
attack of OH$^-$ ion on the sulphur atom, with consequent rupture
of the ring. The validity of the proposed mechanism has been
tested[107] using nucleophiles other than OH$^-$ and the expected
products[109, 110] were obtained. By analogy with the trichloride
(see text) the trifluoride is thought to contain a cyclic six-

membered ring. The nuclear magnetic resonance spectrum[104]

shows all the fluorine atoms to be equivalent, and its

similarity to that of $N_4S_4F_4$ suggests that localised double

and single bonds are present in the molecule.

Trithiazyl trichloride, $N_3S_3Cl_3$

Whilst on careful fluorination of tetrasulphur tetranitride

the eight membered ring remains intact, chlorination[108, 111]

leads to ring contraction with the formation of $N_3S_3Cl_3$.

The structure of this compound has been accurately determined[112].

The molecule has only one direct sulphur-nitrogen distance,

1.605 $\pm$ 0.005Å, which indicates[44, 107b] delocalisation of the

π-bonds and, therefore, an inorganic aromatic ring. The

six-membered ring is in the chair form; the nitrogen atoms

deviate by an average of 0.18Å from the plane of the sulphur

atoms, and the chlorine atoms, all pointing in one direction,

are located in axial positions (Fig.4)

The hydrolysis of the trichloride has already been discussed

(above); further evidence that the sulphur is present in the

sulphur(IV) state is provided by the reaction with hydrochloric

acid[113] which liberates all the sulphur as sulphur dioxide.
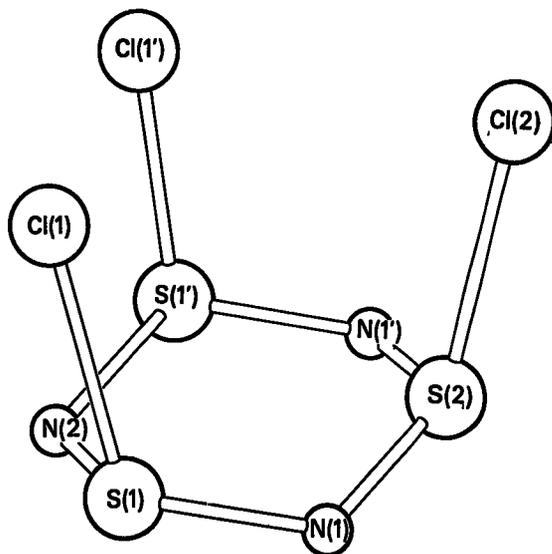
Fig.4.
The structure of (NSCl)$_3$

Trithiazyl trichloride undergoes reactions in which the six-membered ring remains intact as well as reactions in which it is destroyed. Reaction with sulphur trioxide[114] gives the adduct (14) which on heating gives sulphanuric chloride (15).

(14)

(15)
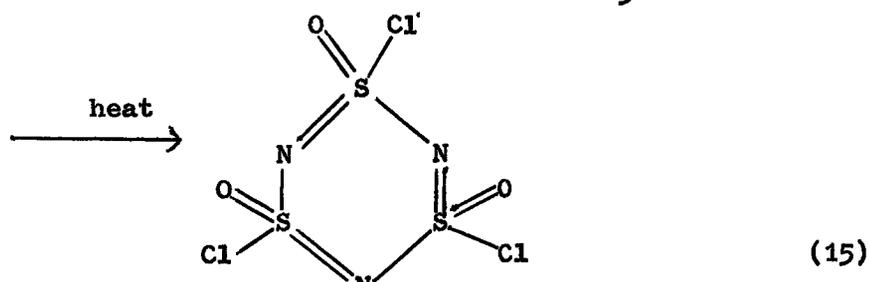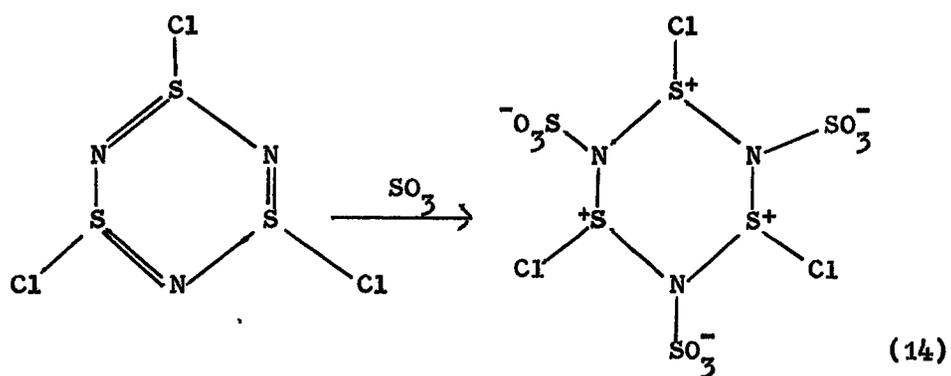
The ring system is also maintained on reaction with ethyl

hypochlorite[113] when the compound.(16) is obtained
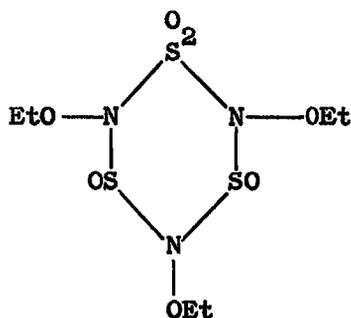
(16)

Other oxidants cause ring breakdown.   Nitrogen dioxide[113]

gives a compound, $(NO)_2S_2O_7$, as it does with tetrasulphur

tetranitride[115], but nitric oxide gives S_3N_2Cl.

Ammonolysis[43] also destroys the ring system.   A red

substance is formed which with mercuric iodide gives $Hg(N_2S)$,

which may also be prepared[83] from $S_2N_2 \cdot NH_3$.   Thus, trithiazyl

trichloride can function as a starting material for the preparation

of derivatives of the imide of orthosulphurous acid, $S_{()}(NH)_2$.

Whilst this imide has not yet been prepared in a pure state its

potassium salt[83], $K_2(N_2S)$, and a butyl derivative[116],

$S(N_2C_4H_9)_2$, are known.

Reduction of $N_3S_3Cl_3$ with tetrasulphur tetraimide[114], or

heptasulphur imide in the presence of pyridine[44], gives S_4N_4.

In the absence of pyridine[117] a brown-red adduct, $S_4N_4 \cdot 4HCl$

is formed which reacts with traces of water to give S_4N_3Cl.

Sulphanuric chloride $N_3S_3O_3Cl_3$

Sulphanuric chloride was first prepared by Kirsanov[13, 118]

by reaction of sulphamic acid with phosphorus pentachloride

and thermal decomposition of the product.

$$HO.SO_2.NH_2 \ + \ 2PCl_5 \longrightarrow Cl.SO_2.N{:}PCl_3 \ + \ POCl_3 \ + \ 3HCl$$

$$3Cl.SO_2.N{:}PCl_3 \longrightarrow (NSOCL)_3 \ + \ 3POCl_3$$
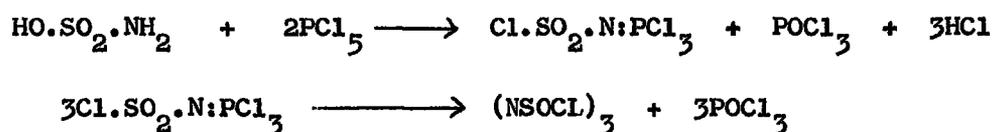
The decomposition reaction is considerably more complex than

this simple equation suggests. The isomeric α- and β-sulphanuric

chlorides are fairly easily obtained from the crude pyrolysis

product, the α-isomer being formed in the greater yield. However,

Kirsanov[118] also reported the presence in the crude product of

at least three other compounds, none of which have been characterised.

Whilst the Kirsanov method is the most convenient route to

sulphanuric chloride it may also be prepared in other ways. The

decomposition of a mixture of thionyl and sulphuryl chlorides

with ammonia[119] gives sulphanuric chloride in low yield, as does

the oxidation[114] of trithiazyl trichloride with sulphur trioxide.

Vandi, Moeller and Brown[120] have reported a modification of the

Kirsanov procedure which differs from the original method in the

mode of treatment of the crude pyrolysis product. Grampel and Vos[121] were unable to obtain sulphanuric chloride in the manner reported by Kirsanov[118]; they reported that pyrolysis of the intermediate, $ClSO_2 \cdot N{:}PCl_3$, in the presence of ultra-violet radiation gave a compound (17)
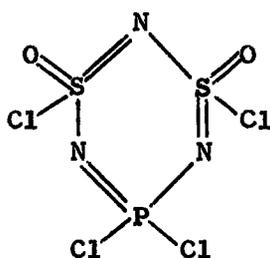
(17)

The significance of this observation is not clear. The author has prepared sulphanuric chloride by the Kirsanov method on several occasions, as have Banister[122] and Vandi et.al.[120] It is possible that the compound reported by Grampel and Vos[121] resulted from the use of ultra-violet radiation.

Sulphanuric acid, $(NSO.OH)_3$ should be the first product of the hydrolysis of sulphanuric chloride. Like trisulphimide, with which it is isomeric, the acid is not known as such and is clearly very unstable. Even on careful acid hydrolysis,[123] imidodisulphamide and sulphuric acid are formed immediately. On the other hand, trisulphimide in an acid medium gives sulphamide,

and sulphamic and sulphuric acids. The difference in the

hydrolysis products from two such similar compounds is striking.

Whilst sulphanuric chloride is hydrolysed by moist air the

corresponding fluoride is particularly stable. Two isomeric

fluorides have been reported by Seel and Simon[124] who caused

∝-sulphanuric chloride to react with potassium fluoride in

carbon tetrachloride at 145°C. Moeller and Ouchi[125] have

reported an alternative synthesis using potassium fluoride in

acetonitrile.

Sulphanuric chloride undergoes solvolytic substitution

reactions only under carefully controlled conditions, in

which respect it seems to resemble the somewhat analogous

trithiazyl trichloride[123]. Reaction with ammonia results in

solvolysis followed by polymerisation[126] to give melam and melem

analogues, and with morpholine[120], at room temperature, N-N'

dimorpholido sulphamide is formed. Under controlled conditions

at low temperature simple metathesis reactions may be affected;

e.g. Failli et.al.[127] have prepared two isomeric trimorpholido

derivatives. It appears that by varying the solvent used one

or other isomer may be made to predominate.

Sulphanuric fluoride[125] is reported to be more stable with

respect to ring cleavage than sulphanuric chloride, and it more

readily undergoes substitution reactions. Reaction with phenyl

lithium in diethyl ether in the corresponding mole ratios

yields the mono-and diphenyl derivatives, both of which are

obtained in only one isomeric form.   The triphenyl compound

cannot be prepared in this manner but may be prepared by

reaction of the fluoride in benzene with aluminium chloride.

The secondary amines, morpholine, 2.6 dimethylmorpholine,

piperidine and pyrolidine form disubstituted products,

irrespective of the mole ratios used, each in two isomeric forms.

The structure of α-sulphanuric chloride has been determined by

X-ray crystallography.[127-130]   The molecule exists as

a ring in the chair form; the nitrogen atoms deviate by an

average of ~0.25Å from the plane of the sulphur atoms.   The

chlorine atoms are all located on one side of the molecule in

axial positions; the oxygen atoms are all in equatorial

positions.   Fig.5 shows the structure of α-sulphanuric

chloride; S_3O_9 which is isoelectronic with $(NSOCl)_3$ has

a similar structure.

The S-N bond lengths are all equal[130] at 1.571 ± 0.004Å;

which is most simply explained as a result of delocalised

p_π-d_π bonding[44,130].   Veigers and Vos[131] have shown that

this equality of bond lengths is probably genuine and not
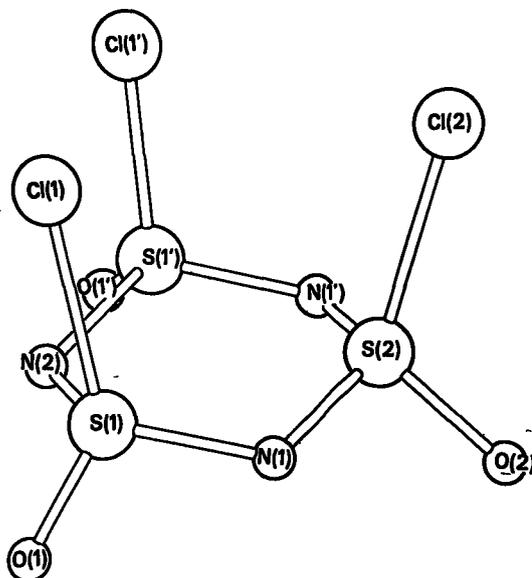
Fig.5.
The structure of α-(NSOCl)$_3$

merely the result of refining in the wrong space group.   The

sulphur atoms have coordination number 4, the bonds pointing to

the corners of a tetrahedron.   The angles N$\hat{S}$N(113°) and

O$\hat{S}$Cl(107°) are more nearly equal than is the case in the

phosphonitrilics[132].   Hazell et.al.[130] consider that the small

difference between the endo-and exocyclic angles in

α-(NSOCl)$_3$ may be due to the double bond character of the

S=O exocyclic bond.   α-Sulphanuric chloride is obtained as

the major product from the Kirsanov preparation and yet of the four

possible isomers it is the one showing maximum steric repulsion

between ring substituents.

This situation may be compared with that in $(NSF)_4$ and

$(NSCl)_3$; in all three compounds the strongly repelling groups

(the lone pair electrons in the sulphur(IV) compounds or the

double bond to oxygen in α-$(NSOCl)_3$) are pointing away from the

mean plane of the ring. A number of factors may be responsible

but two important ones may be (i) the repelling effect of axial

sulphur lone pair electrons or axial S=O bonds exceeds that of an

axial S-Cl bond, (ii) that these structures result in the

closest packing in the solid state or maximum intermolecular

attractions. If this latter reason is important then these

molecules may have different structures in solution than in the

solid phase. A similar situation occurs with the tetrameric

phosphonitrilic chloride and fluoride.[133]

Definite structural data on other sulphanuric

compounds is lacking. The dipole moment studies of Vandi et.al.[120]

suggest that in β-$(NSOCl)_3$ the ring has the chair form present

in the α-isomer. In their calculations these authors made no

allowance for the atom polarisations of the molecules. Rogers

and Gross[134] have determined the dipole moments of both sulphur

and tetrasulphur tetranitride in benzene. They concluded that

for S_4N_4 the moment observed (0.52D) when atom polarisation

is neglected is due to entirely an abnormally large atom

refraction. On the other hand $(NSF)_4$ - which contains localised

bonds - has a zero dipole moment as expected.

The infrared spectra[125, 127] of the isomeric aryl and diarylamino-sulphanuric compounds suggest that the isomerism arises from differences in the orientation of the substituents, as in the chlorides, rather than from differences in the conformation of the ring itself.

Thiotrithiazyl compounds. S_4N_3X

The most stable compounds derived from S_4N_4 are the thiotrithiazyl compounds,[135-137] $(S_4N_3)X$, whre X may be, e.g., halogen HSO_4^-, NO_3^-, SCN^-, BPh_4^-, $SbCl_6^-$ or $SbCl_4^-$. The best known of these compounds is the chloride which is obtained from S_4N_4 by reaction with various non-metal halides,[117,138-143] e.g.,

$$3S_4N_4 + 2S_2Cl_2 \xrightarrow{CCl_4} 4S_4N_3Cl$$
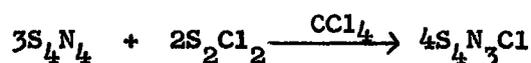
MacDiarmid[117,138] believes that these reactions involve the formation of hydrogen chloride, which then reacts with the S_4N_4. Becke-Goehring[144] has shown that the reaction with sulphur monochloride must proceed via several intermediates since, depending upon the concentration of S_2Cl_2, varying amounts of ^{35}S can be introduced into the S_4N_3Cl. The compound S_3N_2Cl is possibly one such intermediate; it is obtained in the cold from S_4N_4 and S_2Cl_2, and decomposes on heating in carbon tetrachloride.

$$6S_3N_2Cl \longrightarrow 4S_4N_3Cl + S_2Cl_2$$
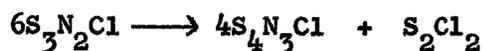
S_4N_3Cl can also be prepared by the reaction[145] between S_2Cl_2

and NH_3 in carbon disulphide, and by treatment[146] of S_2Cl_2

with lithium azide.   All other known sulphur-nitrogen

chlorides can be converted[44] into S_4N_3Cl, e.g. $N_3S_3Cl_3$ and

$S_3N_2Cl_2$ by heating with S_2Cl_2 in CCl_4, or S_3N_3Cl by reaction

with S_2Cl_2 in the presence of chlorine and carbon tetrachloride.

S_4N_3Cl is stable in dry air.   _In vacuo_ at 170° it

decomposes to give S_4N_4. Hydrolysis[141], depending upon the

conditions, gives rise to the black, probably polymeric,

compounds S_4N_3OH and $(S_3N_3OH)_2$ are formed.   Both hydroxides

are unstable and give S_4N_4 on standing.   With sulphur trioxide[147]

the adduct $S_4N_3Cl.2SO_3$ results.   Reaction with metal azides[148]

gives S_4N_4.

The average oxidation number of the sulphur in S_4N_3Cl

is 2.5 as is shown by reaction[149] with piperidine.   The ready

exchange that the chlorine of S_4N_3Cl undergoes with anionic

radicals,[135-137] indicated a salt-like structure, $(S_4N_3)^+X^-$.

Molecular weight determinations[137,150] verified this suggestion

and showed that $(S_4N_3)^+$ cation to be monomeric in solution. The

structure[151] of the cation has been fully worked out from a study of the

nitrate, and is shown in Fig.6.   The molecule is planar in

contrast to the markedly puckered, or non-planar rings of

the parent compound S_4N_4 and the other six-and eight-membered

sulphur-nitrogen rings prepared from S_4N_4, i.e., $S_4N_4H_4$,

$S_4N_4F_4$, $S_3N_3Cl_3$ and $S_3N_3O_3Cl_3$. The average S-N bond distance,

1.54 ± 0.04Å corresponds to a double bond. This high bond order

all around a planar system suggests a well developed π-electron

system. Studies of the electronic spectrum[152] support this and

are best explained on the basis of a ten electron π-system

delocalised over all of the S-N linkages. This hypothesis

requires the participation of sulphur d-orbitals in the π-bonding.
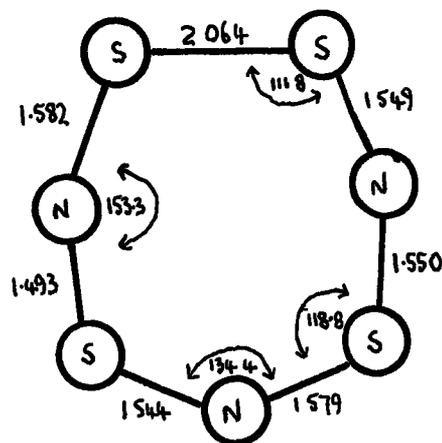
Fig.6.
The structure of the $S_4N_3{}^+$ cation

The acyclic sulphur-nitrogen halides

Thiazyl fluoride NSF.

Thiazyl fluoride, an unstable gas, is prepared by the fluorination of S_4N_4 with mercury[153] silver[153] or cobalt[154] fluorides, or by reaction between ammonia and sulphur tetrafluoride.[155] The structure of NSF has been determined by infrared[104], nuclear magnetic resonance[104] and microwave[156] spectroscopy, and by electron diffraction,[157,158] and is as shown in Fig.7(a).

$1.446\text{\AA}$ $1.646\text{\AA}$

$116°52'$

(a)   (b)
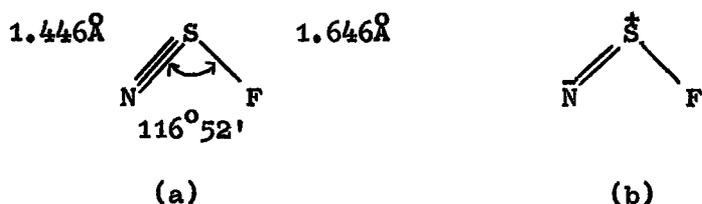
Fig.7.
The structure of thiazyl fluoride

The SN force constant derived from the infrared spectrum corresponds[104,159] to a bond order of 2.3; the SN bond length being $1.446\text{\AA}$. The mesomeric structure (b) contributes[44] to an SN bond order of greater than 2.

Aqueous hydrolysis gives monomeric thionyl imide[160], HNSO, as an intermediate and, finally, SO_3^{2-}, F^- and NH_4^+. Alkaline hydrolysis proceeds similarly though the products are not obtained in quantitative yield.

In glass vessels at room temperature and at pressures of < 760 mm.Hg. NSF decomposes to give $S_3N_2F_2$. At higher temperatures reaction with the glass is rapid and gives S_4N_4, SOF_2, SO_2, SiF_4 and N_2. Chlorination[161] of NSF gives monomeric NSCl. With boron trifluoride the adduct, FSN.BF$_3$ is thought to be formed[162], but is so unstable that it is not well characterised.

Thiazyl chloride. NSCl

The gaseous unstable NSCl may be prepared by the thermal decomposition[163] of $(NSCl)_3$ in vacuo, or by the reaction between ammonium chloride and excess sulphur chloride.[164,165] The infrared spectrum is similar to that of NSF so that both gases must have similar structures[161]. The thionitrosyl halides S=N-F and S=N-Cl which are isomeric with the thiazyl halides are still unknown.

Thiazyl trifluoride NSF$_3$

Thiazyl trifluoride may be prepared by the fluorination of NSF with silver difluoride[44] or by fluorination of S_4N_4 with a mixture of silver difluoride and cobalt trifluoride[154]. This latter reaction is complex; besides NSF$_3$ and NSF, at least ten other volatile compounds are formed. NSF$_3$ is also obtained[44] in low yields when ammonia is introduced into a mixture of sulphur

and AgF_2 in CCl_4. Good yields of NSF_3 are reported[168] from

the reaction between S_2F_{10} and ammonia.

Thiazyl trifluoride is a colourless gas which in contrast

to NSF is extremely stable. Metallic sodium reacts only on

heating to $400^\circ C$; no reaction occurs with gaseous ammonia at

room temperature and NSF_3 is not attacked by dilute acids.

Thiazyl trifluoride reacts[162] with BF_3 to form the compound,

$F_3SN \cdot BF_3$, which in the liquid phase appears to have structure

(18a); in the solid state a fluoroboronium compound (18b) may

be present[169]. The instability of $F_3SN \cdot BF_3$ indicates that the

donor activity of the nitrogen lone pair is weakened by the

inductive effect of the fluorine atoms attached to the sulphur.

$$F-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{S}} \equiv N \longrightarrow \overset{\overset{F}{|}}{\underset{\underset{F}{|}}{B}}-F \qquad \left[NSF_2\right]^+\left[BF_4\right]^-$$
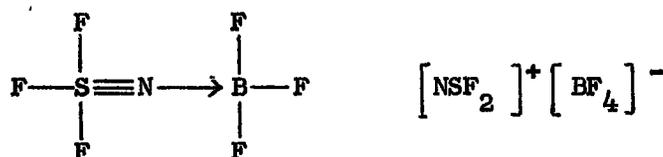
(18a) (18b)

From a study of the infrared and nuclear magnetic resonance

spectra of NSF_3, Richert and Glemser[104] have shown the molecule

to have a tetrahedral structure of C_{3v} symmetry, with all of the

fluorine atoms attached to sulphur in structurally equivalent

positions. The infrared spectrum has great similarity[170] to

that of the tetrahedral compound OPF_3. The spectroscopic study[104]

suggests a sulphur-nitrogen bond order of 2.7. Microwave

studies[156] confirm these results, the very short sulphur-nitrogen bond distance of 1.416Å corresponding[44] to a bond order of ~3.0. The structure of NSF_3 is shown in Fig.8.

1.416Å
F
94°2'
N≡≡≡S———F
1.552Å F
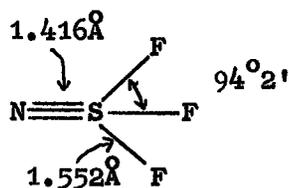
Fig.8.
The structure of NSF_3.

Thiazyl trifluoride is the first compound to contain a sulphur-nitrogen triple bond and may be regarded as derived from the stable SF_6 by substitution of a nitrogen atom for three fluorine atoms. Whilst in SF_6 the sulphur atom exhibits sp^3d^2 (octahedral) hybridisation, in NSF_3, sp^3 (tetrahedral) hybridisation occurs. In addition two p_π-d_π bonds are formed[44] between the nitrogen and the sulphur atoms.

Thiazyl bromide. NSBr

Bromine reacts[166] with S_4N_4 in carbon disulphide to give the bronze coloured compound, $(NSBr)_n$. The molecular weight of this compound is unknown. With acetyl bromide[167] S_4N_4 reacts to give $S_2N_3HBr_4$.

Thiodithiazyl difluoride, $S_3N_2F_2$

Thiodithiazyl difluoride is formed[171] in low yield when NSF

is decomposed in a glass vessel. The crude product appears

to contain two polymorphic forms of the compound $S_3N_2F_2$ for

which if, covalent, two structures, (19a) and (19b) may be

postulated.

$$F\text{---}S\text{---}N\!\!=\!\!\!=\!\!S\!=\!N\text{---}S\text{---}F$$

$$\updownarrow$$

$$F\text{---}S\text{---}\bar{N}\text{---}\overset{+}{S}\!=\!N\text{---}S\text{---}F$$

(19a)

(19b)
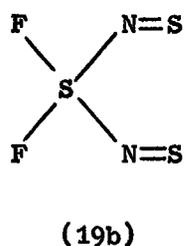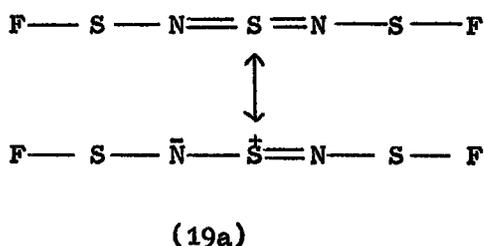
Glemser[44] prefers (19a) on the grounds that the intense colour

of the fluoride requires a structure in which resonance is

possible.

Thiodithiazyl dichloride. $S_3N_2Cl_2$

Thiodithiazyl dichloride may be prepared[172] by gently

heating $(NSCl)_3$ in S_2Cl_2. In the presence of excess chlorine

it reverts to $(NSCl)_3$; possibly in accordance with the equation,[172]

$$3S_3N_2Cl_2 \;+\; 3Cl_2 \longrightarrow \left[6NSCl \;+\; 3SCl_2\right] \longrightarrow 2(NSCl)_3$$

Further heating in S_2Cl_2[139] or S_2Cl_2 in CCl_4[44] or in CCl_4[165]

gives S_4N_3Cl, probably[165] via S_3N_2Cl. Jolly et.al.[165] have

reported a more convenient synthesis from ammonium chloride and

S_2Cl_2 and have suggested the mechanism,

$$NH_4Cl \;+\; 2S_2Cl_2 \longrightarrow NSCl \;+\; 3S \;+\; 4HCl$$

$$2NSCl \;+\; S_2Cl_2 \longrightarrow S_3N_2Cl_2 \;+\; SCl_2$$
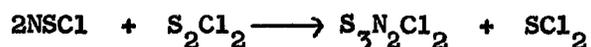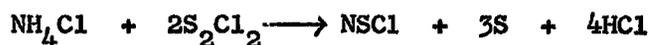
The structure of $S_3N_2Cl_2$ has recently been determined[173]

and is shown in Fig.9. The ring is slightly puckered
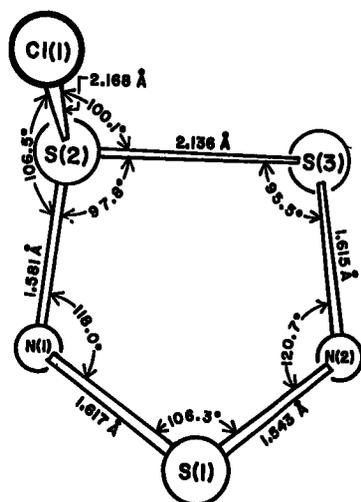
Fig.9.
The structure of $S_3N_2Cl_2$[173]

The properties and reactions of $S_3N_2Cl_2$ have been the

subject of a recent investigation[174].

Thiodithiazyl chloride. S_3N_2Cl

Green crystalline S_3N_2Cl may be obtained[175] from S_4N_4

and S_2Cl_2 in the cold, or by vacuum sublimation[165] of $S_3N_2Cl_2$.

It is also formed[144] when NOCl reacts with S_4N_4, or by reaction

of $(NSCl)_3$ with NO in nitromethane. Structural data is lacking,

in the absence of a molecular weight determination it is possible

that the compound is polymeric.

The compound S_3N_3Cl has been reported and is possibly[44] an intermediate in the chlorination of S_4N_4. The compounds[48] S_2NCl_2 and $S_4N_3Cl_2$ have not yet been confirmed and are of doubtful existence.

SPECTROSCOPIC STUDIES ON SULPHUR-OXYGEN

AND SULPHUR-NITROGEN BONDS

Infrared spectroscopy affords a powerful tool for the

structural characterisation of chemical compounds. The

author has been one of the first members of a new sulphur-

nitrogen research school. It was considered a useful

preliminary to thoroughly review the evidence in the chemical

literature regarding the absorptions of sulphur species, S-X,

where X may be any element, including sulphur itself. The

initial literature survey was done in collaboration with Mr.

J.S.Padley, but the final evaluation of the data relating to

sulphur-oxygen and sulphur-nitrogen bonds was the responsibility

of the author. In this section the available data are collected

and discussed and, in the case of sulphur-nitrogen bonds,

several new empirical correlations are established.

A. SULPHUR-OXYGEN COMPOUNDS

Introduction

The infrared and Raman spectra of compounds containing

sulphur-oxygen bonds have been extensively studied and several

useful correlations have been found[176-180]. In conjunction

with an investigation of the spectroscopic behaviour of compounds

containing sulphur-nitrogen bonds the evidence relating to

sulphur-oxygen bonds has been re-examined in the light of recent

experimental evidence. The previously reported correlations

are confirmed, particularly with respect to inorganic compounds.

Also, the data relating to oxo-anions of sulphur has been

reviewed since many new studies have been reported since these

groupings were last considered[181, 182].

Sulphuryl $(-SO_2-)$ compounds

For $-SO_2-$ compounds several workers[176-178] have

observed a linear relationship between the symmetric S-O

stretching $(\nu_s SO_2)$ and the asymmetric stretching vibration

$(\nu_{as} SO_2)$. Bellamy and Williams[178] have commented that such

a relationship is to be expected since the $-SO_2-$ stretching

vibrations are essentially free from mass and coupling effects.

The data compiled by Robinson[177] are particularly comprehensive

and show that the symmetric and asymmetric S-O vibrations for

compounds of the types X_2SO_2, $XYSO_2$, (including $X(OH)SO_2$), for

ions such as XSO_3^- and SO_4^{2-} and for more complex molecules

containing $-SO_2-$ as part of a ring or chain, all fit the linear

relationship satisfactorily. (Fig.10.) Strictly speaking the

S-O stretching vibrations of the ionic species should not be

described as symmetric and asymmetric. The data considered by

Robinson contained relatively few inorganic compounds, and in

particular, very little data on the simple oxo-anions of sulphur.

Considerably more data referring to inorganic sulphuryl compounds are now available[183-206] and the $\nu_s SO$ and $\nu_{as} SO$ values for these compounds all fit fairly well the line established by Robinson. Points representing these compounds are shown as + in Fig.10. Data for various oxo-anions are also available and the behaviour of these is of interest. Table 2 lists the observed frequencies and these are shown as △ in Fig.10.

Table 2

Symmetric and asymmetric S-O stretching vibrations for
oxo-anions of sulphur

Species	$\nu_s SO (cm^{-1})$	$\nu_{as} SO (cm^{-1})$	Reference
SO_3^{2-}	970	930	207
FSO_2^{-}	1105	1182	208
SO_4^{2-}	981	1104	209
$S_2O_3^{2-}$	995	1123	210
$S_2O_6^{2-}$	1092 / 1000	1235 / 1206	211
$S_2O_7^{2-}$	1059 / 1108	1267 / 1289	212
$RO.SO_2^{-}$	1056-1075	1157-1177	213

The values for SO_4^{2-} and $S_2O_3^{2-}$ fit reasonably well on the Robinson plot (Fig.10). Values for $S_2O_6^{2-}$ and $S_2O_7^{2-}$ fit less well.

41

FIG 10

CORRELATION OF SYMMETRIC AND ASYMMETRIC S-O STRETCHING
VIBRATIONS
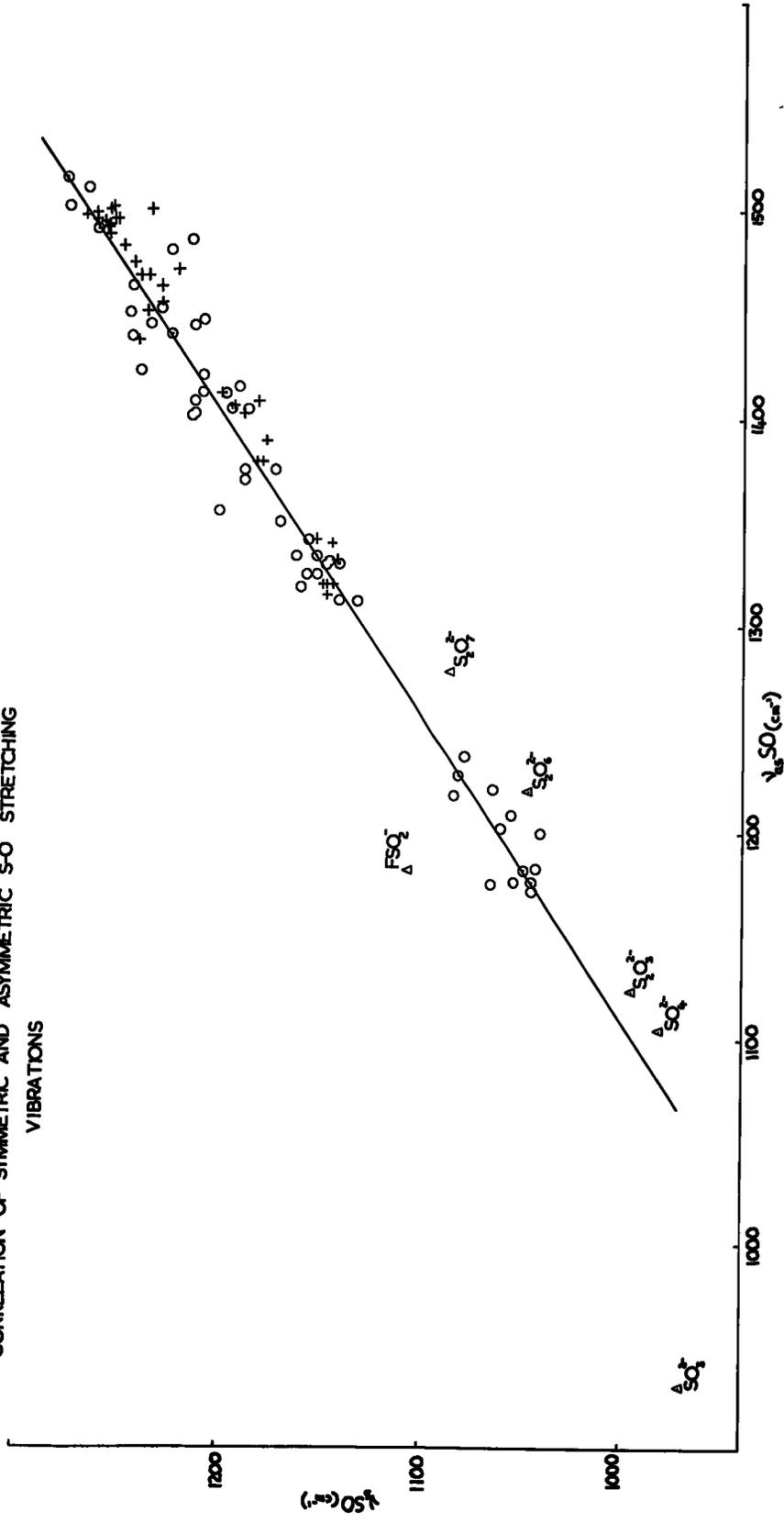
FIG II
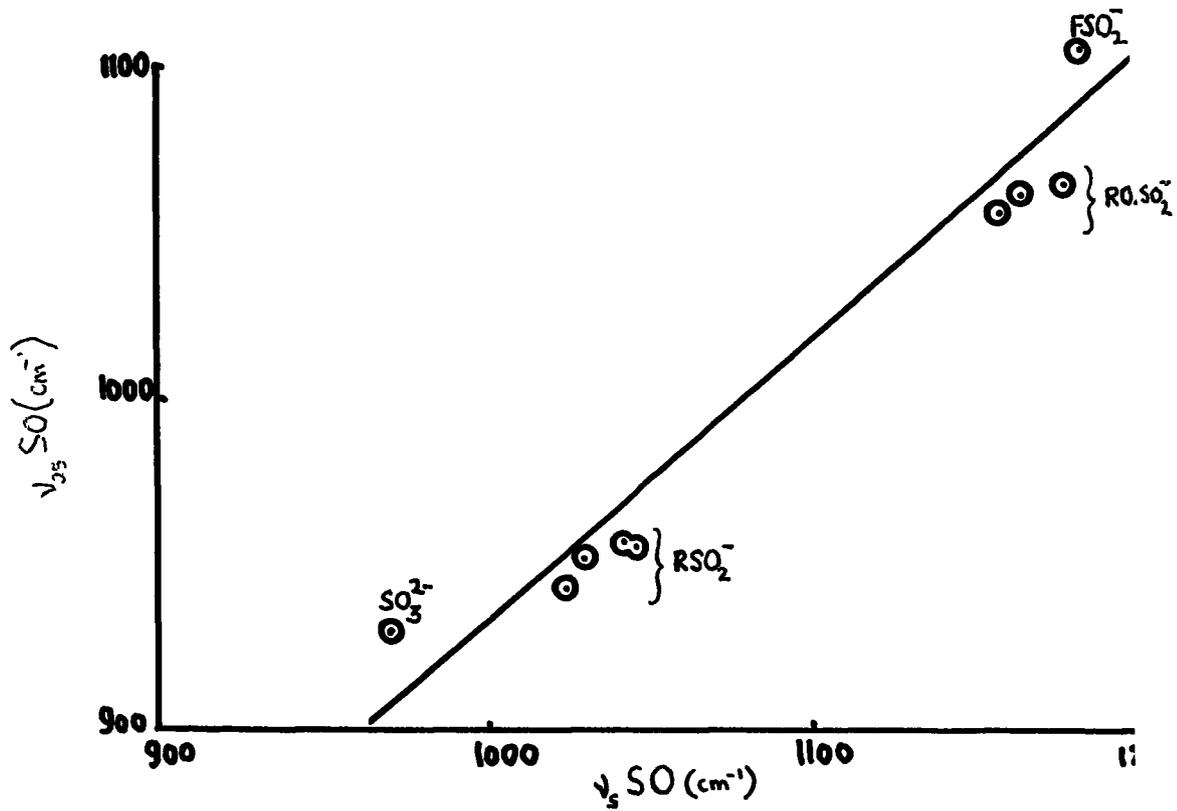
CORRELATION BETWEEN SYMMETRIC AND

ASYMMETRIC S-O FREQUENCIES OF S(IV)

OXO-ANIONS

Possibly the scatter in these values results from the mixed

character of the vibrations or inaccuracy in the reported values

because of the difficulty of resolving bonds in the fairly

complex spectra.   The points representing the sulphur(IV)

species, SO_3^{2-} and FSO_2^- lie well away from the line though the

analogous $RO.SO_2^-$ compounds fit satisfactorily.   The reported

assignments for the XSO_2^- ions are based upon comparison with

sulphur(VI) compounds for which $\nu_{as}SO > \nu_sSO.$ It would seem

more reasonable to assign these sulphur(IV) compounds by analogy

with the sulphite ion for which $\nu_sSO > \nu_{as}SO.$ It is

considered significant that in this case all of the sulphur(IV)

species lie on a new straight line (Fig.11), which suggests that

the line established by Robinson[177] is applicable only to

compounds of sulphur(VI).   Fig.11 contains data for the RSO_2^-

ions[214] for which assignments of the symmetric and asymmetric

stretching modes were made by the author.   The determination

of Raman polarisation data for the XSO_2^- ions would enable an

unambiguous assignment of the symmetric and asymmetric S-O

stretching modes.

Table 3 lists the frequencies observed for various types

of $-SO_2-$ compounds.   In general, as the effective electronegativity

of the attached ligands is increased the S-O stretching vibrations

are shifted to higher frequencies.   This shift indicates

Table 3

Correlation table for S-O symmetric and asymmetric vibrations

Grouping	Type of compound	$S-O^{(cm^{-1})}$ symmetrical	asymmetrical
$C-SO_2-C$	Sulphones(alkyl)	1136-1145	1307-1330
	Sulphones(alkyl-aryl)	1150-1160	1325-1334
	Sulphones(aryl)		
$C-SO_2-N$	Sulphonamides	1152-1169	1336-1358
$C-SO_2-N$	e.g. $F_3CSO_2N_3$	1236	1437
$C-SO_2-O$	Sulphonic acids and esters	1165-1185	1350-1375
$C-SO_2-F$	Sulphonyl fluorides	1203-1210	1401-1412
$C-SO_2-Cl$	Sulphonyl chlorides	1169-1185	1364-1390
$C-SO_2-S$	Thiosulphonates	1144-1154	1331-1342
$N-SO_2-N$	Sulphamide and derivatives.(b)	1140-1168	1320-1398
$O-SO_2-O$	Covalent sulphates	1187-1195	1390-1415
$O-SO_2-O$	e.g. $(SF_5O)_2$ and $SF_5O.SF_4O.SO_2.OSF_2$(b)	1230-1256	1469-1500
$O-SO_2-F$	e.g. $FSO_3F, HSO_3F,$ $S_2O_5F_2, S_2O_8F_2$(c)	1230-1277	1445-1510
$O-SO_2-Cl$	e.g. $HSO_3Cl, S_2O_5Cl_2$ $S_2O_8Cl_2, S_3O_8Cl_2$	1205-1225	1408-1452
$N-SO_2-F$	$\approx NSO_2F$ and $-N(SO_2F)_2$ compounds	1174-1250	1337-1495
	SO_2Cl_2	1269	1502
	SO_2F_2	1182	1414
	Ions, e.g., RSO_3^-, excluding oxo-anions(d)	1026-1080	1175-1221

a: after Robinson[177]

b: groupings not given by Robinson

c: these frequency ranges confirmed by inclusion of data not considered by Robinson

d: see text

increasing strength of the S-O bonds which is most plausibly
explained as resulting, at least in part, from increased double
bond character.

Oxo-anions and complexes

The characteristic ranges over which the S-O stretching
vibrations in oxo-anions occur are given in Fig.13.   For the
less common anions the ranges shown are based upon only a few
reported spectra, usually of alkali metal salts, and are,
thefefore, somewhat tentative.

Sulphites

The free ion has pyramidal C_{3v} symmetry giving rise to four
infrared and Raman active fundamental modes.   The fundamental
frequencies have been calculated[207] as:

ν_1(symmetric stretch), 970 cm.

ν_2(symmetric bend), 630 cm.

ν_3(asymmetric stretch), 930 cm.

ν_4(asymmetric bend), 480 cm.

Both ν_3 and ν_4 are doubly degenerate and any deviation from
C_{3v} symmetry, e.g. coordination through oxygen atoms, can lead to
splitting of modes.   In several reported cases ν_1 and ν_3 are
not resolved,[181, 215-217] or only partially resolved, with the result
that a single broad band is observed with a maximum at $950-970 cm^{-1}$.

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FIG. 13.

S-O STRETCHING FREQUENCIES IN OXO-ANIONS

($\ast$ FEW COMPOUNDS ABSORB AT 1150-1200 cm^{-1})

FREQUENCY (cm^{-1})

| 900 | 1000 | 1100 | 1200 | 1300 |

SO_3^{2-} ν_{ns} ν_s

$SO_4^{2-\ast}$ ν_s ν_{ns}

$S_2O_3^{2-}$ ν_s ν_{ns}

$S_2O_4^{2-}$

$S_2O_5^{2-}$

$S_2O_6^{2-}$ ν_s ν_s ν_{ns}

$S_2O_7^{2-}$ ν_s ν_{ns}

$S_2O_8^{2-}$

$S_nO_6^{2-}$
n=3-6

| 11 | 10 | 9 | 8 |

WAVELENGTH (μ)
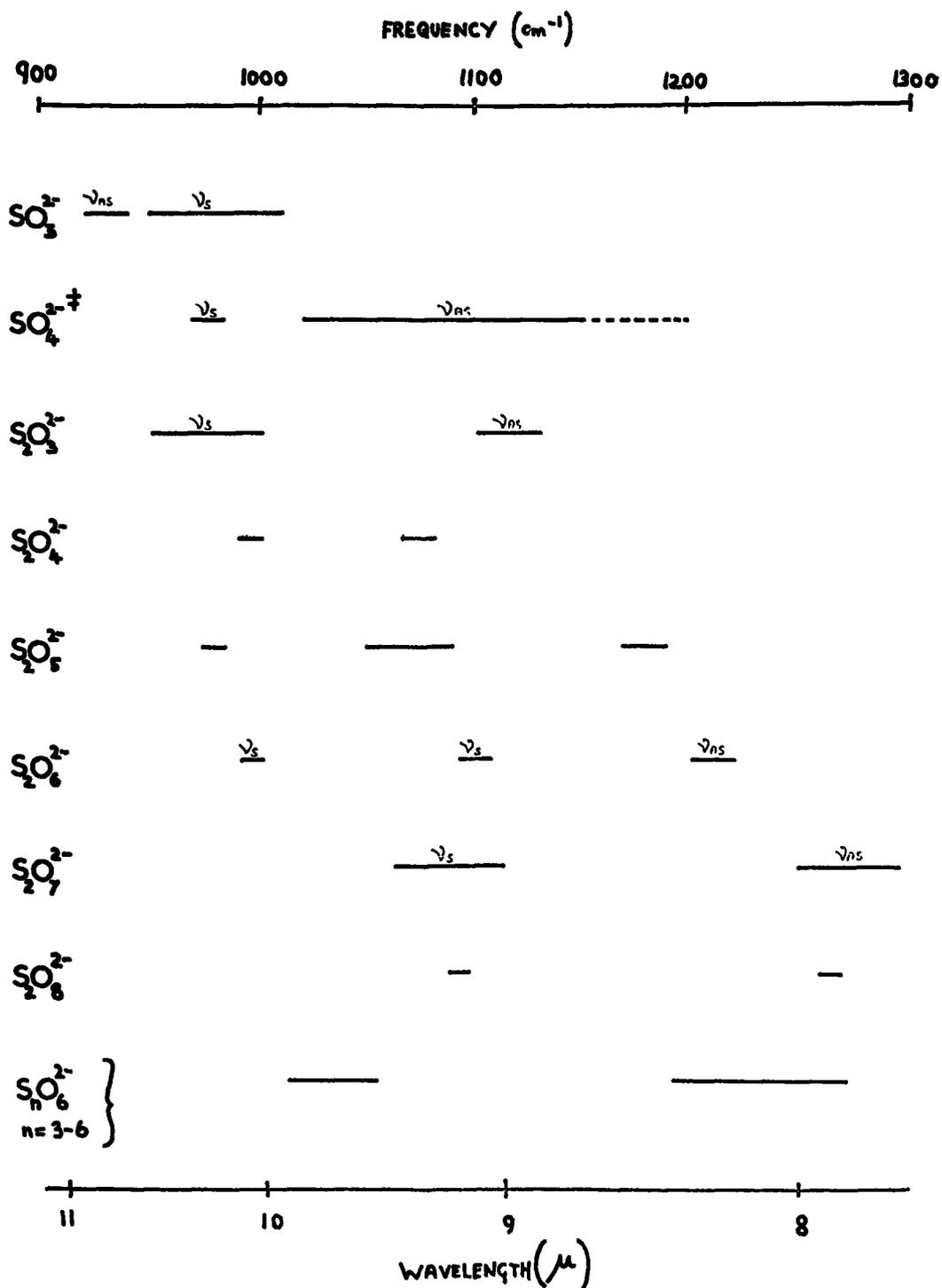
For compounds which have been studied under conditions such that ν_1 and ν_3 are resolved[207,218-220] no splitting of ν_3 is observed, which suggests that in simple compounds the C_{3v} symmetry of the free ion is essentially undisturbed. Since a given compound can be reported with ν_1 and ν_3 resolved by one author and unresolved by another it seems probable that instrumental factors may be the determining factor. The fundamental frequencies observed in the Raman may differ from those in the infrared. Thus, Evans and Bernstein[218] in a study of aqueous solutions of Na_2SO_3 found the fundamentals to occur at $\nu_1 = 967cm^{-1}$, $\nu_2 = 620cm^{-1}$, $\nu_3 = 953cm^{-1}$, and $\nu_4 = 469cm^{-1}$ in the Raman whilst the corresponding infrared frequencies were 1002, 632 and 954 cm^{-1}, ν_4 not being observed. The effect is ascribed to strong intermolecular forces and, as is usual, the infrared bands have the higher frequencies.

Sulphates

The free ion has tetrahedral, T_d, symmetry and hence four fundamental modes for which the calculated frequencies, assuming central forces,[209] are:

ν_1 (symmetric stretch), 981 cm^{-1}

ν_2 (degenerate bend), 451 cm^{-1}

ν_3 (asymmetric stretch), 2204 cm^{-1}

ν_4 (degenerate bend), 613 cm^{-1}

ν_2 is doubly degenerate and both ν_3 and ν_4 are triply degenerate.

All four modes are Raman active but only ν_3 and ν_4 are active in the infrared.   The observed Raman frequencies in various crystalline environments are given in Table 4.   It is seen that doubly and triply degenerate modes may split into two and three components respectively.   Infrared spectra[181, 182] normally show only bands due to ν_3 and ν_4 though in some cases slight lowering of the symmetry brought about by crystal forces causes ν_1 to become weakly infrared active[181].

Table 4

Raman frequencies of sulphate ion in various
crystalline environments.[a]

Compound	$\nu_1(cm^{-1})$	$\nu_2(cm^{-1})$	$\nu_3(cm^{-1})$	$\nu_4(cm^{-1})$
Na_2SO_4	983	454	1106	622
$BaSO_4$	989	(453	(1094	(617
		(462	(1142	(630
			(1167	(648
$CaSO_4$	1018	(415	(1108	(609
		(499	(1128	(628
			(1160	(674

a: from Krishnan[221].

Whilst the perturbing effect of the cation on the sulphate ion symmetry is usually small, in the case of Indium sulphate[222] it is sufficiently great for new polarised lines to appear in the Raman spectrum and these have been accounted for in terms of a $InSO_4^-$ species of C_{3v} symmetry.   Decius[223,224] has shown

that when the alkaline earth sulphates are present in small

amounts in KBr or KCl crystals, the ion symmetry is reduced to

C_{2v}. The general effects of crystal , forces on the spectra

of solid sulphates have been discussed by several workers[225-230]

as have the differences between solid and solution spectra, which

result from the lower symmetry of the solid phase[231-233].

Guerchais et.al.[227] have related displacements of the ν_1 and ν_3

bands to the ionic radius of the cation in a series of alkali

metal sulphates. The displacement is a linear function of the

ionic radius of the cation, the shift being to lower frequency

with increase in ionic radius. The spectra of hydrated

sulphates may differ from those of the corresponding anhydrous

salts, usually as a result of hydrogen bond formation.[234-238]

For compounds of the type $M(H_2O)_6SO_4H_2O$, where M=Mg, Ni, Co,

Zn, ν_3 is at ~1085 cm^{-1} compared with approximately 1150 cm^{-1}

for the anhydrous compounds.[234a] Cho et.al.[239] have suggested

that $MgSO_4H_2O$ exists in the form $Mg(OH)HSO_4$ because of the presence

of a band at ~870 cm^{-1} which they assign to the HSO_4^- ion. On

the other hand Oswald[238] having studied the infrared and N.M.R.

spectra of a series of monohydrates, concluded that the forms

$MSO_3(OH)_2$ and $M(OH)HSO_4$ were not present and that the compounds

were normal sulphates containing strongly bound water molecules.

Tai and Underwood[240] have combined freeze drying with the KBr disc

technique to study the infrared spectra of aqueous sulphate solutions.

The shape of the ν_3 band at ~1120 cm^{-1} was found to vary with the cation and they suggest that the sharp band of K_2SO_4 is the most suitable for analytical purposes.

Considerably more data on the Raman and infrared spectra of the sulphate ion are reported. Ammonium and group 1 sulphates are reported in refs[225, 241-244] group 2 compounds in refs.[245-247]; group 3 compounds in ref.[248] and compounds containing transition metal ions in refs.[249-255]. Compounds of the type $(NH_4)_2M(SO_4)_2 6H_2O$ have been considered by Anantharayanan[256]. The infrared spectrum of iodosyl sulphate shows the $(IO)^+$ cation to be polymeric[257]. Several workers[247, 258-265] have discussed the spectrum of sulphuric acid, which provides evidence concerning possible ionisation processes. The general spectral characteristics of the sulphate ion are reported by various other workers.[266-270] Jaulmes[271] and Keller et.al.[272] have examined the spectra of sulphate minerals and Buijs[273] has examined the spectrum of the sulphate ion when absorbed on an ion exchange resin.

Thiosulphates

The free ion has tetrahedral C_{3v} symmetry and hence six fundamental modes all infrared and Raman active. The calculated frequencies[210] are:

ν_1 (symmetric S-O stretch), 995 cm^{-1}

ν_2 (symmetric S-O bend), 669 cm^{-1}

v_3 (S-S stretch) 435 cm^{-1}

v_4 (asymmetric S-O stretch) 1123 cm^{-1}

v_5 (asymmetric S-O bend) 541 cm^{-1}

v_6 (-SO$_3$ rocking), 335 cm^{-1}

Miller and Wilkins[181] have reported the spectra of several

thiosulphates. The band at 670 cm^{-1} is often broad and the

maximum occurs over the range 640-680 cm^{-1}. The S-O stretching

modes (v_1 = 950-1000 cm^{-1}) are, with the exception of the ammonium

compound, well defined. Buijs[273] has examined the spectra of

thiosulphates on an ion-exchange resin; the spectra are essentially

unchanged though new bands appear due to $S_4O_6^{2-}$ ions formed by

the facile atmospheric oxidation of thiosulphate under these

conditions.

Other oxo-anions

Simon[274] has examined the Raman spectrum of the

dithionite ion ($S_2O_4^{2-}$) and reported S-O stretching modes at

1070 and 998 cm^{-1}. The pyrosulphite ion $S_2O_5^{2-}$ has been studied

by Simon et.al.[275] who concluded that an SOS grouping was present

and interpreted their infrared and Raman data on the basis of

C_{2v} symmetry. However, X-ray analysis shows the presence of an

S-S bond in a structure of C_S symmetry. Buijs[273] in a more recent

examination of the infared spectrum has reported five fundamentals

in the S-O stretching region as expected on the basis of the required

$C_{,S}$ symmetry. The assignment of the fundamental frequencies

of the dithionate ion ($S_2O_6^{2-}$) is subject to some controversy.

Palmer[211] from a study of the Raman and infrared spectra of the

sodium and potassium salts has assigned the S-O stretching

frequencies, on the basis of D_{3d} symmetry, as follows:

ν_7 (asymmetric S-O stretch), 1235-1240 cm^{-1}

ν_{10} (asymmetric S-O stretch), 1206-1216 cm^{-1}

ν_5 (symmetric S-O stretch), 996-1000 cm^{-1}

ν_1 (symmetric S-O stretch), 1092-1102 cm^{-1}

On the other hand, Buijs[273, 276] however has interpreted his

infrared data, in conjunction with the Raman studies of Duval and

Lecomte[271] to suggest that the fundamental should be assigned

as, ν_7 = 994 and 998 cm^{-1}, ν_{10} = 1212 cm^{-1}, ν_5 = 1230 and 1243 cm^{-1}

and ν_1 = 1200 cm^{-1}. Compounds containing S(VI) have been

found to give rise to symmetrical and asymmetrical stretching

frequencies which vary linearly with one another (Fig.10).

The assignments made by Palmer give rise to average values of,

$\nu_s SO$ = 1046 cm^{-1} and $\nu_{as} SO$ = 1221 cm^{-1}, which fit this general

relationship fairly well. The corresponding values from Buijs

assignments are, $\nu_s SO$ = 1237 cm^{-1} and $\nu_{as} SO$ = 1068 cm^{-1}, which

do not fit the straight line. The effect of site symmetry

on the fundamental frequencies has been discussed by Buijs[276].

Simon et.al.[212] have studied the infrared and Raman

spectra of the disulphate ion $(S_2O_7^{2-})$ and have interpreted

their data in terms of C_{2v} symmetry. Symmetric S-O stretching

modes occur in the infrared at 1060 and 1110 cm^{-1}, the

corresponding asymmetric modes being at 1249-1267 and 1289-

1295 cm^{-1}. Similar frequencies are observed in the Raman

spectra. Bands at approx. 740 and 800 cm^{-1} were assigned to

the symmetric and asymmetric SOS stretching modes, respectively,

in agreement with the assignments of Dupuis and Viltange[278].

Gillespie and Robinson[279], however, have assigned frequencies

of ∼150, ∼300 and ∼800 cm^{-1} to the bend, symmetric stretch

and asymmetric stretch, respectively, of the SOS group in

molecules of the type X_nSOSX_n, including $S_2O_7^{2-}$. Further,

these authors have shown that there exist linear relationships

between the symmetric stretching and bending modes of the SOS

group and the square root of the mass of the groups SX_n

attached to the oxygen atom. For the disulphate ion SO

bending modes occur[278] at ∼520 (symmetric) and ∼590 cm^{-1}

(asymmetric).

The Raman and infrared spectra of several peroxodisulphates

$(S_2O_8^{2-})$ have been examined by Simon and Richter[280] who assigned a

band at 1267 cm^{-1} in both spectra to an S-O stretching vibration.

Since the $S_2O_8^{2-}$ ion contains S(VI), its symmetric and asymmetric

frequencies are expected to fit the linear relationship shown

in Fig.10. If the 1267 cm^{-1} band is assigned to the asymmetric mode

then the band observed at 1088 cm^{-1} in the Raman, (not assigned

by Simon and Richter)is in the region expected for the symmetric

stretch.

The spectrum of the tetrathionate ion $S_4O_6^{2-}$ has been discussed

in some detail by Buijs[273]. There are six fundamental S-O stretching

modes and these occur in the regions 1010-1050 cm^{-1} and 1200-

1250 cm^{-1}. As expected these frequencies are close to those

observed for the $S_2O_6^{2-}$ ion. Schmidt and Sand[281] have assigned

bands in these same regions to the S-O vibrations of $K_2S_2O_6$

and these same authors[282] have shown that the infrared spectra

of the ions $S_nO_6^{2-}$, where n = 3 - 6, are similar.

Complexes containing oxo-anions as ligands

(i) Sulphito-compounds

Compounds of the types $M_2^I.M^{II}(SO_3)_2$ and M^ICuSO_3, have

simple spectra typical of the free ion and, therefore, are double

salts and not complexes[217]. When functioning as a unidentate

ligand the sulphite group may bond through either sulphur or

oxygen. The C_{3v} symmetry of the free ion will be essentially

undisturbed if S-bonding occurs and the infrared spectra of complexes

217, 283, 284 of Co^{III}, Rh^{III}, Ir^{III}, Pd^{II}, Pt^{II} and Hg^{II} are in

accordance with this suggestion. Bonding through oxygen lowers

the symmetry to C_s, causing more profound changes in the spectrum; $Tl_2(Cu(SO_3)_2)$ is the only compound for which O-bonding is reported[217].

When occupying two coordination positions the sulphito group may be bidentate or bridging. As is the case with sulphato-compounds it seems doubtful[217] if infrared data can distinguish between the two possibilities. Whilst Baldwin[283] interpreted the infrared spectrum of $(Coen_2SO_3)Cl$ to show that the sulphito group is bidentate, Newman and Powell[217] found that the spectrum of $(Coen_2SO_3)Cl$ was similar to those of $K_2(Pt(SO_3)_2).2H_2O$, $Na_3(Co(SO_3)_3).4H_2O$ and $K_3(Rh(SO_3)_3)2H_2O$. They concluded that infrared data alone could not distinguish between the two possible structures. These latter authors discussed the infrared data in some detail and commented upon Baldwin's[283] interpretation of her data. On the other hand, Babaeva and Kharitonov[285] have suggested that the infrared spectra support the assignment of structures involving bridging sulphito-groups to $(Co(SO_3)_3)^{3-}$ and $(Rh(SO_3)_3)^{3-}$. The spectrum[217] of $K_2(Pd(SO_3)_2)$ indicates that its structure may differ from that previously suggested[286].

(ii) Sulphato-compounds

Nakamoto et.al.[287] have discussed the spectra of both unidentate and bidentate sulphato-groups. When the group

functions as a unidentate ligand e.g. in $(Co(NH_3)_5 \cdot SO_4)X$

compounds[287, 288] the symmetry is lowered to C_{3v}, whilst in

the case that bridging occurs, e.g.

$$\left[(NH_3)_4 Co \overset{NH_2}{\underset{SO_4}{<}} Co(NH_3)_4 \right] (NO_3)_2$$ [287], C_{2v} symmetry is observed.
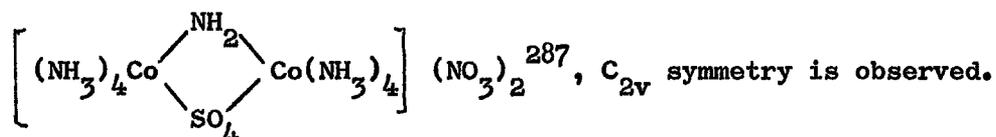
Barraclough and Tobe[289] from a study of the spectrum of

$(Co.en_2 \overset{\smile}{SO_4})Br$ have concluded that it is not possible to

distinguish between bridging and chelating sulphato-groups

using infrared data only.   On the other hand McWhinnie[253]

and Eskenazi et.al.[290] have suggested that the high energy

band of the $\overset{\smile}{\nu}_3$ mode occurs at higher frequencies in complexes

containing chelating sulphato groups $(1210-1240 \text{ cm}^{-1})$ than

in those containing the bridging ligand $(1160-1195 \text{ cm}^{-1})$.

The spectra of some protactinium di- and tri-sulphato complexes

have been reported and discussed[291].   Both uni- and bidentate

sulphato groups may be present and since the various

possibilities could not be differentiated the coordination

of the protactinium remains uncertain.   Baldwin[292] has

discussed the spectra of various complex sulphates and of

compounds of the types, $Y_2SO_4 \cdot MSO_4 \cdot 6H_2O$ and $Y_2SO_4 \cdot X_2(SO_4)_3 \cdot$

$24H_2O$, i.e., Tutton salts and alums.   It appears that these

hydrated compounds may give rise to quite complex spectra and

Baldwin concludes that whilst a simple spectrum indicates an

undistorted sulphato-group it does not necessarily follow

that a complicated band structure shows conclusively coordination

to a metal or even significant deviation from a tetrahedral

structure.

Livingstone[293] has recently reviewed the metal complexes

of ligands containing sulphur as a donor atom; sulphito and

thiosulphato complexes were discussed by this author.

(iii) Thionyl(-SO-) compounds

Table 5 shows the S-O stretching frequencies observed

in various thionyl compounds. With the sulphoxides, R_2SO,

considerable molecular aggregation occurs in the liquid phase

with the result[294-296] that

$$v_{SO_{(liquid)}} < v_{SO_{(solution)}} < v_{SO_{(vapour)}}$$

and because of the considerable solute-solvent interactions that

can arise with these compounds the observed solution frequency

is markedly solvent dependant.[297] The range quoted in Table

5 covers the frequencies observed in CCl_4 and CS_2 solutions.

In contrast to the sulphones it is not possible to differentiate

between compounds having R=aryl and those having R=alkyl.

Barnard et.al.[294] have suggested that the constancy of v_{SO}

at ~1055 cm^{-1} for several sulphoxides arises from the fact that

Table 5

S-O stretching frequencies in thionyl compounds

type of compound	$\nu_{SO}(cm^{-1})$
simple sulphoxides, R_2SO, (R=aryl, alkyl,alkenyl)	$1010\text{-}1070^a$
cyclic sulphoxides, $(CH_2)_nSO$	$1039\text{-}1055, \ 1192^b$
$(CH_2O)_2SO$	1220
disulphoxides	1036-1088
dimethyl sulphoxide-metal complexes	$978\text{-}1037^c$
tetramethylene sulphoxide-metal complexes	950
S-alkylsulphoxonium compounds	1210-1240
O-methylsulphoxonium nitrate	925-1050
SOX_2(X=F,Cl,Br.)	X=F, 1308, X=Cl, 1251 X=Br, 1121
SOF_4	1379

a: see text for variation of v_{SO}.

b: when n=4, $\nu_{SO}=$ 1194 cm^{-1}, this value is anomalously high. A similar situation arises with the cyclic ketones.[296]

c: except Pd^{II} and Pt^{II} complexes, see text.

negligible coupling occurs between the S-O vibration and

the lower frequency C-S vibration, and Price and Gillis[298]

report that negligible conjugation occurs between C=C and

S=O bonds in alkyl-alkenyl sulphoxides. Coupling between

the S-O stretching and CH_3 rocking modes in dimethyl sulphoxide

is, however, well substantiated and leads to some difficulty in

the assignment of ν_{SO} in dimethyl sulphoxide-metal complexes.

Lappert and Smith[301], Cotton et.al.[295] and Holah and Fackler[302]

have assigned a band at 900-950 cm^{-1} to the S-O stretching

vibration in a wide variety of dimethyl sulphoxide complexes

and have concluded that since in these complexes ν_{SO} occurs

at lower frequencies than in the free ligand, the ligand is

bonded through the oxygen atom of the S=O bond. Kaufmann

and Leroy[303] have given a normal coordinate analysis of the

O-bonded complex, $UO_2Cl_2 \cdot 3(CH_3)_2SO$; the bond order of the S=O

bond is decreased by $\sim 12\%$ as a result of complex formation.

Complexes of Pd^{II} and Pt^{II} are exceptions to this general

rule[295, 304,306] as are complexes of the type $C_5H_5Mn(CO)_2D$,

where D may be various sulphoxides[307], in that the ligands are

bound through the sulphur atom with the result that ν_{SO} is

at a higher frequency than in the free ligand. Drago et.al.

[300,308] assign a band at $\sim 1000 cm^{-1}$ to the S-O stretch in the

'normal' O-bonded complexes and suggest that the 900-950 cm^{-1}

band is due to a CH_3 rocking mode since its frequency remains
fairly constant in many complexes, whilst that of the band at
~1000 cm^{-1} varies with the metal ion. These authors suggest
that considerable coupling occurs between these two modes so
that when ν_{SO} is less than 990 cm^{-1}, e.g. in Cu^{II} complexes, the
assignment of "ν_{SO}" is very difficult. Since the extent to
which the S-O vibration is involved in coupling interactions
will vary with the sulphoxide it is dangerous to use the shift in
ν_{SO} which occurs on complex formation as a measure of the
variation of bond strengths for various ligands[304]. The
infrared spectra of sulphoxide complexes with I_2 and ICN
indicate that in these compounds also the bonding is through
the oxygen atom[309].

Correlation between stretching frequency and molecular parameters

The nature of the sulphur-oxygen bond in sulphuryl
$(XYSO_2)$ and thionyl $(XYSO)$ compounds has been discussed by
Gillespie and Robinson[310]. These authors consider that the two
possible extreme forms of the S-O bond may be represented as
(I) and (II)

$$S{=}O \qquad\qquad \begin{array}{c} {+}{-} \\ S{-}O \end{array}$$

$$\text{(I)} \qquad\qquad \text{(II)}$$

Structure (I) represents a situation in which the bonding electrons
are equally shared and arises when the other atoms attached to

sulphur have electronegativities su$\mathbb{G}$ficiently great to raise

the effective electronegativity of sulphur to that of oxygen.

This situation is approached in SO_2F_2 and SOF_4. With

decreasing electronegativity of the attached groups the bond

becomes polar and in the limit the π-bond electron pair resides

essentially on the oxygen atom and structure (II) results.

The observed frequencies for sulphuryl compounds and S^{VI}

containing anions are in agreement with these suggestions (Table3).

The highest frequencies (1270 and 1502 cm^{-1}) are found for

SO_2F_2 and the lowest (981 and 1104 cm^{-1}) are those of the

sulphate ion. Similarly, for the sulphoxides X_2SO the

highest frequency (1308 cm^{-1}) is found for SOF_2. For SOF_4

the frequency is even higher (1379 cm^{-1}) than in SOF_2 which

is consistent with the presence of two additional highly

electronegative ligands. Increasing electronegativity

of the groups X and Y should increase the order of the SO

bond, and since the lengths of the SO bonds may be assumed to

be related to their bond order, a correlation is to be expected

between stretching frequency and bond lengths. This

relationship has been verified by Gillespie and Robinson[310]

and is illustrated in Fig.4. In the case of $-SO_2-$ compounds

the appropriate stretching frequency was calulated[311] from the

equation

$$\nu_{SO} = \frac{1}{x} \nu_s SO + (x-1) \nu_{as} SO) \qquad \ldots\ldots\ldots 1$$

FIG. 14.
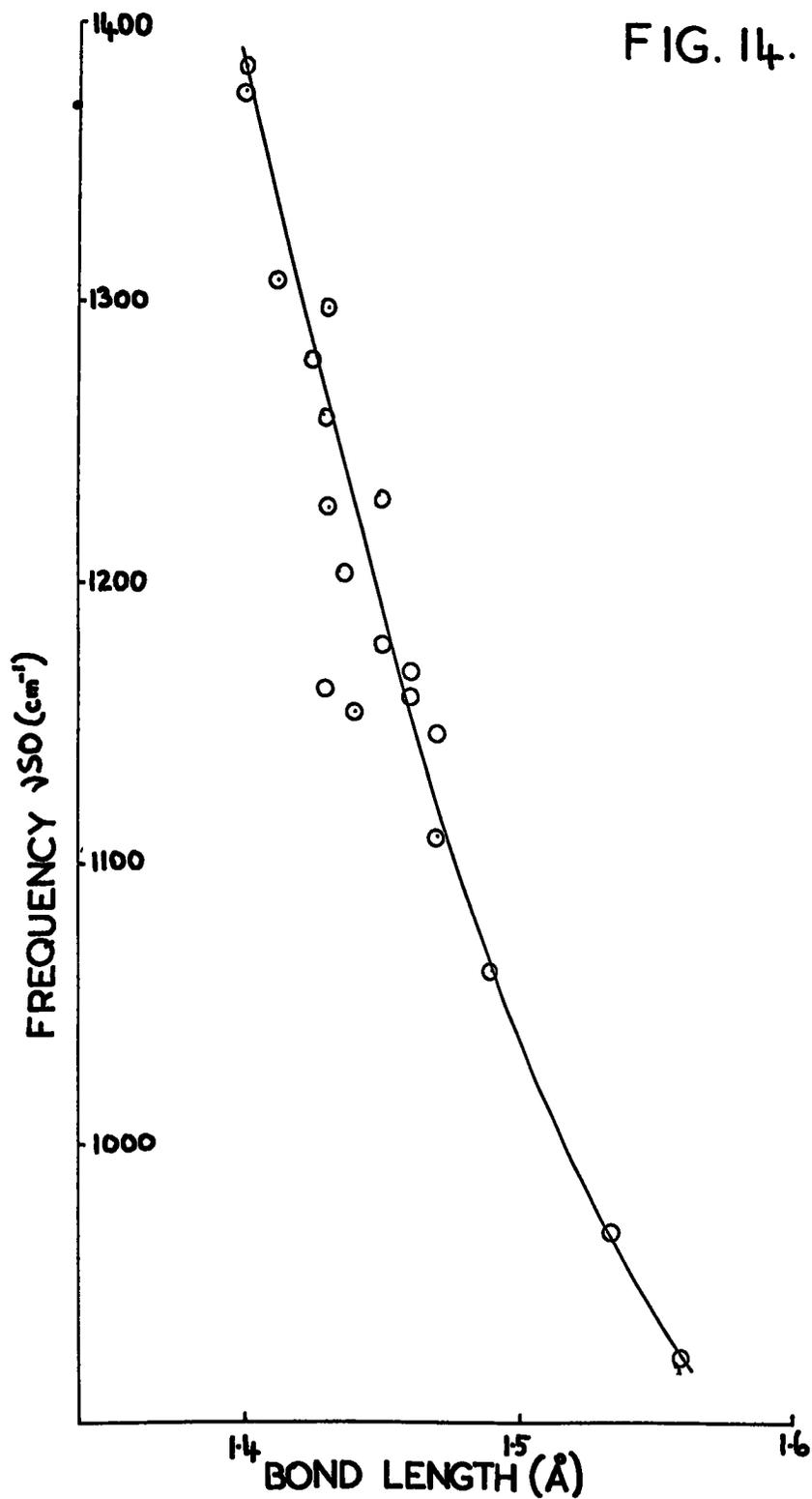
CORRELATION OF S-O STRETCHING FREQUENCY
WITH BOND LENGTH[310]

64

FIG. 15.
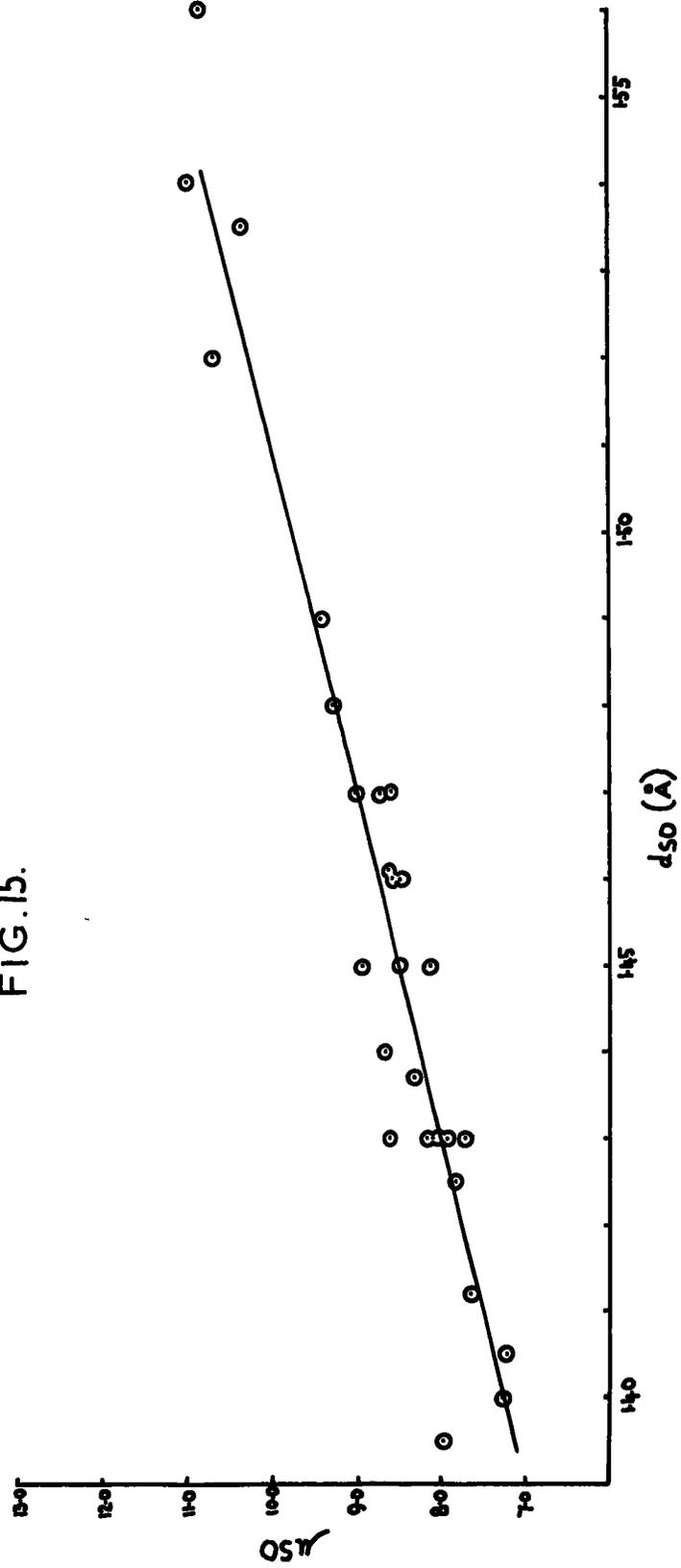
CORRELATION OF WAVELENGTHS (μ) AND BOND DISTANCES FOR

S–O BONDS

where (x-1) is the degeneracy of the asymmetric vibration.

The scatter of the points in Fig.14 is, in general, not greater than $\pm$ 0.02Å which is of the order of the experimental error of most bond lengths determinations.

For several compounds not considered by Gillespie and Robinson both bond lengths and stretching frequencies are now available so that values of the bond length predicted from Fig.14 may be compared with the experimental value. The appropriate data is given in Table 6.

Table 6

Some predicted and observed values of sulphur
oxygen bond length (d_{s-o}).

Compound	ν_{so} cm^{-1}(calc.)[1]	d_{s-o} Å (calc.)[2]	d_{s-o} Å (obs.)[3]
S_2O	1165 [312]	1.46	1.47 [316]
H_2NSO_3H	1180 [313]	1.45	(1.48 [317] (1.44 [318]
$S_2O_3^{2-}$	1080 [210]	1.48	1.48 [319]
$SOBr_2$	1121 [314]	1.47	1.45 [320]
$SO_2(NH_2)_2$	1254 [315]	1.43	(1.39 [321] (1.40 [322]
$(Me_2SO)_2SnCl_4$	920,905 [301]	1.56,1.57	1.54 [323]
$(Me_2SO)BF_3$	938 [301]	1.55	1.52 [323]

(1) calculated from equation (1)

(2) predicted from Fig.14

(3) observed value

For compounds having bond lengths in the range 1.45-1.48$\overset{o}{A}$

agreement between predicted and observed values is particularly

good.   The results for compounds containing shorter ($< 1.45\overset{o}{A}$)

and longer ($> 1.50\overset{o}{A}$) bonds are less satisfactory.

The relationship may be presented more conveniently

if, instead of the frequency (cm^{-1}), the wavelength (μ)

of the absorption maximum is plotted against the bond length.

In this case a straight line is obtained (Fig.15).   Using

the data reported by Gillespie and Robinson[310] in combination

with that in Table 6, a least squares treatment leads to the

relationship,

$$d_{SO} = 3.99 \cdot 10^{-2} (\mu_{SO}) + 1.111$$

where, μ_{SO} is the wavelength of the absorption bond expressed

in microns, and d_{SO} is in $\overset{o}{A}$.

The bond length in the sulphite ion is of interest.   On

the basis of the stretching frequencies[181] $\nu_s SO = 737$ cm^{-1} and

$\nu_{as} SO = 807$ cm^{-1}.   Gillespie and Robinson[310] predicted from

Fig.14 an S-O distance of 1.65$\overset{o}{A}$, and commented that the distance

reported by Zachariassen and Buckely[324] (1.39$\overset{o}{A}$) seemed in error.

Using the more recent values[207] of $\nu_s SO = 970$ cm^{-1} and

$\nu_{as} SO = 930$ cm^{-1} the distance predicted from Fig.15 is 1.53$\overset{o}{A}$.

Since Gillespie's and Robinson's prediction, S-O bond lengths

have been reported for $(Ni(H_2O)_6)SO_3$[325] pf 1.45$\overset{o}{A}$ and for

$Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O^{326}$ of 1.51Å. Only for the latter compound

is the observed value in agreement with the predicted value

of 1.53Å but the S-O distance in this compound may be affected

by the close approach of the sulphur atom of the sulphite group

and one of the copper atoms. It has been shown that the S-O

stretching frequencies of the sulphur(IV) oxo-ahions,

including SO_3^{2-}, do not fit the linear $v_s SO/v_{as} SO$ relationship

established by Robinson[177] but do fit a similar relationship

(Fig.11.) It seems probable, therefore, that for these

compounds the $\mu_{SO} - d_{SO}$ relationship (Fig.15) will not

be applicable, though there may well be a similar relationship

which applies within this class of compounds. Unfortunately

there is as yet insufficient structural data to test this hypothesis.

Gillespie and Robinson[310] have also demonstrated a

linear relationship between stretching frequency and $\widehat{OSO}$

angle in SO_2 compounds, though the correlation is not too

well established since relatively little data were available.

These authors have also discussed the problem of defining

the bond order of sulphur-oxygen bonds and have suggested that

there exists a non linear relationship between the bond length

and the bond order. That the bond order-bond length

relationship for C-C bonds is also non-linear is thought to

support the latter suggestion. On the other hand Cruickshank[322]

has suggested that the bond order-bond length relationship

for S-O compounds is rectilinear.

Deformation Frequencies

The deformation frequencies of the oxo-anions have been

mentioned above. For sulphur dioxide the single symmetric

bending mode occurs[327, 328] at 520-530 cm^{-1}, and for the trioxide

the symmetric and asymmetric bending modes occur at ~495 and

~530 cm^{-1}, respectively[329-331]. The γ and β forms of $(SO_3)_n$

have asymmetric bending modes at ~530 and ~ 566 cm^{-1} respectively[322].

Sulphuryl compounds SO_2X_2 and SO_2XY give rise to an SO_2

scissoring bend and an SO_2 rocking vibration; the values reported

for a series of compounds,[315, 333-335] fall in the range 520-610

and 530-620 cm^{-1} respectively. Feairheller and Katon[336] from

a study of several sulphones concluded that of the four SO_2

bending vibrations only the SO_2 scissoring (545-610 cm^{-1}) and

wagging (496-525 cm^{-1}) are sufficiently localised to be of value

as group frequencies. Bands in the region 500-570 cm^{-1} have

been assigned to bending modes in the alkali methyl sulphonates[337]

and methyl sulphonic acid and its anhydride[338]. For

the sulphamic acid[339] the symmetric and asymmetric bending modes

occur at 640 and 511 cm^{-1}, respectively and in sulphamates[339]

bands at 520-560 cm^{-1} are assigned to SO_3 deformations.

B. SULPHUR-NITROGEN BONDS

Introduction

The infrared and Raman spectra of compounds containing

sulphur-oxygen bonds have been extensively studied and various

empirical correlations established[176-178,180,310]. Robinson[177]

has shown that for sulphuryl compounds a linear relationship

exists between the symmetric and asymmetric S-O stretching

frequencies. Gillespie and Robinson[310] have related the S-O

stretching frequencies of both thionyl and sulphuryl compounds

to the S-O bond lengths and force constants, and these same

authors[180] have demonstrated a linear correlation between the

symmetric stretching and bending modes of the SOS group in

$X_n SOSX_n$ molecules and the square root of the mass of the groups

SX_n attached to the oxygen atom. No such correlations appear

to have been established for sulphur-nitrogen bonds. Since

the nature of the bonding in sulphur-oxygen and sulphur-nitrogen

systems is analogous, similar relationships might be expected

to hold. In this section the available data are summarised and

it is shown that there exists a linear relationship between the

bond lengths and the wave-lengths of the absorption bands of

sulphur-nitrogen bonds. Also, in the case of compounds containing

the NSO group it is shown that the symmetric and asymmetric NSO

stretching frequencies are linearly related.

Discussion

The reported infrared and Raman data are summarised in

Table 7. Since bond orders of up to three may occur a considerable

range of frequency is observed $(630-1690 \text{ cm}^{-1})$; as expected

the frequency increases with increasing bond order. Bond

length measurements[340] show that for compounds which contain

a formal sulphur-nitrogen single bond (e.g. $S(NSO)_2$, $SO_2(NH_2)_2$,

$H_3\overset{+}{N}.SO_3^-$ and $SO_3(N_2O_2)^{2-}$) the experimentally determined bond

distance varies over the range $1.58-1.79\overset{o}{A}$. Small variations

in the bond distance are to be expected, e.g. as a result of

variations in the character of the orbitals used in forming

the bond. These variations will arise with change in the

sulphur valency state and with changes in the number and nature

of the groups attached to the sulphur and the nitrogen atoms.

However, these factors are insufficient to account for the

magnitude of the observed variations and several workers[341-344]

have attempted to explain the observed bond lengths by assigning

to the bond some π character, as a result of p_π-d_π overlap

involving the lone pair electrons of the neutral nitrogen atom

and the empty 3d orbitals of the sulphur atom. The observed

stretching frequencies may also be explained in terms of this

hypothesis.

Table 7

Correlation table for sulphur-nitrogen stretching frequencies

Compound type	$\nu_{SN}(cm^{-1})$
Alkyl thionitrites[349]	620-640
Sulphamic acid[339, 348]	682
$R_3P=NSO_2R'$[378]	760-790
Cyclic $S_n(NR)_{8-n}$ compounds[350-356]	770-840
Sulphamates[339]	788
$R_2S=NCOCHX_2$ (X=Cl, Br)[366]	800-825
Sulphonamides[358-361]	800-920
Sulphamides[362-364]	900-930
SN (short lived)[379]	1204
$(SN)_x$ polymer[379]	1225, 1015
$RN=S(F)CF(CF_3)_2$[372]	1272-1279 or 1295-1300 *
$PhN=S(OMe)_2$[372]	1283
$RN=SF_2$[374,375]	1350-1400
NSF[104]	1372
$(RN=)_2SF_2$[380]	1404-1428
$MeN=SOF_2$[365]	1493
NSF_3[104]	1515
$NS(F)_2NEt_3$[367]	1515
$F_3SN \cdot BF_3$[368]	1690

* see text for preferred assignment

Since a formally single sulphur-nitrogen bond may

exist in widely different chemical environments with consequental

variation in bond strength, any use of the term 'single bond'

is necessarily ambiguous to some extent.   Accordingly we

shall use the term to describe all covalent bonds (including

coordinate bonds) where π contributions make a relatively

small contribution to the bond energy.   Such single bonds

will be expected to have a bond distance close to the value

of 1.74Å which is obtained both from the sum of the Pauling

tetrahedral covalent radii[345] and from the Schomaker-Stevenson

equation[346].

Examination of the data in Table 7 shows that the

absorption range associated with each formal bond type

(single, double, triple) is broad.   Thus compounds containing

a sulphur-nitrogen single bond may absorb over the range

680-930 cm^{-1}, and it will be seen that increases in absorption

frequency can generally be attributed to a strengthening

of p_π-d_π interactions.

The observed bond length[347] in sulphamic acid (1.76Å)

is close to the calculated value of 1.74Å which suggests that

in this compound little or no p_π-d_π bonding occurs.   Sulphamic

acid exists as the zwitterian $H_3\overset{+}{N}\cdot S\overset{-}{O}_3$ so that the nitrogen lone

pair is utilised in bonding the proton of the $H_3\overset{+}{N}$-group and so

is unavailable for donation to the sulphur 3d orbitals.

Hence the sulphur-nitrogen bond is essentially restricted

to two σ-electrons only. The observed stretching frequency

339, 348 (ν_{SN} = 682 cm^{-1}) may, therefore, be taken as being

close to that expected for a sulphur (VI)-nitrogen single bond.

The reported stretching frequencies[349] for the alkyl

thionitrites (RSNO, ν_{SN}≈630 cm^{-1}) suggest that these

compounds contain a sulphur (II)-nitrogen single bond.

However, these absorption bands were not directly observed,

the frequencies were calculated from those of combination bands.

For other compounds which formally contain a sulphur-

nitrogen single bond, e.g., the sulphamate ion, the cyclic

sulphur imines, sulphonamides and sulphamides, the observed

stretching frequencies are higher than that of sulphamic acid

(Table 7). In the sulphamate ion[341] the observed bond length

(1.60Å) suggests some double bond character and, in agreement

with this, the observed stretching frequency[339] (ν_{SN}≈780 cm^{-1})

is considerably higher than that of the free acid. The cyclic

imines[350-356] $S_n(NR)_{8-n}$, R=H, CH$_3$, absorb in the range 770-840

cm^{-1}; when R=CH$_3$ the absorption occurs towards the lower end

of this range. Splitting of the band into two components

may occur if the-NR groups are sufficiently close together[356].

The extent of π-bonding in these compounds is expected to be small

since the d-orbitals of the unsubstituted sulphur (II)

atoms will be of relatively high energy.   In the case of

the sulphonamides the presence of electronegative substituents

causes contraction of the sulphur 3d orbitals[357] so that the

extent of p_π-d_π overlap is increased and accordingly the

stretching frequency[358-361] occurs at 800-920 cm^{-1}.   The

bonding in sulphamide has been discussed by Cruickshank[322]

who has shown that sulphur-nitrogen π-bonding occurs to a

considerable extent; the symmetric and asymmetric SN_2 stretching

modes occur[362-364] in the range 900-930 cm^{-1}.

Compounds formally containing a sulphur-nitrogen double

band may absorb over the very wide range, 780-1500 cm^{-1}

(Table 7), the frequency at which a given compound absorbs

being apparently very sensitive to the nature of substituents

on both the sulphur and the nitrogen atoms.   If the bond

is described of σ and π components then the observed variation

in frequency may be considered to reflect changes in the π-bond

order, and in the relative s, p and d character of the orbitals

utilised in the σ-bond.   Both of these factors will be subject

to electronic effects by the substituents though, in general,

the variation in the π-bond order will be the more important.

For the greater number of compounds studied, the stretching

frequency falls in the much more restricted range 1350-1430 cm^{-1}.

The value of $\dot{v}_{SN}$ = 1493 cm^{-1} reported[365] for CH_3NSOF_2

is particularly high and is in fact greater than the frequency

reported[104] for NSF($\dot{v}_{SN}$ = 1372 cm^{-1}) which formally contains

a sulphur-nitrogen triple bond. For compounds of the type[366]

$R_2S=NCOX$ (X = -CHCl$_2$, -CHBr$_2$, R = alkyl, aryl) $\dot{v}_{SN}$ is found

at 780-820 cm^{-1} which suggests that in these compounds the

sulphur-nitrogen bond is very nearly single in character.

It has been suggested [366] that this situation arises as the

result of polar SN and CO bonds in a strongly conjugated

SNCO bonding system. It seems, therefore, that compounds

which formally contain a sulphur-nitrogen double bond may in

fact contain bonds varying in character between nearly single

and nearly triple bonds. This situation presumably arises

because of the ready polarisability of the π-component of

the double bond.

Few compounds containing sulphur-nitrogen triple bonds

are reported. For both[104] NSF$_3$ and[367] NS(F$_2$)NEt$_2$ $\dot{v}_{SN}$ is

assigned at 1515 cm^{-1}; in the case of the former compound

Richert and Glemser[104] have calculated the bond order of the

sulphur-nitrogen bond as 2.7. In the case of NSF the observed

frequency ($\dot{v}_{SN}$ = 1372 cm^{-1}) suggests that the bond order (2.5)

is less than that in CH_3NSOF_2 for which $\dot{v}_{SN}$ = 1493 cm^{-1},

corresponding [44] to a bond order of ~ 2.6 for the formally

double bond if the vibration is predominantly a localised

sulphur-nitrogen stretching mode. Coordination via the

nitrogen atom of NSF_3 has been found to shift the sulphur-

nitrogen stretching mode to higher frequency. For $F_3SN.BF_3$

Müller et.al.[368] find v_{SN} at 1690 cm^{-1}, so that Δv = 175 cm^{-1}.

A similar situation occurs with adducts of nitriles[369,370]

though in these cases the frequency shifts are smaller

$(\Delta v \sim 25\text{-}110 \ cm^{-1})$. Müller et.al.[368] attribute this increase

in the sulphur-nitrogen stretching frequency to a real increase

in the sulphur-nitrogen bond order.

Since, in general, the stretching frequencies of sulphur-

nitrogen bonds increase with increasing bond order, i.e. as the

bond strengthens and shortens, a relationship between stretching

frequency and bond distance might be expected. There are

relatively few compounds for which both stretching frequencies

and bond lengths of the sulphur-nitrogen bond are available.

The available data which are collected in Table 8 and illustrated

graphically in Fig.16 show that there is a linear relationship

between the wavelengths of the absorption bands and the bond

lengths of sulphur-nitrogen bonds. A least squares treatment

of the data (ignoring that for potassium sulphamate) leads to

FIG 16
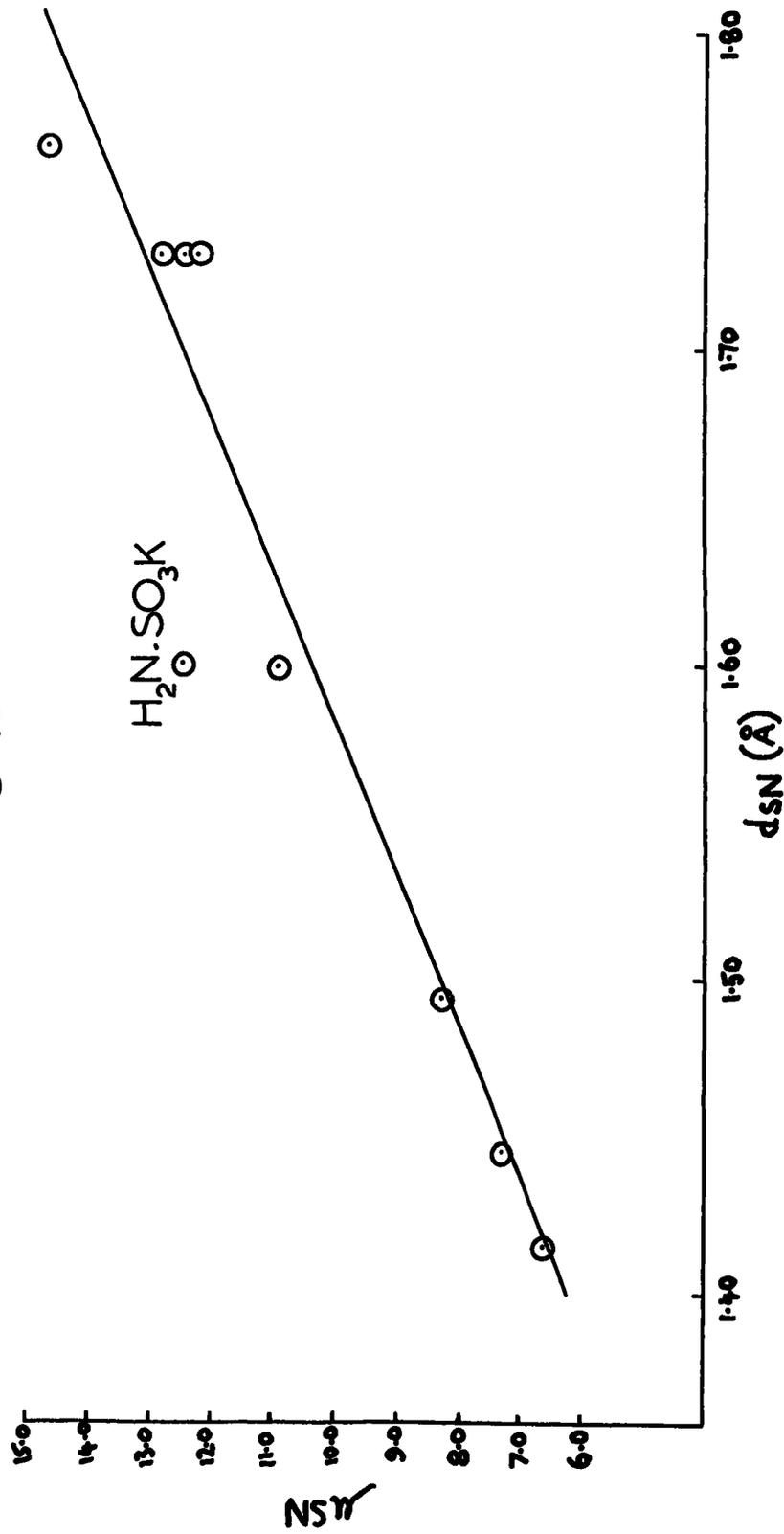
CORRELATION BETWEEN WAVELENGTHS (μ) AND BOND DISTANCES (d)

OF S-N BONDS

the relationship,

$$d_{SN} = 0.0483 \left(\mu_{SN} \right) + 1.099$$

where, μ_{SN} is the wavelength of the absorption band expressed

in microns and d_{SN} is in Angstrom units.

Table 8

Stretching frequencies (ν_{SN}) and bond lengths (d_{SN})

in some sulphur-nitrogen compounds

Compound	ν_{SN} cm^{-1}	ν_{SN} μ	d_{SN} (Å)
$H_3\overset{+}{N}.S\bar{O}_3$	682 [339,348]	14.66	1.764 ± 0.020 [347]
1.4S$_6$(NH)$_2$	780, 819 [356]	12.21, 12.82	1.73 [381]
$H_2N.SO_3K$	805 [339]	12.42	1.60 ± 0.03 [341]
S$_7$NH	806 [356]	12.41	1.73 [382]
SO$_2$(NH$_2$)$_2$	915 [362]	10.93	1.600 ± 0.009 [343]
NS (short lived)	1204 [379]	8.31	1.495 [383]
NSF	1372 [104]	7.29	1.446 [104]
NSF$_3$	1515 [104]	6.60	1.416 [104]

The existence of this correlation implies that for the

compounds considered an essentially pure sulphur-nitrogen

stretching vibration occurs. It is of interest to note
that if the frequency of the absorption band, expressed in
wave numbers, is plotted against the bond lebgth then the
points representing the various compounds fall upon a smooth
curve of similar shape to that reported by Gillespie and
Robinson[310] for SO bonds. Further, if for the compounds
reported by Gillespie and Robinson[310] the wavelength of the
absorption band is plotted against bond length then a linear
relationship is observed. The value of ν_{SN} for sulphamide
used in Fig.16 was calculated as the arithmetic mean of the
symmetric and asymmetric SN_2 stretching vibrations.
Gillespie and Robinson[310] have discussed the assumptions
implicit in this treatment. The scatter in the points is
never greater than $0.04\mathring{A}$ and is less than this for bonds
shorter than $1.70\mathring{A}$ Fig.16 may be used to predict sulphur-
nitrogen bond distances in compounds for which these have
not been measured. Thus, for the compounds, 1.5 $S_6(NCH_3)_2$,
$F_5S.NH_2$, $CH_3N.(SO_2NH_2)_2$, $C_6H_5NS(OCH_3)_2$ and $NS(F_2)NC_2H_5$ the
sulphur-nitrogen stretching frequency has been assigned at 13.00,
12.89, 11.11, 7.79 and 6.60 respectively[354, 371, 363, 372, 369]
corresponding to bond distances of 1.72, 1.72, 1.63, 1.48 and $1.42\mathring{A}$.
The data for potassium sulphamate appears to be anomalous.

If the reported[339] stretching frequency results from a pure

sulphur-nitrogen stretching vibration the bond distance is

in error by about 0.1Å.   However, the reported[341] bond

distance (1.60Å) corresponds to a high degree of double bond

character and it is possible that coupling occurs between the

sulphur-nitrogen and sulphur-oxygen vibrations.   If so then

anamolous behaviour is to be expected.

A knowledge of the manner in which stretching frequency

varies with bond type enables the assignment of sulphur-

nitrogen stretching frequencies for several compounds reported

in the literature.   For $F_5S.NH_2$ Clifford and Duncan[371] have

tentatively assigned a weak band at 1208 cm^{-1} to ψ_{SN}. If

this assignment is correct then the sulphur-nitrogen bond has

a considerable double bond character whereas, on theoretical

grounds an essentially single bond is to be expected.   The

present author favours assignment of the strong band at 776 cm^{-1}

(assigned by Clifford and Duncan to an NH deformation) to the

sulphur-nitrogen stretching vibrations.   Cohen et.al.[373] have

reported the spectrum of $F_5S.NSF_2$; bands at 760 cm^{-1} and 1320 cm^{-1}

may be assigned to the sulphur-nitrogen single and double bands

respectively.   Compounds of the type $RN = S(F)CF(CF_3)_2$ have been

studied by Dresdner at.al.[372] who suggest that for these compounds

ψ_{SN} occurs in the range 1272-1279 cm^{-1}.   For the group $-N=SF_2$

the normal absorption range[374, 375] is 1350-1400 cm^{-1} and

replacement of one F atom by the $-CF(CF_3)_2$ group might be

expected to lower ν_{SN} by only a small amount. The present

author favours assignment of the strong band at 1295-1300 cm^{-1}

to ν_{SN} for these compounds.

Compounds containing the NSO group

Compounds containing the NSO group give rise to absorptions

which are conventionally described as symmetric and asymmetric NSO

Table 9

Symmetric (ν_s) and asymmetric (ν_{as}) stretching frequencies

of -NSO compounds.

Compound type	$\nu_s (cm^{-1})$	$\nu_{as}(cm^{-1})$
RNSO[376]	1120-1135	1238-1252
ArNSO[384]	1137-1179	1272-1300 '
ArSO(NH)NMe$_2$[385]	1135-1160	1260-1270
ArSO(NH)OPh[385]	1160	1295
R$_2$SO(NH)[385]	1099	1212
(NSOF)$_n$[386]	1250	1351
RNSOF$_2$[365,387]	1219-1320	1428-1492

stretching vibrations. The positions and relative

intensities of these vibrations for the aliphatic N-sulphinyl

compounds[376,377] are similar to those observed for SO_2, which

FIG 17
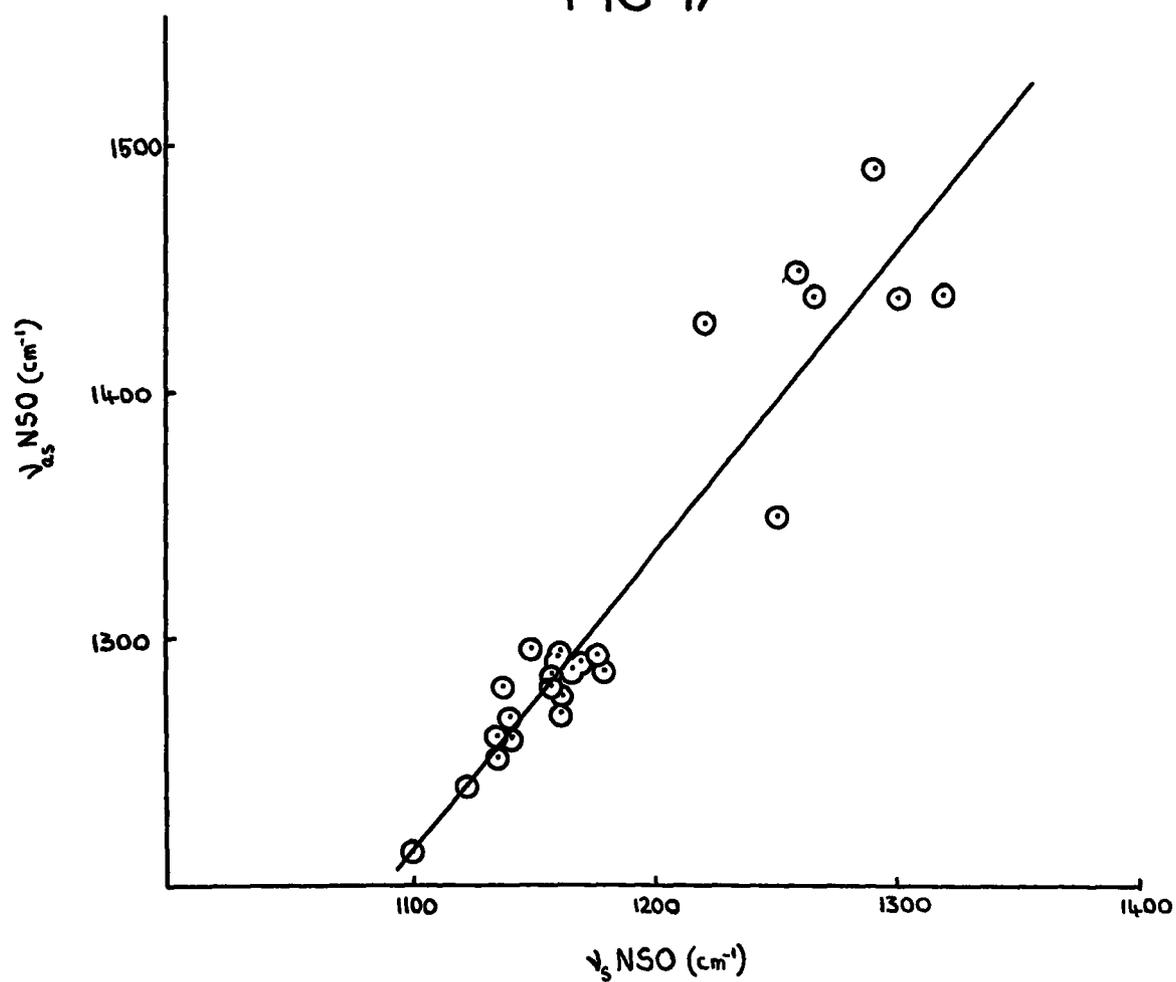
CORRELATION BETWEEN SYMMETRIC AND
ASYMMETRIC NSO FREQUENCIES

suggests[377] a similarly angled structure for the NSO group.

From measurements on N-sulphinyl methyl, ethyl and phenylamines

Glass and Pullin[376] have calculated the angle between

the NS and SO bands as about 120°. For both inorganic

and organic sulphuryl compounds Robinson[177] has shown that

there is a linear relationship between the symmetric and

asymmetric SO stretching frequencies. A similar relationship

might, therefore, be expected to hold in the case of NSO

compounds. The available data are collected in Table 9

and Fig.17. Although rather limited the data are considered

to show a satisfactorily linear relationship between the

symmetric and asymmetric stretching vibrations.

EXPERIMENTAL

(a) <u>Apparatus and techniques</u>

<u>The Nitrogen Supply</u>

As most of the compounds studied react rapidly with moist air almost all of the work was carried out in an atmosphere of dry nitrogen, either in a glove box or in apparatus so designed that counter-current techniques could be used. The nitrogen used for the counter-chrrent work was dried by passage through two efficient traps cooled in liquid nitrogen.

<u>The glove box</u>

The glove box (Lintott III.B) was set up in such a way that its nitrogen atmosphere could be recycled, by means of a small pump inside the box, through two efficient traps cooled in a Dewar vessel containing liquid nitrogen. As a further precaution against traces of moisture trays of P_2O_5 (frequently renewed) were kept in the box. The transfer tube to the glove box was thoroughly purged with nitrogen, also dried by passage through a trap immersed in liquid nitrogen, before the introduction of materials into the box.

<u>Infrared spectroscopy</u>

Infrared spectra over the range $2.5-25\mu$ ($4000-400$ cm^{-1}) were recorded on either a Grubb-Parsons GS.2A or Spectromaster prism-grating spectrophotometers. Far infrared spectra,

$21-50\mu$ $(475-200$ $cm^{-1})$ were recorded on a Grubb-Parsons

DM2/DM3 spectrophotometer.

Samples of moisture sensitive materials were prepared for

spectroscopic analysis in the glove box. Most samples

were prepared in the form of nujol mulls between potassium

bromide, sodium chloride or caesium iodide plates. Where

halogen exchange with the plates was possible, polythene

sheets were inserted between the sample and the plates.

Mass spectra

Mass spectra were recorded on an A.E.I. (M.S.9) mass

spectrophotometer. Most samples were mounted in the glove

box, onto an inert ceramic, and introduced into the ion

source using a direct insertion probe.

(b) The preparation and purification of starting materials and solvents

All solvents were purified and stored under an atmosphere

of nitrogen.

A.R. benzene, A.R. toluene, hexane and heptane were dried

by standing over sodium wire for several days.

Diethyl ether: dried initially over sodium hydroxide and

finally over sodium wire.

Nitromethane and acetonitrile: distilled from P_2O_5 and

stored over anhydrous magnesium sulphate.

Dimethylsulphoxide: twice distilled from sodium hydroxide under reduced pressure.

Carbon tetrachloride: stored over phosphorus pentoxide.

Sulphamic acid: recrystallised from water at 75°C and dried under vacuum at 60°C.

A.R. phosphorus (V) chloride: used as obtained, all loading operations carried out in the glove box.

Triphenylphosphine; vacuum sublimed at 80°C. Triphenylarsine; recrystallised from ethyl alcohol and dried under vacuum. Triphenylstibine; used as obtained after prolonged pumping under high vacuum at room temperature.

p-Toluenesulphonamide; recrystallised from water and dried by prolonged pumping under high vacuum at 50-60°C. m-Nitrobenzenesulphonamide; p-chlorobenzene-sulphonamide, p-methoxybenzenesulphonamide, benzenesulphonamide and pentafluorobenzenesulphonamide were dried by prolonged pumping under high vacuum at 50-60°C.

Thionyl chloride: fractionally distilled, first from quinoline and secondly from linseed oil. The fraction having b.pt.76-78°C/760 mm. was collected.

Sulphuryl chloride: fractionally distilled, the fraction having b.pt. 69.0-69.5°C/760 mm. being collected.

Sodium azide, potassium thiocyanate, diphenyl sulphone,

hexamethylbenzene and mercuric chloride were all dried by

prolonged pumping under high vacuum at room temperature.

Ammonium chloride: dried at $100^{\circ}C$ for 48 hours and then

pumped under high vacuum at room temperature for 8 hours.

Benzenesulphonyl chloride: dried by standing over

anhydrous magnesium sulphate for several days.

Chlor-sulphonic acid and phosphorus oxychloride: fractionally

distilled at atmospheric pressure immediately before use.

Niobium(V) chloride: heated under reflux with an

excess of pure thionyl chloride, filtered and dried under

vacuum.

Beryllium chloride: a pure, anhydrous sample was kindly

provided by Mr.P.D.Roberts.

Diphenylamine: purified by vacuum sublimation at 0.01 mm

and $60-80^{\circ}C$.

Trimethylamine: purified by vacuum distillation and stored

over sodium hydroxide.

Pyridine and triethylamine: dried by standing over sodium

hydroxide and fractionally distilled onto fresh sodium hydroxide.

iso-Quinoline was similarly purified, the distillation being

carried out under reduced pressure.

The preparation of sulphamide

(i) By the reaction between sulphuryl chloride and gaseous ammonia[388]

The ammonia was dried by passage through three 60 cm. columns

filled with, first, soda lime, secondly, potassium hydroxide and, finally, sodium wire.

Fractionally distilled sulphuryl chloride (25 ml.) was dissolved in dry petroleum ether (b.pt. $40-60°$, 800 ml.) and cooled to $0°C$ in an ice/salt bath, with constant stirring. Anhydrous ammonia was added over the surface of the stirred solution at such a rate that the solution temperature was maintained between $0-10°C$. To give satisfactory contact between the reactants the rate of stirring was ~1200 r.p.m. Reaction was complete after 60 minutes. The crude product was warmed to room temperature, the solid material separated by filtration and dried under vacuum. This solid was dissolved in the minimum amount of dilute hydrochloric acid (100 ml. H_2O/5 ml. conc. HCl), the solution warmed to $70-80°C$ for ten minutes, cooled to room temperature and the water removed by vacuum distillation. The solid product was desiccated over P_2O_5 for 24 hours and Soxhlet extracted using A.R. acetone. Vacuum removal of the solvent gave crude sulphamide, 2g., ~ 8% yield. The reaction was repeated on three further occasions the maximum yield obtained being 12% based on sulphuryl chloride.

(ii) <u>By the reaction between sulphuryl chloride and liquid ammonia</u>[24,25]

Liquid ammonia (1000 ml.) was condensed into the reaction flask and cooled to $-78°C$ in an acetone/dry ice bath. A solution

of sulphuryl chloride (100 ml.) in dry hexane (1000 ml.) was

added over four hours with constant stirring at about 1000

r.p.m.   Excess ammonia was allowed to evaporate overnight and

the solid material separated by filtration and dried under

vacuum.   The crude product (210g.) was dissolved in water

(500 ml.), acidified with concentrated HCl (25 ml.) ,

warmed to 70-80°C for 10 minutes, cooled to room temperature

and allowed to stand overnight.   The solution was then

evaporated to dryness under vacuum at 60-70°C and the product

dessicated over P_2O_5.   Extraction with A.R. acetone (3 x 400 ml.)

followed by removal of the solvent under vacuum gave crude

sulphamide, 70.5g., 62%.   Recrystallisation from propanol

gave pure sulphamide 58.5.,m.pt. 91-92°C.

Preparation of ammonium trisulphimide [389]

Sulphamide (6g.) placed in a filtration receiver tube,

the side arm of which was lightly closed with cotton wool.

The tube was heated in an oil-bath to about 100°C and, when

all of the sulphamide had melted, the temperature was raised

to 180°C over one hour.   During the second hour the temperature

was increased to 200-205°C and then maintained for four hours.

After cooling to room temperature the product is obtained as

a fused cake.   Recrystallised three times from H_2O:EtOH,(1:3)

and dried at 100°C.   Found, S= 33.61; N=29.26; H=4.09, calculated

for $(SO_2N.NH_4)_3$, S= 33.36; N=29.16; H= 4.20%.

Preparation of silver trisulphimide [389]

Ammonium trisulphimide (6g.) was dissolved in water

(60 ml.) and the solution diluted with boiling water (1500 ml.)

A solution of AgNO$_3$ (12g.) in water (150 ml.) was then added,

the solution boiled for a few minutes and filtered hot to remove

a small amount of brown precipitate.   On cooling the solution

deposited needles of silver trisulphimide trihydrate which

were removed by filtration and dried at 100°C.

The preparation of benzenesulphinic acid [390]

Benzenesulphonic acid (30g.) was dissolved in ether (150 ml.)

containing a small volume (1.5ml.) of water.   Zinc dust

(30 g.) was then added at a rate such the solution was kept

boiling briskly.   This addition was completed over one hour and

the system heated under reflux for a further hour.   The

precipitate was separated by filtration, washed twice with

water and heated with an aqueous solution of sodium carbonate

(30g./150 ml.) for one hour.   After cooling and filtering

the filtrate was neutralised with concentrated sulphuric acid.

The solid product was separated by filtration and dried under

vacuum at 30°C, m.pt. 82-83°C (reported, 83-84°C.)

The preparation of benzenesulphinyl chloride [390]

Benzenesulphinic acid (14.2g, 0.1 mole) was suspended in

ether (100 ml.) and a slight excess (0.11 mole) of thionyl chloride

added over 20 minutes at room temperature, with constant stirring.

Stirring at room temperature was continued for a further 45

minutes, the solution filtered to remove a small amount of

solid and the ether and excess thionyl chloride removed under

vacuum. The product, which crystallised on cooling, had

m.pt. 33-36°C (reported, 38°C)

The preparation of benzenesulphenyl chloride [391]

Carbon tetrachloride (150 ml.) cooled with stirring to

-10°C in an ice/salt bath. A slow stream of chlorine was

passed through the solvent whilst a solution of thiophenol

(6g.) in carbon tetrachloride (50 ml.) was added dropwise over

30 minutes. Excess chlorine and solvent were then removed

under vacuum to leave a dark red liquid. Found, Cl=25.61%,

calculated for C_6H_5SCl, Cl= 24.51%.

The preparation of NN diethylaminotrimethylsilane [392]

Trimethylchlorosilane (54g., 0.5 mole) was dissolved in

dry ether (500 ml.) and the solution added over 1 hour to a well

stirred solution of diethylamine (73 g., 1.0 mole) in dry

ether (500 ml.). The precipitated amine hydrochloride was

removed by filtration. The ether was removed from the filtrate

under vacuum and the product distilled, the fraction collected

had b.pt. 122-125°C, reported b.pt. 125-126°C.

The preparation of triphenylphosphine dichloride[393]

Triphenylphosphine (25g.) ground to a fine powder, slurried in dry hexane and cooled to -5°C in an ice/salt bath with constant stirring. A steady stream of chlorine, dried by passage through concentrated sulphuric acid, was passed over the surface of the stirred suspension. The gas flow rate was so adjusted that the gas was completely absorbed by the suspension, and the temperature was maintained at 0° to -5°C. After two hours a yellow colour, due to the presence of excess chlorine, rapidly developed. The gas flow was discontinued and excess chlorine immediately removed at a water pump. Evaporation to dryness in vacuo gave a moist, yellow solid. Whilst the yellow colour was presumably due to traces of entrapped chlorine hard pumping under high vacuum had little apparent effect. The solid was washed with 100 ml. of benzene/chloroform mixture $(1:1^{V}/v)$ to give an insoluble white solid and a yellow solution. This mixture was pumped under vacuum until the yellow colour had disappeared, after which evaporation to dryness gave a clean, white solid. This solid was washed with benzene (3 x 20 ml.) and dried under vacuum. Found, Cl=22.00%, calculated for $(C_6H_5)_3PCl_2$, Cl = 21.28%. The infrared spectrum of this compound contained bands at, 1586m, 1488 ms, 1441s, 1370ms, 1342w, 1316m, 1261m, 1181w, 1153w, 1122s, 1110s, 1095s, 996m, 939m, 939w, 868w, 761s, 748s, 728s, 697sh, 691s, 656m, 616m, 585s, 537s, 517s, 494m, 452sh, 444m.

The preparation of sulphanuric chloride

(i) The preparation of trichlorophosphazosulphuryl chloride[13]

A.R. phosphorus pentachloride (426.9g., 2.05 mole) was
pulverised in a glove box and loaded into the reaction flask.
The requisite amount of sulphamic acid (97.1g., 1.0 mole) was then
added, outside the glove box, against a counter-current of nitrogen.
Anhydrous carbon tetrachloride (50 ml.) was added to the mixture
and the whole heated in an oil-bath at 110-120°C. Evolution
of hydrogen chloride began almost immediately. Within 30 minutes
the mixture began to liquefy, and liquefaction was complete after
$2\frac{1}{2}$-3 hours. The reaction mixture was then cooled and filtered
to remove small amounts of unchanged sulphamic acid. Vacuum
distillation removed, first, the carbon tetrachloride at room
temperature, and secondly, the phosphorus oxychloride at 40-60°C.
Finally the product was pumped under vacuum at 90°C to remove
the last traces of the oxychloride and any unchanged phosphorus(V)
chloride. On cooling and filtering the trichlorophosphazosulphuryl
chloride was obtained as a colourless crystals, m.pt. 32-34°C;
reported 35-36°C. Recrystallisation from carbon tetrachloride
raised the m.pt. to 35-36°C. The infared spectrum contained
bands at, 1745m, 1639w, 1538m, 1370vs, 1204vs, 1170sh, 766s,
720w, 621sh, 601s, 572m, 535wm, 503s.

(ii) The pyrolysis of trichlorophosphazosulphuryl chloride[118]

Trichlorophosphazosulphuryl chloride (250.9g.,1.0 mole)

was placed in a two necked flask fitted with a 30 cm Vigreux

column and an inlet tube for dry nitrogen. A condenser

attached to the top of the Vigreux column lead to a receiver

cooled to about -20°C in an acetone/dry ice bath. The

system was evacuated and the nitrogen flow rate so adjusted

that the internal pressure was maintained at 2-5 mm.Hg.

The flask was heated in an oil bath to 140-150°C; the evolution

of phosphorus oxychloride which was initially slow became

more rapid after about 20-30 minutes. The oil bath was

maintained at 140-150°C for two hours and then heated to

160-170°C for 30 minutes. A total of 142g. of phosphorus

oxychloride was recovered, corresponding to a conversion of

about 92% of the starting material.

The crystalline residue was filtered in air and well

pressed out on the frit. The solid obtained was mixed with

ice water (150 ml.) to remove readily hydrolysable impurities

and then the mixture was warmed to 15°C for 10 minutes.

After filtration the solid obtained was desiccated over phosphorus

pentoxide for 24 hours. Recrystallisation from ten times its

own weight of heptane gave fairly pure α-sulphanuric chloride

(23.g., ~24% yield) which was further purified by sublimation at

120°C and 0.01mm Hg.

The filtrate left after removal of the crude α-isomer was extracted with several portions of hot heptane. The bulk of the solvent was removed under vacuum after which cooling of the solution to $0°$ to $-5°C$ gave crystals of the crude β-sulphanuric chloride. After filtration the β-isomer was purified at $40°C$ and 0.01 mm.Hg.

The preparation of the pyridine-sulphur trioxide complex[394]

Pyridine (12.4g.) was dissolved in dry chloroform (70ml.) and the solution cooled to $-10°C$ in an ice-salt bath. Freshly distilled chlorosulphonic acid (7.7g) was added with constant stirring and shaking at such a rate that the temperature remained in the range $0°$ - $5°C$. The resulting slurry was maintained at about $0°C$ for one hour, the solid separated by filtration washed with dry, ice-cold, chloroform (3 x 10 ml) and dried under vacuum. Found, C = 37.8, H = 3.0%: calculated for $C_5H_5N.SO_3$, C = 37.7, H = 3.2%. The infared spectrum contained bands at, 3125s, 3086m, 3058w, 2915w, 1631m, 1613s, 1577w, 1529m, 1477m, 1462s, 1426w, 1385w, 1304;1299 vs (doublet) 1269m, 1232m, 1156m, 1099w, 1075vs, 1062m, 1043ms, 1031w, 1017ms, 879w, 844w, 781s, 753m, 685vs, 676s, 599vs, 561s.

The complex was dissolved in dry acetonitrile and on standing at room temperature the solution slowly deposited needle-like crystals. These were separated by filtration and dried under vacuum. Found, C = 36.82; H = 3.64; N = 8.43; S = 19.41%.

$C_5H_5N.SO_3$ requires, C = 37.73; H = 3.17; N = 8.80; S = 20.41%.

The infared spectrum contained bands at, 3178m, 3106sh, 3067m,

1639sh, 1616s, 1536s, 1490s, 1342sh, 1274vs, 1220sh, 1190s,

1170sh, 1086s, 1058s, 1038vs, 1011ms, 919ms, 889sh, 858w,

784vs, 795vs, 731vs, 681vs, 652w, 613s, 588sh, 575vs, 506ms.

The preparation of the pyridine-selenyl chloride complex[395]

Selenyl chloride (3.32g.,0.01 mole) was dissolved in

dry chloroform (30 ml.) and the solution cooled to 0°C in an

ice-salt bath.   Pyridine (1.58g.,0.02 mole) was added dropwise,

with rapid stirring, over 10 minutes.   A white precipitate

formed immediately.   Dry toluene (20 ml) was added to give a heavy

slurry, the solid separated by filtration, washed with dry

chloroform (3 x 20 ml) and dried under vacuum.   Found, C = 37.10;

H = 3.02; Cl = 22.24% calculated for $SeOCl_2.2(C_5H_5N)$, C =

37.06; H = 3.11; Cl = 21.89%.   The infared spectrum contained

bands at, 3086m, 3058m, 3021m, 2994w, 1919w, 1880w, 1848w,

1694w, 1634m, 1597vs, 1572w, 1447s, 1449vs, 1351wm, 1250m,

1203s, 1155s, 1058vs, 1030vs, 1006vs, 920vs, 879s, 762vs,

746sh, 699sh, 682vs, 634vs, 621sh, 590ms, 423ms, 329s, 298s,

~220s (very broad).

The preparation of pyridine hydrochloride

Hydrogen chloride gas was dried by passage through concentrated

sulphuric acid and passed into a cooled solution of pyridine

in dry ether.   The precipitated hydrochloride was washed several

times with ether and dried under vacuum.   Found, Cl = 31.10%:

calculated for $C_5H_5N.HCl$, Cl = 30.8%.

(c). Attempted synthesis of the sulphanuric system

(i) The reaction between ammonium trisulphimide and thionyl chloride

Ammonium trisulphimide (2.88g., 0.01 mole) slurried with excess

thionyl chloride (5.5ml.) and heated under reflux at 85-95°C

for 6 hours.   Cooled to room temperature.   The solid

material was separated by filtration, washed with dry

hexane (3 x 10 ml.) and dried under vacuum.   The m.p. and

infared spectrum of this material were identical with those

of the starting material.

The reaction was repeated as above but with 10 drops of

dimethylformamide added and the product was recrystallised from

$H_2O:EtOH$ (1:3).   The purified compound decomposed at $\sim 200°C$,

with the evolution of ammonia.   The infared spectrum of

this compound contained bands at, 3175s, 3030sh, 2845sh, 1626w,

1404s, 1253m, 1190m,1117sh, 1081s, 1018m, 860m, 781w,

612s, 595sh, 550w, 532m.   The infared spectrum of the

starting material was very similar and contained bands at,

3425sh, 3175vs, 3030sh, 2841sh, 1634wm, 1404s, 1242s, 1217sh,

1143s, 1081s, 1047s, 825s, 760w, 672 and 667m (doublet)

595sh, 575s.

(ii) The reaction between silver trisulphimide and thionyl chloride

Silver trisulphimide trihydrate (3.06g.,0.005mole) treated,

at room temperature, with an excess of thionyl chloride (2 ml.)

After the initial reaction due to dehydration had occurred the mixture was heated under reflux at 85-95°C for 3 hours.   The system was cooled to room temperature and the residual precipitate separated by filtration, washed with thionyl chloride (2 x 2ml) then with toluene (3 x 5 ml.) and dried under vacuum.   Found, Cl = 25.1%l calculated for AgCl, Cl = 24.8%.   This material was completely transparent in the infrared region.   Evaporation of the filtrate to dryness under vacuum gave a red-brown oil, insoluble in hexane, toluene, carbon tetrachloride and ether, slightly soluble in anhydrous ethyl alcohol.   The infared spectrum of this oil contained bands at, 3426s, 3401s, 3322s, 3289s, 3205s, 1610w, 1527wm, 1379sh, 1348vs, 1307w, 1179sh, 1147vs, 957vw, 889s, 741w, 617w, 576m, 534s.

(iii) The reaction between thionyl chloride and sodium azide

To sodium azide (6.5g.,0.1mole) was added a solution of thionyl chloride (11.9g.,0.1mole) in dry benzene (50ml) and the mixture heated under reflux at 85-95°C for six hours.   The residual solid was separated by filtration and the filtrate vacuum distilled to remove benzene and unchanged thionyl chloride. The residue from the distillation was a very small amount of a dark red-brown, viscous oil which was not investigated further.

The reaction was repeated in the absence of solvent and worked up as above.   Again only traces of a red-brown, viscous oil were obtained.

(iv) <u>The reaction between benzenesulphinyl chloride and</u>
<u>sodium azide</u>

Benzenesulphinic acid chloride (1.6g., 0.01 mole) and

sodium azide (0.65, 0.01 mole) were heated under reflux at

110-120°C for 6 hours. After cooling to room temperature

the mixture was filtered and the filtrate was shown by

infrared spectroscopy to be unchanged benzenesulphinylchloride.

(v) <u>The reaction between benzenesulphenyl chloride and</u>
<u>sodium azide</u>

Benzenesulphenyl chloride (1.4g.,0.01 mole) and sodium

azide (0.65g.,0.01 mole) were heated under reflux

at 130-140°C for 8 hours. After cooling to room temperature

the mixture was allowed to stand for 48 hours. The solid

residue was separated by filtration. The filtrate, a red

liquid, was shown by infrared spectroscopy to be unchanged

benzenesulphenylchloride.

(vi) <u>The reaction between p-toluenesulphonamide and sulphamic acid</u>

p-Toluenesulphonamide (3.42g.,0.02 mole) and sulphamic

acid (2.91g., 0.03 mole) were mixed together and heated at

190-205°C for 16 hoũrs. After cooling to room temperature

the reaction residue was extracted with benzene (2 x 15 ml).

Removal of the solvent under vacuum gave a very small amount

of a cream coloured solid, m.pt. ∼ 80°(dec), the infrared

spectrum of which bore no resemblance th that of sulphanuric

chloride.

(vii) <u>The reaction between thionyl chloride and ammonium chloride</u>

Ammonium chloride (5.4g., 0.1 mole) and thionyl chloride

(47.6g., 0.4 mole) were mixed together and heated at $90-95^{\circ}$C

for 22 hours. After cooling to room temperature the solid

residue was separated by filtration, washed with hexane

(3 x 10 ml.) and dried under vacuum (5.3g.) The infrared spectrum

of this solid contained only bands due to the NH_4^+ ion.

(viii)(a) <u>The reaction between p-toluenesulphonamide and</u>
<u>phosphorus(V) chloride</u> 396

p-Toluenesulphonamide (30.1g., 0.175 mole) and A.R.

phosphorus(V) chloride (36.6g., 0.175 mole) were well mixed

and dry carbon tetrachloride (20 ml.) added. The mixture

was heated in an oil bath at $100-110^{\circ}$C. Evolution of hydrogen

chloride began immediately and the mixture began to liquefy

after about 15 minutes. After heating for one hour the

solution was allowed to cool to $40-50^{\circ}$C and the solvent was

removed under vacuum. The liquid product was heated, under

vacuum, at $90-100^{\circ}$C for 15 minutes to remove any unchanged

phosphorus(V) chloride. On cooling the product solidified

and was recrystallised from carbon tetrachloride. Found,

C = 27.63; H=2.43; Cl-35.20%; calculated for $CH_3.C_6H_4SO_2N$:

PCl_3, C = 27.41; H = 2.30; Cl= 34.71%. m.pt., $105-106^{\circ}$C,

reported 196°C. The infrared spectrum of this compound contained

bands at, 3049s, 2967s, 2916s, 2865w, 2463m, 2404m, 2299w, 2242w,

1961m, 1923m, 1811w, 1757w, 1656w, 1595m, 1492m, 1451sh, 1447vs, 1399w,

1379w, 1316s, 1300s, 1258m, 1202s, 1150vs, 1117m, 1087s, 1043sh,

1017m, 953w, 846m, 812s, 800ms, 762s, 729sh, 705m, 670m, 621s,

590s, 560ms, 515m, 505m.

(b) <u>Pyrolysis of the product, p-tolytrichlorphosphazosulphone</u>

p-Tolytrichlorphosphazosulphone (30.7g., 0.1 mole) was

placed in a two necked flask fitted with a 30 cm Vigreux column

and an inlet tube for dry nitrogen.   A condenser attached to the

top of the Vigreux column lead to a receiver cooled to about

-20°C in an acetone/dry ice bath.   The system was evacuated

and the nitrogeh flow rate so adjusted that the internal pressure

was maintained at 2-5mm.Hg.   The flask was then heated in an

oil bath to 190-200°C.

After about 3 hours the slow distillation of a very

pale yellow liquid began; the temperature of the vapour was

36-38°C.   This distillation continued for about 1 hour,

the residue in the distillation flask becoming progressively

more viscous during this time.   When distillation seemed

complete the compound was allowed to cool to room temperature

under an atmosphere of nitrogen.

The distillate (8g.) had an infrared spectrum identical

with that of an authentic sample of phosphorus oxychloride.

On cooling, the residue in the distillation flask solidified

to a black, glassy mass which was repeatedly extracted with dry

benzene. Removal of the solvent under vacuum gave a pale-brown solid (8.5g.) which was purified by sublimation at 0.005mm. and 60-70°C. Found, C = 43.36; H = 3.56%, calculated for $CH_3C_6H_4SO_2Cl$, C = 44.07; H = 3.71%. The infrared spectrum of this material was identical with that of an authentic sample of p-toluenesulphonylchloride.

The benzene, insoluble material was insoluble in hexane, acetone, acetonitrile, carbon tetrachloride, chloroform, ethyl alcohol, ethyl acetate and carbon disulphide, but was soluble in dimethyl sulphoxide and dimethylformamide. When treated with benzene it 'softened' to a rubber like material which regained its original hardness on drying. The infared spectrum of this material contained bands at, 3030m, 1639w, 1590ms, 1492sh, 1447sh, 1379sh, 1250vs, 1170vs, 1093sh, 1011m, ~910ms (very broad), 810m, 702w, 678m, ~660w, ~550s (very broad).

(ix) The reaction between m-nitrobenzenesulphonamide and phosphorus(V) chloride

m-Nitrobenzenesulphonamide (28.3g.,0.140 mole) and A.R. phosphorus(V) chloride (29.2g., 0.140 mole) were well mixed and dry carbon tetrachloride (20ml.) added. The mixture was then heated in an oil bath at 100-110°C. The slow evolution of hydrogen chloride began immediately and the mixture began to liquefy after about 30 minutes. The reaction

was complete after 2 hours when the solution was cooled

to 40-50°C and the solvent removed under vacuum.   On cooling

the product solidified and was recrystallised three times

from carbon tetrachloride.   Found, C = 21.2; H = 1.5;

N = 8.4; Cl = 30.1%: $O_2N.C_6H_4SO_2N:PCl_3$ requires, C = 21.4;

H = 1.2; N = 8.3; Cl = 31.5%. m.pt. 68-69°C.   The infrared

spectrum of this compound contained bands at, 3115s, 3096sh,

3058w, 2865m, 1931w, 1776w, 1748w, 1613s, 1587m, 1548vs,

1529vs, 1468s, 1431s, 1353vs, 1325vs, 1295sh, 1269sh, 1189sh,

1164vs, 1148s, 1120s, 1081s, 1065s, 1010m, 995m, 934m, 906m,

880vs, 858sh, 818s, 788vs, 745s, 720vs, 637s, 585s, 553s,

510m, ∼474m, ∼437m.

(x)(a) <u>The reaction between p-chlorobenzenesulphonamide and</u>
        <u>phosphorus(V) chloride</u>

p-Chlorobenzenesulphonamide (28.1g.,0.147mole) and A.R.

phosphorus(V) chloride (30.5g.,0.147 mole) were well mixed and

dry carbon tetrachloride (20 ml.) added.   The mixture was

then heated at 100-110°C for one hour after which time liquefaction

was complete.   The solution was cooled to 40-50° C and the

solvent removed under vacuum.   On cooling, the product

solidified and was recrystallised twice from carbon tetrachloride.

Found, C = 22.6; H = 1.4; N = 4.5; Cl = 43.0%. $ClC_6H_4SO_2N$:

PCl_3 requires, C = 22.0; H = 1.2; N = 4.3; Cl = 43.4% m.pt.65-66°C.

The infrared spectrum of this compound contained bands at,

3096m, 1923wm, 1923wm, 1589ms, 1582ms, 1563sh, 1473s, 1397s,

1325s, 1290sh, 1280s, 1214vs, 1172sh, 1152vs, 1088vs, 1012s,

954w, 839s, 824s, 784vs, 743s, 705ms, 643sh, 617s, 595sh,

548s, 521s, ~ 483m, ~425m.

(x)(b) <u>Pyrolysis of the product, p-chlorophenyltriphlorphosphazosulphone</u>

p-Chlorophenyltrichlorphosphazosulphone (32.7g., 0.1 mole)

was placed in a two necked flask fitted with a 30 cm. Vigreux

column and an inlet tube for dry nitrogen.   A condenser attached

to the top of the Vigreux column lead to a receiver cooled to

about -20°C in an acetone/dry ice bath.   The system was evacuated

and the nitrogen flow rate so adjusted that the internal pressure

was maintained at 1-3 mm.Hg. The flask was then heated in an oil-

bath at 210-230°C for 6 hours, after which time the system was

allowed to cool to room temperature under an atmosphere of nitrogen.

Only a very small amount of ($\leqslant$1m.) of distillate had

collected in the condenser receiver and this had an infrared

spectrum identical with that of an authentic sample of phosphorus

oxychloride.   The residue from the distillation flask was twice

recrystallised from carbon tetrachloride.   Found, C = 23.1; H = 1.32;

Cl = 43.6%: calculated for $Cl.C_6H_4SO_2N:PCl_3$, C = 22.0; H = 1.2;

Cl = 43.4%.   The infared spectrum of this material was identical

with that of the pure starting material.

(xi) **The reaction between p-methoxybenzenesulphonamide and phosphorus(V) chloride**

p-Methoxybenzenesulphonamide (23.8g., 0.127 mole) and

A.R. phosphorus(V) chloride (26.5g., 0.127 mole) were well

mixed and dry carbon tetrachloride (20 ml.) added.   The mixture

was then heated in an oil-bath at 100-110°C for one hour, after

which time liquefaction was complete.   After cooling to 40-50°C

the solvent was removed under vacuum and the solid product

was twice recrystallised from carbon tetrachloride.   Found,

C = 25.4; H = 2.3; N = 4.2; Cl = 32.4%: $CH_3OC_6H_4SO_2N:PCl_3$

requires, C = 26.1; H = 2.2; N = 4.3; Cl = 33.0%. m.pt. 82-83°C.

The infrared spectrum of this compound contained bands at,

3015m, 3067w, 3030wm, 2994s, 2950s, 2915m, 2849m, 1964m,

1931m, 1916m, 1887m, 1783w, 1689w, 1661m, 1631w, 1600s, 1582s,

1563sh, 1504vs, 1464s, 1451sh, 1445s, 1412m, 1379w, 1315vs,

1299vs, 1266vs, 1212s, 1176s, 1152s, 1088s, 1018vs, 944w, 841s,

822m, 816sh, 807s, 754s, 722sh, 633s, 620s, 584sh, 570s, 543ms,

513m, 451m, 445sh, ∿410m.

(xii) **The reaction between p-toluenesulphonamide and triphenylphosphine dichloride**[397]

p-Toluenesulphonamide (12.3g., 0.072mole) and triphenylphosphine-

dichbride (23.9g., 0.072 mole) were well mixed and heated in an

oil-bath at 140-150°C for $2\frac{1}{2}$ hours.   On cooling, the viscous

liquid set to a glassy solid which was recrystallised four times

from toluene. During the first crystallisation the hot solution

was filtered to remove a small amount of unchanged starting

material. Found, C = 69.22; H = 5.61%: calculated for

$CH_3C_6H_4SO_2N:P(C_6H_5)_3$, C = 69.52; H = 5.15%. m.pt. 187-188°C

(reported 186-187°C). The infrared spectrum of this compound

contained bands at 3367m, 3268m, 3067w, 3030w, 2924w, 1923w,

1605m, 1590m, 1534w, 1492m, 1486ms, 1443s, 1399w, 1368w, 1335w,

1309m, 1290w, 1266vs, 1253sh, 1178m, 1163sh, 1151vs, 1139s, 1112s,

1105sh, 1085m, 1029w, 1017w, 999m, 909w, 853w, 837w, 820ms,

813ms, 787m, 763ms, 749ms, 725s, 707sh, 694s, 681m, 654m, 579m,

560s, 529sh, 522vs, 487w.

(d) **Reactions between α-sulphanuric chloride and donor molecules**

(i,a) **The reaction between α-sulphanuric chloride and pyridine**

Pyridine (0.48g., 0.006 mole) was added, at room temperature,

to a solution of α-sulphanuric chloride (0.59g., 0.002 mole)

in toluene (10ml.) An immediate turbidity was formed and a

pale-yellow oil was slowly deposited from the solution. After

24 hours at room temperature the oil had darkened to a golden-

red colour and was very viscous. The solvent was removed by

careful decantation and the oil washed with toluene (3 x 10 ml.),

then chloroform (2 x 10ml.) and dried under vacuum. Found,

C = 31.8; H = 3.0; N = 15.3; S = 20.1; Cl = 20.1%: $3(C_5H_5N)$.

$(NSOCl)_3$ requires, C = 34.0; H = 2.9; N = 15.9; S = 18.2; Cl = 20.2%.

The product was insoluble in hexane, toluene, chloroform, carbon
disulphide, ethyl alcohol and acetone. Hydrolysis with sodium
hydroxide solution followed by ether extraction gave a liquid
which was identified as pyridine from its infrared spectrum
and elemental analysis. The infrared spectrum of the adduct
contained bands at, 3058s, 3012s, 2941m,~2597s (very broad),
2083ms, 1643m, 1613s, 1538s, 1488s, 1408w, 1385m, 1300vs, 1253sh,
1198sh, 1166s, 1122s, 1110sh, 1059vs, 1011s, 930sh, 813ms, 800ms,
750s, 702sh, 681vs, 659s, 636w, 609ms, 569s, 529ms, 524ms, 489w.

The adduct was dissolved in dimethylsulphoxide and an excess
of toluene added to give a new oil, the infrared spectrum of
which contained bands at, 3067sh, 2994s, 2915m, ~2600ms (very
broad), 2089ms, 1634m, 1613ms, 1536m, 1486s, 1433s, 1418sh, 1350sh,
1330sh, 1300s, 1250sh, 1221s, 1161s, 1134s, 1045vs, 1015sh,
953s,~ 855s (broad), 752s, 733sh, 684s, 667w, 610m, 580s,
559s, 530w, 488ms.

(i,b) <u>Pyrolysis of the adduct</u> $3(C_5H_5N).$ $(NSOCl)_3$

The adduct was heated at 70-80°C under a pressure of ~2mm.
Hg. and the pyrolysis product collected on a cold finger cooled
to -78°C with an acetone-dry ice mixture. The product, a white
solid, was resublimed a further two times. Found, C = 41.3;
H = 3.86; Cl = 23.81. The infared spectrum contained bands at,
3125sh, 2597s(very broad), 2092s, 2028sh, 1653sh, 1631s, 1610vs,

1529s, 1501w, 1547s, 1412s, 1338s, 1333ms, 1304m, 1269w, 1248ms,

1192ms, 1165m, 1148m, 1135m, 1110w, 1081m, 1053s, 1040sh, 1021sh,

1002s, 915ms, 875w, 832m, 820m, 810vs, 705w, 676vs, 669sh,

664sh, 607s, 529m, 516sh, 485m, 444sh, 430wm (broad).

Hydrolysis followed by ether extraction gave pyridine which was

identified by its infrared spectrum and elementary analysis.

(iii,a) <u>The reaction between α-sulphanuric chloride and iso-quinoline</u>

α-Sulphanuric chloride (0.59g., 0.002 mole) was dissolved

in toluene (10 ml.) and a solution of iso-quinoline (0.77g.,

0.006mole) in toluene (10 ml.) added at room temperature. The

separation of a pale-yellow oil began immediately. The

reaction was complete in one hour, after which time the oil had

darkened to a red-brown colour. The solvent was removed by

careful decantation, the oil washed with toluene (3 x 10ml.)

and dried under vacuum. Found, C = 47.5; H = 3.6; Cl = 16.1%;

$3(C_9H_7N).(NSOCl)_3$ requires, C = 47.7; H = 3.1; Cl = 15.6%. The

solubilities of this compound were similar to those of the

corresponding pyridine compound. The infared spectrum

contained bands at, 3086sh, 3012s, 2976sh, 2604s(very broad),

2299sh, 1066ms, 1642s, 1611s, 1590w, 1543m, 1493m, 1477m,

1408sh, 1387s, 1370ms, 1357ms, 1342sh, 1297vs, 1274sh, 1253sh,

1238sh, 1215w, 1165s, 1136sh, 1120s, 1059s, 1033sh, 1011sh,

990sh, 977ms, 970sh, 945w, 922w, 866m, 824s, 799s, 772m, 747m,

700sh, 683s, 657s, 601w, 623w, 610s, 539sh, 525m, 508s, 474s.

Hydrolysis with sodium hydroxide solution followed by ether

extraction gave iso-quinoline which was identified by its

infrared spectrum and elemental analysis.

The adduct was dissolved in dimethylsulphoxide and

an excess of toluene added.   The red-brown solution was decanted

from the precipitated oil and evaporated under vacuum to give

a red-brown solid.   This solid was twice recrystallised from a

dimethylsulphoxide-toluene mixture.   Found, C = 38.8;

H = 3.7; N = 9.8; Cl = 16.8%: $2(C_9H_7N).(CH_3)_2SO.(NSOCl)_3$

requires, C = 38.2; H = 3.2; N = 11.1; Cl = 16.9%.   The

infrared spectrum contained bands at, 3226w,, 3030sh, 2976s,

2898m, 2618s, 2398w, 2105wm, 2058wm, 1653s, 1639vs, 1607s, 1541m,

1490m, 1433ms, 1418m, 1408m, 1391m, 1374m, 1355w, 1311s, 1282m,

1259m, 1131w, 1086w, 1047sh, 1033s, 1010ms, 945ms, 910vs, 855ms,

833ms, 800ms, 754w, 723s, 680wm, ∿560wm (broad), 508m, 484w,

473w.

(ii,b) Pyrolysis of the adduct, $3(C_9H_7N).(NSOCl)_3$

The adduct was heated at 70-80°C under a pressure of 1-2

mm.Hg. and the pyrolysis product collected on a cold finger

cooled to -78°C with an acetone-dry ice mixture.   The product,

a white solid, was resublimed and then recrystallised from a

dimethylsulphoxide-toluene mixture.   Found, C = 55.85; H = 3.64;

Cl = 1670%. The infrared spectrum contained bands, at 3076sh,

3030sh, 2353s (very broad), 2060 ms, 1639s, 1610s, 1587sh, 1538w,

1488sh, 1408w, 1361s, 1333sh, 1287m, 1272wm, 1250w, 1220w,

1170sh, 1149ms, 1053wm, 1033w, 1012w, 966m, 947w, 922w, 868m,

837s, 800ms, 769w, 754s, 727s, 623ms, 538w, 512s, 506sh, 473s.

Hydrolysis with sodium hydroxide solution followed by ether

extraction gave iso-quinoline which was identified by its infrared

spectrum and elementary analysis.

(iii) <u>The reaction between α-sulphanuric chloride and trimethylamine</u>

α-Sulphanuric chloride (0.59g., 0.002 mole) was dissolved

in toluene and the solution cooled in liquid nitrogen.   An

excess ($\sim$ 270 N.c.c, $\sim$ 0.012 mole) of trimethylamine was condensed

into the flask, which was then kept at $-25^{\circ}C$ for 4 hours.

The solid product was separated by filtration, washed with

toluene (3 x 10 ml.) and dried under vacuum.   Found, C = 23.6;

H = 5.9; Cl = 21.1%: $3\left[(CH_3)_3N\right].(NSOCl)_3$ requires, C = 23.2;

H = 5.8; Cl = 22.7%.   The infrared spectrum contained bands

at, 2725sh, 2667sh, 2631s, 2481m, 1634w, 1481s, 1456vs,

1425w, 1330s, 1312s, 1263w, 1245m, 1185m, 1136s, 1076s, 1052m,

991ms, 966sh, 953m, 813w, 773m, 738sh, 722wm, 690m, 639w,

614wm, 594s, 559m, 515m.

(iv) <u>The reaction between α-sulphanuric chloride and triphenylphosphine</u>

To a solution of α-sulphanuric chloride (0.59g., 0.002 mole)

in toluene (5 ml.) was added, at room temperature, a solution of

triphenylphosphine (1.57g., 0.006 mole) in toluene (5 ml.)

A golden red oil slowly separated from the solution. The

reaction seemdd complete after 22 hours. The solvent was

removed by decantation and the extremely viscous oil was washed

with toluene (3 x 10 ml.) and dried under vacuum. Found, C =

61.5; H = 4.7; Cl = 9.2%: $\left[(C_6H_5)_3P\right]_3 \cdot (NSOCl)_3$ requires,

C = 60.1; H = 4.2; Cl = 9.9%. Insoluble in hexane, toluene,

chloroform and carbon tetrachloride. The compound dissolved

in nitromethane, and toluene added to give triphenylphosphine

dichloride, which was identified by its infrared spectrum and

elemental analysis.

(e) Reactions between other sulphur(VI) compounds and donor molecules

(i) The reaction between pyridine and sulphuryl chloride

   (a) Preparation of the 2:1 adduct, $2(C_5H_5N)SO_2Cl_2$

Sulphuryl chloride (4.05g., 0.03 mole) was dissolved in dry

heptane (20 ml.) and cooled to $0^\circ C$ in an ice bath. An excess

of pyridine (10 ml.) was added over 5 minutes with vigorous

stirring. A pale-yellow oil began to separate immediately.

The mixture was allowed to warm to room temperature and was

maintained at this temperature, with constant stirring, for

3 hours. During this time the oil darkened to a red-brown

colour and its viscosity greatly increased. The solvent was

removed by decantation and the oil washed with dry heptane

(3 x 20ml.) then with dry chloroform (2 x 20 ml.) and dried

under vacuum.

When dry the oil was very viscous and 'frothed' badly under

vacuum.   Found, C = 42.40; H = 3.70; Cl = 25.79%: $2(C_5H_5N)$.

SO_2Cl_2 requires, C = 41.27; H = 3.44; Cl = 24.15%.   The

infrared spectrum contained bands at 3125sh, 3058s, 3021sh,

2932m, 2849w, ~ 2500s, (very broad), 2096ms, 1618s, 1595vs,

1520s, 1475vs, 1464sh, 1403s, 1374m, 1328sh, 1271s, 1244s,

1182s, 1156m, 1115ms, 1105sh, 1049ms, 1019w, 993vs, 928w,

901w, 887w, 870w, 838m, 819m, 789ms, 751vs, 723w, 679vs, 659sh,

636sh, 606s, 588ms, 552sh, 524ms.   On standing for about

24 hours the oil began to solidify and after about 7 days had

set to a solid mass.

(b) **Pyrolysis of the adduct**

The oily adduct was heated at 90-100°C under a pressure

of 0.01mm.Hg and the decomposition product was collected on a

cold finger cooled with liquid nitrogen.   The white solid

collected on the cold finger was purified in the following

manner.   The solid was dissolved in nitromethane and toluene

added in portions to the solution.   During the initial stages

of the addition the compound separated as an oil but as the

solution became more dilute, crystals began to separate.   At

this stage the solution was separated from the oil and further

diluted with toluene.   The crystals so obtained were similarly

recrystallised a further two times and were dried under vacuum.

Hydrolysis with sodium hydroxide solution followed by ether

extraction gave a liquid which was identified as pyridine by its

infrared spectrum and elemental analysis.　Analysis of the

recrystallised product gave, C = 46.24; H = 4.98; N = 10.71; Cl =

28.05%.　The infrared spectrum, which was identical with that

of the crude product, contained bands at, 3134w, 3095w, 3049s,

~2410s (very broad) 2096ms, 1631ms, 1621w, 1605s, 1529s, 1504sh,

1488s, 1387wm, 1342w, 1316m, 1242ms, 1202wm, 1161m, 1104m,

1055ms, 1026w, 1001s, 942m, 837w, 814ms, 749vs, 722sh, 680vs,

668sh, 609s.

(c) **Attempted preparation of the 1:1 adduct,** $C_5H_5N.SO_2Cl_2$

Sulphuryl chloride (4.05g., 0. 03 mole) was dissolved in

dry heptane (20 ml.) and cooled to 0^oC in an ice bath.　Pyridine

(2.37g., 0.03 mole) was added with vigorous stirring.　A

pale-yellow oil began to separate immediately and was worked up

as in (a) above.　Found, C = 40.10; H = 3.35; Cl = 26.00%:

$2(C_5H_5N).SO_2Cl_2$ requires, C = 41.27; H = 3.44; Cl = 24.15%.

(ii) The reaction between triethylamine and sulphuryl chloride

Sulphuryl chloride (2.70g., 0.02 mole) was dissolved in

dry toluene (10 ml.) and cooled to 0^oC in an ice bath.　A

solution of triethylamine (2.02g., 0.02 mole) in dry toluene

(10 ml.) was added over 10 minutes with vigourous stirring.

A rapid, exothermic, reaction occurred with the formation of a white

precipitate.   The precipitate was separated by filtration,

washed with dry toluene (3 x 10 ml.), dried under vacuum and

recrystallised twice from a nitromethane-toluene $(1:2^{v}/v)$

mixture.   Found, C = 52.19; H = 11.14; N = 9.43; Cl = 24.60%:

calculated for $(C_2H_5)_3N.HCl$, C = 52.34; H = 11.73; N = 10.17;

Cl = 25.75%.   Evaporation to dryness of the original filtrate

gave traces of a red-brown oil.

(iii) The reaction between triphenylphosphine and sulphuryl chloride

(a) Preparation of the 1:1 adduct, $(C_6H_5)_3P.SO_2Cl_2$

Triphenylphosphine (7.86g., 0.03 mole) was dissolved in

dry heptane (20 ml.) and a solution of sulphuryl chloride

(4.05g., 0.03 mole) in dry heptane (10 ml.) was added over 10

minutes, with constant stirring, at room temperature.   A

mildly exothermic reaction occurred and a pale-yellow, mobile

oil separated slowly from the solution.   The solution was allowed

to stand overnight at room temperature.   The solvent was removed

by careful decantation and the oil washed with dry heptane (2 x 10 ml.)

dissolved in dry chloroform (20 ml.) and reprecipitated by the

addition of heptane (20 ml.)   On standing for 5 minutes the

oil solidified.   The solid was separated by filtration, washed

with dry heptane (2 x 10 ml.) and dried under vacuum.   Found,

C = 53.46; H = 3.23; Cl = 16.84%: $(C_6H_5)_3P.SO_2Cl_2$ requires, C =

54.43; H = 3.81; Cl = 17.84:. m.pt. 60-80°C.

To the solid product was added chloroform (20 ml.), a

large proportion of the solid was insoluble, even in the boiling

solvent. The insoluble portion was separated by filtration

and dried under vacuum. Found, C = 53.61; H = 3.26; Cl =

18.91%: $(C_6H_5)_3P.SO_2Cl_2$ requires, C = 54.43; H = 3.81;

Cl = 17.84% m.pt., 180°(dec). The product was insoluble in

hot toluene, hexane and carbon tetrachloride. The infrared

spectrum contained bands at, 3082w, 3058w, 2481m, 1919w, 1835w,

1695w, 1580s, 1570sh, 1479s, 1438vs, 1342wm, 1314ms, 1263s,

1188wm, 1161wm, 1145w, 1107vs, 1099s, 1072w, 1031w, 996s,

853w, 760vs, 747vs, 727vs, 697sh, 669sh, 656s, 616s, 565s,

535m, 513ms.

The filtrate containing the chloroform soluble portion

was evaporated to small bulk (~5 ml.) and hexane (20 ml.) was

added. A colourless oil separated. The solvent was removed

by careful decantation and the oil dried under vacuum. Found,

C = 53.32; H = 3.24; Cl = 18.70%: $(C_6H_5)_3P.SO_2Cl_2$ requires,

C = 54.43; H = 3.81; Cl = 17.84%. On standing several days

the oil slowly solidified, m.pt. 65-70°C. The infrared

spectrum contained bands at, 3158w, 3086m, 3062m, 3021m, 2915w,

2869w, 2519vw, 2309vw, 2203vw, 1908vw, 1818vw, 1681vw, 1605m,

1582s, 1493s, 1481s, 1435vs, 1332sh, 1312sh, 1279vs, 1185wm,

1163wm, 1120sh, 1106vs, 1096sh, 1077w, 1040vs, 1026w, 993m,

935w, 749s, 729vs, 696s, 685s, 617s, 578s, 536vs, 513s.

(b) <u>Pyrolysis of the chloroform insoluble product</u>

The solid was heated at 170-180°C under a pressure of

0.01mm.Hg and the decomposition products were collected on a

cold finger cooled to -78°C with an acetone-dry ice mixture.

A white solid collected on the cold finger and traces of a

liquid collected on the upper part of the flask. The solid

material after removal from the cold finger was subjected to

prolonged pumping under high vacuum. Its infrared spectrum

was identical with that of the starting material.

(c) <u>Attempted preparation of the 2:1 adduct</u>, $[(C_6H_5)_3P]_2 \cdot SO_2Cl_2$

Triphenylphosphine (7.86g., 0.03 mole) was dissolved in

dry heptane (20 ml.) and a solution of sulphuryl chloride

(2.03g., 0.015 mole) in dry heptane (5 ml.) was added over

5 minutes at room temperature. The pale-yellow oil which

separated from the solution was worked up as in (ɑ) above.

Found, C = 53.91; H = 3.12; Cl = 17.63%: $(C_6H_5)_3P \cdot SO_2Cl_2$

requires, C = 54.43; H = 3.81; Cl = 17.84%.

(iv) <u>The reaction between triphenylstibine and sulphuryl chloride</u>

Triphenylstibine (3.35g., 0.01 mole) was dissolved in

dry toluene (10 ml.) and cooled to 0°C in an ice-salt bath.

A solution of sulphuryl chloride (1.35g., 0.01 mole) in dry

toluene (10 ml.) added over 10 minutes with constant stirring.

The solution was allowed to warm to room temperature and dry

hexane (20 ml.) added. Colourless crystals were deposited

immediately and were separated by filtration, washed with dry

hexane (2 x 10 ml.) and dried under vacuum. Found, C = 50.52;

H = 3.94; Cl = 16.02%: calculated for $(C_6H_5)_3SbCl_2$, C = 50.98;

H = 3.57; Cl = 16.73%.

(v) <u>The reaction between triphenylarsine and sulphuryl chloride</u>

Triphenyl arsine (3.06g., 0.01 mole) was dissolved in

dry toluene (10 ml.) and cooled to $0^\circ C$ in an ice-salt bath.

A solution of sulphuryl chloride (1.35g., 0.01 mole) in dry

toluene (10 ml.) was added over 10 minutes with constant stirring.

Colourless crystals separated during the addition. These were

separated by filtration, washed with dry, ice-cold toluene

(2x5 ml.) and dried under vacuum. Found, C = 57.89; H = 4.20;

Cl = 17.95%: calculated for $(C_6H_5)_3AsCl_2$, C = 57.32; H = 4.02;

Cl = 18.80%.

(vi) <u>The reaction between pentafluorobenzene sulphonamide and pyridine</u>

Pentafluorobenzene sulphonamide (2.47g., 0.01 mole) mixed

with an excess of pyridine (5 ml.) and warmed to $50-55^\circ C$, at

which temperature the sulphonamide was soluble. A deeply orange

coloured solution was obtained. The solution was maintained at $50-55^\circ C$

with constant stirring, for 4 hours, cooled to room temperature,

dry toluene (40 ml.) added, the precipitate separated by filtration

washed with dry heptane (2 x 10 ml.) and dried under vacuum.

The solid material had an infrared spectrum identical with

that of pentafluorobenzene sulphonamide, and a mixed melting

point confirmed it as unchanged starting material.

(vii) The reaction between diphenyl sulphone and pyridine

Diphenyl sulphone (2.18g., 0.01 mole) was dissolved in

dry toluene and an excess of pyridine (5 ml.) added over 5

minutes at room temperature with constant stirring. The

temperature of the solution rose to 40-50°C during the addition;

when the solution had returned to room temperature dry heptane

(50 ml.) was added, and the white crystals obtained were

separated by filtration and dried under vacuum. A mixed melting

point showed these to be unchanged diphenyl sulphone.

(viii) The reaction between sulphamide and pyridine

Sulphamide (0.96g., 0.01 mole) dissolved in an excess of

pyridine (8 ml.) and maintained at room temperature for 17 hours.

The solution was then warmed to 50-60°C for 30 minutes after which

time an excess of dry toluene (50 ml.) was added. The

resultant precipitate was separated by filtration, washed with

toluene (10 ml.) and then with hexane (10 ml.) and dried under

vacuum. A mixed melting point showed the solid to be unchanged

sulphamide.

(ix) <u>The Reaction between benzene sulphonamide and pyridine</u>

Benzene sulphonamide (3.14g., 0.02 mole) was mixed with

pyridine (3.16g., 0.04 mole) and warmed to 75-85° at which

temperature the sulphonamide was completely soluble. The

solution was maintained at this temperature for 24 hours, cooled

to room temperature and dry toluene (20 ml.) added. After

filtration the solid material was washed twice with dry toluene

(10 ml.) and dried under vacuum. A mixed melting point showed

the solid to be unchanged benzene sulphonamide.

(x) <u>The reaction between benzenesulphonyl chloride and pyridine</u>

(a) <u>Using only a small excess of pyridine</u>

Benzenesulphonyl chloride (3.53g., 0.02 mole) was dissolved

in dry heptane (10 ml.) and a solution of pyridine (1.96g.,

0.025 mole) in dry heptane (10 ml.) added over 5 minutes, with

constant stirring at room temperature. After some 30 minutes

a very faint turbidity developed. The reaction was

maintained at room temperature for a further 4 hours, with only

little increase in the volume of precipitate. The solution

was then warmed to 50-60° for 30 minutes and, after cooling

to room temperature, filtered. Only mg. quantities of solid

material was obtained and this had m.pt., 128-130°C.

(b) <u>Using a large excess of pyridine</u>

Benzene sulphonyl chloride (3.53g., 0.02 mole) was dissolved
in dry toluene (10 ml.) and pyridine (12 ml.) added over 10
minutes, with constant stirring, at room temperature. The
solution was maintained at room temperature for 72 hours, after
which time it was evaporated to small volume (~2 ml.) under
vacuum. Dry hexane (30 ml.) was then added and the very small
amount of solid material separated by filtration, washed three
times with dry hexane (10 ml.) and dried under vacuum. m.p.
128-130°. Found, Cl = ~1.0%; calculated for $C_5H_5N.C_6H_5SO_2$
Cl, Cl = 13.9%.

(xi) <u>The reaction between benzenesulphonyl chloride and
triphenylphosphine</u>

Benzenesulphonyl chloride (1.77g., 0.01 mole) was dissolved
in 5 ml. of a mixture of toluene and heptane (1:1 ^{v}/v). To this
solution was added over 10 minutes a solution of triphenylphosphine
(2.62g., 0.01 mole) in 40 ml. of the same solvent mixture. An
immediate turbidity developed and a colourless oil began to
separate; after a further 10 minutes this oil crystallised to a
white solid. The reaction mixture was maintained at room
temperature, with constant stirring, for 3 hours, after which time the
solid product was separated by filtration, dissolved in dry
acetonitrile, reprecipitated by addition of dry hexane, filtered
and dried under vacuum. m.pt. 152-154°C, Found, C = 77.3; H = 5.7;
Cl = 0.0%, calculated for $(C_6H_5)_3PO$, C = 77.7; H = 5.4%; m.pt.156°C.

(f) <u>Thionyl chloride and phosphorus oxychloride with donor molecules</u>

(i) <u>The reaction between thionyl chloride and pyridine</u>

Thionyl chloride (3.57g., 0.03 mole) was dissolved in dry

carbon tetrachloride (30 ml.) and cooled to 0°C in an ice bath.

An excess of pyridine (10 ml.) was added over 5 minutes with

constant stirring. The system was allowed to warm to room

temperature and was kept at this temperature for 2 hours.   The

temperature was then increased to 50°C for 2 hours after which

time only traces of a white precipitate had formed.   Dry

heptane (50 ml.) was then added to give a slight increase in the

amount of precipitate.   The solid was then separated by

filtration and dried under vacuum.   Found, Cl = 31.0%;

calculated for $C_5H_5N.HCl$, Cl = 30.8%.   The infrared spectrum

of this material was identical with that of an authentic sample

of pyridine hydrochloride.

(ii) <u>The reaction between phosphorus oxychloride and pyridine</u>[399]

(a) <u>Under anhydrous conditions</u>

Pyridine (5.54g., 0.07 mole) was dissolved in dry carbon

tetrachloride (25 ml.) and phosphorus oxychloride (4.60g.,

0.03 mole) was added at room temperature, with constant stirring.

A very small amount of a white precipitate formed over about 1

hour.   The temperature was then increased to 50-55°C for 16

hours, no further increase in the amount of precipitate being

observed. Evaporation to dryness under vacuum gave traces

of a white solid the infrared spectrum of which was identical

with that of an authentic specimen of pyridine hydrochloride.

This reaction was repeated in other solvents, hexane and toluene,

without solvent and using a large excess of pyridine. In all

cases only trace quantities of pyridine hydrochloride could be

obtained.

(b) Using unpurified reagents

An exßess of pyridine (10.0 mole) was added to phosphorus

oxychloride (4.60g., 0.03 mole) and the solution allowed to stand

at room temperature for one hour. To the solution hexane (50 ml.)

was added and the precipitated white solid was separated by

filtration, washed with hexane (3 x 10 ml.) and dried under vacuum.

Found, C = 49.22; H = 3.21; Cl = 33.39%, $(C_5H_5N)_2 \cdot POCl_3$ requires,

C = 38.51; H = 3.20; Cl = 34.23%. m.pt. 50-70°C.

(g) The donor properties of α-sulphanuric chloride

(i) The reaction between α-sulphanuric chloride and hexamethyl benzene

(a) With reactants in 1:1 mole ratio.

α-Sulphanuric chloride (0.585g., 0.002 mole) was dissolved in

dry toluene (5 ml.) and a solution of hexamethylbenzene (0.324g.,

0.002 mole) in dry toluene (5 ml.) was added rapidly, with constant

stirring, at room temperature. The solution gradually acquired a

faint pink colour. After standing for 24 hours a very small amount

of a flocculent precipitate had separated from a dark red solution.

The solid material was separated by filtration and dried under

vacuum. Found, Cl = 16.1%: $(NSOCl)_3 . 2[C_6(CH_3)_6]$, requires Cl =

17.3%. The filtrate when evaporated to dryness gave a red-

brown solid. Found, Cl = 20.7%: $(NSOCl)_3 . C_6(CH_3)_6$, requires

Cl = 23.4%.

(b) With reactants in 1:2 mole ratio

α-Sulphanuric chloride (0.585g., 0.002 mole) was dissolved

in dry toluene (5 ml.) and a solution of hexamethylbenzene

(0.648g., 0.004 mole) in dry toluene (10 ml.) was added rapidly

at room temperature. As in (a) after 24 hours only a small

amount of a pale-yellow solid had precipitated from solution.

(c) With the hexamethylbenzene in excess

α-Sulphanuric chloride (0.585g., 0.002 mole) was dissolved

in toluene (5 ml.) and a solution of hexamethylbenzene (1.62g.,

0.01 mole) in toluene (15ml.) was added at room temperature.

After 24 hours at this temperature no pink colour had developed

and no precipitate had formed. Hexane (30 ml.) was added and a

cream coloured precipitate obtained which was separated by

filtration and dried under vacuum. Found, C = 20.5; H = 4.2;

Cl = 15.8%: $(NSOCl)_3 . 2[C_6(CH_3)_6]$ requires, C = 23.4; H = 2.9;

Cl = 17.3%. Attempted purification by sublimation or recrystallisation

from hot solvents caused decomposition to a red-brown solid.

(ii) <u>The reaction between α-sulphanuric chloride and beryllium chloride</u>

Beryllium chloride (0.40g., 0.005 mole) was slurried with dry toluene (20 ml.) and a solution of α-sulphanuric chloride (1.46g., 0.005 mole) in dry toluene (20 ml.) was added over 10 minutes, with constant stirring, at 40°C. Undissolved beryllium chloride was still present under these conditions. The system was maintained at $40-50^{\circ}$C for 70 hours after which time the residual solid was separated by filtration. The filtrate was evaporated dryness and the solid obtained recrystallised from heptane. m.pt. $142-144^{\circ}$C (α-$(NSOCl)_3$, 144°C). The infrared spectrum of this material was identical with that of an authentic sample of α-sulphanuric chloride.

(iii) <u>The reaction between α-sulphanuric chloride and mercury(II) chloride.</u>

Mercury(II) chloride (0.54g., 0.002 mole) was dissolved in dry ether (10 ml.) and a solution of α-sulphanuric chloride (0.59g., 0.002 mole) was added rapidly at room temperature. The solution was maintained at this temperature, with constant stirring, for 24 hours. The solvent was removed under vacuum and the solid residue extracted with toluene (10 ml.) After filtration the solvent was removed under vacuum and the solid obtained was shown by its m.pt. and infrared spectrum to be unchanged α-sulphanuric chloride.

(iv) **The reaction between α-sulphanuric chloride and titanium(IV) chloride.**

α-Sulphanuric chloride (0.29g., 0.001 mole) was dissolved in dry toluene and an excess of titanium(IV) chloride (0.006 mole) was added at room temperature. An orange-red colour developed immediately. The solution was maintained at room temperature, with constant stirring, for 16 hours after which time a small amount of a black oil had separated from the solution. Addition of hexane caused the separation of more black oil. The solvent was removed by decantation and the oil dried under vacuum to give a viscous, black, tarry material which was not investigated further.

(v) **The reaction between α-sulphanuric chloride and niobium(V) chloride.**

Niobium(V) chloride (0.39g., 0.0015 mole) was slurried with dry carbon tetrachloride (10 ml.) and a solution of α-sulphanuric chloride (0.429g., 0.0015 mole) was added over 10 minutes, with constant stirring, at room temperature. A deep red colour developed immediately. After about 10 minutes an orange-red solid began to precipitate from the solution and after a further 10 minutes decomposition to give a brown-black solid occurred. The reaction was not investigated further.

(h) <u>Metathesis reactions of α-sulphanuric chloride</u>

     (i) <u>The reaction between α-sulphanuric chloride and butyl
lithium</u>

α-Sulphanuric chloride (1.46g., 0.005 mole) was dissolved

in benzene (20 ml.) and cooled to $0^\circ C$ in an ice bath. A

solution of n-butyl lithium (6.1 ml., 2.45M, 0.015 mole) was

then added with constant stirring. A white precipitate

formed immediately. The solution was warmed to room temperature

and maintained at this temperature for 3 hours. The precipitate

was separated by filtration and the filtrate evaporated to

dryness under vacuum to give only a small amount of a low

melting ($\sim 40^\circ C$) solid. The original precipitate was then

further extracted with benzene, then ether, to give further

small amounts of the low melting solid. The infrared spectrum

of this material contained bands at, 2950s, 2920sh, 1543w,

1560w, ~1250s (broad), 1111sh, ~990vs (broad), ~275 cm^{-1}),

813w, 725w, ~650m (broad).

(ii) <u>The reaction between α-sulphanuric chloride and methyl lithium</u>

     α-Sulphanuric chloride (0.59g., 0.002 mole) was dissolved in

ether and cooled to $-10^\circ C$ in an ice bath. A solution of methyl

lithium (12.5 ml. 0.48M, 0.006 mole) was then added with constant

stirring. An orange colour developed immediately. The solution

was warmed to room temperature when a white precipitate was

deposited from a colourless solution. After standing for

3 hours the solid was separated by filtration and dried

under vacuum. The infrared spectrum contained bands at,

1613w, 1410w, 1205s (broad) 1058sh, 1020s (very broad),

950sh, 900sh, 813w, 722m. The filtrate when evaporated

to dryness gave a small amount of a white solid which was

transparent in the infrared.

(iii) The reaction between α-sulphanuric chbride and potassium thiocyanate.

A solution of α-sulphanuric chloride (1.46g., 0.005 mole)

in acetonitrile (10 ml.) was added, with constant stirring, to

a slurry of potassium thiocyanate (1.46g., 0.015 mole) in

acetonitrile (10 ml.) An intense orange-brown colour

developed immediately and an orange precipitate was deposited.

After 2 hours at room temperature the solid was separated by

filtration and dried under vacuum. This solid was insoluble

in benzene, acetone, ethyl alcohol, water, carbon disulphide and

dimethylsulphoxide; slightly soluble in acetonitrile and

dimethylformamide. The infrared spectrum contained bands

at, 1543w, 1481sh, 1449m, 1299s, 1227sh, 1163s, 1129sh, 1064m,

1019m, 922w, 855w, 787w, 683m, 637sh, 615s, 533w.

(iv) The reaction between α-sulphanuric chloride and and phenylmagnesium bromide

(a) Using mole ratio 1:3

α-Sulphanuric chloride (0.70g., 0.0024 mole) was dissolved

in ether (10 ml.) and the solution cooled to $0^{\circ}C$ in an ice-bath.

An ethereal solution of phenylmagnesium bromide (8.0 ml., 0.90M,

0.0072 mole) was added over 10 minutes with constant stirring.

A deep red-brown colour developed but no precipitate formed.

The solution was kept at $0^{\circ}C$ for 1 hour, and then at room

temperature for a further 2 hours. Removal of the solvent under

vacuum gave a red-brown solid, insoluble in ether, hexane, toluene

and chloroform. Extraction with acetonitrile gave a red-brown

solution which was separated from the residual white solid by

filtration. Removal of the solvent under vacuum gave a pale

red-brown solid, the infrared spectrum of which contained bands

at, 3175ms, 3077sh, 2315s, 2288vs, 1679w, 1623m, 1560w, 1479sh,

1408m, 1449s, 1375s, 1368m, 1277sh, 1264m, 1163w, 1109sh, 1077w,

1035s, 995w, 930ms, 803w, 749m, 729w, 702m, 687m. Found, C =

26.93; H = 3.17; N = 8.85; S = 7.17%. $\left[NS(O)C_6H_5 \right]_3$ requires,

C = 51.76; H = 3.62; N = 10.07; S = 23.02%.

(b) Using mole ratio 1:1

α-Sulphanuric chloride (0.70g., 0.0024 mole) was dissolved

in ether and the solution cooled to $-20^{\circ}C$ in an acetone-dry ice

bath. An ethereal solution of phenylmagnesium bromide (26.6 ml.,

0.09M, 0.0024 mole) was added dropwise, with stirring, over 45

minutes. The solution was maintained at $0^{\circ}C$ for a further

45 minutes and then warmed to room temperature for 22 hours.

After this time a white solid and a red-brown oil had separated from

the solution. Removal of the solvent under vacuum gave a red-brown solid from which only traces of a red-brown oil could be extracted with heptane and toluene. Extraction with nitromethane gave, after removal of the solvent, a red-brown oil which was vacuum distilled onto a micro-cup cold finger. Found, C = 48.06; H = 3.25%: calculated for C_6H_5NSO, C = 51.77; H = 3.63%. The infrared spectrum contained bands at, 3077s, 3040m, 2967w, 2933w, 1605w, 1587w, 1560m, 1490m, 1464s, 1449sh, 1389m, 1319sh, 1276ms, 1235m, 1193m, 1172ms, 1163ms, 1077w, 1047vw, 1028w, 1012w, 907w.

(v) The reaction between α-sulphanuric chloride and N,N diethylamino-trimethylsilane

α-Sulphanuric chloride (0.80g., 0.0027 mole) was dissolved in toluene (10 ml.) and cooled to -78°C in an acetone-dry ice bath. A solution of N,N diethylaminotrimethylsilane (1.17g., 0.0081 mole) in toluene (11.7 ml.) was then added, with constant stirring. The solution was maintained at -78°C for 30 minutes and then at room temperature for 21 hours. The golden-red solution was evaporated under vacuum to give a golden-red oil. Found, C = 33.5; H = 6.96%: $(NSON(C_2H_5)_2)_3$ requires, C = 35.80; H = 7.52%. Attempts to purify this oil by sublimation and recrystallisation were unsuccessful. The infrared spectrum contained bands at, 3125w, 2994sh, 2950sh, 2882w, 1615w, 1563ms, 1446ms, 1449sh, 1385ms, 1347w, 1290sh, 1250s, 1193m, 1143m, 1064ms, 1010ms, 917m, 847ms, 784m, 760sh, 690w, $\sim$560m. Many of these bands were rather broad and poorly resolved.

DISCUSSION

A. Attempted Syntheses of the cyclic sulphanuric system

The preparation[118] of the most readily accessible sulphanuric

compound, sulphanuric chloride, involves the isolation and pyrolysis

of the extremely hygroscopic trichlorophosphazosulphuryl chloride.

Further, the impure trichlorophosphazosulphuryl chloride does

not pyrolyse to give sulphanuric chloride so that, to avoid

recrystallisation of the intermediate, the use of pure starting

materials is essential. This entails handling of the

phosphorus(V) chloride in an inert atmosphere. Other

sulphanuric compounds are at present only obtainable via

metathesis reactions of the chloride. Attempts were, therefore,

made to devise alternative syntheses which (i) did not involve

such moisture sensitive materials, and (ii) might be more

economical on an industrial scale.

(i) Attempted syntheses from trisulphimide salts

The synthesis investigated may be represented as,

$$SO_2Cl_2 \quad \xrightarrow{\quad NH_3 \quad} \quad SO_2(NH_2)_2 \qquad (1)$$

$$SO_2(NH_2)_2 \quad \xrightarrow{\quad heat \quad} \quad (NH_4 \cdot NSO_2)_3 \quad \xrightarrow{\quad SOCl_2 \quad} \quad (NSOCl)_3 \qquad (2)$$
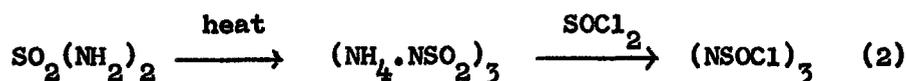
and may be considered to involve two separate aspects which are

now discussed.

(a) The preparation of sulphamide

Sulphamide is normally prepared[24-26] by the low temperature (-78°C) reaction between sulphuryl chloride and liquid ammonia. Recently Andreson and Miller[388] have reported good yields (~70%) from a process involving the use of gaseous ammonia at 0°C. Such a process is of considerably greater convenience than that normally used. In this work several attempts to prepare sulphamide by the method of Andreson and Miller resulted in a maximum yield of only ~12%. This result is in agreement with the observations of previous workers[20-23]. It is concluded that high yields of sulphamide can only be obtained by the use of liquid ammonia. However, for the preparation of small amounts (~10g.) of sulphamide the method of Andreson and Miller is convenient.

(b) Reactions of derivatives of trisulphimide

Trisulphimide derivatives are readily obtained from sulphamide. The ammonium salt is formed when sulphamide is subjected to prolonged heating[36-38] at 200°C and metal salts are easily prepared[36] from this compound. Two extreme canonical forms (20) (21) may be written for the trisulphimide anion.
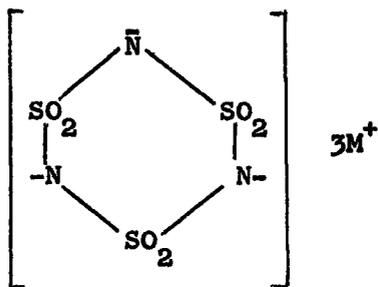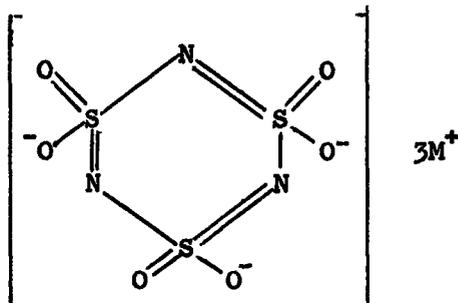
(20)   (21)

It is probable that bpth forms contribute to the structure

of the anion. Since the electronegativity of oxygen is greater

than that of nitrogen it is to be expected that (21) will

make the larger contribution. If (21) is of importance

then chlorinating agents may be capable of reacting with this

form to give the corresponding acid chloride, viz., sulphanuric

chloride. Thionyl chloride was chosen as the chlorinating

agent in preference to phosphorus(V) chloride since the use

of the latter involves the separation of the product from

phosphorus oxychloride.

Under the conditions used neither ammonium nor silver

trisulphimide underwent reaction with thionyl chloride. However,

reaction between ammonium trisulphimide and thionyl chloride did

not occur in the presence of dimethylformamide. The product

was not desired sulphanuric chloride but was an ammonium

compound, the infrared spectrum of which was similar to that

of the starting material. The formation of this compound

suggests that when chlorination does occur it does so in other

than the required manner.   Hence, the use of other chlorinating

agents was not examined.

The reaction between silver trisulphimide trihydrate and

thionyl chloride gave an oil, the infrared spectrum of which

contained bands, at $\sim 3400\text{-}3300$ cm^{-1}, attributed to -NH

groups.   It is suggested that this compound is trisulphimide

itself, which is formed as below:

$$(AgNSO_2)_3 3H_2O + 3SOCl_2 \longrightarrow (AgNSO_2)_3 + 6HCl + 3SO_2$$

$$(AgNSO_2)_3 + 3HCl \longrightarrow (HNSO_2)_3 + 3AgCl$$
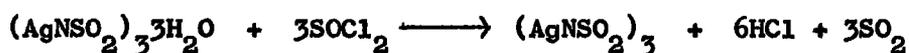
(ii) <u>Reactions between inorganic azides and sulphur-halogen compounds</u>

Various cyclic non-metal-nitrogen compounds may be

prepared by thermal decomposition of the appropriate azides.

Phosphonitrilic compounds may be obtained from the reaction,[400,401]

$$R_2PX + NaN_3 \xrightarrow{\text{heat}} \frac{1}{n}(R_2PN)_n + N_2 + NaX$$
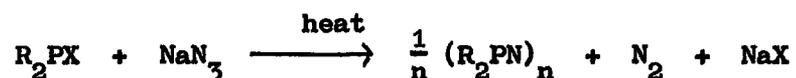
where X = Br, Cl and R = Br, Cl, Ph, CF$_3$.   Usually the

products are highly polymeric though in some cases[400] the

lower polymers can be isolated.   Azides of the group IV

elements[402] Si, Ge, Sn and Pb are prepared by the general

reaction.

$$R_3MX + LiN_3 \xrightarrow{\text{solvent}} R_3MN_3 + MX$$
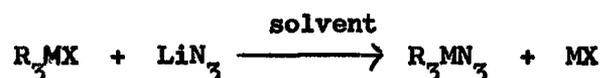
These azides show a relatively high degree of thermal
stability due to π-bonding between the central metal atom
and the azide group but pyrolysis of the silicon compound,
Ph_3SiN_3, gives a high yield of cyclic polymers. Dimesitylboron
azide may similarly be prepared[403] from the corresponding
fluoride and decomposes to a linear polymer on heating and
benzenesulphonyl azide has been prepared[404] by the reaction
between sodium azide and benzenesulphonyl chloride.

It was thought reasonable to attempt the synthesis of
cyclic sulphur-nitrogen compounds from the appropriate azides.
No attempt was made to isolate the azide it being considered
preferable to decompose it as formed. By analogy with the
examples quoted above the following equations represent
possible reactions between thionyl chloride or benzenesulphinyl
chloride and sodium azide.

$$SOCl_2 + NaN_3 \xrightarrow{\text{heat}} \frac{1}{n}(NSOCl)_n + NaCl + N_2$$

$$PhSOCl + NaN_3 \xrightarrow{\text{heat}} \frac{1}{n}(PhSON)_n + NaCl + N_2$$
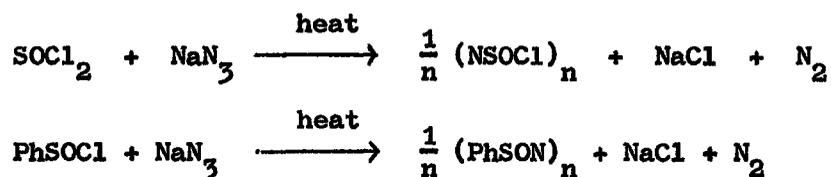
Under the conditions used neither of these reactions occurred.

Trithiazyl trichloride, $(NSCl)_3$ may be oxidised[114] to
sulphanuric chloride so that convenient syntheses of trithiazyl
compounds might also afford the corresponding sulphanuric
compounds. Accordingly the preparation of $(NSPh)_3$ was unsuccessfully

attempted via the reaction,

$$PhSCl \ + \ NaN_3 \ \xrightarrow{\text{heat}} \ \frac{1}{n} \ (PhSN)_n \ + \ NaCl \ + \ N_2$$
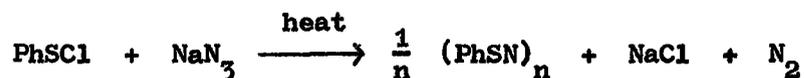
The failure of these sulphur-halogen compounds to react

with sodium azide is in marked contrast to the facile reaction

that occurs with benzenesulphonyl chloride, and is also

surprising in view of the widespread occurrence of the analogous

reaction with other elements. It is possible that the azide

used is of importance since in the case of the phosphonitrilic

compounds the use of lithium azide rather than sodium azide

results in improved yields.

(iii) <u>Reactions between ammonium chloride and sulphur-halogen</u>
     <u>compounds</u>

The formation of phosphorus-nitrogen and boron-nitrogen cyclic

compounds by the reactions between phosphorus(V) chloride[133]

or boron trichloride[405] respectively, and ammonium chloride

is well known. For the case of phosphorus(V) chloride the

reaction may be represented as,

$$PCl_5 \ + \ NH_4Cl \ \longrightarrow \frac{1}{n} \ (NPCl_2)_n \ + \ 4HCl$$
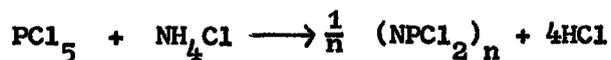
though this simple equation conceals some complexity;

according to the conditions either linear or cyclic compounds can

predominate[133]. Maguire <u>et.al.</u>[164] and Jolly <u>et.al.</u>[165] have

studied the reaction between ammonium chloride and sulphur

chloride. When an excess of sulphur chloride is used, thiazyl

chloride is formed.

$$NH_4Cl + S_2Cl_2 \longrightarrow NSCl + 3S + 4HCl$$
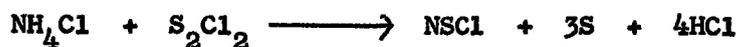
Using excess ammonium chloride thiodithiazyl dichloride results; from reaction between the thiazyl chloride initially formed with more sulphur chloride.

$$2NSCl + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + SCl_2$$

By analogy with the case of P-N or B-N compounds, the equation,

$$NH_4Cl + 2SOCl_2 \longrightarrow \frac{1}{n}(NSOCl)_n + 4HCl + \tfrac{1}{2}S + \tfrac{1}{2}SO_2$$

represents a possible reaction between ammonium chloride and thionyl chloride. Attempts to bring about this reaction were unsuccessful.

(iv) The attempted dehydration of sulphonamides by sulphamic acid

Carboxylic acid amides are readily converted into the corresponding nitriles by heating with sulphamic acid[406]

$$RCONH_2 + H_2N.SO_2OH \xrightarrow{\ 180^\circ/220^\circ\ } RCN$$
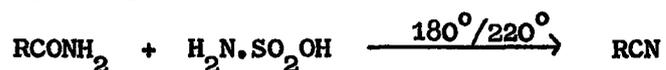
An analogous reaction involving a sulphonic acid amide would yield a sulphanuric derivative.

$$RSO_2NH_2 + H_2NSO_2OH \xrightarrow{\ heat\ } (RSON)_n$$
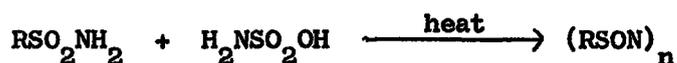
Under the conditions examined this reaction did not occur.

B. The pyrolysis of aryl trichlorophosphazosulphones

Whilst sulphanuric chloride is prepared by the pyrolysis of trichlorophosphazosulphuryl chloride, $ClSO_2N:PCl_3$, the pyrolysis of analogous compounds does not appear to have been investigated, though if the reaction occurs in general a wide variety of sulphanuric compounds is readily accessible. Kirsanov[407] has reported that aryl trichlorophosphazosulphones decompose when vacuum distilled but has not examined the decomposition products. Alkyl trichlorophosphazosulphones[408] appear to be thermally more stable in that they can be vacuum distilled without decomposition. Bis(trichlorophosphazo) sulphone is also unstable[409] and decomposes to a considerable extent when vacuum distilled.

If the decomposition of aryl trichlorophosphazosulphones proceeds similarly to that of trichlorophosphazosulphuryl chloride then aryl substituted sulphanuric compounds should result.

$$ArSO_2N:PCl_3 \longrightarrow \tfrac{1}{n}(ArSON)_n + POCl_3$$
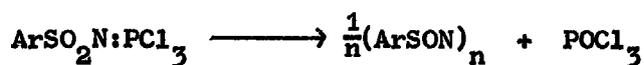
Four compounds, $XC_6H_4SO_2N:PCl_3$, (X = p-CH_3, p-CH_3O, p-Cl and m-NO_2) have been prepared and the pyrolysis of two of these compounds (X = p-CH_3 and p-Cl) has been studied.

In the preparation of these compounds it was observed

that the rate of reaction decreased along the series,

$CH_3O > CH_3 > Cl > NO_2$.   In the original sulphonamide,

$XC_6H_4SO_2NH_2$, the extent to which the nitrogen lone pair

is involved in p_π - d_π bonding to the sulphur atom will

vary with the nature of the group X.   When X is electron

attracting (e.g. $m-NO_2$) the extent of π-bonding will be

greater than when X is electron releasing (e.g., $p-CH_3O$).

Since increasing π-bonding effectively decreases the ability

of the nitrogen atom to act as a donor, the observed order of

relative reaction rates is explained if the first step

in the reaction is the formation of a donor-acceptor complex.

$$XC_6H_4 \underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}} \underset{\overset{|}{H}}{\overset{\overset{H}{|}}{N}} \rightarrow PCl_5$$
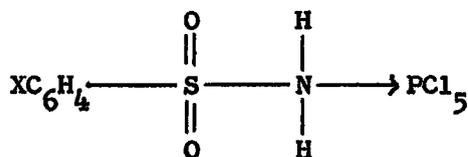
Pyrolysis of p-tolytrichlorophosphazosulphone im

resulted in elimination of $POCl_3$, but only to about 50% of the

amount required for the formation of the sulphanuric derivative.

$$CH_3C_6H_4SO_2N:PCl_3 \longrightarrow \frac{1}{n} (CH_3C_6H_4SON)_n + POCl_3$$
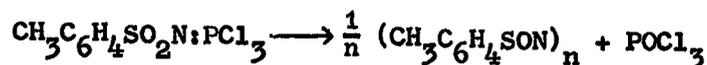
Also formed in the pyrolysis was p-tolysulphonyl chloride,

$CH_3C_6H_4SO_2Cl$.   The formation of this compound is thought to

result from the elimination of phosphonitrilic chloride, in

accordance with the equation,

$$CH_3C_6H_4SO_2N{:}PCl_3 \longrightarrow CH_3C_6H_4SO_2Cl + \frac{1}{n}(NPCl_2)_n$$

The solubilities and infrared spectrum of the black reaction

residue suggest it to be a polymeric material, formed by reaction

between $(CH_3C_6H_4SON)_n$ and $(NPCl_2)_n$.

p-Chlorobenzenetrichlorophosphazosulphone is thermally

more stable and underwent only slight decomposition during the

attempted pyrolysis. That traces of $POCl_3$ were obtained,

and a strong odour of the sulphonyl chloride was noted, suggests

that decomposition occurs in the same way as for the p-tolyl

compound.

The mass spectra of these compounds have been recorded and

compared with that of trichlorophosphazosulphuryl chloride.

The more abundant species observed are given in Tables 11 and

10 respectively. For trichlorophosphazosulphuryl chloride the

probable breakdown pattern is given in Fig.18

Fig.18

Mass spectroscopic breakdown pattern of $ClSO_2N{:}PCl_3$

(Routes involving species not observed in the
spectrophotometer are shown ......)

$ClSO_2N{:}PCl_3 \longrightarrow ClSO_2NPCl_2 \longrightarrow ClSO_2NPCl \longrightarrow ClSO_2NP$

$ClSONPCl_2 \cdots\cdots \rangle ClSONPCl \cdots\cdots \rangle ClSONP$
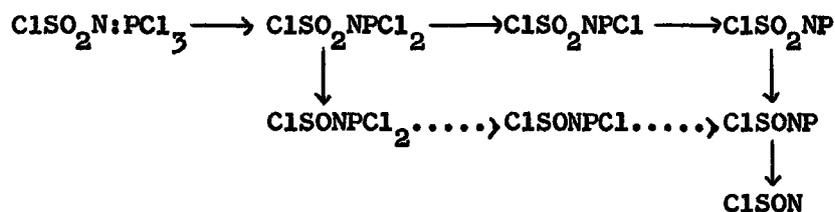
$ClSON$

It is significant that this breakdown pattern parallels that

obtained on thermal pyrolysis. No peaks which resulted from

the early rupture of the ClSON unit were detected. The spectra

of the aryl trichlorophosphazosulphones are quite different.

The breakdown pattern for all of these compounds is of the type

illustrated in Fig.19. The main breakdown route involves

Table 10

Mass spectrum of $ClSO_2N:PCl_3$. Accelerating potential 70ev.
Source temperature, 240°C.

Nominal mass	Species	Rel.Int.
293 294 295	$(NSOCl)_3$	3.5 4.3 2.2
214 216 218 220	$ClSO_2NPCl_2$	99.7 100.0 43.2 7.9
198 200	$ClSONPCl_2$	3.7 2.9
179-183	$ClSO_2NPCl$	$\lesssim$4.0
144	$ClSO_2NP$	<2.0
128	$ClSONP$	<2.0
99 97	$ClSON$	6.0 2.0

Masses corresponding to SO_2, NSO, SO, NS, Cl and to $POCl_3$

and its breakdown products were also observed.

Table 11

Mass spectra of $XC_6H_4SO_2N:PCl_3$ compounds.   Accelerating potential 70 ev.

Species type	Rel. Int.			
	$CH_3O^{1,2}$	CH_3^3	Cl^4	NO_2^5
$XC_6H_4SO_2N:PCl_3$	29.6	30.3	17.3	10.1
$XC_6H_4SO_2NPCl_2$	~1.0	2.3	1.4	2.3
$XC_6H_4NPCl_3$	~3.0	12.0	7.3	5.4
SO_2NPCl_3	~3.0	5.5	9.3	29.7
$SONPCl_3$	56.0	100.0	100.0	100.0

1, $CH_3OC_6H_4 = 100$,

Source temperature, 2 = 150, 3 = 215, 4 = 225, 5 = 235 ^oC.

loss of the XC_6H_4 fragment to give $(SO_2NPCl_3)^+$ and then the

particularly abundant $(SONPCl_3)^+$ ion.   Breakdown via the alternative

route involves, eventually, rupture of the S-N bond.   Both

routes involve rupture of the XC_6H_4SON grouping and, therefore,

cannot result in the formation of a sulphanuric derivative.

It was concluded that the thermal pyrolysis of a sulphone containing

the $N:PCl_3$ group is unlikely to lead to a sulphanuric compound unless

the mass spectroscopic breakdown of the compound differs from that

shown in Fig. 19

Fig. 19

Mass spectroscopic breakdown pattern for $XC_6H_4SO_2N:PCl_3$ compounds.

Species arising from combination reactions are shown........

$$XC_6H_4SO_2N:PCl_3$$

$XC_6H_4SO_2NPCl_2$ SO_2NPCl_3

$XC_6H_4SO_2NPCl$ $SONPCl_3$

$XC_6H_4SO_2NP$ $SNPCl_3$

$XC_6H_4SO_2N$ $XC_6H_4NPCl_3$ ← · · · · · · · · · · $NPCl_3$

$XC_6H_4SO_2$ $XC_6H_4NPCl_2$ PCl_3

XC_6H_4 XC_6H_4NPCl

XC_6H_4NP

XC_6H_4N
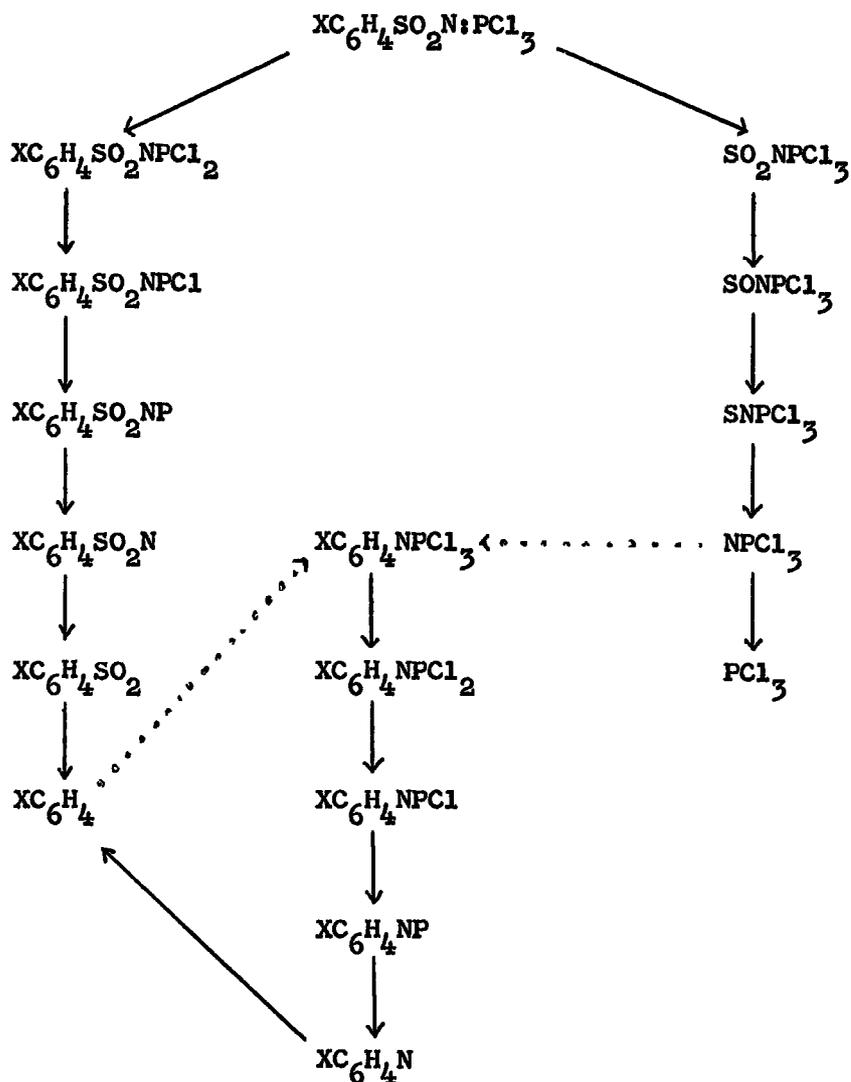
Since thermal pyrolysis of $p\text{-}CH_3C_6H_4SO_2N:PCl_3$ resulted

in elimination of the $NPCl_2$ grouping, the corresponding triphenyl

compound, p.$CH_3C_6H_4SO_2N:PPh_3$, was prepared. It was thought

that elimination of the $NPPh_2$ grouping might less readily

occur. However, the mass spectrum of this compound showed

an analogous breakdown pattern to that observed for chloro

compounds, Fig. 19 .   In view of this the thermal pyrolysis

of the compound was not carried out.

The infrared spectra of these compounds have also been

recorded. Wiegrabe et.al.[378] have reported the spectra of

p-$SH_3C_6H_4SO_2N:PCl_3$ and p-$CH_3C_6H_4SO_2N:PPh_3$; by analogy with

their assignments the spectra of the $XC_6H_4SO_2N:PCl_3$ compounds

prepared in this work are assigned as in Table 12. There

are no marked variations from one compound to another,

in particular the ν_{SN} and ν_{SO_2} modes show no systematic

variation with the electronic character of the substituent

X as expressed by its Hammett σ constant. For all of the

compounds strong bands occur at $\sim$1600 and $\sim$1500 and $\sim$1450 cm^{-1}

and are assigned[410] to the C=C skeletal in-plane vibrations.

For the p-substituted compounds the C-H out-of-plane

deformations occur[410] in the normal range, 860-880 cm^{-1};

the m-NO_2 compound having this mode at 788 cm^{-1} (normal range,

810-750 cm^{-1}). Vibrations involving the substituent X

occur in the expected regions. Alkyl aryl ethers[410] show

one band at 1270-1230 cm^{-1} corresponding to a C-O vibration, a

second band at 1150-1060 cm^{-1} may result from a CH_2-O- vibration.

Aromatic nitro compounds[410] show N-O vibrations in the ranges,
1527 $\pm$ 16 cm^{-1} and 1348 $\pm$ 11 cm^{-1}. The C-Cl stretching
vibration normally occurs[410] in the range 750-700 cm^{-1} but for
dichloroethylene and chlorinated aromatic compounds may be as
high as 845 cm^{-1}. p-ClC$_6$H$_4$SO$_2$N:PCl$_3$ shows two absorption
modes in this region, 743 and 784 cm^{-1}. By analogy with
the other XC$_6$H$_4$SO$_2$N:PCl$_3$ compounds the band at 743 cm^{-1} is
assigned to ν_{SN} and the band at 784 cm^{-1} is tentatively
assigned to the C-Cl mode.

Table 12

The infrared spectra of XC$_6$H$_4$SO$_2$N:PCl$_3$ compounds

$\nu_{cm^{-1}}$ \ X	p-CH$_3$O	p-CH$_3$	p-Cl	m-NO$_2$	assignment
	1212	1206	1214	1190	$\nu_{P:N}$
	754	762	743	745	ν_{SN}
	1316	1316	1325	1325	$\nu_{as}SO_2$
	1152	1150	1152	1148	$\nu_s SO_2$
	584	590	595	585	$\nu_s PCl$
	633	621	643	637	$\nu_{as}PCl$
	543	541	548	553	δSO_2(scissor)
	513	515	521	510	δSO_2(wag)
			784		ν_{CCl}
	1266				$\}\nu_{CO}$
	1088				
				1548	$\}\nu_{NO}$
				1353	

The infrared spectrum of $ClSO_2N:PCl_3$ is given in Table 13.

The ν_{SN}, $\nu_{P:N}$ and ν_{SO_2} modes occur at frequencies similar to those

observed for the aryl trichlorophosphazosulphones.   Values

of ν_{SN} for both $ClSO_2N:PCl_3$ and the $XC_6H_4SO_2N:PCl_3$ compounds

suggest[44] that in all of these compounds the S-N bond order

is close to unity.   This is perhaps surprising since the

pyrolysis experiments and mass spectra of these compounds

suggèst that the S-N bond in $ClSO_2N:PCl_3$ is stronger than that

in the $XC_6H_4SO_2N:PCl_3$ compounds.

Table 13

The infrared spectrum of $ClSO_2N:PCl_3$

$\nu\,cm^{-1}$	assignment
1754m	
1639w	
1538wm	$2 \times \nu_{SN} = 1532$
1370vs	$\nu_{as}SO_2$
1204vs	$\nu_{P:N}$
1170vs	$\nu_s SO_2$
766s	ν_{SN}
720w	
621m	$\nu_{as}PCl$
601s	$\nu_s PCl$
572m	$\delta\,SO_2$ (scissor)
535m	$\delta\,SO_2$ (wag)
503s	

C. α-Sulphanuric chloride as an acceptor molecule

The first reaction in this series, viz the reaction between α-sulphanuric chloride and pyridine, was initially performed, (a) as part of a general investigation into the chemistry of the sulphanuric system, and (b) as a preliminary experiment to the use of pyridine as an acceptor of HCl in other experiments which involved the elimination of this acid. It being observed that an adduct was formed a more general investigation was made of the acceptor properties of α-sulphanuric chloride, and then of other sulphur(VI) compounds. These adducts are unusual in that they contain sulphur(VI) at the acceptor site already

linked to three ~~coordinated~~ covalent nitrogen and each α-sulphanuric

chloride molecule is bonded to three donor molecules.

(i) Reactions with tertiary amines

The viscous oils obtained by reaction of α-sulphanuric chloride with aromatic tertiary amines were insoluble in most solvents but dissolved, with reaction, in the polar solvents dimethylsulphoxide and dimethylformamide. Attempted distillation in vacuo lead to decomposition. Analysis of the products as obtained suggested that these were compounds of the type $(NSOCl)_3 \cdot 3B$, where B = pyridine, iso-quinoline. The infrared spectra of these compounds suggest that the sulphanuric ring remains intact;

that of the pyridine adduct (Table 14) is discussed in some

detail since the spectra of pyridine complexes have been

extensively studied.

α-Sulphanuric chloride itself has strong bands at;

(1) 1812m; (2) 1335s, 1326s (doublet); (3) $\sim$1100s (broad);

(4) 812m; (5) 713ms; (6) 702ms; (7) 663s; (8) $\sim$540ms (broad) cm^{-1}.

Corresponding bands in the spectrum of the pyridine adduct were

assigned at; (1) 1818w; (2) 1319s, 1300s (doublet); (4) 813ms,

800ms (doublet); (6) 702sh; (7) 658s; (8) $\sim$530ms (broad) cm^{-1}.

The broad band which appears at $\sim$1100 cm^{-1} for α-sulphanuric

chloride is difficult to assign for the adduct since it occurs

in a region in which pyridine itself shows five strong absorption

bands. Whilst the spectrum of α-sulphanuric chloride is as yet

unassigned some of the observed bands are expected to be due

to vibrations involving the S-N ring, and hence would be

expected to disappear if ring opening occurred.

The changes that occur in the infrared spectrum of pyridine

when it functions as a donor have been discussed by several

authors.[411-414]. In general there is a close similarity between

the spectrum of the free base and those of complexes involving metal

halides. This has been attributed[412] to back bonding from the

d-orbitals of the metal to the π-electron system of the base.

This concept is supported by the more marked changes in the spectra which occur when pyridine is protonated[415] or coordinated to BX_3 compounds[413] since in these systems back coordination cannot occur. The following discussion is based upon the pyridine assignments given by Wilmshurst and Bernstein[416] using the nomenclature of Kline and Turkevitch[417]. The (C_{2v}) pyridine molecule has 27 fundamental modes of vibration. Ten modes are in the plane of the ring and are symmetrical with respect to the C_{2v}-axis (Class A1); nine are in the plane of the ring but are antisymmetrical with respect to the C_{2v}-axis (Class B1); five modes involve out-of-plane vibrations which are antisymmetric to the two-fold axis (Class B2); and the remaining three symmetrical out-of-plane (A2) modes are forbidden in the infrared. The active modes are numbered 1-20 with suffixes a,b where necessary to distinguish degenerate vibrations.

For pyridine itself (Table 14) the symmetric and antisymmetric in-plane ring deformations occur at 1430-1600 cm^{-1} and these same modes occur at 1480-1640 cm^{-1} for the adduct. These frequency shifts are somewhat greater than those observed for pyridine-metal halide adducts[411] (Table 14) but are comparable with those reported for $C_5H_5N.BCl_3$,(8a, 1624; 8b, 1576; 19a, 1540; 19b, 1462 cm^{-1})[413] and pyridine hydrochloride, (8a, 1631; 8b, 1603;

19a, 1530; 19b, 1481cm^{-1})[415]   A new fairly weak band at 1253 cm^{-1}

present in the spectra of neither α-sulphanuric chloride nor

pyridine, is characteristic of pyridine complexes and salts.[411]

The region 1200-1000 cm^{-1} is complex and appears to be a

superimposition of the expected five strong pyridine bands and

the broad band which occurs at ∿1100 cm^{-1} for α-sulphanuric

chloride.   Assignments (Table 14) in this region are tentative.

Other bands at 750, 681 and 609 cm^{-1} correspond to those which

occur at 749, 652 and 605 cm^{-1} for pyridine itself.   A strong

band at 569 cm^{-1}, present in the spectra of neither pyridine

nor α-sulphanuric chloride is in the region expected for a

N→S bond, (part 2, this thesis).   An interesting feature of

the spectrum is the presence of a strong, broad, band at ∿2600 cm^{-1}.

If the compound is a simple adduct involving donation of the

nitrogen lone pair electrons to vacant sulphur orbitals, then the

band must be assigned to a C-H stretching mode.   Its low

frequency can then be explained as due to involvement of the C-H

bond in a hydrogen bond.   Alternatively, the band can, in

principle, be assigned to a N-H (hydrogen bonded) mode.   These

two possibilities are now discussed.

(a) That the band at ∿2600 cm^{-1} is due to a N-H vibration.

    For this to be so the compound must have some such structure

as (22).   Pyridinium compounds normally also show[418,419] non

Table 14

The infrared spectra of $3(C_5H_5N)(NSOCl)_3$ and C_5H_5N.[416]

$3(C_5H_5N)(NSOCl)_3$ (cm^{-1})	C_5H_5N (ν_{cm}^{-1})	Range observed[411] in complexes (cm^{-1})	assignment
3058s	3054		)
3012sh			) νCH
2941sh			)
385μ. 2597s (broad)			)
480μ 2083m			
1818w			$(NSOCl)_3$
1634sh	1583	1578-1615	ν_{8a}
1613s	1572	1562-1576	ν_{8b}
1538s	1482	1471-1490	ν_{19a}
1488s	1439	1436-1461	ν_{19b}
1408w			
1385m	1375		
1319)			} $(NSOCl)_3$
1300)			
1253m			
1198sh			
1166s	1148	1144-1170	ν_{15}
1122s			
1110sh			
1059s	1030	1035-1047	ν_{12}
1011s	992	1004-1022	ν_1
813)			)
800)			} $(NSOCl)_3$
750	749	741-769	ν_4
702sh			$(NSOCl)_3$
680	652	645-650	ν_{6b})
658s			$(NSOCl)_3$
609m	605	620-641	ν_{6a} ?
569s			$(NSOCl)_3$
529ms)			} $(NSOCl)_3$
524ms)			

hydrogen bonded N-H modes at $\sim3200-3100$ cm^{-1}, not present.

$$\left[\begin{array}{c} O=S \underset{}{} C_5H_4\overset{+}{N}H \\ N \quad\quad N \\ O=S \quad\quad S=O \\ \overset{+}{C_5H_4NH} \quad N \quad \overset{+}{C_5H_4NH} \end{array}\right] \quad 3Cl^-$$

(22)

for the adduct and, the band which occurs at ~540 cm^{-1} for

α-sulphanuric chloride and at ~530 cm^{-1} for the adduct is in the

region expected for the S-Cl stretching frequency[340]. Further,

attempted metathesis reactions and mass spectroscopic studies

reported later indicate that ionisation of the chlorine atoms

generally results in ring opening. An ionic compound such as

(22) is also expected to be a crystalline material.

(b) That the band at ~2600 cm^{-1} is due to a C-H vibration.

Two possible extreme structures arise; (23) represents a

simple donor-acceptor adduct and (24) represents a situation in

$$\begin{array}{c} C_5H_5N \\ O= S \downarrow Cl \\ N \quad\quad N \\ C_5H_5N \longrightarrow S \quad\quad S \longleftarrow NH_5C_5 \\ Cl \quad N \quad Cl \end{array}$$

$$\left[\begin{array}{c} O= S \quad NH_5C_5 \\ N \quad\quad N \\ O= S \quad\quad S=O \\ C_5H_5N \quad N \quad NH_5C_5 \end{array}\right]^{3+} \quad 3Cl^-$$

(23)   (24)

which formation of the adduct is followed by ionisation of the
chlorine atoms.   Most of the points raised in (a) favour
structure (23), though the solubilities of the adduct show it
to be a very polar compound which may result, in part, from a
highly polar S-Cl bond, i.e. (24) may make an appreciable
canonical contribution to the structure.   Whilst the spectrum
does not allow one to distinguish between C-H....Cl and C-H...O
hydrogen bonding the latter is the more likely since hydrogen
bonds to oxygen are stronger than those to chlorine,[420] because
of the greater electronegativity of the oxygen atom.   If the
band at $\sim$2600 cm^{-1} is assigned to a C-H (hydrogen bonded) mode
then the frequency shift, relative to CH in pyridine, is
$\Delta\nu\sim$ 450 cm^{-1}.   This shift is much greater than those normally
associated ($\Delta\nu \sim$ 30-100 cm^{-1}) with C-H hydrogen bonds.[420, 421]
If, as is suggested by the viscosity of the adduct, the hydrogen
bonding is intermolecular then it is possible that pairs or
arrays of (hydrogen bonded) protons may move in unison.
Cooperative movements of this sort give rise to particularly stable
hydrogen bonded systems, e.g. Reid[422] has discussed the bonding in
KH_2PO_4 from this standpoint.

Because of its insolubility, the N.M.R. spectrum of the adduct
could not be examined in solution, and its high viscosity causes
the spectrum obtained for the compound itself to be ill-defined.

However, the observed spectrum is consistent with the suggestion that hydrogen bonds are present.[420] At 25°C, apart from the normal pyridine triplet, a new broad band appears at low field. Using cyclohexane as an external reference the shift, relative to the C_α pyridine peak, is ~8.0 p.p.m. This new band moves to higher fields with increasing temperature.

The infrared spectra of the iso-quinoline and trimethylamine adducts are more difficult to assign precisely since much less is reported with regard to the frequency shifts observed when these molecules act as donors. Tentative assignments of the bands due to α-(NSOCl)$_3$ in these adducts are given in Table 15. Bands at 610 cm^{-1} and 594 cm^{-1} in the spectra of the iso-quinoline and trimethylamine adducts, respectively, are assigned to the N→S bonds. The spectra of both compounds show broad bands at ~2600-2500 cm^{-1} which are attributed to C-H hydrogen bonds by analogy with the pyridine adduct.

Similar adducts are formed with other donors. With triphenylphosphine the product, which corresponds to $3(Ph_3P).(NSOCl)_3$, was a sticky semi-solid material the infrared spectrum of which could not be obtained as it was impossible to prepare a satisfactory mull. The adduct was insoluble in non-polar solvents but when dissolved in nitromethane decomposed to give triphenylphosphine dichloride.

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Table 15

Bands assigned to α-(NSOCl)$_3$ in iso-quinoline and trimethylamine adducts ($\sqrt{}$cm^{-1})

α-(NSOCl)$_3$	$3(C_9H_7N)(NSOCl)_3$	$3\left[(CH_3)_3N\right](NSOCl)_3$
1335s)	1342sh)	1330s)
1326s)	1297s)	1312s)
~1100s	1120s	1076s
812m		
713ms		722wm
702ms	700sh	690m
666s	683s	
~540ms	~530m	~515ms

Infrared spectra were obtained for the triphenylarsine, $3Ph_3As.(NSOCl)_3$ and triphenylstibine, $3Ph_3Sb.(NSOCl)_3$ adducts and bands due to α-(NSOCl)$_3$ are given in Table 16. All other bands in the spectra of these compounds corresponded to those expected for the donor molecules.[423] In contrast to the amine adducts no bands were observed at ~2600 cm^{-1}. The triphenylstibine adduct, in contrast to those of phosphorus and arsenic, is a solid compound. The preparation of this compound also resulted in the formation of triphenylstibine dichloride.

Table 16

Bands assigned to α-(NSOCl)$_3$ in triphenylarsine and
triphenylstibine adducts (ν cm^{-1})

α-(NSOCl)$_3$	3Ph$_3$As(NSOCl)$_3$	3Ph$_3$Sb.(NSOCl)$_3$
1335s)	1342sh)	1333m)
1326s)	1335s)	1285s)
~1100s	1110s	1110sh
812m	804ms	805wm
713ms		
702ms	697sh	694sh
666s	632m	631wm
~540ms	~550m	~550w

D. Other sulphur(VI) compounds as acceptor molecules

As a result of the formation of the α-sulphanuric chloride

adducts (above) in which it is suggested that sulphur(VI) functions

as the acceptor site, the possibility that other sulphur(VI) compounds

behave similarly has been investigated. It was thought that a study

of the properties of any such compounds might provide further

evidence concerning the structures of the α-sulphanuric chloride

adducts.

Adducts of sulphur trioxide with organic bases are well known[424]

though little attention has been paid to the structures of these

adducts. Watari[425] has reported the infrared spectrum of

$Me_3N.SO_3$; the frequencies calculated assuming C_{3v} symmetry

are in good agreement with those observed. The order of the

N-S bond is computed as 0.68 so that the compound appears to

be a true donor-acceptor complex. These compounds appear to be the

only reported examples where sulphur(VI) functions as an acceptor.

Baumgarten[426] has reported that pyridine reacts with sulphuryl

chloride to give a complex, oily, product which is thought to

contain $(C_5H_5NCl)SO_2Cl$ and $(C_5H_5NCl)_2SO_2$. This reaction has

been repeated in order that the infrared spectrum of the product

might be examined. The viscous, oily, product corresponded to

$2(C_5H_5N)SO_2Cl_2$ irrespective of the mole ratio of the reactants.

The infrared spectrum is complex and is difficult to assign with

any precision. However, it is characteristic of coordinated

rather than salt-like pyridine[411]. The symmetric and asymmetric

S-O stretching modes occur at 1403 and 1182 cm^{-1}, respectively

compared to 1414 and 1182 cm^{-1} for sulphuryl chloride itself[427].

As with the α-sulphanuric chloride adducts a strong broad band

occurs at ~2500 cm^{-1} and is thought to be due to C-H hydrogen

bonding. By analogy with the α-sulphanuric chloride derivatives it

is suggested that the oil initially formed is a simple adduct.

However, on standing ($>$ 24 hours) the oil appears to decompose with

loss of SO_2, possibly in a complex manner as suggested by Baumgarten.[426]

Because of the presence of the band at ~2500 cm^{-1} it was

decided to prepare the pyridine-sulphur trioxide and pyridine-

selenyl chloride complexes in order to examine the infrared

spectra of these compounds.

Whilst the infrared spectrum[425] of the $Me_3N.SO_3$:_

complex does not show a band at ~2500 cm^{-1}, it was felt that an

aromatic amine complex might behave differently. Further,

if for the pyridine complex the band at ~2500 cm^{-1} were observed,

this would suggest that the hydrogen bonding involved the

C-H...O system. The selenyl chloride complex, $2(C_5H_5N).SeOCl_2$,

whilst not completely analogous to the sulphur(VI) adducts, was

thought to be of interest in view of its peculiar structure.

This compound, which has a tetragonal pyramidal structure,[428]

contains two long, 2.57 and 2.39Å, Se-Cl bonds (calculated, 2.16Å).

The longer bond is thought to be due to a briding chlorine which

approaches the unfilled octahedral position in a neighbouring

molecule. However, if in the sulphur(VI) adducts the band at

~2600 ⊕ 2500 cm^{-1} is due to the C-H...Cl system, then a similar

situation might exist in this compound, for which the infrared

spectrum does not appear to have been reported. The infrared

spectrum is given in Table 17. The band at 1250 cm^{-1} is

characteristic of coordinated pyridine[411]. The band at 920 cm^{-1}

is assigned to νSe-O which in selenyl chloride[429] itself occurs

Table 17

The infrared spectrum of $2(C_5H_5N) \cdot SeOCl_2$

ν cm^{-1}	assignment		ν cm^{-1}	assignment
3086m)			920vs	ν Se-O
3058m)	ν CH		879s	ν_{10b}
3021m)			762vs	ν_4
2994w			746sh	
1919w			699sh	
1880w			682vs	ν_{11}
1694w			634vs	ν_{6b}
1634m	ν_{8a}		621sh	ν_{6a}
1597vs	ν_{8b}		590ms	
1572s			423ms	ν_{16b}
1527w			329s	ν_{as} Se-Cl
1477s	ν_{19a}		298s	δ_s ClSeCl
1449vs	ν_{19b}		~220s	δ_{as} OSeCl
1351wm	ν_{14}			
1250m				
1203s	ν_{9a}			
1155s	ν_{15}			
1058vs	ν_{18a}			
1030vs	ν_{12}			
1006vs	ν_1			

at 995 cm^{-1}. Bands in the region 450-200 cm^{-1} are tentatively

assigned by analogy with selenyl chloride[429] for which ν_{as}Se-Cl,

δ_sClSeCl and δ_{as}OSeCl occur at 347, 279 and 255 cm^{-1} respectively.

In the region 770-620 cm^{-1} all of the strong bands are associated

with pronounced shoulders and the assignments are tentative.

The mass spectrum of this compound showed only peaks due

to pyridine, Se and SeO. It seems that simple breakdown into

the two components occurs. That peaks due to $SeOCl_2$ and $SeOCl$

are not observed is reminiscent of the behaviour of $SOCl_2$ for

which the parent peak is insignificant, and that due to SOCl is

of low intensity[102].

The infrared spectrum of the pyridine-sulphur trioxide complex

is given in Table 18. The band at 652 is characteristic of

coordinated pyridine[411]. A doublet at 1304, 1299 cm^{-1} and the

band at 1075 cm^{-1} are assigned to ν_{as} S-O and ν_sS-O respectively,

these modes occur at 1330 cm^{-1} and 1069 cm^{-1} for the trioxide

itself[330]. The doublet at 658-676 cm^{-1} is difficult to assign

since both pyridine (652 cm^{-1}) and sulphur trioxide (652 cm^{-1})

absorb in this region, which may also contain νS-N. The spectrum

seems to be as expected for a simple adduct and it is suggested

that this form of the compound is a true donor-acceptor complex.

The pyridine-sulphur trioxide complex is difficult to purify

because of its insolubility[424] in most solvents. The compound

was dissolved in nitromethane, at room temperature, and the solution

Table 18

The infrared spectra of the two compounds, $C_5H_5N.SO_3$

α (ν cm^{-1})	assignment	β (ν cm^{-1})	α (νcm^{-1})	assignment	β (ν cm^{-1})
3125s ⎫		3178m			919ms
3086m ⎬ ν_{CH}		3106sh	879w		889sh
3058w ⎭			844w		858w
2915w					794vs ⎫
1631m	ν_{8a}	1639sh	781s		784vs ⎬
1613s	ν_{8b}	1616s	753m	ν_4	731vs ⎭
1577w			685vs		681vs
1529m		1536s			652w
1477m	ν_{19a}	1490s	676s		613s
1462s	ν_{19b}				588sh ⎫
1426w			599vs	ν_{6a}	575vs ⎭
1385w	ν_{14}	1342sh ⎫	561s	δ_dS-O	
1304vs ⎫ ν_{as}S-O					506ms
1299vs ⎭					
1269m		1274vs ⎪			
1232m		1220sh ⎬			
1207m	ν_{9a}				
1156m	ν_{15}	1190s ⎪			
1099w		1170sh ⎭			
1075vs	ν_sS-O	1086s			
1062m	ν_{18a}	1058s			
1043ms	ν_{12}	1038s			
1031w					
1017ms	ν_1	1011ms			

allowed to stand at this temperature for several hours.

Needle like crystals were slowly deposited and analysis showed

the molecular formula still to be $C_5H_5N.SO_3$. It seems,

therefore, that this compound can exist in two solid forms (α and β).

The infrared spectrum of the second (β) form is also given in

Table 18 and is more complex than that of the (α) form first

isolated. The regions 1300-1150, 800-730 and 590-570 cm^{-1}

contain broad complexes absorptions; it seems probable that in

this β form the pyridine is bonded through oxygen, or that the

sulphur trioxide is present in a polymeric form.

The mass spectra of both forms of $C_5H_5N.SO_3$ were identical.

In each case simple decomposition into the constituents, C_5H_5N

and SO_3, occurred. In this respect these compounds resemble the

selenyl chloride adduct, $2(C_5H_5N).SeOCl_2$.

In conclusion, a study of the adducts, $C_5H_5N.SO_3$ and

$2(C_5H_5N).SeOCl_2$, has revealed no evidence for C-H hydrogen

bonding in these compounds. However, they do illustrate the

general infrared and mass spectroscopic behaviour which is to

be expected for simple donor-acceptor adducts.

The reactions of sulphuryl chloride with other donors has

also been investigated. With triphenylphosphine two compounds,

a colourless oil and a white amorphous solid were isolated; the

analyses for each compound indicated a molecular structure,

$Ph_3P.SO_2Cl_2$. On the basis of the infrared spectra of these

compounds it is thought that both are simple adducts, the oil

containing the ligand bonded to the sulphur atom, whilst in the

solid the ligand is bonded to one of the oxygen atoms. The

infrared spectra are given in Table 19; as is that of Ph_3P itself.

For the oil the strong broad band at 1279 cm^{-1} is assigned to

$\nu_{as}S-O$ and appears to obscure the weak absorption at 1274 cm^{-1} of

triphenylphosphine itself. This mode occurs[427] at 1414 cm^{-1} in

SO_2Cl_2 itself. This rather large shift ($\Delta\nu = 135$ cm^{-1}) is

probably due, in part, to the high mass of the ligand though

other factors must also be involved since mass effects do not

normally result in changes of this magnitude. Bands at 1106

and 578 cm^{-1} correspond to the ν_sS-O and SO_2 bending modes which

occur[427] at 1182 and 560 cm^{-1} for SO_2Cl_2 itself. All of the

other bonds observed correspond to those of the free ligand.

In the case of the solid the strong ($\nu_{as}S-O$) band which occurs

at 1279 cm^{-1} for the oil has disappeared, and the band at 1263 cm^{-1}

is thought to correspond to the weak 1274 cm^{-1} band of triphenyl-

phosphine. The strong band at 1006 cm^{-1} is assigned to an S-O

stretching vibration and that at 565 cm^{-1} to an SO_2 bending mode.

The new band at 656 cm^{-1} (not present for the oil) is thought to

be due to a vibration involving the $S-O-PPh_3$ group. The

remaining bands correspond to those observed for the free ligand,
though the bands at 1031 and 996 cm^{-1} appear to be reversed in
intensity as compared with those at 1023 and 996 cm^{-1} for Ph$_3$P itself.

Table 19

The infrared spectra of the Ph$_3$P.SO$_2$Cl$_2$ adducts

oil (ν cm^{-1})	Ph$_3$P(ν cm^{-1})	solid (ν cm^{-1})	oil (νcm^{-1})	Ph$_3$P(νcm^{-1})	solid (νcm^{-1})
1582s	1582ms	1580s	617s	617wm	616s
		1570sh	578s		565s
1493s			536vs	539w,	535m
1481s	1472vs	1479s	513s	511s	513ms
1435vs	1431vs	1438vs			
	1370w				
1322sh	1324w	1342wm			
1312sh	1305ms	1314ms			
1279vs	1274w	1263s			
1185wm	1176wm	1188wm			
1163wm	1153wm	1161wm			
1120sh	1117w	1145w			
1106vs		1107vs			
1096sh	1088s	1099s			
1077w	1068m	1072w			
1040vs	1023s	1031w			
1026w					
993w	994m	996s			
935w	916wm				
	853w	853w			
	752s	760vs			
749s	746s	747vs			
729vs	741s	727vs			
696s	695s	697sh			
685s	691s	690s			
		699sh			
		656s			

Since the adduct is initially obtained as the oil, which
then largely isomerises to the solid, it would seem that the O-
bonded form is slightly the more stable. Mass spectroscopic

studies support this suggestion. The mass spectra of both

isomers are identical and correspond to cleavage of the adduct

into triphenylphosphine oxide and thionyl chloride.

Attempts to prepare a 2:1 adduct, $2(Ph_3P).SO_2Cl_2$, were

unsuccessful, in contrast to the reaction with pyridine when only

the 2:1 adduct could be obtained.

With triphenylarsine and triphenylstibine simple adducts

were not isolated, but the dichlorides, Ph_3AsCl_2 and Ph_3SbCl_2

were obtained in almost quantitative yields. It seems probable

that these compounds were obtained via the initial formation of

an adduct, which then decomposed with elimination of SO_2, e.g.

$$Ph_3As + SO_2Cl_2 \longrightarrow (Ph_3As.SO_2Cl_2) \longrightarrow Ph_3AsCl_2 + SO_2$$
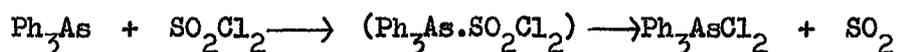
The preparation of these dichlorides in this manner does not appear

to have been previously reported, and is more convenient than the

normal preparation by the action of chlorine on the triphenyl derivative.

Attempts to prepare adducts with other sulphur(VI) compounds,

aryl sulphonamides and sulphonyl chlorides, diphenylsulphone and

sulphamide, were unsuccessful. The compound $(C_5H_5N.SO_2Ph)Cl$

has been reported[430] but could not be obtained in this work. The

reaction between benzenesulphonyl chloride and triphenylphosphine

gave triphenylphosphine oxide and, presumably, benzenesulphinyl

chloride, though this was not isolated. Brzozowski[431] has reported

the preparation of a variety of amine complexes with sulphonamides

containing acyl substituents. These compounds are thought to
contain the amine bonded via the carbon of the acyl group, except
in the case of sulphonyl guanidines for which bonding via the
sulphur of the SO_2 group is postulated. The author has
unsuccessfully attempted to prepare adducts of pyridine with benzene-
and pentafluorobenzene-sulphonamides. Whilst in the latter case
only the starting materials could be recovered, the formation of
a strong colour on mixing the reactants suggests that an unstable
adduct may have been formed in solution.

It seems that adducts can only be prepared for sulphur(VI)
compounds in which the sulphur atom is surrounded by four highly
electronegative ligands. For such compounds the energies of the
unfilled sulphur d-orbitals are lowered by the presence of the
substituents[357] and it seems reasonable to assume that it is these
orbitals which accommodate the donor electrons. Adducts of
α-sulphanuric chloride are more stable than those of sulphuryl
chloride. Thus, α-sulphanuric chloride forms adducts with Ph_3As
and Ph_3Sb (though the latter is rather unstable) whilst sulphuryl
chloride does not form adducts with these weaker ligands. Again,
α-sulphanuric chloride forms stable adducts with both aromatic and
aliphatic tertiary amines, whilst sulphuryl chloride-aromatic
amine adducts seem rather unstable and with aliphatic amines no
simple adduct is formed (see later). A possible explanation is that

for the α-sulphanuric chloride adducts the donor electrons are

accommodated in molecular orbitals which, to some extent, are

delocalised over the sulphur-nitrogen ring.

E. Similar complexes of amines with elements other than sulphur

If the above hypothesis is correct then compounds of

other covalently saturated main group element (X) containing

low-lying d-orbitals should also be capable of forming adducts.

In particular, if X = O or X - Cl bonds are present the resultant

compounds may contain C-H hydrogen bonds.   Phosphorus oxychloride

seemed to satisfy the requirements and the formation of an adduct,

$2(C_5H_5N).POCl_3$, has been reported[399].   The preparation of this

compound was attempted in order that its infrared spectrum might

be examined.   Under anhydrous conditions it was only possible to

isolate traces of pyridinium chloride.   However, using unpurified

reagents a product was obtained for which the analyses were

approximately those required for the adduct.   The m.p. of this

product (50-70°C) indicate it to be impure and it is thought to be a

mixture of pyridine salts of phosphorus oxychloride hydrolysis

products.

Complexes of acyl halides with pyridine and other tertiary

bases have been examined by Paul and Chadha[432] who have proposed structures

such as (25) because of the presence of a band at 2300-2100 cm^{-1}

$$\left(\begin{array}{c} \overset{+}{O} \longleftarrow C_5H_5N \\ R\text{---}C \end{array} \right) \quad Cl^-$$
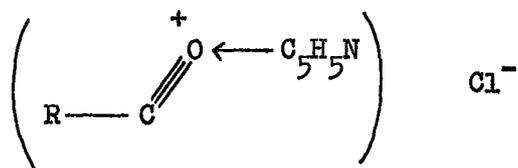
(25)

which they assign to the $C \equiv \overset{+}{O}$ group.

$$\left(\begin{array}{c} C_5H_5\overset{+}{N} \\ | \\ C \\ O \quad R \end{array} \right) Cl^- \qquad \begin{array}{c} C_5H_5N \\ \downarrow \\ R\text{---}C \overset{O}{\underset{Cl}{<}} \end{array} \qquad \begin{array}{c} C_5H_5\overset{+}{N} \\ | \\ R\text{---}C \overset{O^-}{\underset{Cl}{<}} \end{array}$$
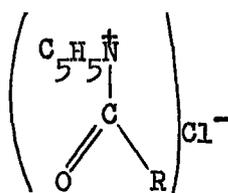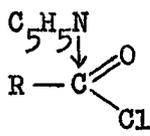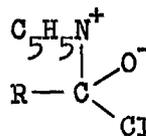
(26)   (27a)   (27b)

Because of the high electronegativity of the oxygen atoms it

seems likely that the positive charge in the $(RCO)^+$ ion will

be largely associated with the acyl carbon atom. It is thought,

therefore, that these complexes are more likely to have structures

such as (26) and (27), which involve bonding via the acyl carbon

atom. These structures are analogous to those proposed for the

α-sulphanuric chloride-amine adducts, (23) and (24), and may be

regarded as extreme possibilities representing the formation of salts

(26) or donor-acceptor complexes (27). Structure (27a) which

requires four-covalent carbon to act as an acceptor site is

unlikely but it can be alternatively written as (27b) in which

form it may make a canonical contribution.

The spectra of these acyl halide-amine complexes show a

strong broad band at 2700 cm^{-1} which is assigned by Paul

and Chadha[432] to a C-H stretching mode, but with no explanation

as to its low frequency$\frac{1}{2}$ On the basis of structures (26) and

(27) this may be explained as due to C-H hydrogen bonding, as in the

case of the sulphur(VI) adducts.

F. The amine adducts and dimethylsulphoxide

The reaction between $3(C_9H_7N)(NSOCl)_3$ and dimethylsulphoxide

gave a compound for which the analyses corresponded to,

$2(C_9H_7N).(CH_3)_2SO.(NSOCl)_3$, i.e. one iso-quinoline ligand was

replaced by dimethylsulphoxide. The assignment of $\sqrt{}$S-O

in complexes containing dimethylsulphoxide is the subject of some

controversy, as has been discussed in part 2 of this thesis.

For this compound the infrared spectrum is complex and the

band expected at ~1000 cm^{-1} is in a region where pyridine itself

absorbs strongly. A new strong band at 910 cm^{-1} may be

assigned to either the S-O stretching or the CH_3- rocking vibration.

It seems probable that the dimethylsulphoxide is bonded through its

oxygen atom as in most other complexes. Dimethylsulphoxide also

reacted with the pyridine adduct to give a compound the infrared

spectrum of which was similar to that of the mixed iso-quinoline-

dimethylsulphoxide adduct.

G. The pyrolysis of the amine adducts

All of these compounds decomposed when heated at $100^{\circ}C$

under vacuum. In the case of the adduct, $2(C_5H_5N) \cdot SO_2Cl_2$,

analysis of the product indicated a molecular formula, $C_5H_{4-6}NOCl$,

but did not precisely fix the number of hydrogen atoms present

(Table 20).

Table 20

Analysis of the $2(C_5H_5N) \cdot SO_2Cl_2$ pyrolysis product

	Calculated (%)			Found (%)
	C_5H_4NOCl	C_5H_5NOCl	C_5H_6NOCl	
C	46.35	45.99	45.64	46.24
H	3.12	3.87	4.61	4.98
N	10.81	10.72	10.65	10.71
Cl	27.37	27.16	26.95	28.05

The infrared spectrum was characteristic of the pyridinium ion[411]

and, with the exception of two moderately strong bands at 1104

and 814 cm^{-1} was identical with that of pyridinium chloride.

The N.M.R. spectrum in nitromethane was identical with that of

pyridinium chloride in the same solvent. Alkaline hydrolysis

liberated pyridine though, in contrast, the mass spectrum contained

peaks at masses (113, 115) corresponding to C_5H_4NCl.

It has not been possible to suggest a completely satisfactory

structure for this compound. The molecular formula

C_5H_5NOCl was rejected since it requires an odd-electron

molecule. For the species C_5H_4NOCl and C_5H_6NOCl various

structures (28-30) may be written.

$$
\begin{array}{ccc}
\text{(28)} & \text{(29)} & \text{(30)}
\end{array}
$$

Structure with ring bearing CCl and N→O   (28)

Structure with OH on N and Cl^- (29)
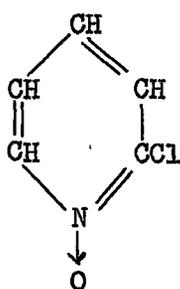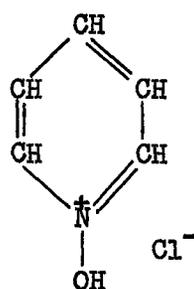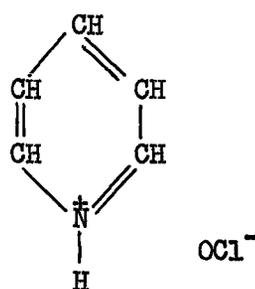
Structure with H on N and OCl^- (30)

Structures (28) and (29) involving N-O bonds seem plausible

by analogy with the O-bonded form of the $Ph_3P.SO_2Cl_2$ complex,

though (28) is unlikely since it requires the hydrolysis product

to be an hydroxypyridine. On the basis of structures (29)

and (30) it is difficult to account for the presence of C_5H_4NCl

in the mass spectrum. The mass spectrum of $C_5H_5N.HCl$

shows only peaks due to C_5H_5N and HCl so that, as expected,

the Cl^- ion is not capable of chlorinating the pyridine nucleus

under the conditions used in the spectrophotometer. However,

the hypochlorite ion is a stronger chlorinating agent and it is

perhaps possible that, at the temperatures used ($\sim 200^\circ C$),

thermally induced chlorination could occur before the sample volatilised into the ioh source.

The formulation of this pyrolysis product as a pyridine salt receives some support from the reaction between triethylamine and sulphuryl chloride from which only triethylamine hydrochloride could be isolated. However, evaporation of the solution to dryness gave traces of a red-brown oil which suggests that an unstable adduct may have been formed initially. A similar situation occurs in the reactions of thionyl chloride with pyridine and some other tertiary bases[102] which also yield only the amine hydrochlorides.

The pyridine and iso-quinoline adducts of α-sulphanuric chloride appear to decompose in an analogous manner to the pyridine-sulphuryl chloride adducts. The products appear to have molecular structures C_5H_6NSCl and C_9H_8NSCl i.e, they are thio-analogous of the product from the pyridine-sulphuryl chloride adduct, and presumably, have analogous structures.

H π-Complexes of α-sulphanuric chloride

α-Sulphanuric chloride reacts with excess hexamethylbenzene to give a compound for which the analyses correspond approximately to, $2(C_6Me_6).(NSOCl)_3$. Attempts at purification lead to decomposition with the formation of a red-brown solid which was similar in appearance to that obtained from reactions using a

lower proportion of hexamethylbenzene. It seems possible that

this red-brown solid is an impure, unstable 1:1 adduct, $C_6Me_6 \cdot$

$(NSOCl)_3$.

Similar products are formed, in the solid phase, by the

amino- and chloro-cyclophosphazenes[433]. The chlorocyclophosphazenes

are strong acceptors towards hexamethylbenzene. The cyclo-

tri-and penta-phosphazenes each form only a 2:1 complex, e.g.

$2(C_6Me_6) \cdot (NPCl_2)_3$; the cyclo-tetra- and hexa-phosphazenes form

both 2:1 and 1:1 adducts.

I. α-Sulphanuric chloride as a donor molecule

These experiments were carried out as part of a general

examination of the chemical properties of α-sulphanuric chloride.

In principle α-sulphanuric chloride may function as an electron

donor via (i) the ring nitrogen atoms (ii) the exocyclic oxygen

atoms and (iii) the delocalised $p_\pi - d_\pi$ ring orbitals.

(i) the ring nitrogen atoms

Other cyclic sulphur-nitrogen systems form adducts in this

manner. Thus $(NSF)_4$ forms[106] the weak adduct $(NSF)_4 \cdot BF_3$ and

S_4N_4 forms adducts[96-101] with a variety of metal-halides, e.g.,

$S_4N_4 \cdot SbCl_5$ for which structural studies[434] show the presence

of a Sb-N bond.

(ii) The exocyclic oxygen atoms

Such behaviour, though less likely than (i), would be analogous to that of dimethylsulphoxide which forms numerous adducts with metal halides[300-308].

(iii) The π-delocalised system

Such behaviour is unusual, however, it has been suggested[435] that this type of bonding occurs in the complex $(NPMe_2)_4 \cdot Mo(CO)_4$.

Attempts to form adducts with beryllium and mercury(II)-chlorides were unsuccessful. More promising results were obtained with transition metal halides. The colour changes which occur with both $TiCl_4$ and $NbCl_5$ suggest that some interaction, possibly weak charge transfer, occurs. However, in both cases the initial product decomposed on standing at room temperature. It is possible that an examination of these reactions at lower temperatures would lead to isolation of complexes. However, it may be more desirable to examine the donor properties of other, particularly amino, sulphanuric derivatives. Thus, it has been shown that the phosphonitrilic chlorides are only weakly basis[436,437] and do not intereact with metal halides[438]. In contrast the amino phosphonitriles[439,440] are more strongly basic and form complexes with Co(II), Cu(II) and Ni(II) ions[438]. It has been suggested[438]

that this difference may result from the ability of the

halide atom to decrease ring electron density. Analogously,

though benzene acts as a Lewis base, C_6F_6 is a Lewis acid[441].

Electron donor substituents such as amines may have the opposite

effect and, therefore, enhance the donor capacity of the ring or

the ring nitrogen atoms. Similar arguments may apply in the

case of sulphanuric compounds.

J. Metathesis reactions of α-sulphanuric chloride

One aim of the research was to attempt the preparation of

a series of sulphanuric compounds, $(NSOX)_3$, and to investigate

the properties of these compounds utilising, e.g., infrared

N.M.R. and mass spectroscopy and measurement of dipole moments

in solution. It was hoped that in this way the stability of the

compounds could be shown to be related to the nature of the

substituent X.

Reactions with lithium alkyls lead to the formation of

compounds whose infrared spectra bore no resemblance to

those of sulphanuric chloride or other sulphanuric derivatives[125, 127].

In an attempt to prepare the triphenyl derivative, $(NSOPh)_3$,

by reaction with phenylmagnesium bromide only a small amount of

an oil was isolated. The infrared spectrum of this oil was almost

identical with that reported for phenyl thionylimine, PhNSO. The

analyses were quite close to those required and it was concluded

that the oil was impure PhNSO. Presumably the phenylmagnesium

bromide added initially across the S=O double bond and this

was followed by ring opening and rearrangement.
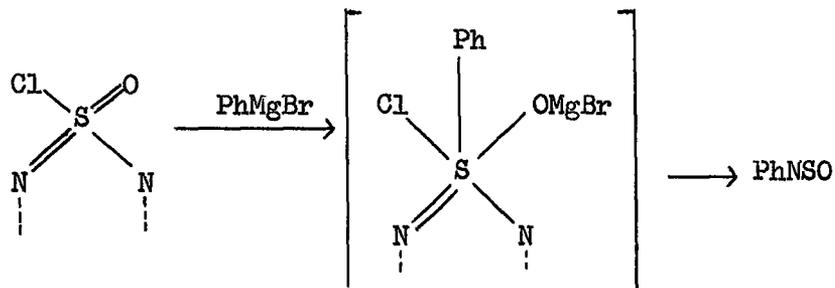
The low yield of PhNSO suggests that other modes of breakdown

also occur. Attempts to prepare the mono-phenyl derivative in

like manner apparently resulted in a similar ring cleavage.

The product obtained by extraction of the crude reaction residue

with acetonitrile was analysed for C,H,N and S which were found

to account for only 46% of the compound. Qualitative tests showed

the presence of magnesium, chlorine and bromine. Analysis for

total halogen in conjunction with the elemental analyses suggested

that the material could best be represented as $(PhNSO).2(CH_3CN).$

$Mg_2BrCl_2.$ The infrared spectrum could be rationalised on the

assumption that both PhNSO and CH_3CN were present; the C≡N mode

occurs at 2288 cm^{-1} which is characteristic of the nitrile group

acting as a donor to a rather weak acceptor.[369-370]. No reasonable

structure could be postulated for molecular formula and it was

concluded that the material was probably a mixture of PhNSO and a

magnesium halide - acetonitrile adduct. It is possible that these two components weakly interact in the solid phase.

Reaction with potassium thiocyanate gave an orange solid, insoluble in organic solvents so that separation from the by-product, potassium chloride, was impossible. The analogous reaction with phosphonitrilic chloride leads to the formation of the isothiocyanate derivative[442] and a similar result might be expected in this case. The infrared spectrum of the crude product bore no resemblance to that of sulphanuric chloride and did not show an absorption at ~ 2000 cm^{-1} which is characteristic[443] of the -NCS group. The orange-red pyridine-2-isothiocyanate which exists as a dimer does not show this absorption. It was concluded that the product was a polymeric isothiocyanate.

N,N diethylaminotrimethylsilane is a useful reagent for the introduction of -NEt_2 groups. Thus, Abel and Armitage[444] have reported the reactions,

$$RSO_2Cl + Et_2N.Si.Me_3 \longrightarrow Me_3SiCl + RSO_2NEt_2 \quad (R=Me,Ph)$$

$$SO_nCl_2 + 2Et_2N.Si.Me_3 \longrightarrow 2Me_3SiCl + (Et_2N)_2SO_n \quad (n=1,2)$$
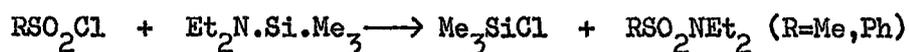
Reaction with α-sulphanuric chloride gave an oil, the analyses for which approximate to those required for the diethylamino derivative, $(NSONEt_2)_3$. The crude product is expected to be a mixture of at least two isomers but attempts to separate these by sublimation or recrystallisation were unsuccessful.

The infrared spectrum of the oil is very similar to those reported[125,127] for other sulphanuric derivatives.

It seems that, in general, α-sulphanuric chloride undergoes ring cleavage rather than simple metathesis reactions. Low temperature reactions with nucleophiles of low basicity, e.g., morpholine[127] and N,N diethylaminotrimethylsilane do, however, result in substitution. During the course of this work Moeller and Ouchi[125] have reported the synthesis of some derivaties of sulphanuric fluoride which undergoes metathesis reactions more readily than the chloride. These authors have suggested that the lack of substitution of α-sulphanuric chloride by more basic reagents may be a consequence of the exothermic vigour with which the chlorine atoms are solvolytically removed. The mass spectrum of α-$(NSOCl)_3$, Table 21 and Fig.20, is of interest in this context. Few of the species formed are sufficiently stable to give rise to measurable peaks and the suggested breakdown pattern is somewhat tentative. The most abundant peaks are those due to $(N_3S_3O_3Cl_2)^+$, which is formed by loss of one chlorine atom. It seems that further ionisation processes lead to the formation of very unstable species and that the sulphur-nitrogen ring is readily cleaved. Possibly the formation of cyclic cations involves profound changes in the ring geometry with consequent breakdown in the delocalised p_π - d_π system. Similar factors may operate in methathesis reactions if these proceed via solvolytic removal of the chlorine atoms.

Fig.20

The mass spectroscopic breakdown of α-(NSOCl)$_3$. Routes involving species not observed in the spectrophotometer are shown ....

$$N_3S_3O_3Cl_3$$

$$N_3S_3O_3Cl_2 \longrightarrow N_3S_3O_2Cl_2$$

$$N_3S_3O_3Cl \qquad\qquad N_3S_3O_2Cl$$

$$N_2S_3O_3Cl \qquad\qquad N_2S_3O_2Cl$$

$$N_2S_2O_3Cl$$

$$N_2S_2O_2Cl$$

$$N_2S_2OCl$$

$$NS_2OCl$$

$$NSOCl \longrightarrow SOCl \longrightarrow SO + Cl$$

$$NSO \longrightarrow NS + O$$
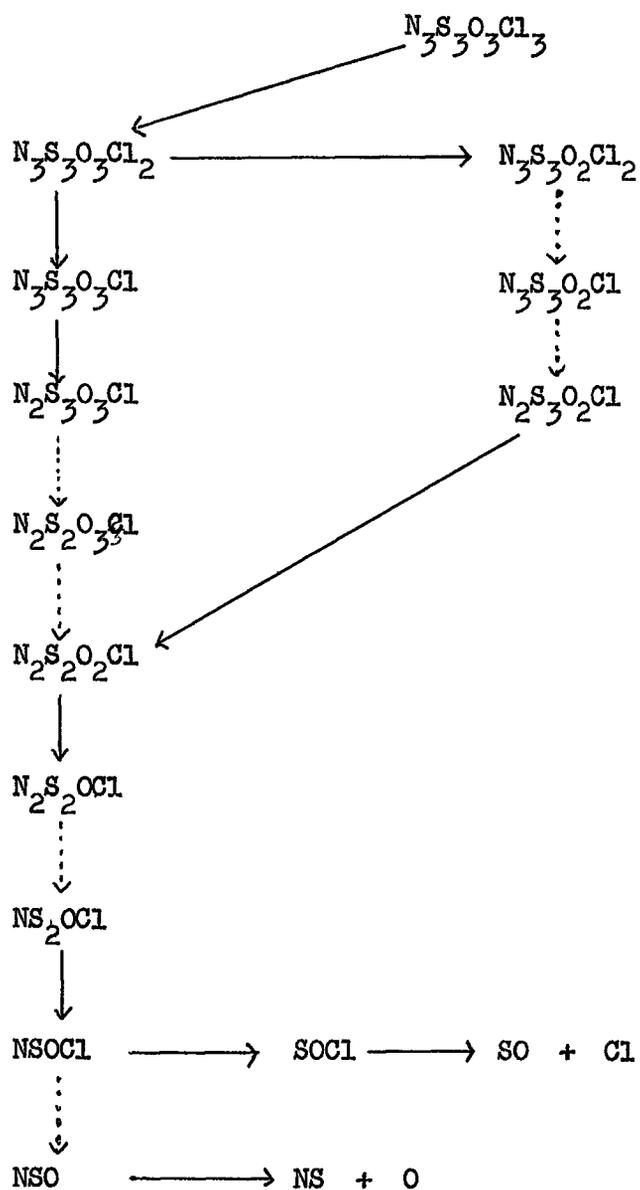
Table 21

The mass spectrum of α-(NSOCl)$_3$. Accelerating potential 70 ev.,

Source temperature 90°C

Nominal mass	rel. int.	species
291	4.8 ⎫	
293	5.3 ⎬	$N_3S_3O_3Cl_3$
295	2.4 ⎭	
256	100.0 ⎫	
258	81.6 ⎬	$N_3S_3O_3Cl_2$
260	24.1 ⎭	
240-244	<2.0	$N_3S_3O_2Cl_2$
221	<1.0	$N_3S_3O_3Cl$
207-209	<1.0	$N_2S_3O_3Cl$
143	<1.0	N_2S_2OCl
99	<1.0 ⎫	
97	2.4 ⎭	NSOCl
85	2.5 ⎫	
83	7.5 ⎭	SOCl
48	21.6	SO
46	37.4	SN

The infrared spectrum of α-(NSOCl)$_3$ is given in Table 22.

Table 22

The infrared spectrum of α-(NSOCl)$_3$

ν cm^{-1}	assignment
1812w	1100+713 = 1813
1335s	ν_{S-O}
1326s	2 x 663 = 1326
~1100s (broad)	
812m	
713ms	
702ms	
669sh	
663s ν 510m s	ν_{S-Cl}

Using the measured S-O bond length (1.407Å), and the relationship

between S-O bond lengths and stretching frequencies derived in the

spectroscopic section, the predicted value of νS-O in α-(NSOCl)$_3$

is 1334 cm^{-1}. The observed band at 1335 cm^{-1} overlaps with

one at 1326 cm^{-1} which appears to be an overtone of the band

at 663 cm^{-1}. The band at 540 cm^{-1} is in the region expected

for the S-Cl stretching vibration.[340] From the relationship

between S-N bond lengths and stretching frequencies

(spectroscopic section)νS-N is predicted at 1025 cm^{-1}. No

band is observed at this frequency. It seems that exocyclic

groups give rise to stretching frequencies in the expected regions

and that other bands (1100-660 cm^{-1}) are to be associated with

ring stretching and deformation modes.

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773s, 694sh, 687ms, 669w, 631w, ~550wm, ~440m.

Evaporation of orange-red solution to dryness gave

a red-brown solid which was recrystallised from toluene-hexane

mixture. The infrared spectrum of the recrystallised material

was identical with that of an authentic sample of Ph_3SbCl_2.

Chapter 5

Structural Studies on Sulphur Species

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CONTENTS

1. Infrared and Raman spectroscopy: Introduction

With few exceptions infrared and Raman spectra can be obtained for all covalent molecules and all ionic species containing covalently bound atoms. Infrared and Raman spectra provide similar molecular data and either method can supplement or complement the other

Information of three types is obtainable from such spectra

(i) Most ions and certain functional groups give rise to absorptions at characteristic positions in the infrared and Raman spectra Consequently the spectra can be used for qualitative diagnosis and in favourable cases can be used for quantitative analysis

(ii) The shape and symmetry of the system can be derived from the number of observed features arising from fundamental vibrations, and from other details such as vapour phase band envelopes in the infrared, and Raman depolarisation ratios.

(iii) For a few simple molecules in the gas phase precise values of bond lengths and interbond angles can be calculated A consideration of such calculations is outside the scope of this Chapter

The main purpose of the following treatment is to summarise the theory, some practical aspects, and literature relevant to the task of identifying (1) inorganic substances containing sulphur and (2) sulphur-containing functional groups and ions

2. Infrared spectra

(a) The origins of infrared spectra

As a first approximation, it is possible to consider the non-translational energy of

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a molecule as being composed of three additive components due to (1) the energy state of the electrons in the molecule, (2) vibrations of the constituent atoms and (3) the rotation of the molecule as a whole Absorption of one or more quanta of radiation will increase the appropriate molecular energy level (Fig 5 1) Excitation of the mole-

Wavelength (μ)	0 1		1 0	10	100	1000	10000
Wavenumber (cm⁻¹)			10000	1000	100	10	1 0
		Visible					Microwave
Region of spectrum							
	Ultraviolet			Infrared			
Energy of radiation (Kcal mole⁻¹)	2 86		286	2 86	0 286	2 86x10⁻²	2 86 x10⁻³
Nature of transitions	Electronic						
			Vibrational				
						Rotational	
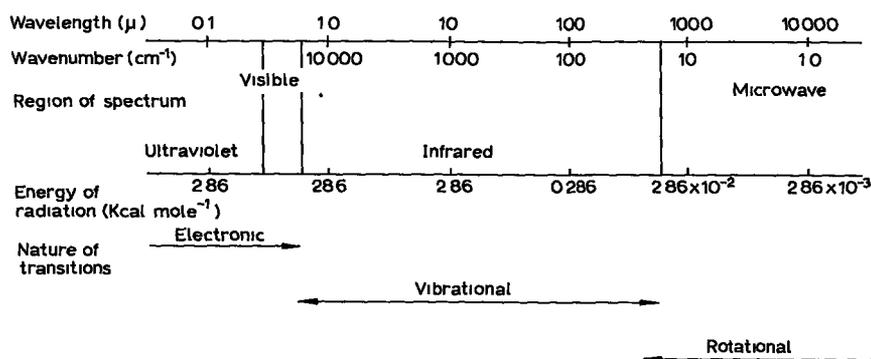
Fig 5 1 The electromagnetic spectrum Wavelength, λ, is expressed in microns (μ ~ 10⁻⁴ cm⁻¹) The wavenumber, ν̄, is 10⁴/λ

cule to higher vibrational levels only, generally requires infrared radiation The energy required to excite pure rotational transitions falls in the far infrared region of the spectrum However, both vibrational and rotational excitations can occur simultaneously and so each feature in an infrared spectrum is composed of a number of very closely spaced lines present in the vibration-rotation band are often observable (cf section 2 V) Theory shows that when a pure vibrational excitation occurs, the frequency of the infrared radiation absorbed is nearly equal to the' mechanical frequency of the vibration Consequently it can be appreciated using a mechanical molecular model that the frequency of the molecular vibration, and hence of the radiation absorbed, will depend upon the masses of the vibrating atoms and the strengths of the bonds between them We now consider this approach in more detail to show how the details of an infrared spectrum are dependent upon molecular structure and intermolecular forces

(b) Theory

(i) Introduction

The position, intensity and contour of an infrared absorption band are determined by molecular parameters and intermolecular forces The often interdependent factors which determine the overall characteristics of an infrared spectrum can be subdivided and treated separately as follows

(i) atomic mass,

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(ii) bond strength

(iii) molecular geometry and symmetry

(iv) overtones and combination bands.

Variables which can modify one or more of (ii)–(iv) are.

(v) phase,

(vi) Fermi resonance,

(vii) electronic effects (inductive, mesomeric and π electron delocalisation)

(viii) molecular strain and steric hindrance,

(ix) "field" effects which may occur internally within the molecule or as a result of the influence of an external field in a crystal or dielectric

(x) solvent effects.

These factors are now discussed

(ii) Absorption frequency as a function of mass and bond strength

The complex behaviour of a vibrationally excited molecule can be analysed as the combination of a number of simple oscillations ("fundamental" or "normal" modes of vibration). During a fundamental vibration of a group of atoms, the centre of gravity of the group does not move and all the constituent atoms move with the same frequency and in phase. Adjacent atoms at the extremities of each bond can be taken to be point masses M_1 and M_2 which execute an approximately simple harmonic motion about an equilibrium point. If linkages with the remaining atoms are ignored, the frequency of a fundamental oscillation is given by Hooke's law.

$$\tilde{v}(\text{in cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}} \tag{I}$$

Where c is the velocity of light, f is the stretching force constant of the bond (i e the restoring force per unit displacement from the equilibrium point) and μ is the reduced mass of the system Reduced mass is defined $\cdot$ $1/\mu = 1/M_1 + 1/M_2$ and so

$$\tilde{v}(\text{in cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{f(M_1 + M_2)}{M_1 M_2}} \tag{II}$$

An approximate value for the force constant, f, can often be calculated using Gordy's rule (III)[1] or Badger's rule (IV)[2] These are purely empirical relations; they occasionally lead to a highly inaccurate value for f

$$f = a \ N \left[\frac{x_1 x_2}{r^2} \right]^{\frac{3}{4}} + b \qquad \text{(Gordy's rule)} \tag{III}$$

N is the bond order, x_1 and x_2 are the Pauling electronegativity values and r is the internuclear separation in Ångstrom units The constants a and b are about 1.67 and 0 30 respectively for stable molecules in which the atoms show normal covalencies

$$r = \left(\frac{c}{f} \right)^{\frac{1}{3}} + d \qquad \text{(Badger's rule)} \tag{IV}$$

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The values of the constants c and d depend on the positions of the atoms in the Periodic Table. It is found that the force constant in most (including sulphur) compounds falls within the range $4-6 \times 10^5$ dynes cm^{-1} for single bonds and approximately two or three times this value for double bonds and triple bonds respectively As indicated by equation (II) above the absorption position becomes $\sqrt{2}$ and $\sqrt{3}$ times higher in frequency respectively

Thus, the equations above show that in principle the approximate frequency of an infrared band can be calculated from mass, bond order and bond length values Useful values can be obtained even for polyatomic systems where some interference from neighbouring bonds is to be expected Fig 5 8 shows how the stretching frequency of sulphur bonds to oxygen, varies with bond length

Bending force constants are usually about one tenth of the magnitude of stretching force constants and so the bending frequencies of a molecular skeleton of heavy atoms often lie in the far infrared region

(iii) *Number of vibrations as a function of molecular geometry and symmetry*

For a molecule of n atoms there are $3n$ degrees of freedom corresponding to motion of the individual atoms along the three Cartesian axes Of these degrees of freedom, 3 are translational (motion of the molecule as a whole along the three axes) and 3 rotational (2 for a linear molecule) Thus there are $3n-6$ ($3n-5$ for linear molecules) possible modes of vibration and theoretically each of these fundamental modes can absorb energy of a particular frequency In practice the theoretical number of absorptions is unlikely to be observed because overtones and combination bands (section 2 v) can increase, and other factors can reduce, the number of bands observed The number of bands can be reduced by theoretical [(i) and (ii)] and by practical [(iii) and (iv)] limitations

(i) "Forbidden" transitions If the symmetry of the vibration is such that it results in no (or only slight) change in the dipole moment of the molecule, then absorption will be forbidden in the infrared spectrum (or may be too weak to be detected).

(ii) Degeneracy Absorptions will occur at identical frequencies if the vibrations responsible for them involve identical *relative* movements of the atoms In a condensed phase the superimposed absorptions may however be split into a closely spaced multiplet (cf section 2X).

(iii) Fundamental frequencies may occur outside the range studied

(iv) Absorption peaks may be too close together to be resolved (accidental degeneracy)

Bond vibration modes are roughly divisible into three distinct types, stretching, bending (or deformation) and torsion The first consists of periodic stretching of the bond along the bond axis Bending vibrations are displacements occurring at right angles to the bond axis and consequently involve a change in bond angles Torsion involves twisting about a bond.

Absorption occurs when the frequency of the oscillating field of the infrared radia-

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tion is equal to the frequency of the oscillating dipole produced by the molecular vibration The magnitude of the molar extinction coefficient is proportional to the square of the change in the dipole moment of the molecule[3]. This results in stretching vibrations often producing the most intense peaks in the spectrum, though certain symmetrical vibrations produce no absorption at all ("infrared inactive", due to no overall change in dipole moment) For instance, the totally symmetric stretching vibrations of SO_3 and SO_4^{2-}, and the totally symmetric stretching (breathing) vibration of SF_6 do not appear in the infrared spectrum Unlike tetrahedral SO_4^{2-}, the totally symmetric stretching vibration of the trigonal bipyramidal molecule SF_4 is infrared active Consequently the number of absorption peaks observed may yield some structural information

More detailed treatments of vibration spectra can be found in a number of text books[4-11]

Groups of the type AX_2 (e.g $-CH_2-$, $-NH_2$, $-SO_2-$) occur so frequently, particularly in organic compounds, that trivial names have been devised to describe the various possible types of vibration (Fig 5 2)
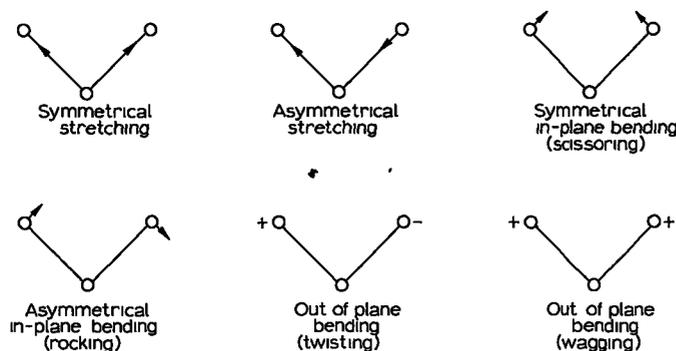
Fig 5 2 Vibrational modes of the AX_2 group + and − represent relative movements perpendicular to the surface of the page

(iv) Overtones and combination bands

These are the two main types of absorption bands which appear in a spectrum additional to the fundamental stretching and deformation modes

Overtones occur at 2,3 . n times the fundamental frequency ($\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{n}$ of the wavelength) The first overtone often has $\frac{1}{10}$-$\frac{1}{100}$ of the intensity of the fundamental and intensity rapidly diminishes with increasing n A first overtone can, however, be unexpectedly weak or unexpectedly strong in an infrared spectrum

Combination bands occur when infrared radiation (of frequency $v_a + v_b + ..$) excites two or more fundamentals (of frequencies v_a, v_b etc) simultaneously. Commonly, except in very weak absorptions, only two fundamentals contribute Combination bands can be quite strong and numerous and may extend into the near infrared In sulphur chemistry the population of the near infrared (generally wholly due to over-

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tones and combination bands) is appreciably less than for many organic compounds
If, for some reason, some of the lower frequency fundamentals are inacessible it may
be difficult to determine the origin of the overtone and combination bands that they
cause

Difference bands (at frequencies equal to e g $v_a - v_b$, $v_a + v_b - v_c$) are also possible
but they are normally weak.

(Overtones, combination bands and difference bands are generally very much
weaker in Raman spectra than in infrared spectra)

(v) *Characteristic band shapes for gases, liquids and solids*

(1) *Gases.* In the gas phase, molecules are free to rotate and so changes in the
rotational energy of the molecule can accompany a vibrational transition The
vibrational band is split into a large number of sharp peaks close together and almost
equally spaced on each side of the original vibration frequency For a diatomic
molecule treated as a rigid rotator the frequencies of the sharp peaks are given by the
equation.

$$v = v_0 + \frac{hm}{4\pi^2 I}$$

where v_0 is the fundamental vibration frequency in sec^{-1}, h is Planck's constant,
I is the moment of inertia for the rotation and $m = 0, \pm 1, \pm 2, \pm 3, ...$

Rotational fine structure therefore offers a means of calculating moments of inertia
and hence bond distances and bond angles For all molecules the spacing of the lines
depends primarily upon the magnitudes of the principal moments of inertia. In small
molecules with low moments of inertia, the individual rotational lines will be resolved
[e.g , in the water vapour bands at 5 0–7 5μ (1950–1350 cm^{-1})] and accurate mole-
cular parameters can in principle be calculated In heavier molecules, the individual
rotational levels lie too close together to be resolved, the vibration-rotation band
then has a smooth contour

The overall contours of vibration-rotation band systems vary considerably (cf
ref 5 p 206) but are composed essentially of three parts, the P, Q and R branches, as
required by the above equation. The Q branch ($m = 0$) corresponds to a change in
vibration quantum number without change in rotational quantum number The P
and R branches correspond respectively to decrease and increase in the rotational
quantum number. The relative intensities of the P, Q and R branches are determined
by the symmetry of the vibration and the ratios of the three moments of inertia In
certain cases, the Q branch is not observed Thus, for linear molecules the Q branch
will be absent if the vibration produces an oscillating molecular dipole parallel to the
molecular axis, and asymmetric top molecules (three different principal moments of
inertia) give rise to bands with a PR structure only, on account of low intensity of
the Q branch

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(2) *Liquids.* In the liquid state, the translational kinetic energy of a molecule may be affected as a result of the vibrational excitation; the kinetic energy may contribute to or benefit from the energy involved in the transition. The probability that energy will be transformed in this way falls sharply as the quantity of energy involved in the transfer increases. Consequently intermolecular forces and collisions eliminate not only rotational fine structure (with a few exceptions), but also prevent the occurrence of a sharp line vibrational absorption The absorption bands of liquids and solutions appear as compressed bellshaped curves of about 10–30 cm^{-1} band width at half the peak height.

(3) *Solids* In the solid state, lattice forces prevent molecular rotation; rotational modes are replaced by the excitation of lattice vibrations (*cf* section 2.ix) Pure solids normally give sharp bands but contour is sensitive to the sampling technique

(vi) *Fermi resonance*

When two vibrational states of the same symmetry fortuitously give rise to absorptions of close frequency, resonance interaction will occur between them Both frequency and intensity will be affected and may be to such an extent that the absorptions cannot be assigned to any particular vibration Perturbation theory shows that the magnitude of the interaction increases with frequency proximity.

In classical terms the interaction can be compared with linked mechanical oscillations in which the molecule gradually transfers its vibration from one mode to the other A quantum mechanical treatment[6] shows that the coupling pushes the bands further apart (the lower frequency absorption moves down and the higher frequency absorption moves to still higher frequency) and mixes their character (each of the resonating levels takes some of the character of the two contributory vibrations) Also, the weaker absorption "borrows" intensity from the stronger one so that two roughly equally intense bands may be recorded

The effects of Fermi resonance are most noticeable when an overtone or combination tone has a frequency very close to that of another fundamental. The result is that instead of there being only one strong fundamental absorption band, the normally weak overtone transition acquires some fundamental character and two fairly strong bands are observed

Despite its restriction to vibrations of similar symmetry the occurrence of Fermi resonance (or "coupling") in infrared (or Raman) spectra is widespread, especially among large molecules

(vi) *Electronic effects*

Absorption frequencies characteristic of a particular chemical group are often sensitive to electronic effects within the molecule The relation between frequency and minor changes in constitution has frequently been interpreted in terms of inductive, mesomeric and/or π delocalisation effects The influence of "field effects"

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between non-bonded atoms has not been studied to a great extent in sulphur chemistry but their presence is indicated, for instance, in phase change effects (section 2 x) The importance of electronic interactions is shown by correlations, which have been proposed for organic compounds, between group frequencies and Hammett σ[12-18] and Taft σ^* factors[19-25], ionisation potentials[26,27], electronegativities[28-31], half wave potentials[32,33] and redox potentials[34,35] References include work on sulphur compounds[12,13,19-21,28].

Extensive work on organic (and some inorganic) compounds has shown that correlations between frequency shifts and physical properties appear to work best when the comparison involves some experimental measurement of the bond polarity (e g , change in covalent bond distance, ionisation potential or reactivity) Correlations with more general functions such as electronegativity are less likely to be meaningful Substituent groups show a consistent order of effectiveness provided that the study is limited to groups well removed from the vibrating group The so-called inductive effect of a polar group upon a given linkage can usually be regarded as a composite of true induction effects working along the bonds and non-bonded interactions working across intramolecular space (e g., electrostatic repulsions between two non-bonded but neighbouring strongly electronegative atoms).

(viii) Molecular strain and steric hindrance

Work with some cyclic organic compounds[36] has shown that vibration frequencies may be modified by the presence of molecular strain, e g the variation of $\nu(SO)$ with n in the compounds $(CH_2)_n SO$

Steric hindrances can give rise to electronic interactions between neighbouring but not mutually linked atoms and these interactions may result in appreciable frequency shifts In extreme cases geometrical isomerism becomes possible, each isomer having its own spectrum.

Little similar work has been done on inorganic sulphur compounds but the possible influence of molecular strain and steric hindrance should not be overlooked.

(ix) Frequency shifts within one phase

(1) *Gases* Since the appearance of resolvable rotational lines depends upon relatively unhindered molecular rotation (*cf* section 2 v), it will tend to disappear as pressure or temperature increase[37-39] Chemical interactions typical of the liquid phase can also occur though the effects are less marked

(2) *Liquids* Infrared spectra of pure liquids are affected by interactions such as molecular association and selfionisation[40,41] Additional or modified absorptions may also be caused by solvent impurities particularly water Spectral changes arising in solution have been studied extensively especially for organic systems Almost all the recently reported inorganic and organic studies of solvent effects in infrared

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spectra concluded that the predominant interactions were specific solute molecule-solute molecule or solute molecule-solvent molecule interactions rather than effects due to change in dielectric constant or refractive index The last two factors generally appear to have only a minor effect. The shifts in infrared absorption peaks from one solvent to another ("solvent shifts") have been related to solubility differences[43,44], and bond moment changes. Solvent shifts, Δ, are commonly expressed as fractions of the group frequency

$$\Delta = \frac{\nu(\text{standard solvent}) - \nu(\text{solvent 2})}{\nu(\text{standard solvent})}$$

Structural information can be gained in a number of ways from detailed studies of solution spectra For instance, molecular association through hydrogen bonding is minimised in dilute solution and no solution studies at several concentrations assist the study of molecular association Hydrogen bonding (X–H---) greatly increases the integrated intensity of the X–H stretching absorption peak and moves it to lower frequency[36,44-48] If the hydrogen bonding is strong the band becomes quite broad

Solution shift data can also be used to check an assignment If a band in a particular molecule A is suspected as being due to the bond X–Y, solution spectra are measured in a number of different solvents, for this and a similar compound also containing the same group X–Y A graph is plotted of solvent shift for vibration X–Y, compound A versus shift for vibration X–Y, compound B A straight line supports the allocation of the band in A to the vibration X–Y

The most marked solvent shifts encountered when coordination and charge transfer complexes are formed with solvent molecules[49-51].

(3) *Solids* Solid state spectra are invaluable for qualitative indentification but they are less reliable for correlations between absorption frequencies and molecular structure This is because the electronic environments of the atoms (and hence the number of absorptions, frequencies and band shapes) may be seriously affected by the numerous types of intermolecular forces (particularly crystal forces, dipolar interactions and hydrogen bonding)[44,52-66] Polymorphic forms of the same substance also give different spectra As a result of these complications, solid state spectra may be difficult to interpret (also see section 2 x 2)

(x) *Phase change effects*
A Change from the gaseous state to the pure liquid or dissolved state produces in the vibrational spectrum of the solute several characteristic effects

(i) rotational fine structure disappears or is replaced by a simple band contour
(ii) liquid bands are usually displaced with respect to the corresponding gas bands, stretching frequencies are often displaced to lower frequencies and bending vibrations sometimes to higher frequencies (These tendencies may be much disturbed by inter-molecular interactions)

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(iii) band half widths may be greatly increased,

(iv) band intensities may change by factors of ten or more,

(v) there are often more bands in the liquid state than in the gaseous state of a substance.

B. Change in phase from the liquid to the solid state also produces new bands and changes in band frequency and intensity A major cause of the new bands which frequently appear below about 150 cm^{-1} (66μ) is lattice vibrations, that is, absorptions due to translational or torsional oscillations of the molecule or ion in the crystal These new vibrations can form combination bands with existing vibrations with consequential frequency shifts and new absorptions at higher frequencies.

Brief mention has been made (section 3.(iii)) of the part played by molecular symmetry in determining the form of an infrared spectrum In the solid state there is the additional complication of environmental effects

(i) Field effects. Shifts of frequency are often found for a given ion in different crystal environments (in which the same environmental symmetry is maintained) For instance, displacements of two of the four fundamental frequencies of the sulphate ion have been related[284] to the ionic radius of the cation

(ii) Site symmetry. If the crystallographic site symmetry of a molecule or ion differs from the point symmetry of the species, further absorption bands may appear due to (a) splitting of existing degeneracies and (b) relaxation of selection rules[68,69] The methods for computing these changes have been reviewed in several places[589].

Scattering (see Christiansen effect below) may also modify solid state spectra relative to spectra obtained on liquids. The variations in band position, intensity and contour which occur during change in phase are often unpredictable and may be surprisingly large This is especially true of band intensity from vapour to liquid states. The less pronounced changes that occur within one phase are better understood Since intermolecular forces produce spectral complications in both liquids and solids, spectra are best measured in the vapour phase if this is possible, or in solution in a relatively inert solvent
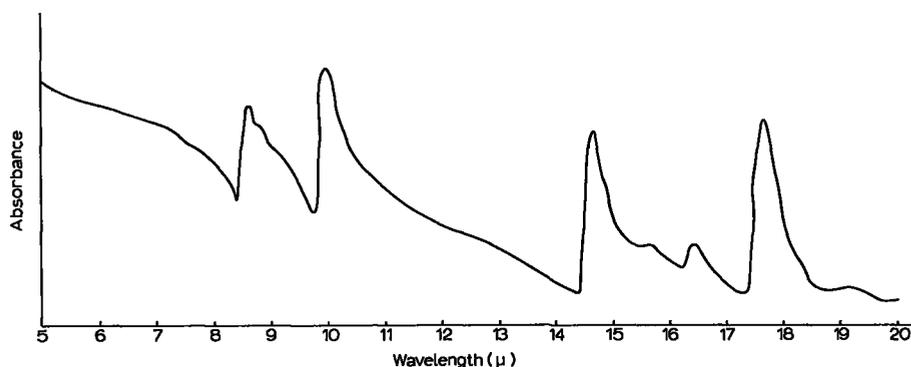

Fig 5 3 Infrared absorption spectrum of the S$_4$N$_3^+$ ion from 5μ to 20μ Band distortion due to Christiansen effect

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Christiansen Effect[67]. If the refractive indices of solid particle and surrounding medium differ appreciably, the infrared absorption peaks will be distorted The effect arises because in the region of an absorption band, the refractive index of a material changes sharply and causes an increase in transmittance on the high frequency side of the band (Fig 5 3)

The effect becomes more serious as particle size approaches the wavelength of the radiation It is therefore more pronounced at short wavelengths and is minimised by careful grinding. It is never completely eliminated when obtaining spectra of powdered crystalline materials

3. Raman spectra

(a) Origin of Raman effect

When a gas or a liquid is illuminated with monochromatic light, the scattered light is mainly of the same frequency (Rayleigh scattering) A very small proportion (usually < 1   ) may be of higher or lower frequency This is the Raman effect. This process differs from that occurring in ultraviolet, infrared and microwave spectroscopy in that the illuminated molecules cause a modification of the energy of the incident photons rather than a complete absorption of a certain proportion of them. It is, therefore, not surprising that the Raman effect depends upon a different molecular property.

Absorption spectroscopy depends upon the interaction of the electric field of the light wave with a change in the electric dipole of the molecule But the transfer of energy in *scattering* experiments depends upon the facility with which the radiation can induce a dipole in the molecules that is to say, it depends upon their polarisability A theoretical treatment shows that the intensity of Rayleigh scattering is proportional to the molecular polarisability but that of the Raman scattering arises from *changes* in the polarisability produced by vibration and/or rotation Just as infrared absorption frequencies are equal to the frequencies of the oscillating dipoles (i e the vibration or rotation frequencies), so the Raman frequency shifts are equal to the frequencies at which the polarisability is changing—again the frequencies of vibration and rotation Hence Raman scattered light has frequencies $v + v_R$ where $v =$ incident frequency and $v_R =$ the Raman shift

As in infrared spectroscopy, Raman frequencies and intensities are governed by molecular and vibrational symmetry But since the selection rules for the appearance of absorption peaks or Raman lines differ, it frequently happens that fundamental frequencies active in Raman scattering are inactive in the infrared, though lines may appear in both Raman data may therefore supplement or complement the information obtainable from an infrared spectrum For instance, weak infrared bands (e g , from certain symmetrical vibrations involving S–S or S–H) may show clearly in the

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Raman spectrum and some medium or strong infrared bands (e g , overtones and combination bands) may be weak or absent.

Because of the basic similarity between the two techniques, many of the comments made in previous sections, concerning the theory of infrared absorption and the interpretation of spectra, are also applicable to Raman spectra This similarity between the two techniques forms the background to the following section in which some of the points of difference are briefly considered.

(b) Polarisation of Raman lines

Further valuable structural information can be obtained from a study of the polarisation of the scattered light.

The light incident on the Raman sample can be regarded as effectively composed of two oscillating electric vectors mutually at right angles and of equal amplitude, likewise, the scattered light may be analysed into two plane-polarised components but the amplitudes (and hence the intensities) are no longer equal In the Raman experiment, observations are made at right angles to the direction of the incident light; then if i represents the intensity of the scattered component oscillating *parallel* to this direction and I the corresponding intensity of the component *perpendicular* to it, the ratio i/I is called the *depolarisation ratio, ρ*. The magnitude of ρ can be determined in practice, at least qualitatively, by using incident light with the plane of polarisation first parallel and then perpendicular to the axis of the sample

The general rules of polarisation are that *all* vibrational modes that are not totally symmetric will give Raman lines for which ρ has the maximum value of $\frac{6}{7}$ (so-called depolarised lines), or else will be inactive Only totally symmetric vibrations will give rise to polarised Raman lines ($i e$ $\rho < \frac{6}{7}$) When laser excitation is used, ρ has the value $\frac{3}{4}$ for depolarised lines

Rules particular to molecules with a centre of symmetry (*e.g* , CS_2, *trans*-form of XS_2X molecules) are·

(1) all vibrations which are antisymmetric with respect to the centre of symmetry are forbidden in Raman scattering

(2) transitions that are allowed in the infrared are forbidden in the Raman spectrum, and *vice versa* (rule of Mutual Exclusion). In certain centro-symmetric molecules, a vibration may appear in neither (*e.g* , one of the vibrations of SF_6[71,72]).

4. X-ray diffraction

The way in which X-ray diffraction can be used for the determination of molecular structure is outlined in many text books, *e g* , refs 590–594. The accuracy with which molecular dimensions can be measured is comparable with or better than that attainable by spectroscopic methods Also X-ray analysis can be applied to a much

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wider range of materials including molecules of great complexity Published data on sulphur bond distances and bond angles are included in the following sub-sections.

The X-ray determination of molecular structure requires the diffraction pattern of a single crystal If a powder is used the resulting powder diagram is characteristic of the sample and can be used for identification purposes[595-597].

Literature review

Most references were obtained from Chemical Abstracts up to and including December, 1965 Except where stated otherwise, structural information and spectral data are quoted as given by the original authors

5. Hydrogen

(a) H_2S,D_2S and HDS

All three isotopic species are bent triatomic molecules (C_{2v} or C_s) in the gas phase The vibrational spectra are summarised in Table 5 1 A number of discrepancies occur

TABLE 5 1

INFRARED AND RAMAN BANDS OF H_2S, HDS, D_2S AND THE POLYSULPHIDES

	$\nu_1(cm^{-1})$		$\nu_2(cm^{-1})$	$\nu_3(cm^{-1})$		References
H_2S gas	2610 8[a]		1290	2684		78
H_2S liq	2573 6[a]					78
H_2S solid	2446	2523		2532	2544	84
	2520 8[a]	2553 7[a]		2545 8[a]		84
D_2S gas	1891 6[a]		934	1999		73
D_2S liq	1866 3[a]					96
D_2S solid	1835	1753		1843	1854	84
	1832 5[a]	1853 4[a]		1848 5[a]		73
HDS gas			1090	(2684)		
	ν(S–H)					
H_2S_2	2509[a]					85
H_2S_3	2513[a]					87
H_2S_5	2513[a]					88
H_2S_6	2513[a]					88

[a] indicates Raman band

in the reported data for the combination and overtone bands, especially in the earlier reports where it is often not clear as to whether ν_{vac} or ν_{air} has been measured The frequencies and assignments reported by Bailey, Thompson and Hale[73] appear to be most widely accepted as being correct

Work on the vibration-rotation bands of H_2S has been carried out with instruments of low dispersion by Bailey, Thompson and Hale[73] and under higher dispersion by Nickless   Ch 5   /4/   1st proof

Nielson[76], and Cross[75] Similar studies have been carried out[73,76] on HDS and D_2S.

Force constants of H_2S and D_2S were calculated by Penney and Sutherland[77], and good agreement was obtained for the two isotopic species The values of 4 14×10^5 and $4 \cdot 46 \times 10^5$ dyne cm^{-1} for k_{HS} and k_{OS} respectively were calculated using the fundamental vibrational frequencies obtained by Bailey et al.

The rotational constants and moments of inertia quoted by Crawford[78] have recently been recalculated by Herzberg[79] using the more recent value of the numerical factor $h/8\pi^2 C$ due to Birge[80]. The results obtained are consistent with the values obtained from microwave spectra[81], and are listed in Table 5 2

TABLE 5 2

ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA OF H_2S IN THE LOWEST VIBRATIONAL STATE[68]

$A_0 = 10\,393\ cm^{-1}$, $I_a^0 = 2\,694 \times 10^{-40}\ g\ cm^2$
$B_0 = 9\,040\ cm^{-1}$, $I_b^0 = 3\,097 \times 10^{-40}\ g\ cm^2$
$C_0 = 4\,723\ cm^{-1}$, $I_c^0 = 5\,927 \times 10^{-40}\ g\ cm^2$

$l_0(S-H) = 1\,334\ Å$

$\widehat{HSH} = 92° 16'$

The Raman spectra of liquid H_2S and D_2S and D_2S have been reported[82], the shifts in Raman frequency accompanying the change from gas to liquid have been determined as 37 2 and 25.3 cm^{-1} respectively to lower frequencies[83]

Three different crystalline phases exist for H_2S and D_2S but their structure and the nature of the phase transitions between them are unknown[84] The lowest temperature phase, III, undergoes transition to phase II at 103 6°K and 107.8°K respectively for H_2S and D_2S The infrared spectra of phase III can be assigned on the basis of an eight-molecule unit cell with symmetry D_{4h}, the observed number of Raman lines is also consistent with this model

(b) Polysulphides

Infrared and Raman data have been reported[85-88] for H_2S_2, H_2S_3, H_2S_5 and H_2S_6 The sulphur-hydrogen stretching frequency falls within the range 2480–2557 cm^{-1}, and the sulphur–sulphur stretching frequency falls in the region 467–509 cm^{-1}

(c) Thiols

The sulphur–hydrogen stretching frequency in both the alkyl and aryl thiols appears[89-92,385] in the region 2564–2620 cm^{-1}, but assignment of the bands within this region has been a matter of some controversy[93-95] Cole, Little and Mitchell[46] have recently found bands at 2585 and 2572 cm^{-1} in the infrared spectra of phenyl thiol in carbon tetrachloride, and have suggested that these result from the presence of

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monomer and hydrogen-bonded cyclic dimer in solution. The S–H bonds lengths/ in thiols show little deviation[97-102], and generally the S–H bond length is reported as 1.323–1 350 Å

6. Boron

Boron trisulphide has been studied spectroscopically and its symmetry deduced from the spectra obtained. There are several plausible models for B_2S_3: a linear molecule ($D_{\infty h}$), a bipyramidal (D_{3h}), a plane V or W-shaped molecule (C_{2v}) or a twisted zigzag (C_2). Infrared emission and absorption spectra of gaseous B_2S_3 have been observed for the normal isotopic mixture and for a sample prepared with ^{10}B by Greene and Margrave[103], and examination of the isotopic shifts with the aid of the Redlich-Teller product rule, gives support to a twisted zigzag model with C_2 symmetry

Six and four membered sulphur-boron ring compounds have been known for several years[104], but few have been investigated spectroscopically. Recently Forster and Muetterties[105] have reported the infrared spectrum of $(Et_2NBS)_2$ which has still to be assigned.

Organic boron-sulphur compounds have been recently reviewed by Cragg and Lappert[111] who have tabulated the ν_{B-S} assignments for several types of cyclic molecules. In some cases the B–S bond is associated with two well separated absorption bands[106,112-114], e g , compounds of the type $(RS)_3B$ have B–S stretching bands at 910–1000 cm^{-1}, and 740–755 cm^{-1} and $(RS)_2BR'$ compounds have B–S stretching bands at 1000–1100 cm^{-1} and 740–755 cm^{-1}. The strong Raman bands for $B(SEt)_3$ at 460 and 450 cm^{-1} are attributed to $^{10}BS_3$ and $^{11}BS_3$ symmetric stretching vibrations respectively[106].

7. Carbon: Thiocyanates

In general the thiocyanate ion can coordinate either through nitrogen or sulphur, and many factors influence the way in which the group is bound. The C–N stretching frequency has been used[107] to distinguish between S- and N-bonding, since among complexes whose structures are known, those which are S-bonded generally have the higher values for the C–N stretching frequency. There is a certain amount of overlap however, and it has proved more useful to use the C–S stretching frequency which occurs at 690–720 cm^{-1} and 780–860 cm^{-1} for S bonded and N bonded complexes respectively[108-110,115,116]. Nuclear Magnetic Resonance has also been used to distinguish between N and S bonded groups, since in the S bonded complexes the ^{14}N resonance is shifted downfield compared to the free SCN$^-$ ion, and in N bonded complexes it is shifted upfield[117]

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Raman[118] and infrared[119] spectral evidence suggests that the predominant species present in molten and aqueous alkali metal thiocyanates is linear $[S-C=N]^-$. In N bonded complexes $M-N\equiv C-S^-$ and $M-\overset{+}{N}=C=S$ are predominant, and in S-bonded complexes $M-S-C\equiv N$ is important[108]. Lewis, Nyholm and Smith[108] suggest that when the thiocyanate ion is the only ligand bound to a metal M, then the way in which the group is bound is decided by the relative bond energies of a covalent M–S bond and the more ionic M–N bond.

The position of the thiocyanate ion in the spectrochemical series[49,120] depends on whether it is S- or N-bonded, when S-bonded it occupies a position approximately equal to Cl⁻ but when N-bonded it lies between H_2O and NH_3.

Livingstone[121] has recently reviewed cyanates, thiocyanates and selenocyanates, and discusses the factors which influence the predominance of one canonical form over another.

The M–SCN linkage is always angular, but the M–NCS linkage can be collinear or angular with the M–N–C angle as low as 111°. The S–C bond length falls within the range 1.55–1.80 Å for both types of linkage[122–126,586]. Hazell has reported an apparent correlation between the M–N–C angle (110–180°) and the carbon–nitrogen and sulphur–carbon distances[586], the sulphur–carbon bond lengths are generally shorter than predicted; this may be attributed to d_π–p_π-bonding between sulphur and carbon atoms.

8. Silicon, germanium, tin and lead

The infrared and Raman spectra of disilyl sulphide, $(H_3Si)_2S$, have been studied in detail[127,128]. The intense and polarised Raman line at 480 cm⁻¹, assigned to the symmetrical skeletal stretching mode also occurs in the infrared. A strong band at 517 cm⁻¹, not shifted by deuteration, is assigned to the asymmetric stretch and appears in both spectra. There is therefore little doubt that the Si–S–Si skeleton is non-linear[127], a value of about 100° has been proposed for the Si–S–Si angle. Low temperature infrared spectra suggest a C_{2v} molecular symmetry. Infrared and Raman data (frequency assignments, selection rules and band envelopes) for $S(GeH_3)_2$ have been used[137] to deduce that the Ge–S–Ge angle is approximately 120°. Hooton and Allred[129] have tentatively assigned the Si–S and Ge–S stretching frequencies in organo silyl and germyl sulphides, and Schumann and Schmidt[130] have examined the stretching frequency of Sn–S and Pb–S bonds in compounds of the type Ph_3M–S–MPh_3. The available data are summarised in Table 5.3.

TABLE 53

FREQUENCY RANGES OF CHARACTERISTIC ABSORPTIONS OF SOME GROUP IV ELEMENTS BONDED TO SULPHUR

		References				References	
ν(Si-S)	430-600 cm^{-1}	129,	130	ν(Sn-S)	267-392 cm^{-1},	130	
ν(Si-S-Si)	400-530 cm^{-1}	{129, 135,	132 136	ν(Sn-S-Sn)	330-380 cm^{-1}	130	135
ν(Ge-S)	400 cm^{-1}	130	131	ν(Pb-S)	305 cm^{-1}	130	
ν(Ge-S-Ge)	385-420 cm^{-1}	130 137	135	ν(Pb-S-Pb)	275-340 cm^{-1}	130	135

9. Nitrogen

(a) Spectral data

Relatively little data on sulphur–nitrogen stretching frequencies have been reported Since bond orders of up to three can occur a considerable range of frequency is observed (see Fig 5.4) In this respect the situation is akin to that encountered with respect to sulphur–oxygen bonds (section 12), but whereas in this latter case several correlations between stretching frequency and other bond properties have been found, no such correlations are reported in the case of sulphur–nitrogen compounds Since the nature of the bonding in sulphur–oxygen and sulphur nitrogen systems is analo-
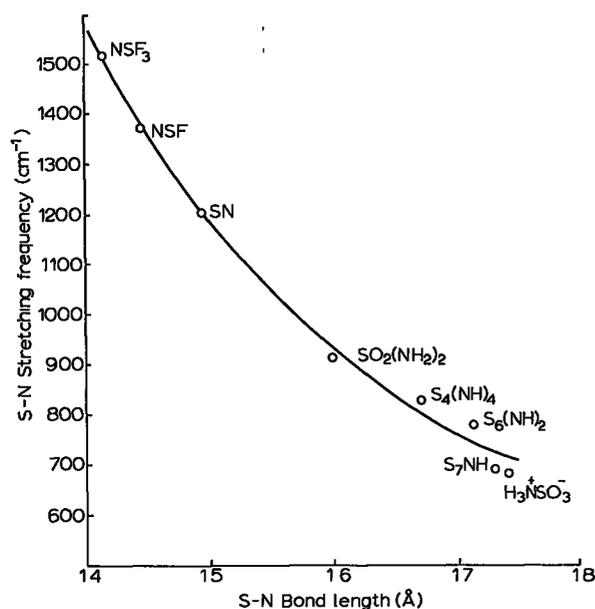

Fig 5 4 Correlation of S-N stretching frequencies and bond lengths

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gous, similar relationships might be expected to hold Unfortunately the available data are limited but as presented in Fig 5.4 they do suggest a correlation between the sulphur–nitrogen stretching frequency and bond length (cf Fig 5 8 for the similar S–O correlation) The scatter in the points is never greater than ± 0.02 Å, which is only about twice the estimated error of the more accurate bond lengths used.

TABLE 5 4

SULPHUR–NITROGEN STRETCHING FREQUENCIES

Grouping	Compound type	$\nu_{SN}(cm^{-1})$	References
N–S–N	cyclic $S_n(NR)_{8-n}$	770–840	142–149
N–SO$_2$–N	sulphamide and derivatives	900–930	150, 151
C–SO$_2$–N	sulphonamides	800–920	152–155
C–S–N	alkyl thionitrites	620–640	156
N–SO$_3^-$	sulphamic acid	682	
	sulphamates	788	138, 139
$(-N=)_nSF_2$	$(RN=)_2SF_2$	1404–1428	157
	$RN=SF_2$	1350–1400^a	158, 159
	$PhN=S(OMe)_2$	1280	160
N≡S–	NSF	1372	161
N≡S<	NSF$_3$	1515	161
	$NS(F_2)NEt_2$	1515	162
	SN (short lived)	1204	163
	$(SN)_n$ polymer	1225, 1015	163

^{a} except the fluorocarbon-compound[160] $C_3F_7N=SF_2$ for which $\nu_{SN} \approx 1275\ cm^{-1}$

The available spectral data is summarised in Table 5.4 the lowest S–N stretching frequencies are observed for sulphamic acid (682 cm^{-1}) and alkyl thionitrites ($\sim 630\ cm^{-1}$) For sulphamic acid, Vuagnat and Wagner[138] and Nakagawa et al[139] agree in assigning ν_{SN} to a band at $\sim 685\ cm^{-1}$, but Bicelli[140,141] assigned a band at $\sim 565\ cm^{-1}$ to ν_{SN}. Vuagnat and Wagner[138] assigned this latter band to an –SO$_3$ deformation Compounds containing a formal sulphur–nitrogen double bond may absorb over a wide range, 1280–1500 cm^{-1}, the frequency at which a given compound absorbs being apparently very sensitive to the presence of substituents on either the sulphur or the nitrogen atoms. If the double bond is described in terms of σ and π components then the observed variations in frequency may be considered to a first approximation to reflect changes in the π-bond order resulting from the electronic effects of the substituents Few compounds containing SN triple bonds are reported, the frequency observed for NSF(1372 cm^{-1}) suggests that its bond order is less than that in NSF$_3$(1515 cm^{-1})[161]

Cyclic compounds of the type $S_n(NR)_{8-n}$, where R=H or CH$_3$, absorb in the range 770–840 cm^{-1}, when R=CH$_3$ the absorption occurs toward the lower end of this range. Splitting of the band into two components may take place if the >NR groups are sufficiently close together[147]. The π-delocalised systems S_4N_4[142] and $S_4N_3^+$ [164,]

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[165] give rise to several bands involving S–N stretching but the precise origins of each absorption have not been determined The spectra of some sulphanuric compounds $(NSOX)_3$, where X=Cl[166], F[167], are reported but not assigned.

(b) Structural data

The reported structural data are given in Table 5 5 Many of the reported bond lengths are intermediate between the values calculated[168] for a single bond (1.73 Å)

TABLE 5 5

BOND DISTANCES AND ANGLES IN SULPHUR–NITROGEN COMPOUNDS

Compound	r_{S-N}(Å)	$\widehat{NSN}$	$\widehat{NSX}$, SNX	References
SN⁺ (short lived)	1 250			176
SN (short lived)	1 495			177
S_4N_4	1 616±0 010	104 5±1 5°		178, 179
$S_4N_4H_4$	1 674±0 012	108 4°	122 2° (SNS)	172, 180
$S_4N_4F_4$	1 660±0 01 (S–N)	111 7±0 6°	91 5±0 4° (FS–N)⎫	173
	1 540±0 01 (S=N)		106 2±0 4° (FS=N)⎭	
$S_4N_3NO_3$	1 54±0 04	118 9±1 5°	152 4±1 3°⎫	
			134 4±1 2°⎬(SNS) ⎫	182, 183
			111 3±1 0° (SSN) ⎭	
S_7NH	1 73		115 8 (SNS) ⎫	184
			108 6 (NSS) ⎭	
1,4-$S_6(NH)_2$	1 73		110° (NSS) ⎫	185
			118° (SNS) ⎭	
1,5-$S_6(NH)_2$	1 62		112 3, 107 2 (NSS) ⎫	186
	1 68		120 3, 117 3 (SNS) ⎭	
$N_3S_3Cl_3$	1 605±0 01	113 4±0 5°	123 8±0 5 (SNS) ⎫	187
			113 8±0 5 (NSCl) ⎭	
$N_3S_3O_3Cl_3$	1 571±0 004	112 8±0 4°	122 0±0 4 (SNS) ⎫	
			106 3±0 3 (NSCl) ⎬	181
			111 9±0 4 (NSO) ⎭	
$SO_2(NH_2)_2$	1 600±0 009	112 1±0 7°		171
$SO_2[N(CH_3)_2]$	1 623±0 005	112 6±0 4°		170
$S_3N_2O_2$	1 58	120 0°		189
	1 69			
$H_3\overset{+}{N}SO_3$	1 764±0 020			190
H_2NSO_3K	1 60±0 03			191
$KNH(SO_3)_2$	1 655±0 005		124 7±0 5° (SNS)	192
$KNHOH(SO_3)$	1 67±0 02			193
$(NH_4)_2SO_3(N_2O_2)$	1 79±0 01		116 5° (SNN) ⎫	169
			103 9° (NSO) ⎭	
NSF	1 446			161
NSF_3	1 416			161

and for a double bond (1 54 Å) It is generally accepted that the bonds possess some π character as a result of overlap involving the lone pair electrons on the nitrogen atom and the empty $3d$-orbitals of the sulphur atom[169-172] Wiegers and Vos[173a] have,

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however, commented that a conclusive explanation of relative sulphur–nitrogen bond lengths has not yet been given. In S_4N_4[174] and $S_4N_3^+$[175] dimensions and also electronic spectra have been rationalised using a molecular orbital treatment. Pure single S–N bonds are rarely encountered The value reported for $1,4\text{-}S_6(NH)_2$ of 1.73 Å results from a preliminary refinement only, so that $S_7(NH)$, (1.73 Å), $H_3NSO_3^-$ (1 76 Å), and $(NH_4)_2SO_3(N_2O_2)$ (1 79 Å) are the only reliable examples of compounds containing S–N single bonds The bond length in $S_7(NH)$ may be contrasted with the shorter bonds found in $S_4(NH)_4$ (1 67 Å), and $1,5\text{-}S_6(NH)_2$ (1 62, 1 68 Å). In the case of the sulphamate and dinitrososulphite ions the sulphur $3d$-orbitals are utilised in the π-bonding systems of the $-SO_3$ and $-SO_3(N_2O_2)$ groups, (the S–O bond lengths in both ions correspond approximately to double bonds) so that the sulphur–nitrogen bond is restricted to two σ-electrons only Data in Table 5.4 suggest that in some

TABLE 5 6

SYMMETRIC AND ASYMMETRIC STRETCHING FREQUENCIES OF NSO COMPOUNDS

Compound type	v_s (cm^{-1})	v_{as} (cm^{-1})	References
RNSO	1120–1135	1238–1252	194
ArNSO	1137–1179	1272–1300	195
ArSO(=NH)N(CH$_3$)$_2$	1135–1160	1260–1270	196
ArSO(=NH)OC$_6$H$_5$	1160	1295	196
R$_2$SO(=NH)	1099	1212	196
(NSOF)$_n$	1250	1351	197
RN=SO$_2$F	1219–1320	1428–1492	198, 199
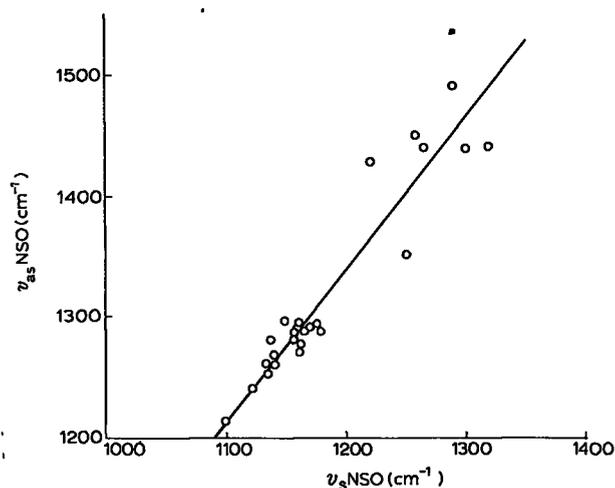
Fig 5 5 Correlation of symmetric (v_sNSO) and asymmetric (v_{as}NSO) stretching frequencies of the NSO group

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compounds which formally contain S–N single bonds, $e\,g$, sulphonamides and sulphamides, considerable π-bonding may occur since for these compounds ν_{SN}(800–930 cm^{-1}) is at a higher frequency than that which is associated with the single bond in sulphamic acid (682 cm^{-1}) The spectra of several other S–N compounds[237–243] are reported without assignment of ν_{SN}.

Compounds containing the NSO group give rise to symmetric and asymmetric stretching modes. The available data are listed in Table 5.6, and in Fig 5 5 the symmetric stretching frequency (ν_s) is plotted against the asymmetric frequency (ν_{as}) Though the data are somewhat limited a reasonably satisfactory relationship is observed In this respect the NSO group may be compared with the SO$_2$ group for which a similar relationship is well established (section 12.a)

TABLE 5 7

P=S STRETCHING FREQUENCIES OF COMPOUNDS XYZR=S

Compound			Frequency, ν_{PS} (cm^{-1})		References
X	Y	Z	Raman	Infiared	
F	F	F	695	g 694	216, 609, 614
F	F	Cl	729		216
F	F	Br	711		216
Cl	Cl	F	737		217
Cl	Cl	Cl	753	751, g 768	215, 606, 614
Cl	Cl	Bi	743		215
Bi	Cl	F	729		217
Bi	Br	F	713		217
Br	Br	Cl	729		215
Br	Bi	Br	718		215
I	I	I		1 673	603
Me	Me	Me		s 570	598, 200
Et	Et	Et		s 538, 1 552	598, 200
n-Pr	n-Pi	n-Pr		583, 596	598
n-Bu	n-Bu	n-Bu		596	598, 605
n-Am	n-Am	n-Am		588, 599	598
C$_6$H$_{11}$	C$_6$H$_{11}$	C$_6$H$_{11}$		s 619	598
CF$_3$	CF$_3$	CF$_3$		x 800	604
SMe	SMe	SMe		685	223
SEt	SEt	SEt		685	218, 223
Ph	Ph	Ph		s 627	598
Cl	Cl	Me	671	672, g 696	219, 218
Cl	Cl	Et		646, 676	200
Cl	Cl	OMe		705, 725	218
Cl	Cl	OEt		695, 725	218
OMe	OMe	H		633, 654	218
OMe	OMe	OMe		603, 620	200, 221
OMe	OMe	SH		660	218

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10. Phosphorus

Phosphorus–sulphur linkages are of two main types, (ı) terminal, P=S and (ıı) bridge, P–S– Infrared and Raman data are available for both types

The effect of the nature of X on the P=O or P=S stretching frequencies of POX_3 and PSX_3 compounds has been discussed in detail[28,200,201,598,599,610,611] The P=S force constant has been calculated[202] to be $4 2 \times 10^5$ dyne cm^{-1} for $PSCl_3$ and this value leads to a P=S stretching frequency of 675 cm^{-1} for an isolated P=S group The thiophosphoryl halides[539] absorb in the region 695–753 cm^{-1} Replacement of halogen by alkyl or alkoxy groups shifts this region down to 535–725 cm^{-1} (see Table 5 7; some compounds give rise to two peaks) The highest observed frequency

Compound			Frequency, ν_P (cm^{-1})		References
X	Y	Z	Raman	Infrared	
OMe	OMe	SMe		660	218
OMe	OMe	Cl		660	218
OEt	OEt	H		636, 658	218
OEt	OEt	OH		618, 655	218
OEt	OEt	OEt		580, 600	200, 220
OEt	OEt	OEt	610, 629		200, 222
OEt	OEt	SH		660	218, 220
OEt	OEt	SEt		660	218
OEt	OEt	SCl		652	214, 612
OEt	OEt	Cl		655	218, 220
OEt	OEt	CCl₃		635	612
Ph	Ph	Me		609, 618	598
Ph	Ph	Et		s 598, 599ᵃ, 601ᵃ	598
Ph	Ph	n-Bu		s 605, 617	598
Ph	Ph	Cl		660	598
Me	Me	Ph		s 585	598
Me	Me	P(S)Me₂		s' 568, 1' 572	608
Et	Et	Ph		578	598
ı-Pı	ı-Pı	SH		595	605
ı-Pı	ı-Pı	Cl		593	605
n-Bu	n-Bu	Ph		597	598
s-Bu	s-Bu	SH		617	605
s-Bu	s-Bu	Cl		626	605
I	I	P(S)I₂		s' 725	607

s – spectrum of solid in KBr disc   ᵃ shoulders on absorption peak
s' – spectrum of solid in Nujol mull
1 – spectrum of solution in CS_2
1' – spectrum of solution in $CHCl_3$
g – gas spectrum
x – conditions not recorded
Pure liquid used for all other spectra

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for the P=S fundamental vibration is that at 860 cm^{-1} for $PS(NH_2)_3$[600]. These shifts are apparently[203,204,598] caused, as in the case of phosphoryl compounds, by a combination of four variables mass and steric effects of the groups attached to phosphorous, their inductive effect and π donation by halogen, particularly fluorine, to phosphorous. Slight shifts are also caused by coupling of the P–X and P=S vibrations when their natural frequencies are close.

The infrared spectra of numerous organic derivatives of thiophosphoric acids have been studied[205-209]. Two bands of widely different frequency have been found to be characteristic of terminal P=S bonds These occur within the overall ranges 625–862 cm^{-1} and 530–730 cm^{-1} Both bands appear to be characteristic of the P=S bond, since both disappear during the isomerisation of phosphorothionates to phosphorothiolates
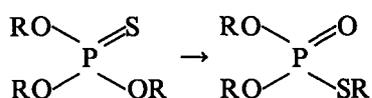
No wholly satisfactory explanation of their origin has so far been suggested. The infrared spectra of the diphenyl thiophosphinates of dimethyl aluminium and gallium ($[Me_2MOP(S)Ph_2]_2$) have been reported and the S–P stretching frequencies are consistent with a dimeric structure with donation through the sulphur atoms[210]. The overall frequency limits within which stretching vibrations of the P–S–(X) bond are found are 440–613 cm^{-1} Chittenden and Thomas[209] have discussed the effects of changes in the nature of the substituent groups attached to phosphorus on the P=S stretching frequency and have tabulated the infrared absorption frequencies of the P=S, P–S–(C), P–S–(P), P–S–(H) and P=Se bonds as a function of the overall chemical structure of the molecule

Phosphorotetrathioates have been found[205] to absorb strongly in the region 520–570 cm^{-1} Dialkylphosphorodithioates of Zn, Ni and Pb are reported to show P=S absorptions at 625–665 cm^{-1} and P–S at 530–560 cm^{-1} Compounds of the general type $XS–P(S)(OR)_2$ (X = alkyl, acyl) show a well defined P=S absorption in the region 640–680 cm^{-1}, the frequency decreasing with the electronegativity of X[207] Phosphoromonothioates[206] absorb near 560 cm^{-1}.

The force constant for the P–S single bond in P_4S_3 has been calculated[211] to be 1.65×10^5 dyne cm^{-1} This would lead, in an isolated P–S bond to a vibration frequency of 422 cm^{-1} It has been found[205,208,212,213] that P–S bonds with bridging sulphur generally absorb in the region 400–700 cm^{-1}

Corbridge[205] tentatively suggested 400–500 cm^{-1} as the absorption region characteristic of P–S–P linkages. McIvor and Hubley[208] investigated over 40 organophosphorus compounds containing sulphur Weak diffuse bands at 488 cm^{-1} for two P–S–P compounds were ascribed to the P–S links Their conclusions as regards P=S absorption (terminal sulphur) agree with the findings of Hooge and Nickless   Ch $\mathcal{5}$ *$\mathcal{14}$*   1st proof

Christen[200] (described above and in Table 5.7). Compounds [(RO)$_2$P(S)]$_2$S show[214] a fairly strong absorption due to P–S–P at 485–515 cm^{-1}.

P–S–H compounds absorb at similar frequencies, phosphorodithioic acids[208] at 493–548 cm^{-1} and (CF$_3$)$_2$–P–S–H at 508 and 522 cm^{-1} ν_{PS} in other (CF$_3$)$_2$P–SX compounds[212] [X = Me, t-Bu and –P(CF$_3$)$_2$] occurs at 508–530 cm^{-1}

Structural data for sulphur–phosphorus compounds are given in Table 5 8

TABLE 5 8

SULPHUR–PHOSPHORUS BOND LENGTHS AND ANGLES

Compound	l_{P-S} (Å)	P–S–P(°)	References
SPEt$_3$	1 86		224
SPF$_3$	1 85		225
(S$_2$P(OMe)$_2$)K	1 96		226
P$_2$S$_6$Br$_2$	1 98		227
BPS$_4$	2 16		228
K$_3$PS$_4$	2 02, 2 04 2 08, 2 08		229
(CH$_3$PS$_2$)$_2$	1 94 (exocyclic) 2 14 (cyclic)	85 46±0 23	230, 231
P$_4$S$_3$	2 10	102	232, 233
P$_4$S$_5$	1 94 (exocyclic) 2 08–2 21 (cyclic)	108, 102, 99 and 88	234
P$_4$S$_7$	1 95 (exocyclic) 2 08 (cyclic)	106	235, 236
P$_4$S$_{10}$	1 95 (exocyclic) 2 08 (cyclic)	109±1	235

11. Arsenic and antimony

The intense band located in the range from 470–490 cm^{-1} in the spectra of the trialkylarsine sulphides has been assigned[245] to the fundamental arsenic–sulphur stretching frequency The assignment of ν_{As-S} in monosubstituted arsine sulphides and in arsine sulphides bearing phenyl and cyclohexyl groups cannot be made with the high level of confidence possible for the trialkyl compounds Bands at 490 cm^{-1} and 476 cm^{-1} have been assigned with reasonable certainty to the As–S stretching vibration in triphenyl- and tricyclohexyl arsine sulphides respectively. The As–S stretching frequency has been found to depend almost entirely upon the mass of the organic constituents on the arsenic atom[245] There is a brief reference[244] to Raman shifts for Na$_3$AsO$_3$S, Na$_3$AsO$_2$S$_2$, Na$_3$AsOS$_3$, Na$_3$AsS$_4$, and Na$_3$SbS$_4$

12. Oxygen

(a) Sulphuryl ($-SO_2-$) compounds

The infrared and Raman spectra of compounds containing sulphur–oxygen bonds have been extensively studied and several useful correlations have been established For $-SO_2-$ compounds several workers[19,28,246] have observed a linear relationship between the symmetric S–O stretching (v_sSO) and the asymmetric stretching vibration ($v_{as}SO$). Bellamy and Williams[246] have commented that such a relationship is to be expected since the $-SO_2-$ stretching vibrations are essentially free from mass and

TABLE 59

SYMMETRIC AND ASYMMETRIC STRETCHING VIBRATIONS FOR OXO-ANIONS OF SULPHUR

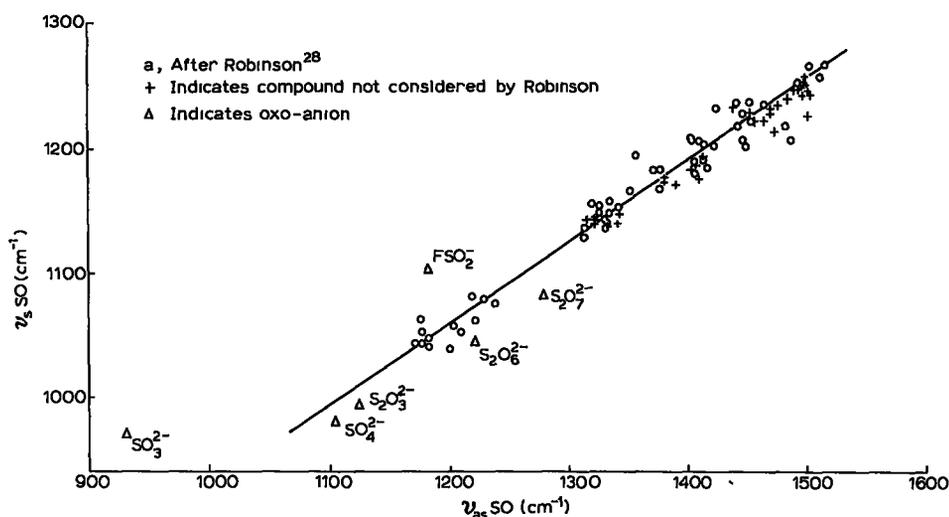| Species	v_s (cm^{-1})	v_{as} (cm^{-1})	References
SO_3^{2-}	970	930	264
FSO_2^-	1105	1182	265
SO_4^{2-}	981	1104	266
$S_2O_3^{2-}$	995	1123	267
$S_2O_6^{2-}$	1092	1235	268
	1000	1206	
$S_2O_7^{2-}$	1059	1267	269
	1108	1289	

Fig 5 6 Correlation of symmetric and asymmetric S–O stretching frequencies[a]

[a], after Robinson[28] + indicates compound not considered by Robinson $\triangle$ indicates oxo-anion

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coupling effects The data compiled by Robinson[28] is particularly comprehensive and shows that the symmetric and asymmetric S–O vibrations for compounds of the types X_2SO_2, (including $X(OH)SO_2$), for ions such as XSO_3^- and SO_4^{2-} and for more complex molecules containing $-SO_2-$ vibrations or inaccuracy in the reported values because of the difficulty of resolving bands in the fairly complex spectra. On the other hand, the values for the SO_3^{2-} and FSO_2^- ions lie well away from the line All of the compounds reported by Robinson contain sulphur in the S(VI) state, as do the oxo-anions which fit the linear relationship The ions SO_3^{2-} and FSO_2^-, however, contain S(IV), which perhaps suggests that the line established by Robinson is applicable only to compounds containing S(VI).

Table 5 10 lists the frequencies observed for various types of $-SO_2-$ compounds. It is seen that, in general, as the effective electronegativity of the groups attached to the $-SO_2-$ group is increased the S–O stretching vibrations are shifted to higher

TABLE 5 10

CORRELATION TABLE FOR S–O SYMMETRIC AND ASYMMETRIC VIBRATIONS [a]

Grouping	Type of compound	$\nu_{S-O}(cm^{-1})$	
		symmetrical	asymmetrical
$C-SO_2-C$	Sulphones(alkyl)	1136–1145	1307–1330
	Sulphones(alkyl-aryl)	1150–1160	1325–1334
	Sulphones(aryl)		
$C-SO_2-N$	Sulphonamides	1152–1169	1336–1358
$C-SO_2-N$	e g , $F_3CSO_2N_3$	1236	1437
$C-SO_2-O$	Sulphonic acids and esters	1165–1185	1350–1375
$C-SO_2-F$	Sulphonyl fluorides	1203–1210	1401–1412
$C-SO_2-Cl$	Sulphonyl chlorides	1169–1185	1364–1390
$C-SO_2-S$	Thiosulphonates	1144–1154	1331–1342
$N-SO_2-N$	Sulphamide and derivatives[b]	1140–1168	1320–1398
$O-SO_2-O$	Covalent sulphates	1187–1195	1390–1415
$O-SO_2-O$	e g , $(SF_5O)_2SO_2$ and SF_5O SF_4O SO_2 OSF_2[b]	1230–1256	1469–1500
$O-SO_2-F$	e g , FSO_3F, HSO_3F, $S_2O_5F_2$, $S_2O_8F_2$[c]	1230–1260	1445–1510
$O-SO_2-Cl$	e g , HSO_3Cl, $S_2O_5Cl_2$, $S_2O_8Cl_2$, $S_3O_8Cl_2$	1205–1225	1408–1452
$N-SO_2-F$	$=NSO_2F$ and $-N(SO_2F)_2$ compounds[b]	1174–1250	1337–1495
	SO_2F	1269	1502
	SO_2Cl_2	1182	1414
	Ions, e g , FSO_3^- $MeSO_3^-$, excluding oxo-anions[d]	1026–1080	1175–1221

[a] after Robinson[28]

[b] groupings not given by Robinson

[c] these frequency ranges confirmed by inclusion of data not considered by Robinson

[d] frequency ranges for oxo-anions are in section 12 b

frequencies This shift indicates increasing strength of the S–O bonds which is most plausibly explained as resulting, at least in part, from increased double bond character (*cf* section 12 e)

(b) Oxo-anions and complexes

The characteristic ranges over which the S–O stretching vibrations in oxo-anions occur are given in Fig 5 7 For the less common anions the ranges shown are based
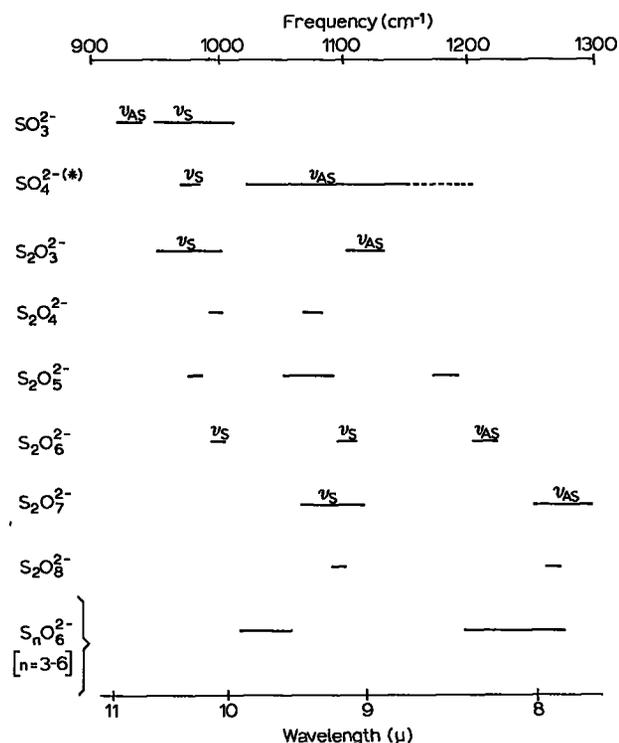
Fig 5 7 Observed frequency ranges of S–O stretching vibrations in oxo-anions
* The range for SO_4^{2-} is normally 1020–1150 cm^{-1}, relatively few compounds absorb at 1150–1200 cm^{-1}

upon only a few reported spectra, usually of alkali metal salts, and are, therefore, somewhat tentative

Few XSO_2^- ions have been studied Houlton and Tartar[277] examined the Raman spectra of several sodium alkyl sulphinites and observed S–O stretching modes at 942–956 cm^{-1} and 1024–1046 cm^{-1}, though these were not assigned to any specific vibrations Paetzold and Aurich[265] have assigned bands at 1182 and 1105 cm^{-1} for potassium fluorosulphite to the asymmetric and symmetric S–O stretching vibrations respectively

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(i) *Sulphates*

The free ion has tetrahedral, T_d, symmetry and hence four fundamental modes for which the calculated frequencies, assuming central forces[266], are·

v_1 (symmetric stretch), $981\ cm^{-1}$, v_2 (degenerate bend), $451\ cm^{-1}$
v_3 (asymmetric stretch), $1104\ cm^{-1}$, ' v_4 (degenerate bend), $613\ cm^{-1}$

v_2 is doubly degenerate and both v_3 and v_4 are triply degenerate All four modes are Raman active but only v_3 and v_4 are active in the infrared. The observed Raman frequencies in various crystalline environments are given in Table 5 11 It is seen that doubly and triply degenerate modes may split into two and three components respectively. Infrared spectra[271,278] normally show only bands due to v_3 and v_4 though in some cases slight lowering of the symmetry brought about by crystal forces causes v_1 to become weakly infrared active[271]

TABLE 5 11

RAMAN FREQUENCIES OF SULPHATE IONS IN VARIOUS CRYSTALLINE ENVIRONMENTS[a]

Compound	$v_1\ (cm^{-1})$	$v_2\ (cm^{-1})$	$v_3\ (cm^{-1})$	$v_4\ (cm^{-1})$
Na_2SO_4	983	454	1106	622
$BaSO_4$	989	453 462	1094 1142 1167	617 630 648
$CaSO_4$	1018	415 499	1108 1128 1160	609 628 674

[a] from Krishman[279]

Whilst the perturbing effect of the cation on the sulphate ion symmetry is usually small, in the case of indium sulphate[280] it is sufficiently great for new polarised lines to appear in the Raman spectrum, and these have been accounted for in terms of a $InSO_4^-$ species of C_{3v} symmetry. Decius[281,282] has shown that when the alkaline earth sulphates are present in small amounts in KBr or KCl crystals, the ion symmetry is reduced to C_{2v}. The general effects of crystal forces on the spectra of solid sulphates have been discussed by several workers[61,283-287] as have the differences between solid and solution spectra, which result from the lower symmetry of the solid phase[68,69,288]. Guerchais et al [284] have related displacements of the v_1 and v_3 bands to the ionic radius of the cation in a series of alkali metal sulphates The displacement is a linear function of the ionic radius of the cation, the shift being to lower frequency with increasing ionic radius

The spectra of hydrated sulphates may differ from those of the corresponding anhydrous salts, usually as a result of hydrogen bond formation[64,289-293]. For compounds of the type $M(H_2O)_6SO_4\ H_2O$, where M = Mg, Ni, Co, and Zn, v_3 is at $\sim1085\ cm^{-1}$ compared with approximately $1150\ cm^{-1}$ for the anhydrous com-

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pounds[64] Cho et al.[294] have suggested that $MgSO_4H_2O$ exists in the form $Mg(OH)$ HSO_4 because of the presence of a band at $\sim 870\,cm^{-1}$ which they assign to the HSO_4^- ion. On the other hand, Oswald[293] having studied the infrared and NMR spectra of a series of monohydrates, concluded that the forms $MSO_3(OH)_2$ and $M(OH)HSO_4$ were not present and that the compounds were normal sulphates containing strongly bound water molecules Tai and Underwood[295] have combined freeze drying with the KBr disc technique to study the infrared spectra of aqueous sulphate solutions The shape of the v_3 band at $\sim 1120\,cm^{-1}$ was found to vary with the cation and they suggest that the sharp band of K_2SO_4 is the most suitable for analytical purposes

Considerably more data on the Raman and infrared spectra of the sulphate ion is reported Ammonium and group 1 sulphates are reported in refs [61,66,296-298], group 2 compounds in refs [299-301], group 3 compounds in ref.[302], and compounds containing transition metal ions in refs [303-309] Compounds of the type $(NH_4)_26H_2O$ have been considered by Ananthanarayanan[310] The infrared spectrum of iodosyl sulphate shows the $(IO)^+$ cation to be polymeric[311]. Several workers[301,312-319] have discussed the spectrum of sulphuric acid, which provides evidence concerning possible ionisation processes The general spectral characteristics of the sulphate ion are reported by various other workers[41,320-323]; Jaulmes[324] and Keller, Spotts and Biggs[325] have examined the spectra of sulphate minerals and Buijs[326] has examined the spectrum of the sulphate ion when absorbed on an ion exchange resin

(ii) Thiosulphates

The free ion has tetrahedral C_{3v} symmetry and hence six fundamental modes all infrared and Raman active. The calculated frequencies[267] are.

v_1 (symmetric S–O stretch), 995 cm^{-1}, v_2 (symmetric S–O bend), 669 cm^{-1},

v_3 (S–S stretch),   435 cm^{-1}, v_4 (asymmetric S–O stretch),

                                                1123 cm^{-1},

v_5 (asymmetric S–O bend), 541 cm^{-1}, v_6 ($-SO_3$ rocking),   335 cm^{-1}

Miller and Wilkins[271] have reported the spectra of several thiosulphates. The band at $\sim 670\,cm^{-1}$ is often broad and the maximum occurs over the range 640–680 cm^{-1} The S–O stretching modes ($v_1 = 950$–1000 cm^{-1}, $v_4 = 1100$–1130 cm^{-1}) are, with exception of the ammonium compound, well defined Buijs[326] has examined the spectra of thiosulphates on an ion-exchange resin, the spectra are essentially unchanged though new bands appear due to $S_4O_6^{2-}$ ions formed by the facile atmospheric oxidation of thiosulphate under these conditions

(iii) Other oxo-anions

Simon[327] has examined the Raman spectrum of the dithionite ion ($S_2O_4^{2-}$) and reported S–O stretching modes at 1070 and 998 cm^{-1} The pyrosulphite ion $S_2O_5^{2-}$ has been studied by Simon et al.[328] who concluded that an SOS grouping was present and interpreted their infrared and Raman data on the basis of C_{2v} symmetry

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However, X-ray analysis shows the presence of an S–S bond in a structure of C_s symmetry Buijs[326] in a more recent examination of the infrared spectrum has reported five fundamentals in the S–O stretching region as expected on the basis of the required C_s symmetry. The assignment of the fundamental frequencies of the dithionate ion $(S_2O_6^{2-})$ is subject to some controversy. Palmer[268] from a study of the Raman and infrared spectra of the sodium and potassium salts has assigned the S–O stretching frequencies, on the basis of D_{3d} symmetry, as follows

ν_1 (asymmetric S–O stretch), 1235–1240 cm^{-1},
ν_{10} (asymmetric S–O stretch), 1206–1216 cm^{-1},
ν_5 (symmetric S–O stretch), 996–1000 cm^{-1},
ν_1 (symmetric S–O stretch), 1092–1102 cm^{-1}

On the other hand, Buijs[70,326] has interpreted his infrared data, in conjunction with the Raman studies of Duval and Lecomte[329] to suggest that the fundamentals should be assigned as, $\nu_7 = 994$ and 998 cm^{-1}, $\nu_{10} = 1212$ cm^{-1}, $\nu_5 = 1230$ and 1243 cm^{-1}, and $\nu_1 = 1200$ cm^{-1}. Compounds containing S^{VI} have been found to give rise to symmetrical and asymmetrical stretching frequencies which vary linearly with one another (Fig 5 6 section 12 a) The assignments made by Palmer give rise to average values of, $\nu_s SO = 1046$ cm^{-1} and $\nu_{as} SO = 1221$ cm^{-1}, which fit this general relationship fairly well. The corresponding values from Buijs assignments are, $\nu_s SO = 1237$ cm^{-1} and $\nu_{as} SO = 1068$ cm^{-1}, which do not fit the straight line of Figure 6 The effect of site symmetry on the fundamental frequencies has been discussed by Buijs (loc. cit.)

Simon and Wagner[269] have studied the infrared and Raman spectra of the disulphate ion $(S_2O_7^{2-})$ and have interpreted their data in terms of C_{2v} symmetry Symmetric S–O stretching modes occur in the infrared at ~ 1060 and ~ 1110 cm^{-1}, the corresponding asymmetric modes being at 1249–1267 and 1289–1295 cm^{-1} Similar frequencies are observed in the Raman spectra Bands at approx 740 and 800 cm^{-1} were assigned to the symmetric and asymmetric SOS stretching modes, respectively, in agreement with the assignments of Dupuis and Viltange[330] Gillespie and Robinson[331], however, have assigned frequencies of ~ 150, ~ 300 and ~ 800 cm^{-1} to the bend, symmetric stretch and asymmetric stretch, respectively, of the SOS group in molecules of the type X_nSOSX_n including $S_2O_7^{2-}$ Further, these authors have shown that there exist linear relationships between the symmetric stretching and bending modes of the SOS group and the square root of the mass of the groups SX_n attached to the oxygen atom. For the disulphate ion SO bending modes occur at ~ 520 (symmetric) and ~ 590 cm^{-1} (asymmetric).

The Raman and infrared spectra of several peroxodisulphates $(S_2O_8^{2-})$ have been examined by Simon and Richter[332] who assigned a band at 1267 cm^{-1} in both spectra to an S–O stretching vibration Since the $S_2O_8^{2-}$ ion contains S(VI), its symmetric and asymmetric frequencies are expected to fit the linear relationship shown in Fig 5 6 If the 1267 cm^{-1} band is assigned to the asymmetric mode then the band observed

at 1088 cm^{-1} in the Raman, (not assigned by Simon and Richter) is in the region expected for the symmetric stretch.

The spectrum of the tetrathionate ion ($S_4O_6^{2-}$) has been discussed in some detail[326, 482]. There are six fundamental S–O stretching modes and these occur in the regions 1010–1050 cm^{-1} and 1200–1250 cm^{-1} As expected these frequencies are close to those observed for the $S_2O_6^{2-}$ ion. Schmidt and Sand[333] have assigned bands in these same regions to the S–O vibrations of $K_2S_2O_6$ and these authors[334] have shown that the infrared spectra of the ions $S_nO_6^{2-}$, where $n = 3$–6, are similar

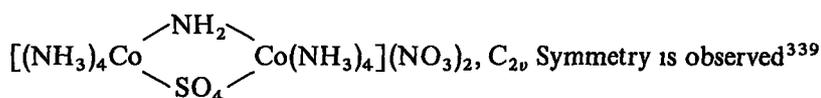### (iv) Complexes containing oxo-anions as ligands

(1) *Sulphito-compounds* Compounds of the types $M_2^I M^{II}(SO_3)_2$ and M^ICuSO_3, have simple spectra typical of the free ion and, therefore, are double salts and not complexes[273] When functioning as a unidentate ligand the sulphite group may bond through either sulphur or oxygen The C_{3v} symmetry of the free ion will be essentially undisturbed if S-bonding occurs and the infrared spectra of complexes[273,335,336] of Co^{III}, Rh^{III}, Ir^{III}, Pd^{II}, Pt^{II} and Hg^{II} are in accordance with this suggestion Bonding through oxygen lowers the symmetry to C_s, causing more profound changes in the spectrum, $Tl_2[Cu(SO_3)_2]$ is the only compound for which O-bonding is reported[273]

When occupying two coordination positions the sulphito-group may be bidentate or bridging As is the case with sulphato-compounds it seems doubtful[273] if infrared data can distinguish between the two possibilities

Baldwin[335] has interpreted the infrared spectrum of $[Coen_2SO_3]Cl$ to show that the sulphito group is bidentate Newman and Powell[273] found that the spectrum of $[Coen_2SO_3]Cl$ is similar to the spectra of $K_2[Pt(SO_3)_2]$ 2 H_2O, $Na_3[Co(SO_3)_3]$ 4 H_2O and $K_3[Rh(SO_3)_3]$ 2 H_2O, they concluded that infrared spectral data alone cannot distinguish between the two possible structures. These latter authors discussed the infrared data in some detail and commented upon Baldwin's[335] interpretation of her data. On the other hand, Babaeva and Kharitonov[337] have suggested that the infrared spectra support the assignment of structures involving bridging sulphito-groups to $[Co(SO_3)_3]^{3-}$ and $[Rh(SO_3)_3]^{3-}$ The spectrum[273] of $K_2[Pd(SO_3)_2]$ indicates that its structure may differ from that previously suggested[338].

(2) *Sulphato-compounds.* Nakamoto et al.[339] have discussed the spectra of both unidentate and bidentate sulphato-groups When the group functions as a unidentate ligand e g in $[Co(NH_3)_5 SO_4]X$ compounds[339,340], the symmetry is lowered to C_{3v}, whilst in the case that bridging occurs, e g ,

$$[(NH_3)_4Co\begin{array}{c} \diagup NH_2 \diagdown \\ \diagdown SO_4 \diagup \end{array}Co(NH_3)_4](NO_3)_2, \quad C_{2v} \text{ Symmetry is observed[339]}$$

Barraclough and Tobe[341] from a study of the spectrum of $[Coen_2SO_4]Br$ have con-

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cluded that it is not possible to distinguish between bridging and chelating sulphato-groups using infrared data only On the other hand, McWhinnie[307] has suggested that a band at $\sim 1220\ cm^{-1}$ may be used to differentiate between the two possibilities The spectra of some protactinium di- and tri-sulphato complexes have been reported and discussed[342] Both uni- and bidentate sulphato groups may be present and since the various possibilities could not be differentiated the coordination of the protactinium remains uncertain Baldwin[343] has discussed the spectra of various complex sulphates and of compounds of the types, Y_2SO_4 $MSO_4 \cdot 6\ H_2O$ and $Y_2SO_4 \cdot X_2(SO_4)_3\ 24\ H_2O$, i e Tutton salts and alumns. It appears that these hydrated compounds may give rise to quite complex spectra and Baldwin concludes that whilst a simple spectrum indicates an undistorted sulphato-group it does not necessarily follow that a complicated band structure shows conclusively coordination to a metal or even significant deviation from a tetrahedral structure.

Livingstone[121] has recently reviewed the metal complexes of ligands containing sulphur as a donor atom; sulphito and thiosulphato complexes were also discussed by this author

(c) Thionyl (-SO-) compounds

Table 5.12 shows the S—O stretching frequencies observed in various thionyl compounds With the sulphoxides, R_2SO, considerable molecular aggregation occurs in the liquid phase with the result[36,344,345] that

$$\nu_{SO_{(liquid)}} < \nu_{SO_{(solution)}} < \nu_{SO_{(vapour)}}$$

TABLE 5 12

S—O STRETCHING FREQUENCIES IN THIONYL COMPOUNDS

Type of compound	$\nu_{SO}\ (cm^{-1})$
simple sulphoxides, R_2SO, (R = aryl, alkyl, alkenyl)	$1010–1070^a$
cyclic sulphoxides, $(CH_2)_nSO$	$1039–1055,\ 1192^b$
$(CH_2O)_2SO$	1220
disulphoxides	1036–1088
dimethyl sulphoxide-metal complexes	$978–1037^c$
tetramethylene sulphoxide-metal complexes	950
S-alkylsulphoxonium compounds	1210–1240
O-methylsulphoxonium nitrate	925–1050
SOX_2 (X = F, Cl, Br)	X = F, 1308, X = Cl, 1251} ^{d} X = Br, 1121
SOF_4	1379

^{a} see text for variation of ν_{SO}
^{b} when $n = 4$, $\nu_{SO} = 1192\ cm^{-1}$, this value is anomalously high
A similar situation arises with the cyclic ketones[36]
^{c} except Pd(II) and Pt(II) complexes, see text
^{d} see Table 5 20 section 15

Nickless   Ch 5-33   1st proof

and because of the considerable solute-solvent interactions that can arise with these compounds the observed solution frequency is markedly solvent dependant[346] The range quoted in Table 5.12 covers the frequencies observed in CCl_4 and CS_2 solutions. In contrast to the sulphones it is not possible to differentiate between compounds having R = aryl and those having R = alkyl. Barnard, Fabian and Koch[344] have suggested that the constancy of v_{SO} at ~ 1055 cm^{-1} for several sulphoxides arises from the fact that negligible coupling occurs between the S–O vibration and the lower frequency C–S vibration, and Price and Gillis[347] report that negligible conjugation occurs between C=C and S=O bonds in alkyl-alkenyl sulphoxides Coupling between the S–O stretching and CH_3 rocking modes in dimethyl sulphoxide is, however, well substantiated[348,349] and leads to some difficulty in the assignment of v_{SO} in dimethyl sulphoxide-metal complexes. Lappert and Smith[350], and Cotton Francies and Horrocks[345] have assigned a band at 900–950 cm^{-1} to the S–O stretching vibration in a wide variety of dimethyl sulphoxide complexes and have concluded that since in these complexes v_{SO} occurs at lower frequencies than in the free ligand, the ligand is bonded through the oxygen atom of the S–O bond. Complexes of Pd^{II} and Pt^{II} are exceptions to this general rule[345,351,352], as are complexes of the type $C_5H_5Mn(CO)_2$ D, where D may be various sulphoxides[353], in that the ligands are bound through the sulphur atom with the result that v_{SO} is at a higher frequency than in the free ligand Drago and Meek[349,354] assign a band at ~ 1000 cm^{-1} to the S–O stretch in the "normal" O-bonded complexes and suggest that the 900–950 cm^{-1} band is due to a CH_3 rocking mode since its frequency remains fairly constant in many complexes, whilst that of the band at ~ 1000 cm^{-1} varies with the metal ion These authors suggest that considerable coupling occurs between these two modes so that when v_{SO} is less than ~ 990 cm^{-1}, e.g., in Cu^{II} complexes, the assignment of "v_{SO}" is very difficult. Since the extent to which the S–O vibration is involved in coupling will vary with the sulphoxide it is dangerous to use the shift in v_{SO} which occurs on complex formation as a measure of the variation of bond strengths for various ligands[351] The infrared spectra of sulphoxide complexes with I_2 and ICN indicate that in these compounds also the bonding is through the oxygen atom[40]

(d) Structural data · Bond lengths and bond angles

(i) Introduction

For the S–O single bond Pauling's covalent radii[168] give a value of 1 70 Å, and the Schomaker–Stevenson[335] rule gives 1 69 Å In the case of double bonds the corresponding values are 1.49 Å and 1 47 Å respectively. To date no compound is known in which the S–O bond is as long as the predicted value for the single bond. The longest reported bonds[356-358] are 1 66 Å in SF$_5$O OSF$_5$; 1 64 Å in SF$_5$OF, and 1.64 Å in HS$_2O_7^-$ The value of 1 72 Å in $(NO_2)_3S_3O_{10}$ is not considered reliable[359] In these compounds the 3d-orbitals normally used for double bonding with oxygen[360,361] are largely utilised in forming single bonds to other oxygen atoms However, there is

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some evidence[361] that even for these long bonds some $d_\pi-p_\pi$ overlap occurs so that they may be expected to be somewhat shorter than a true single bond The situation with respect to double bonds is less satisfactory The shortest observed bond lengths* are 1 39 Å in $SO_2(NH_2)_2$[171], 1 405 Å in SO_2F_2,[424] 1 412 Å in SOF_2[430], and 1.40 Å in S_3O_9[387], all of which are appreciably shorter than the predicted double bond value Gillespie and Robinson[362] comment that the double bond radii may well be incorrect and take the value of 1 40 Å as that of a true SO double bond Abrahams[363] has used Moffitt's bond order assignments[360] to predict a double bond length of 1 425 Å, and since the observed bond lengths in many compounds expected to contain S=O bonds are reasonably constant at about 1.44 Å this assignment has found fairly wide acceptance Cruickshank[361] has considered the S–O bond from a theoretical standpoint and proposed a linear relationship between bond lengths and bond order However, the bond orders calculated by this author lead to an unsatisfactorily short length of about 1 30 Å for the double bond

(ii) Compounds derived from the SO_4^{2-} tetrahedra

Table 5.13 lists most of the important published data Further data are available for some types of compounds, e g., sulphates, but most of this is referred to in the literature quoted For most simple hydrated and anhydrous sulphates the reported S–O distances fall within the range 1 47–1.53 Å, though recent high resolution studies[364-368] on several hydrates all report average S–O distances in the range 1.473 ±0.003 Å. In many cases the tetrahedral symmetry of the sulphate group is only slightly distorted[367,369,370], though in a few cases[371], e.g CdSO4 and HgSO4, the distortion is more marked These two compounds are also unusual in that the metal ions are surrounded by a very distorted tetrahedron of oxygen atoms, whilst for all other $M^{II}SO_4$ compounds only the very small beryllium ion has a tetrahedral coordination, and Mg, Mn, Fe, Co, Ni, Cu, and Zn, all of which have an ionic radius smaller than cadmium or mercury, are octahedrally coordinated The high temperature form of $CdSO_4$ has the expected octahedral coordination[372]

Ananthanarayanan[287] has studied the effect of crystal forces on S–O distances and O–S–O angles in anhydrous sulphates by Raman spectroscopy Atoji and Rundle[373] from a neutron diffraction study of $CaSO_4 H_2O$ have shown the deviations of the O–S–O angles from the tetrahedral angle to be insignificant, whereas both the Raman[374] and infrared[375] spectra have been interpreted to suggest that the sulphate group summetry is distorted. Atoji and Rundle conclude that spectroscopic methods are apparently the more sensitive in detecting the effects of crystalline field effects Larsen[367] has summarised the available high resolution data for various hydrated sulphates, and has shown that these fall into two classes, having average corrected S–O distances of 1.480 Å and 1 486 Å respectively In the compounds having the

* The reported value of 1 38 Å in $(NO_2)_2S_3O_{10}$ is considered unreliable[359], the value of 1 37 Å in $S_3N_2O_2$, the shortest SO bond length reported[189], must be used with caution in the absence of a confirmatory analysis

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TABLE 5 13

Compound	r_{S-O} (Å)	$\widehat{XSO}$	$\widehat{OSO}$	References
SO	1 4933			379
S₂O	1 46±0 01	118 0±0 5°		380
SO₂	1 43±0 01		119 5±1 5°	381, 382
	1 4321±0 0005		119 0±0 5°	383, 384
SO₃	1 43±0 02		120±2°	386
ice-like (SO₃)₃	1 40±0 05		122° (O=S=O)	387
	1 60±0 05		100° (O–S–O)	
asbestos, (SO₃)ₙ	1 59±0 04		128°	388
	1 63±0 04		102°	
LiSO₄H₂O	1 47		109 5±0 1	367
ZnSO₄	1 48		109 5°	389
HgSO₄	1 50		107 6°, 116 5°	371
CuSO₄	1 51±0 03		109 5°	389, 369
CdSO₄	1 53		103 0, 115 8°	371
VOSO₄	1 43			390
Li(N₂H₅)SO₄	1 43		109 8°	391
	1 56			
H₂SO₄	1 43		104°, 117°	392, 393
	1 54			
NaHSO₄	1 613±0 013		101 25±1 0°	394
	1 450±0 013		112 75±1 0°	
KHSO₄	1 56±0 015		107°, 112°	395
	1 56±0 015			
H₂NSO₃H	1 439±0 022	103 5°	115 1°	190, 396
H₂NSO₃K	1 42±0 03	107 5±0 5°	111 5±0 5°	191, 397
K₂NH(SO₃)₂	1 447±0 005		112 75±1 0°	192
K₂CH₂(SO₃)₂	1 461±0 005	107 3±0 5°	113 1±0 7°	376
MgS₂O₃6H₂O	1 48±0 02	108 1±0 8°	111 0±1 1°	398, 399
Na₂S₂O₄	1 51±0 02	98 7°	108 2°	400
K₂S₂O₅	1 50±0 01 (–SO₂⁻)	100 5°	100 3° (–SO₂⁻)	377
	1 43±0 01, 1 47±0 01, }(–SO₃⁻)	106 6°	111 9° (–SO₃⁻)	
K₂S₂O₆	1 43±0 05	105±1°		401, 402, 403
NaK₅Cl₂(S₂O₆)₂	1 48±0 05			404
(NO₂)₂S₃O₁₀	1 38, 1 42, 1 54 1 72		101°, 122°	359
NO₂HS₂O₇	1 64±0 03 (S–O(H))		133° (OSO(H))	358
	1 47±0 03		107°–118°	
Na₂S₄O₆2H₂O	1 46±0 02	107 8±1 0°	113 6±1 4°	405
BaS₄O₆2H₂O	1 43±0 04	105°	113°	406, 407
(NH₄)₂SO₃N₂O₂	1 44±0 01	103 9°	115 1°	169, 408
Ni(H₂O)₆SO₃	1 45±0 03		95 4°	409, 410
BaSe(S₂O₃)₂	1 40	106°	113°	411
(NH₄)₂Te(S₂O₃)₂	1 43	106°	112°	412
(C₆H₅SO₂)₂Se	1 43			413
(CH₃SO₂S)₂Te	1 43			414
[Ru(II)(NH₃)₄SO₂Cl]Cl	1 428±0 010		113 8±0 6°	415
(C₆H₅)₂SOSbCl₅	1 53			416
(CH₃)₂SOBF₃	1 52			416
[(CH₃)₂SO]₂SnCl₄	1 51, 1 54			416
S₃N₂O₂	1 37	115 3°		189
(NSOCl)₃	1 407±0 007	(ClSO)107 9° (NSO)111 9°		181

longer S–O distance (1 486 Å), the sulphate group has only hydrogen atoms as nearest neighbours whilst in the other compounds at least two of the sulphate oxygen atoms have cations as nearest neighbours. The individual S–O distances within the sulphate group reflect the slight distortions caused by the cations or hydrogen atoms. Ions such as $S_2O_6^{2-}$, $S_2O_7^{2-}$, $S_3O_{10}^{2-}$, $HN(SO_3)_2^{2-}$, and $[SO_3N_2O_2]^{2-}$ and molecules such as $SO_3^-NH_3^+$ and $(SO_3)_n$ may be regarded as derived from the tetrahedral SO_4^{2-} group Cruickshank[361] has discussed the bonding in some of these compounds and has suggested that in the SO_4^{2-} ion two strong π-bonding molecular orbitals are formed by overlap of the $3d_{x^2-y^2}$ and $3d_{z^2}$ of the sulphur and the appropriate $2p_\pi$ and $2p_{\pi'}$ orbitals of oxygen By an extension of this concept the structures of many sulphur containing anions are explained and the observed bond lengths correlated with their π-bond order Cruickshank suggests that the use of $3d$-orbitals for π-bonding is of potential importance whenever sulphur is tetrahedrally coordinated and that the ability of doubly linked oxygen and triply linked nitrogen to share in these π-bonds is widespread Cruickshank's predicted bond lengths for $K_2(CH_2(SO_3)_2)$ have been essentially confirmed by Truter[376] which lends support to this theory. On the other hand, Lindquist and Mörtsell[377] have used the observed O–S–O bond angles in $S_2O_4^{2-}$, $S_2O_5^{2-}$ and $S_2O_6^{2-}$ ions to determine the hybrid orbitals used by sulphur in these compounds, assuming that these are orthogonal combinations of $3s$- and $3p$-orbitals only. The results indicate that this assumption is essentially correct for the thionate group and that the bond lengths are principally determined by the s-character of the hybrid orbitals forming the σ-bonds The possibility that d-orbitals are used in the thionite group was not eliminated Truter[378] has discussed the structures of various S(II), S(IV), and S(VI) compounds and concludes that there is as yet no theory which accounts satisfactorily for the bond lengths in all the oxo compounds of sulphur. She concludes that theories that imply a gradation from S(II) to S(VI) do not explain the essentially anomalous character of S(IV) which forms the longest single bonds and has the smallest bond angles A possible explanation is that hybridisation is essentially the same (sp^3) in S(II) and S(VI) but is different in S(IV), the small angles around S(IV) indicating a tendency to pure p-bonds with a predominantly s lone pair. The p-bonds would result in a larger radius and a smaller electronegativity for S(IV)

It would seem that many factors combine to determine bond lengths These factors which are often interdependent include the oxidation state of sulphur, its hybridisation, the electronegativities of all the atoms and the existence of π-bonding.

(iii) Sulphoxides and sulphones
The molecular dimensions of these groups illustrated in Tables 5 14 and 5.15 Little new data has appeared since these groupings were reviewed by Abrahams[363] In the case of the sulphoxides the three sulphur bonds form a shallow pyramid; the XSO angle has a particularly constant value at $106°-108°$ and the XSX angle varies from $93°$ to $114°$ The tetrahedral structure of the sulphate, and related groups, is

Nickless   Ch *5 – 5y*   1st proof

TABLE 5 14

MOLECULAR DIMENSIONS IN THE SULPHOXIDE GROUP

Molecule	X-S-O (°)	X-S-X (°)	r_{S-O} (Å)	References
F_2SO	106 8±0 1	92 8±0 1	1 412±0 001	430
Cl_2SO	106 0±1 0	114 0±2 0^a	1 45±0 02	425
Br_2SO	108 0±2 0	96 0±2 0	1 45 (assumed)	429
$(CH_3)_2SO$	107 0±5 0	100 0±5 0	1 47±0 03	431
$(C_6H_5)_2SO$	106 2±0 7	97 3±1 0	1 473±0 015	432
CH_3SO $CH_2CH(NH_2)$ $C(O)OH$	107 5±0 7	96 7±1 0	1 488±0 012	433

^{a} Angles smaller than 106° were not used in the models tiied

TABLE 5 15

MOLECULAR DIMENSIONS IN THE SULPHONE GROUP

Molecule	X-S-O (°)	X-S-X (°)	O-S-O (°)	r_{S-O} (Å)	References
F_2SO_2		100 0±8 0	130 0±10	1 43±0 02	225
		96 1±0 2	124 0±0 2	1 405±0 003	424
Cl_2SO_2	106 5±2 0	111 2±2 0	119 8±5 0	1 43±0 02	425
$(CH_3)_2SO_2$	105 3±3 0	115 0±15	125 0±15	1 43±0 02	426
$C_6H_5SO_2CH_3$	107 0 (av)	112 0	120 0	1 455±0 015	427
$[(CH_3)_2N]_2SO_2$		112 6	119 7	1 499	428
$(H_2N)_2SO_2$	106 2±0 5	112 1±0 7	119 4±0 8	1 391±0 008	171

essentially maintained in the sulphones. Comparison of the data in Tables 5 14 and 5 15 shows the geometry of the two groupings to be similar Thus, the XSO angle in the sulphones has nearly the same constant angle, 107°, as in the sulphoxides and the XSX angles in related pairs of compounds are also similar, e.g , the FSF angles in SOF_2 and SO_2F_2 are 92 8° and 96.1° respectively The OSO angle in the sulphone group is invariably the largest sulphur bond angle in a given molecule, and is always greater than the tetrahedral value This is because electron repulsions due to multiple bonds are stronger than repulsions due to single bonds[417] The structural similarity between sulphoxides and sulphones is particularly well established in the case of the diphenyl derivatives[418,419] Diphenyl sulphoxide dissolves in diphenyl sulphone to form a continuous series of solid solutions and it has been suggested that the sulphur lone pair of diphenyl sulphoxide occupies the same direction and effective volume as one of the sulphur oxygen bonds in diphenyl sulphone Three other organic sulphones[420-422] and one cyclic compound[426] are reported and were discussed by Abrahams A theoretical treatment of the bonding in both groupings has been given by Moffitt[360].

(e) Correlations between stretching frequency and molecular parameters

The nature of the sulphur–oxygen bond in sulphuıyl ($XYSO_2$) and thıonyl ($XYSO$)

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compounds has been discussed by Gillespie and Robinson[362] These authors consider that the two possible extreme forms of the S–O bond may be represented as (I) and (II)

$$S=O \qquad \overset{+}{S}-\overset{-}{O}$$

(I)   (II)
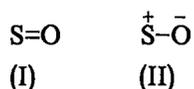
Structure (I) represents a situation in which the bonding electrons are equally shared and arises when the other atoms attached to sulphur have electronegativities sufficiently great to raise the effective electronegativity of sulphur to that of oxygen This situation is approached in SO_2F_2 and SOF_4 With decreasing electronegativity of the attached groups the bond becomes polar and in the limit the π-bond electron pair resides essentially on the oxygen atom and structure (II) results. The observed frequencies for sulphuryl compounds and S(VI) containing anions are in agreement with these suggestions. The highest frequencies (1270 and 1502 cm^{-1}) are found for SO_2F_2 and the lowest (981 and 1104 cm^{-1}) are those of the sulphate ion. Similarly, for the sulphoxides X_2SO the highest frequency (1308 cm^{-1}) is found for SOF_2 For SOF_4 the frequency is even higher (1379 cm^{-1}) than in SOF_2 which is consistent with the presence of two additional highly electronegative ligands. Increasing electronegativity of the groups X and Y should increase the order of the SO bond and since the lengths of the SO bonds may be assumed to be related to their bond order a correlation is to be expected between stretching frequency and bond lengths This relationship has been verified by Gillespie and Robinson and is illustrated in Fig 5 8 In the case of $-SO_2-$ compounds the appropriate stretching frequency was calculated[434] from the equation·

$$v_{SO} = \frac{1}{x}[v_s SO + (x-1)v_{as}SO] \tag{1}$$

where $(x-1)$ is the degeneracy of the asymmetric vibration The scatter of the points in Fig 5 8 is, in general, not greater than ± 0 02 Å which is of the order of the experimental error of most of the bond length determinations

For several compounds not considered by Gillespie and Robinson both bond lengths and stretching frequencies are now available so that values of the bond length predicted from Fig 5 8 may be compared with the experimental values The appropriate data is given in Table 5 16.

For compounds having bond lengths in the range 1 45–1 48 Å agreement between predicted and observed values is particularly good The results for compounds containing short (~ 1.40 Å) and long (~ 1 55 Å) bonds are rather less satisfactory, the predicted values deviating by ± 0 03 Å from the observed value Further, the bond length in the sulphite ion is of interest Gillespie and Robinson[362] predicted a value of 1.65 Å and commented that the value (1 39 Å) reported by Zachariasen and Buckley[440] seemed in error Using the values $v_s SO = 970$ cm^{-1} and $v_{as}SO = 930$ cm^{-1} (Table 5 9) the predicted value is 1 55 Å. More recent bond lengths have been reported by

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TABLE 5 16

SOME PREDICTED AND OBSERVED VALUES OF SULPHUR-OXYGEN BOND LENGTH (r_{s-o})

Compound	$\nu_{so}(cm^{-1})$ (calc)[a]	r_{s-o}Å (calc)[b]	r_{s-o}Å (obs)[c]
S_2O	1165 (435)	1 46	1 47 (380)
H_2NSO_3H	1180 (436)	1 45	1 48 (438)
			1 44 (396)
$S_2O_3^{2-}$	1080 (267)	1 48	1 48 (439)
$SOBr_2$	1121 (437)	1 47	1 45 (429)
$SO_2(NH_2)_2$	1254 (150)	1 43	1 39 (171)
			1 40 (361)
$(Me_2SO)_2SnCl_4$	920, 905 (350)	1 56, 1 57	1 54 (416)
$(Me_2SO)BF_3$	938 (350)	1 55	1 52 (416)

[a] calculated from equation 1, page
[b] predicted from Fig 5 8
[c] observed value
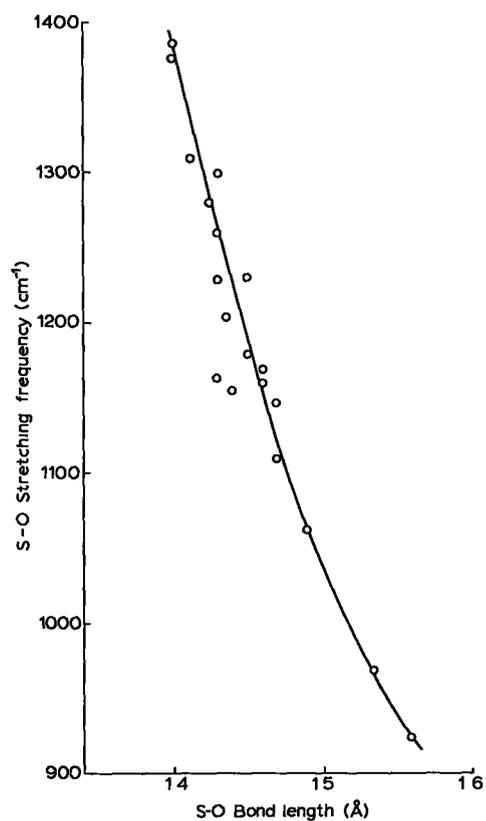
Fig 5 8 Correlation of S-O stretching frequencies with bond length[a]
a, from R J Gillespie and E A Robinson[162]

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Grand–Jean, Weiss and Kern[410] (1 45 Å) and Kierkegaard and Nyberg[441] (1.51 Å). Only the latter value is in even approximate agreement with the predicted value. Since the values of v_{as}SO and v_sSO for the sulphite ion do not fit the linear relationship shown in Fig 5 6, it is inadvisable to use the $v_{SO}-r_{SO}$ plot for predicting r_{SO} values for S(IV) species which contain sulphur bonded to more than one oxygen atom

Gillespie and Robinson[362] have also demonstrated a linear relationship between stretching frequency and OSO angle in $-SO_2-$ compounds, though the correlation is not too well established since relatively little data was available. These authors have also discussed the problem of defining the bond order of sulphur–oxygen bonds and have suggested that there exists a linear relationship between the force constant and the bond order, and a non-linear relationship between the bond length and the bond order That the bond order-bond length relationship for C–C bonds is also non-linear is thought to support the latter suggestion On the other hand Cruickshank[361] has suggested that the bond order-bond length relationship for S–O compounds is rectilinear

(f) Deformation frequencies

The deformation frequencies of the oxo-anions have been mentioned in section 12 b For sulphur dioxide the single symmetrical bending mode occurs[442,443] at 520–530 cm^{-1}, and for the trioxide the symmetrical and asymmetrical bending modes occur at ~ 495 and ~ 530 cm^{-1}, respectively[444–446] The γ and β forms of $(SO_3)_n$ have asymmetric bending modes at ~ 530 and ~ 566 cm^{-1} respectively[452] Sulphuryl compounds SO_2X_2 and SO_2XY give rise to an SO_2 scissoring bend and an SO_2 rocking vibration, the values reported for a series of compounds[12,150,447,448] fall in the ranges 520–610 and 530–620 cm^{-1}, respectively. Feairheller and Katon[449] from a study of several sulphones concluded that of the four SO_2 bending vibrations only the SO_2 scissoring (545–610 cm^{-1}) and wagging (495–525 cm^{-1}) are sufficiently localised to be of value as group frequencies Bands in the region 500–570 cm^{-1} have been assigned to bending modes in the alkali methyl sulphonates[450] and methyl sulphonic acid and its anhydride[451]. For sulphamic acid[138] the symmetric and asymmetric bending modes occur at 640 and 511 cm^{-1} respectively, and in sulphamates[138] bands at 520–560 cm^{-1} are assigned to SO_3 deformations

13. Sulphur

Stretching frequencies and structural data for S–S bonds are given in Table 5 17. X-ray analysis of rhombic sulphur[453] has shown the molecule to be a crown shaped S_8 ring (point group D_{4d}) All Raman lines are due to internal vibrations, since they are all present in solution[455] From the Raman spectra of the solid[454] the strongly polarised lines at 470 and 216 cm^{-1} can be assigned to v_1 and v_2 respectively. Of the

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three allowed infrared active fundamentals $(\nu_4, \nu_5$ and $\nu_6)$, ν_5 is assigned at 465 cm^{-1} since it is a stretching mode, and hence at a higher frequency than ν_4 and ν_6 which are bending modes The observed Raman shifts are in close agreement with the calculated values[456,461] The far infrared spectra of S_8 in CS_2 solution and in discs have been discussed in a preliminary communication[460] Sulphur chains consisting of S_2, S_6, and S_n have been studied spectroscopically and by electron diffraction and the structural parameters determined[457-459].

Molecules of the type XS_2S are generally assumed to be non-planar as found for S_2Cl_2 (C_2 symmetry and similar to H_2O_2) Electron diffraction measurements[573] and vibrational spectra[461] of S_2Cl_2 are consistent with such a model and exclude the planar arrangements trans (C_{2h}) and cis (C_{2v}). The infrared frequencies reported by

TABLE 5 17

STRETCHING FREQUENCIES AND STRUCTURAL DATA FOR S–S BONDS

Compound type	ν_{S-S} (cm^{-1})	l_{S-S} (Å)	$\widehat{SSX}$(°)	References
S_8	^{a}	2 060	108 0	473–475, 541
S_2	668	1 887		457, 458, 476
S_n		2 1	100	459
S_2H_2	509R, 501, 510	2 05	95	85, 86, 99
S_2X_2	510–540	1 98–	104–	86, 462, 463, 477–479
		2 07	105	
S_2R_2	495–520	2 04–2 05	102–110	370, 466, 480
$S_2O_n^{2-}$	324–434	1 97–2 39	98–110	400–402, 439, 481, 482
RS_nX	450–500^R			483
S_nH_2	467–509			87, 88
RS_nH	450–500^R			483
$(RNS)_n$	480–490			144
$RN(S)_nNR$	418–448			467
$ROC(S)SSC(S)OR$	505–510			467
MS_x		1 99–2 18	103–110	484–489
R = Raman				

^{a} Raman shifts for S_8 are 152, 185, 216, 243, 434, 470 and 520 cm^{-1}

several investigators are in good agreement. There are, however, many discrepancies between the assignments made for these compounds[86,462,463], particularly in the cases of Me_2S_2 and S_2Cl_2

The variation of the vibrational frequencies in the compounds H_2S_2, Me_2S_2, S_2F_2, S_2Cl_2, and S_2Br_2, with the mass of the atoms attached to sulphur lends support to the assignments due to Hooge and Ketelaar[86] In these XS_2X molecules the highest frequency remains fairly constant at 510–540 cm^{-1}. Since the vibration is not greatly influenced by substituents on the sulphur atoms, it was assigned to the S–S stretching vibration For S_2Cl_2, Gerding and Westrik[462], and Vogel–Högler[464] disagree with the assignments made by Hooge and Ketelaar[86]. Assignment of the Raman frequencies of S_2Br_2 by Stammreich and Forneris[465] has been made by analogy with

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the assignment for S_2Cl_2 by Gerding and Westrik[462] The infrared spectra of Et_2S_2 and $(C_3H_7)_2S_2$ show S–S stretching frequencies at 507 and 502 cm^{-1} respectively[86] Cyclic molecules containing sulphur–sulphur linkages have been investigated by several workers[144,147,466–470], the S–S stretching frequency falling within the range 400–500 cm^{-1}. Many organic sulphur compounds also absorb within this range

There is little spectral information on compounds containing S=S double bonds. Disulphur monoxide[471] is a bent triatomic molecule with two stretching modes (v_{SO} at 1165 cm^{-1}, v_{SS} at 679 cm^{-1}) and one bending mode (388 cm^{-1}) The S=S stretching frequency in S=SF$_2$ has been reported[472] at 715 cm^{-1}

Abrahams[363] has reviewed the observed variations in S–S bond lengths and S–S–S bond angles The data in Table 5.17 show that for many classes of compound the S–S bond lengths fall within the range 1 97–2 18 Å Lindquist and Mörtsell[377] have suggested that the variations of S–S distance in the ions $S_2O_4^{2-}$ (2 39 Å), $S_2O_5^{2-}$ (2.21 Å) and $S_2O_6^{2-}$ (2 15 Å) supports their thionite-thionate structure for the $S_2O_5^{2-}$ ion For the greater number of compounds the S–S–S angle is 102–108°

14. Selenium and tellurium

No reports of characteristic stretching frequencies for sulphur-selenium or sulphur-tellurium bonds have been found in the literature Structural data[411–414,490–492] are available for a few compounds of the type $(RSO_2S)_2Se$ and $(RSO_2S)_2Te$ The S–Se and S–Te bond lengths are reported in the ranges 2 17–2 20 Å and 2 35–2.41 Å respectively The S–Se–S and S–Te–S bond angles fall in the range 96–103°.

15. Halogens

Infrared frequencies, Raman shifts and X-ray data are summarised in Tables 18–21

(a) Sulphur (II) halogen compounds

XS–SX. The disulphur dihalides have been studied in some detail, especially with regard to the problem of the relative positions of the two halogen atoms Infrared and Raman data for S_2Cl_2 were originally interpreted in terms of a planar cis C_{2v} model[462,494,495] Raman polarisation measurements were later reinterpreted[461] to support a non-planar (C_2) structure The calculated frequencies for S_2Cl_2 (C_2 model) agree with the observed values, so that along with results obtained from electron diffraction[496], the total evidence is in accordance with a non planar molecular arrangement

SX$_2$ Infrared[499] and Raman[500] spectra, electron diffraction data[480,496,501] and force constant calculations[501,502] for SCl_2 are all consistent with C_{2v} symmetry

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(b) *Sulphur (IV) halogen compounds*

SF_4 (point group, C_{2v}). The infrared and Raman spectra[503] are in accordance with a trigonal bi-pyramidal structure with one equatorial position occupied by a sulphur lone pair Infrared assignments[503] are. $v_1 = 889$, $v_6 = 867$, $v_8 = 728$, $v_7 = 523$, $v_9 = 463$ cm^{-1}. Raman frequencies are close to these values. The infrared band at at 889 cm^{-1} is assigned to the S–F symmetric stretch and those at 867 and 728 cm^{-1} involve asymmetrical S–F stretching SF_4 reacts with BF_3, AsF_5 or SbF_5 to form trifluorosulphonium (SF_3^+) salts The SF stretching vibrations in solid $SF_3^+BF_4^-$ absorb[504] at 940 cm^{-1} (v_s SF) and 908 cm^{-1} (v_{as} SF).

$S=SF_2$. The infrared spectrum of $S=SF_2$ has been reported (see section 13), and the bands at 757 cm^{-1} and 684 cm^{-1} assigned to the symmetric and asymmetric S–F stretching frequencies respectively[472,497,498].

SOX_2. The thionyl halides show six infrared and Raman active fundamental vibrations Their Raman spectra have been shown[505,506] to be consistent with a pyramidal molecular structure (C_s symmetry, leading to 4 polarised and 2 depolarised lines) rather than a planar arrangement (C_{2v}, 3 polarised and 3 depolarised lines) Depolarisation factors are not available for SOF_2

TABLE 5 18

FREQUENCY ASSIGNMENTS FOR THIONYL HALIDES

SOF$_2$			SOCl$_2$		SOBr$_2$	Approximate description[437]
Infrared[507]	Raman[508]	Raman[509,437]	Infrared[510–512]	Raman[513]	Raman[506]	
1333	1308	1312	1251		1121	SO stretch
808	801	795	492	490	405	SX$_2$ stretch(s)
630	526	529		194	267	SO wag
410		326		344	120	SX$_2$ bend
748	721	720	455	443	379	SX$_2$ stretch(as)
390	393	395		284	223	SX$_2$ rock

Long and Bailey[437] have investigated a six constant Urey–Bradley–Simanouti force field for the thionyl halides and although for each molecule a set of force constants can be found which exactly reproduce the observed frequencies, these force constants are not satisfactorily consistent with the physical model underlying the UBS field This failure arises principally from the neglect of interactions involving the lone pair on the sulphur atom. These authors prefer the SOF_2 assignment of O'Loane and Wilson[597] to that of Gillespie and Robinson[505].

NS(IV) Compounds The sulphur–halogen stretching frequency[159,161] has been assigned in the following compounds –NSF (640 cm^{-1}), RNSF$_2$ (727 and 764 cm^{-1})

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(c) *Sulphur (VI) halogen compounds*

S_2F_{10} The infrared spectrum of S_2F_{10} and the Raman spectrum of the liquid can be interpreted[514-516] on the basis of a staggered F_5S-SF_5 model (D_{4d}). This structure is confirmed by electron diffraction experiments[517], Dodd, Woodward and Roberts [514,515] calculated the frequencies of the eight fundamental modes and these are in agreement with the observed Raman shifts The seven S–F stretching modes appear in the infrared and Raman spectra between 684 and 938 cm^{-1}. The S–F bond force constant was calculated to be $4\,27 \times 10^5$ dyne cm^{-1}. The solid state infrared spectrum is similar to the vapour spectrum[514] with additional absorptions due to combination bands intensified by Fermi resonance.

SF_6 (point group O_h) has six normal modes of vibration, three are Raman active and only two are infrared active[6,60,71,503,518-520]. The five fundamental frequencies are observed at· 940(IR), 775(R), 644(R), 615(IR) and 524 cm^{-1}(R), the symmetric SF stretching vibration scatters at 775 cm^{-1} The nature of the vibrational modes of XY_6 molecules has been discussed in some detail by Herzberg[521]

SF_5X. Replacement of one of the fluorine atoms by chlorine in SF_6 lowers the symmetry to C_{4v}. Cross and coworkers[522] have assigned the Raman shifts at 834 and 404 cm^{-1} to SF and SCl stretching vibrations respectively. A study[613] of compounds containing $-SF_5$ showed that this group leads to bands of diagnostic value in the regions 580–610 cm^{-1} (strong) and 860–910 cm^{-1} (very strong)

SOF_4 The Raman spectrum of the liquid, and the infrared spectrum of the gas indicate[523] that the structure is analogous to SF_4, *i e.* based on a trigonal bipyramid in which the oxygen atom occupies the equatorial position, which in SF_4 is occupied by the lone pair. The point group is hence C_{2v} and of the twelve Raman fundamentals, eleven are infrared active. The SF_2 stretching vibrations have been assigned[523] at 741, 797 and 933 cm^{-1} in the Raman spectrum

SO_2F_2. Sulphuryl fluoride has a slightly aspherical top structure, and electron diffraction[524] and microwave spectra[525] indicate C_{2v} symmetry Of the nine normal modes of vibration, eight are infrared active and by analogy with thionyl fluoride where the asymmetric SF_2 stretch occurs at a higher frequency than the symmetric stretch, the infrared bands at 885 and 848 cm^{-1} are assigned[526] to v_{as}(S–F) and v_s(S–F) respectively.

RSO_2X. The Raman[447,527,528] and infrared spectra[21,243,254,257,258,261,262,374, 529-531] of a large number of sulphonyl halides have been reported.

Sulphonyl fluorides absorb in the region 780–852 cm^{-1} and this is assigned[527] to the SF stretching frequency King and Smith[21] report that all sulphonyl chlorides gave a band at 370–390 cm^{-1} characteristic of the S–Cl stretching vibration, and that the introduction of electron withdrawing substituents is accompanied by a shift to higher frequencies Although S–Cl frequencies of aromatic sulphonyl halides show no precise correlation with the ordinary Hammett substituent parameters, they do give a good linear plot with Taft's σ-values, indicating a direct connection between

stretching frequency and inductive effect of the substituents

The Raman spectra of some sulphonyl bromides[528] give an extraordinarily strong band at about 285 cm^{-1} By comparison with the corresponding chlorides and fluorides, this is assigned to an S–Br stretching vibration Force constant and bond energy calculations indicate that in all cases the C–S bond is stronger than the S–halogen bonds[528].

SO_2Cl_2 Raman[505,532,533] and infrared[510,534] data for sulphuryl chloride are consistent with a roughly tetrahedral molecule (C_{2v} symmetry) Such symmetry gives rise to nine fundamentals, all are Raman active and eight are infrared active. There has, however, been some disagreement over the assignments[505,510,533] The SCl vibrations in the Raman spectrum were assigned[505,533] $\nu_s(SCl_2)$ 405 cm^{-1}, $\nu_{as}(SCl_2)$ 362 cm^{-1}, SCl$_2$ rock 282 cm^{-1}, SCl$_2$ bend 218 cm^{-1}.

SO_2XY The infrared spectrum[248,249] of SO_2BrF, and the infrared[247] and Raman[533] spectra of SO_2ClF have been reported The S–Hal stretching frequencies in SO_2BrF have been assigned[248,505,533]. $\nu(SBr)$ 270 cm^{-1}, $\nu(SF)$ 814 cm^{-1} The Raman shifts for SO_2ClF have been assigned[533] $\nu(SCl)$ 430 cm^{-1}, $\nu(SF)$ 823 cm^{-1}.

Infrared and Raman data are available for many other sulphur halogen compounds (Table 5 21) but the sulphur–halogen absorption regions remain within the following limits·

$$\nu(SF)\ 496\text{–}941\ cm^{-1};\ \nu(SCl)\ 372\text{–}545\ cm^{-1},\ \nu(SBr)\ 280\text{–}531\ cm^{-1}$$

16. Transition metals

For the purposes of this review "transition metals" will be taken to include the elements zinc, cadmium and mercury

The fundamental metal-sulphur stretching frequencies of some binary sulphides

TABLE 5 19

STRETCHING FREQUENCIES AND BOND LENGTHS IN S(II)–HALOGEN COMPOUNDS

Compound	ν_{SI} (cm^{-1})		ν_{SCl} (cm^{-1})		ν_{SB} (cm^{-1})		r_{SCl} (Å)	r_{SC} (Å)	References
	s	as	s	as	s	as			
S$_2$X$_2$	745	807	443^R	537^R	302^R	529^R	1 99	2 24	386, 461, 462, 465,
			438	538		531			477–479, 535–538, 540
SX$_2$			514^R	535^R				2 02	386, 480, 500–502, 542
ArSX			495–514						543, 544
NCSX			520		451				545
NCSX$_3$			542		450				545, 546
Cl$_3$CSX			533^R						547, 548
			532						

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TABLE 5 20

STRETCHING FREQUENCIES AND BOND LENGTHS IN $S(VI)$–HALOGEN COMPOUNDS

Compound	ν_{sf} (cm⁻¹)		ν_{sCl} (cm⁻¹)		ν_{sB} (cm⁻¹)		l_{sf} (Å)	r_{sCl} (Å)	r_{sB} (Å)	References
	s	as	s	as	s	as				
SX₄	889	867					1 58			50, 503
		728								548–550
SOX₂	801	721	490	443	405	378	1 60	2 07	2 27	263, 429, 437, 480, •
										496, 505–507, 510,
										511, 551
NSX	640						1 446			161
(NSX)₄								2 150		187
								2 084		
(NSX)₄							1 602			173
RN=SX₂	764	727								159

TABLE 5 21

STRETCHING FREQUENCIES AND BOND LENGTHS IN $S(IV)$–HALOGEN COMPOUNDS

Compound	ν_{SI} (cm⁻¹)		ν_{sCl} (cm⁻¹)		ν_{sB} (cm⁻¹)	l_{SI} (Å)	r_{sCl} (Å)	References
	s	as	s	as				
SX₆	775ᴿ	615				1 56		71, 72, 552–553
SX₅Y	624ᴿ		404ᴿ			1 597		
	834ᴿ							522
	703ᴿ							
	916ᴿ							
S₂X₁₀	913	690				1 56		30, 357, 514–517, 554
SOX₄	933ᴿ,	797ᴿ, 741ᴿ						523, 550, 555, 556
SO₂X₂	848	885	403	388ᴿ		1 53	1 99	496, 505, 510, 513,
			408					524; 557
SO₂XY	813							247–249, 533
SF₅OF						1 56		357
RSO₂X	780–852		372–390	285				21, 243, 254, 257, 258,
								261, 262, 374, 529–531
ROSO₂X	832–852							262
R₂NSO₂X	794–901							199, 247, 252, 253
S₂O₅X₂	872ᴿ		412ᴿ	427ᴿ				505
S₂O₆X₂	843							529
S₂O₈X₂			412ᴿ	434ᴿ				251
S₂O₅XY			432ᴿ					318
XOSO₂X	852							261
SO₂X⁻	496							257
R₃C–SX₅	850–903							559
(RN=)₂SX₂	833–883							560
(NSOX)ₙ	833							199
NSX₃	775					1 416		161
(NSOX)₃							2 003	181

are given in Table 5.22 As expected the frequency decreases in passing from zinc to cadmium[575] The anomalously high frequency for cinnabar[576] results from the tendency of Hg(II) to become linearly two coordinated The rare zinc blende form of mercuric sulphide would presumably[601] absorb at 200 cm^{-1}. Downs, Ebsworth and Emeléus have assigned the strongly polarised Raman line at 243 cm^{-1} in $(CF_3S)_2Hg$ to ν_{Hg-S} and have reported similar absorptions in related compounds[577] Goggin and Woodward[578] in a tentative assignment of the Raman spectrum of the (MeHg $SMe_2)^{2+}$ ion in aqueous solution, place ν_{Hg-S} at 302 cm^{-1} There is, however, substantial mixing of this and the $-SC_2-$ bending mode

Recent infrared studies[562,574,585] of $M_2^I(MoS_4)$, $M_2^I(WS_4)$, and $M_2^I(CuS_4)$ compounds have shown the asymmetric M–S stretching frequency (ν_3) to lie within the range 440–480 cm^{-1}, one of the deformation modes (ν_4) occurs near 150 cm^{-1}.

TABLE 5 22*

MI TAL–SULPHUR STRETCHING FREQUENCIES BENTRALIZE

Compound	$\nu_{M-S}(cm^{-1})$	References
ZnS	310	575
CdS	220	575
HgS(cinnabar)	349	576
$Hg(SCF_3)_2$	243	577
$Hg(SCF_3)Cl$	251	577
$Hg(SCF_3)Br$	264	577
$NMe_4[Hg(SCF_3)_2Cl]$	223	577
$NMe_4[Hg(SCF_3)_2Br]$	222	577
$NMe_4[Hg(SCF_3)_2I]$	219	577

* From Adams (Ref 601)

Adams[561] has presented a preliminary report of infrared and Raman investigations of metal complexes with various sulphur ligands, including thiourea, dithiolates and dialkyl sulphides Nakamoto et al. have made two important studies using normal coordinate analysis, of the in-plane vibrations of dithiocarbamate[579] and dithiooxalate[580] systems For the latter system the band at 322 cm^{-1} and the doublet at 436,422 cm^{-1} (split by interaction between the rings) can be described as $\nu(Pt-S)$ For the dithiocarbamates a band at 375 cm^{-1} is due largely to $\nu(Pt-S)$, but two further absorptions at 560 and 288 cm^{-1} are complex modes involving both Pt–S bond stretching and ring deformation Watt and McCormick[582] have investigated the spectra of the related xanthate complexes and assigned bands at 360 and 330 cm^{-1} to $\nu(M-S)$, and by analogy with this, Schrauzer and Mayweg[581] have assigned bands near 400 and 350 cm^{-1} in diethietene complexes $M(S_2C_2R_2)_2$ to $\nu(M-S)$.

For $PdCl_2(RS\cdot C_2H_4 SR)$, R = Me, Coates and Parkin[584] assigned a strong band at 338 5 cm^{-1} as $\nu(Pd-S)$, but were unable to find a similar band for the corresponding ethyl complex For R = Ph however, strong bands at 331 and 312 cm^{-1} have been

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TABLE 5 23

METAL–SULPHUR STRETCHING FREQUENCIES IN CHELATE SYSTEMS

Compound	M–S(cm^{-1})			References
	M= Ni	Pd	Pt	
$M(S_2C_2O_2)_2$			436	
			422	580
			322	
$M(S_2CNH_2)_2$			560	579
			288	
			375	579
$M(S_2COMe)_2$	383	347	362	582
	360	335	330	
$M(S_2C_2Ph_2)_2$	408	401	403	581
	352	352	373	

* From Adams (Ref 601)

TABLE 5 24

Compound	M–S bond length (Å)	References
MnS_2	2 59	488
FeS_2	2 26	488
CoS_2	2 315	488
Co_9S_8	octahedral 2 39	566
	tetrahedral 2 21	566
NiS_2	2 396	488
$Ni(CH_3N_3S)_2$	2 155	567
$Ni[P(CH_2CH_2S)_2CH_2CH_2SH]$	2 16 and 2 22	587
$Ni(CH_5N_3S)_2SO_43H_2O$	2 16	588
$Cu_{12}Sb_{14}S_{18}$	2 234, 2 272 and 2 342	568
ZrOS	2 74	569
MoS_2	2 41	602
Mo_2S_3	2 36	564
MoS_4^{2-}	2 17	565
$Mo(C_2H_2S_2)_3$	2 33	570
$Pt(SN)_4$	2 23 and 2 25	571
$Pd[S=C(NH_2)_2]_4Cl_2$	2 33 and 2 35	572
Pd_4S	2 34 and 2 48	563

assigned to $\nu(Pd–S)$ by Pluscec and Westland[583], who have also prepared $MX_2(PhS, C_3H_6\ SPh)$, $(M = Pd, Pt; X = Cl, Br.)$. M–S stretching frequencies in chelate systems are summarised in Table 5.23.

Structural data on several first and second row transition metal sulphides and complexes is available and is given in Table 5.24. The M–S bond length varies from 2 15 Å in $Ni(SN_3CH_3)_2$ to 2.74 Å in ZrOS

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Acknowledgement

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