CYCLIC SULPHUR IMIDES

PROPERTIES AND DERIVATIVES
OF
CYCLIC SULPHUR IMIDES

By

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
(October) 1968

MASTER OF SCIENCE
(Chemistry)

McMaster University
Hamilton, Ontario

TITLE: Properties and Derivatives of Cyclic Sulphur Imides

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SUPERVISOR: Dr. F. P. Olsen

NUMBER OF PAGES: ix, 76

SCOPE AND CONTENTS:

The methylation of three isomeric hexasulphur diimides under basic conditions has been investigated. Both mono- and dimethylated products have been obtained from the 1,5- and 1,4-hexasulphur diimides. The anion formed from the 1,3 isomer was found to undergo decomposition, the major products being polysulphides and N-methyl heptasulphur imide. The usefulness of proton NMR, mass spectra, and infrared spectra in conjunction with these compounds has been considered.

ACKNOWLEDGMENTS

I would like to express my appreciation for the guidance and interest of Dr. F. P. Olsen during the course of this work. Thanks are also due to Mr. Paul Rasmussen for recording the mass spectra, and to Mrs. Beryl Spiers for obtaining the Raman data.

Financial assistance from the National Research Council, the Ontario Department of University Affairs, and the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

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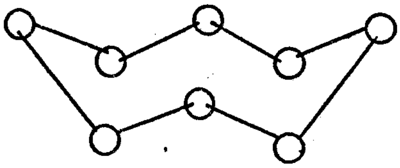
INTRODUCTION

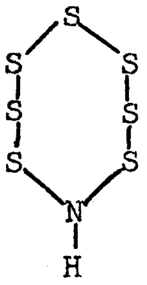
1. THE SULPHUR IMIDES

Within the group of compounds known as sulphur imides, there exists a series whose structures are based on the eight-membered, puckered ring found in α-sulphur (I),



I

with one or more sulphur atoms replaced by N-H groups. The series consists of heptasulphur imide (S_7NH, II), hexasulphur diimide ($S_6(NH)_2$), which has three isomeric structures (III-V), pentasulphur triimide ($S_5(NH)_3$), which has two isomers (VI, VII), and tetrasulphur tetraimide ($S_4(NH)_4$, VIII). The term "sulphur imides" will henceforth be used to refer specifically to this series. Excluded will be imides based on six-membered rings such as tetrasulphur diimide ($S_4(NH)_2$).



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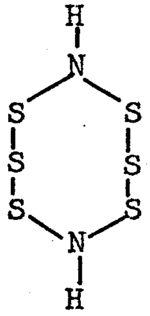

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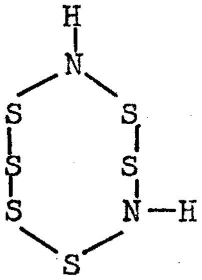

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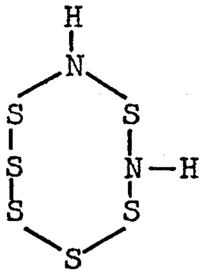

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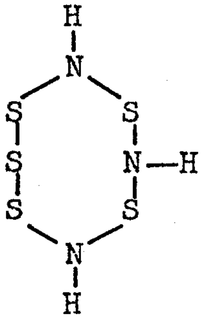

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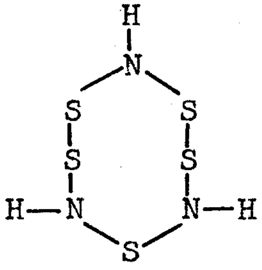

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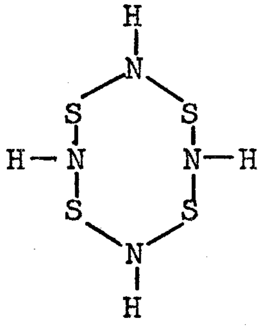
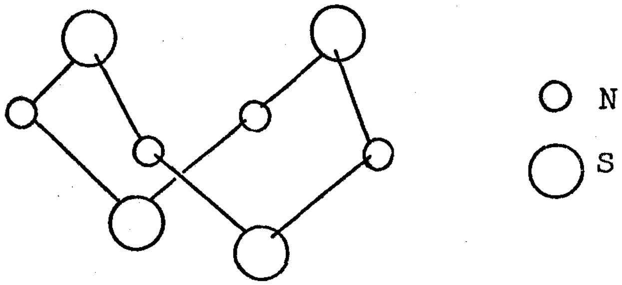


VIII

It can be seen that all possible isomers are represented except those with neighbouring nitrogen atoms; although several attempts to prepare these are implied in the literature, they remain unknown.

In addition, one other compound should be mentioned. Tetrasulphur tetranitride (S_4N_4, IX), if not a member, is at least a relative of this series. It has an eight-membered ring structure, is a product of the reaction which produces the higher sulphur imides; and is the starting material in the preparation of tetrasulphur tetraimide.

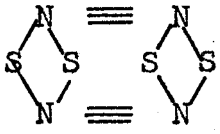


IX

2. DISCOVERY AND CHARACTERIZATION

Sulphur of course has been known from earliest times, due to its natural occurence. A route to the sulphur imides was discovered more or less accidentally, and it has been only in the last ten years that most of the series has been characterized. It is interesting to note that although nearly all members are prepared from the same reaction, individual members were discovered over a period covering more than sixty years. These compounds possess similar structures, and most are produced only in very small yields. Thus it has only been with the recent use of chromatography, rather than recrystallization, as a separative method, that the existence of most of the sulphur imides could be detected.

In 1835, the reaction between sulphur monochloride (S_2Cl_2) and ammonia was found by Gregory (28) to yield a compound of sulphur and nitrogen only; in 1896 the molecular formula was determined to be $(SN)_4$ (1, 45). A large number of formulations were proposed on the basis of chemical evidence, including those of Schenk (45) (X), Ruff and Giesel (43) (XI, XII), and Arnold and co-workers (4) (XIII, XIV).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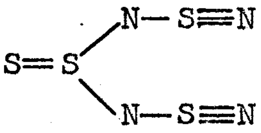
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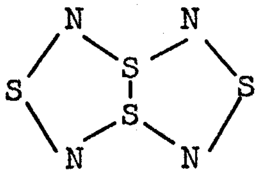
XII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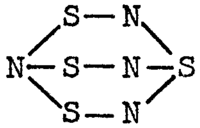

XIV

Lu and Donohue (36) in 1944 determined the structure (IX) using electron diffraction methods; this was further supported by Clark's X-ray study (10) in 1952, although in the next year infrared data (35) were interpreted to favour an earlier electron diffraction study (29) giving a cage structure with N-N bonds. A three-dimensional X-ray analysis (46) finally settled the controversy in favour of structure IX. Salient features are the short S-S distance (2.58 A, nearly 1.1 A less than the sum of the van der Waals radii, but 0.6 A longer than an S-S single bond), and the equal S-N bond distances (1.616 A). These points make the molecule one of theoretical interest, with questions of

S-S and N-N bonding, π-electron delocalization, and sulphur d-orbital involvement being much discussed (49).

Tetrasulphur tetraimide was discovered in 1908 as the reduction product of tetrasulphur tetranitride and alcoholic tin (II) chloride (53). Meuwsen suggested a tetramer on the basis of the molecular weight determination, although his structure contained S-H, rather than N-H, bonds (38). From chemical evidence (2, 16) and finally from the infrared spectrum (34), N-H bonds were accepted. The crystal structure, reported in 1958 (44), gave structure VIII, with a puckered eight-membered ring; packing considerations are also said to support N-H bonds, although the hydrogen atoms were not directly located.

Heptasulphur imide, S_7NH, was first formulated as S_6NH_2 by Macbeth and Graham (37) and as $S_{18}N_3H_5$ by Arnold, Hugill, and Hutson (4). It was finally correctly elucidated by Arnold and Perry (3,5) and by Becke-Goehring (17); the ring form was accepted on the basis of chemical behaviour and similarity to tetrasulphur tetraimide until in 1960 it was determined crystallographically (52). Like tetrasulphur tetranitride, this compound is prepared from sulphur monochloride and ammonia; a procedure at 0°, using dimethylformamide as solvent, makes this the major product (aside from sulphur). The mechanism proposed by Becke-Goehring <u>et al</u> (20) for this reaction has the S_2Cl_2 dissociating in the polar solvent, to give the cation S_2Cl+, which acts toward NH_3 as a Lewis base:

$$\mathrm{Cl{-}S{-}S{-}Cl} \rightleftharpoons \mathrm{Cl{-}S{-}S^+} + \mathrm{Cl^-} + \mathrm{NH_3} \longrightarrow (\mathrm{Cl{-}S{-}S{-}NH_3^+})\mathrm{Cl^-}$$

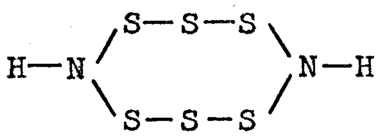
The adduct is said to react further via a stepwise path:

$$\mathrm{Cl^-({}^+H_3N{-}S\big[S{-}Cl)} + \mathrm{Cl\big]S{-}S{-}Cl} \longrightarrow \mathrm{Cl^-({}^+H_3N{-}S{-}S{-}S{-}Cl)} + \mathrm{SCl_2}$$

$$\longrightarrow \mathrm{Cl^-({}^+H_3N{-}S_7{-}Cl)} \rightleftharpoons \mathrm{HCl} + \mathrm{H_2NS_7Cl} \longrightarrow \mathrm{S_7NH} + \mathrm{HCl}$$

While some sort of chain-lengthening reaction must take place, this mechanism does not seem reasonable for two reasons. First, formation of SCl_2 from S_3Cl_2 or S_2Cl_2 is too slow to account for the rate of the reaction, and second, S_2Cl_2 is present in small concentration compared to the more reactive ammonia. Recent workers (12) have shown that the yield of heptasulphur imide is not significantly improved by using heptasulphur dichloride (S_7Cl_2) as the starting chlorosulphane. They suggest that heptasulphur imide is formed and subsequently decomposed under the alkaline conditions used. This might account for the hexa- and pentasulphur imides formed; evidence however is lacking.

The hexasulphur diimides, which are produced in the above reaction, had escaped detection due to the small yield and the similarity of their crystal form to heptasulphur imide. Weiss in 1959 separated by column chromatography a compound which analyzed as $S_6(NH)_2$ and had a melting point of 140° (51); the following year he published an X-ray study showing that this was the symmetrical isomer (III) (52):



III

In 1963, two groups independently reported the isolation of three compounds of formula $S_6(NH)_2$ (31, 48). Both groups assigned the structures on the basis of the infrared spectra, one group using the splitting of the N-H band, the other the splitting of the S-N band. Their assignments disagree with respect to the 1,5 and 1,4 isomers. Although an X-ray study had been done on the 1,5 isomer, the only physical property given was the melting point, and this did not correspond to any of those now reported (nor did these two new sets of melting points correspond well to each other, presumably due to the difficulty of separating the isomers completely). In 1965, a preliminary report on an X-ray determination settled the assignment of the 1,5 and 1,4 isomers, and the 1,3 was assigned by elimination (50). It is interesting that the only isomer isolated by Weiss was said by later workers to be formed in smallest yield (0.1% based on sulphur monochloride) and to be one of the pair of isomers most difficult to separate. The only reliable method of correlating the structures and the compounds appears to be through the order of R_f value using carbon disulphide/silica gel thin layer chromatography. The order of increasing R_f value corresponds to that of decreasing dipole moment, as determined by Heal (Table 1).

Table 1

Dipole Moments and R_f Values of the Hexasulphur Diimides

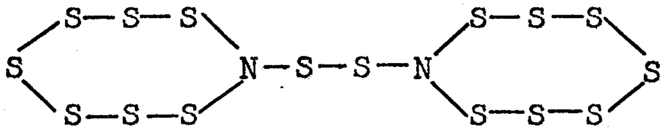
Isomer	R_f	Dipole Moment
1,4	0.34	1.23
1,5	0.24	1.74
1,3	0.22	2.28

Finally, the pentasulphur triimides were reported to be among the reaction products of sulphur monochloride and ammonia (32); yields were 0.3% for the presumed 1,4,6 isomer, and less than 0.1% for the 1,3,5 isomer. Structural assignments were on the basis of dipole moments, the 1,3,5 isomer (VI) being expected to possess the higher dipole moment. This latter isomer was also reported as a product of the reaction between tetrasulphur tetranitride and hydrazine adsorbed on silica gel (13).

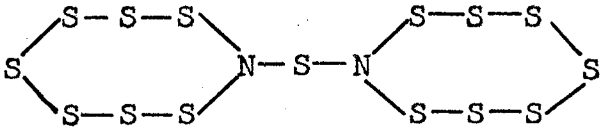
3. DERIVATIVES OF THE SULPHUR IMIDES

Most of the chemistry which has been done on the sulphur imides concerns heptasulphur imide and tetrasulphur tetraimide, since these are the most readily available. A number of derivatives have been prepared in which the cyclic S-N skeleton is unbroken; these include inorganic adducts and salts, as well as organic derivatives.

Reactions of heptasulphur imide with the boron trihalides have resulted in the adducts S_7NBCl_2 and (probably) S_7NBBr_2; with BI_3 the ring is destroyed and with BF_3 there is no reaction (30). A sulfonic acid derivative, S_7NSO_3H, has been prepared from sulphur trioxide (18). Reactions of heptasulphur imide with sulphur mono- and dichloride lead to compounds of composition $S_{16}N_2$ (XV) and $S_{15}N_2$ (XVI) by loss of two moles of hydrogen chloride (21).



XV



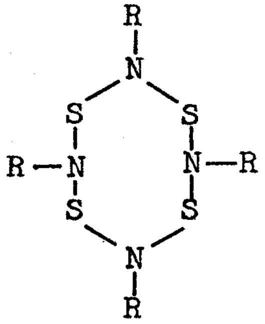
XVI

Organic derivatives of the sulphur imides have been prepared in two ways:

(1) reaction of primary amines with chlorosulphanes

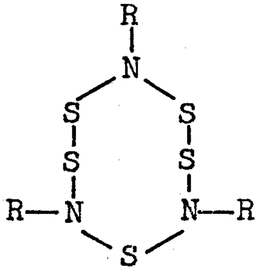
(2) direct substitution of an organic group for the acidic proton.

The first method has been used successfully to prepare alkyl derivatives only; it has the disadvantage of producing mixtures and polymeric products. Derivatives produced from the reaction of sulphur dichloride, SCl_2, and alkylamines are the methyl (47), ethyl (42), benzyl, and β-ethylbenzyl (23) of XVIII, the methyl (47), benzyl, and β-ethylbenzyl (42) of XIX, and the methyl (47) of XX.



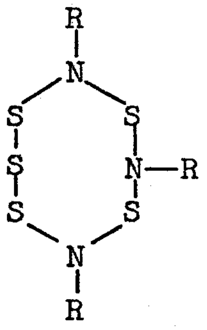
$R = CH_3$, CH_2CH_3,
$CH_2C_6H_5$,
$CH_2CH_2C_6H_5$.

XVIII



$R = CH_3$, $CH_2C_6H_5$,
$CH_2CH_2C_6H_5$.

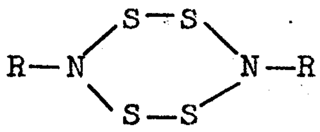
XIX



$R = CH_3$.

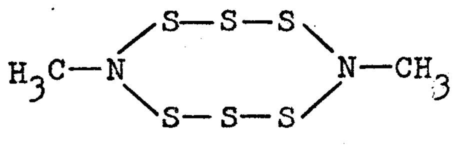
XX

Reports of the reaction between sulphur monochloride and primary amines (19) indicate that six-membered rings are formed under conditions of high dilution (XXI).



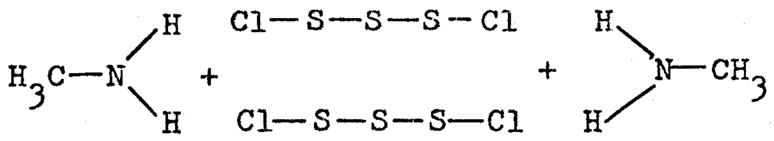
XXI

Brasted and Pond (8) reacted trisulphur dichloride, S_3Cl_2, with monomethylamine, and obtained a cyclic compound which they assigned the structure (XXII):

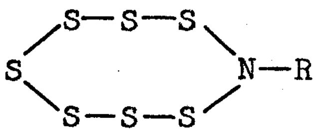


XXII

on the basis of a cyclization in which the S_3Cl_2 chains are unbroken:



The second method, direct substitution, has been mostly confined to acyl and hydroxy methyl derivatives of heptasulphur imide. Compounds of the form (XXIII):



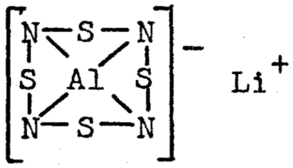
XXIII

where R = $\underset{\underset{O}{\|}}{C}\text{-}CH_3$, $\underset{\underset{O}{\|}}{C}\text{-}C_6H_5$, and CH_2OH (22) were reported soon after the structure of heptasulphur imide was determined; the first two were prepared from the organic acid chloride, the third from formaldehyde, with sodium hydroxide or pyridine as acid scavenger. Further derivatives, prepared from the carboxylic acids, with R = $\underset{\underset{O}{\|}}{C}\text{-}CH_3$, $\underset{\underset{O}{\|}}{C}\text{-}CH_2Cl$, $\underset{\underset{O}{\|}}{C}\text{-}C_6H_5$, $\underset{\underset{O}{\|}}{C}\text{-}CH_2C_6H_5$, $\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7CH_3$, $\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_{16}CH_3$, $\underset{\underset{O}{\|}}{C}\text{-}CH{=}CH\text{-}C_6H_5$, $\underset{\underset{O}{\|}}{C}\text{-}C_6H_4\text{-}\underline{o}\text{-}Cl$, and $\underset{\underset{O}{\|}}{C}\text{-}C_6H_4\text{-}\underline{p}\text{-}NO_2$, were reported in 1963 (11).

A formaldehyde derivative of tetrasulphur tetraimide, $S_4N_4(CH_2OH)_4$, has been prepared by Meuwsen (38); from it, Arnold has made the tetra-acetate and the tetra-p-nitrobenzoate. He also prepared the phenylcarbamyl derivative, $S_4N_4(CONHC_6H_5)_4$, by the addition of phenyl isocyanate to the tetraimide (2).

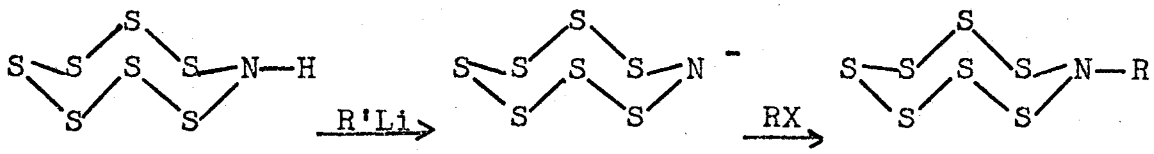
The only application to other imides is the acylation of the hexasulphur diimides. From the reaction with acetyl or benzoyl chloride and pyridine in chloroform, all three diacetyl derivatives, and the 1,5 and 1,4 dibenzoyl derivatives, have been reported (33).

It has generally been held that heptasulphur imide will decompose in the presence of base, and in all of the above reactions, neutral or acidic conditions have been maintained. There are, however, reports of a number of salts containing anions of sulphur imides. Sodium salts, of formula $Na(NS_7)$ and $Na_4(NS)_4$, are reported to be very unstable and reactive (24). Two mercury salts of heptasulphur imide are reported. The compound $S_7N\text{-}Hg\text{-}Hg\text{-}NS_7$ is said to be prepared from reaction with mercury (I) nitrate (26), while $S_7N\text{-}Hg\text{-}NS_7$ is prepared from mercury (II) acetate (40). With tetrasulphur tetraimide, mercuric acetate in pyridine gives a compound analyzing as $Hg_5(NS)_8$, possibly composed of $3Hg_2(NS)_4$ and $Hg_4(NS)_4$ (39). A complex aluminum salt, $Li(Al(NS)_4)$ has also been reported (25); structure XXIV has been suggested since careful hydrolysis appears to regenerate the tetraimide.



XXIV

Recent work (41) has shown that anions of heptasulphur imide can be prepared by proton abstraction in a basic medium, and that once formed they are sufficiently stable to be reacted with alkyl halides:



This reaction was shown to constitute a general method of preparing primary and secondary alkyl derivatives of heptasulphur imide. Examples included reactions with methyl, ethyl, allyl, benzyl and isopropyl halides.

4. INFRARED STUDIES

Reported infrared data on the sulphur imides consists of the positions of the N-H and S-N stretches, which vary only slightly from one compound to another. Several recent papers have investigated the relationship between the S-N stretch in various compounds and their structural features. Banister, Moore, and Padley (6), considering a wide variety of sulphur-nitrogen compounds for which both ν (SN) and S-N bond length are known, have derived the relationship:

$$r_{SN} = 0.0483(\mu_{SN}) + 1.099$$

(where μ_{SN} is the wavelength in microns and r_{SN} is the bond length in Angstroms). This implies an essentially pure S-N stretching vibration. The authors suggest that their equation allows predictions of unmeasured bond lengths; for 1,5-$S_6(NCH_3)_2$, for example, they predict a bond distance of 1.72 A.

In a paper dealing only with the cyclic sulphur imides, Garcia-Fernandez (15) has shown linear relationships between the following quantities:

(1) S-N bond order and oxidation state of S
(2) S-N distance and ν(SN)
(3) S-N distance and oxidation state of S
(4) S-N bond order and ν (S-N)
(5) S-N distance and S-N-S angle
(6) number of N atoms and S-N bond order.

However in most cases the uncertainty in individual measurements is so great with respect to the overall range that the significance of the relationships seems questionable.

An earlier paper (35) giving a normal coordinate analysis for the infrared spectrum of tetrasulphur tetranitride is the only work of a more specific nature which has been done. However, this work was carried out before the X-ray study had been completed, and the infrared and Raman data given were interpreted in favour of a structure which was later shown to be incorrect.

5. AIMS OF PRESENT WORK

(a) Synthesis of Derivatives of the Hexasulphur Diimides.

The recent work showing that the S-N skeleton of heptasulphur imide was sufficiently stable under basic conditions to undergo proton abstraction and alkylation made an extension of this method to the hexasulphur diimides seem feasible. It is possible that the method might provide a route to both di- and monoalkylated derivatives. The latter in particular have not previously been prepared, while reliable methods of preparing the former are not available. Besides providing a route to these compounds, such studies would provide more information concerning the stability of sulphur-nitrogen compounds in general.

By preparing dialkyl derivatives directly from the imides, the isomeric structures would be known, based on the configuration of the starting imide. Therefore it would be possible to check if the structure of the only dialkyl derivative known, $S_6(NCH_3)_2$, does have the 1,5 arrangement, as proposed.

(b) Identification of the Sulphur Imide Structures.

Evidence for the structures of the sulphur imides and their derivatives has so far been based either on X-ray crystallography or dipole moments, neither of which is suitable for quick routine identification. In several cases, non-rigorous methods have been used to assign structures. Thus when two compounds of formula $S_5(NCH_3)_3$ were obtained from the reaction of sulphur dichloride and methylamine, their structures were tentatively assigned by comparing the yields to the probability of sulphur chlorides with two- and three-sulphur chains being present; i.e., the 1,4,6 isomer would be more probable than the 1,3,5 isomer.

Obviously a more reliable method of making such assignments is required; a method of characterizing derivatives based on a relatively invariant property of the S-N skeleton would be useful.

In this work, NMR, mass spectra, and infrared spectra are examined as methods for characterizing the various isomers. The proton resonance spectra of the imides themselves are sufficiently broad due to quadrupole relaxation on nitrogen to obscure small differences in position; however it is possible that the chemical shifts of organic derivatives might be significantly different. Mass spectra is also a plausible means of differentiating between isomers, since there is a possibility of differing fragmentation patterns. Infrared spectra in the conventional region from 4000 to 600 cm^{-1} show only N-H and S-N stretches, and are very similar for the different sulphur imides. Hence a study of the far infrared spectra of these compounds was undertaken in an attempt to find spectral features which could be used as a method of identification.

It is the purpose of this work to apply and evaluate these various methods as potential sources of structural information in conjunction with the synthesis of alkyl derivatives of the hexasulphur diimides under basic conditions.

RESULTS

1. PREPARATION OF ORGANIC DERIVATIVES OF THE HEXASULPHUR DIIMIDES

(a) Methylation of 1,4-Hexasulphur Diimide

Preliminary work was done on 1,4-hexasulphur diimide, since it is formed in highest yield, and is the most easily purified, of the three isomers. Attempted methylation was carried out under three sets of conditions. First, a 1:1 molar ratio of ethyl lithium to hexasulphur diimide was used to generate the mono-anion; next, a 2:1 molar ratio of ethyl lithium was used to generate the di-anion; and third, a 2:1 molar ratio of the weaker base, lithium hydroxide, was used.

(i) Reaction with a 1:1 Molar Ratio of Ethyl Lithium

The 1,4 isomer of hexasulphur diimide was reacted with ethyl lithium, followed by methyl iodide, in anhydrous tetrahydrofuran at 0^{o}. Colour changes indicated the formation and subsequent reaction of a highly coloured intermediate, presumably an imide anion. Thin layer chromatography of the reaction mixture demonstrated the presence of four products plus a small amount of sulphur. A chromatographic separation resulted in pure samples of each of these components which were subsequently identified by their infrared, NMR, and mass spectra.

The first compound, after sulphur, to be eluted was a colourless oil which hardened to a white solid melting at 24.5-25.5°. The infrared spectrum (Table 9) showed bands characteristic of S-N (798 cm^{-1}), C-N (1094, 1058, 1019 cm^{-1}) and C-H (2965, 2920, 2850 cm^{-1}) bonds, but no bands which could be attributed to an N-H group. The proton NMR spectrum showed a single sharp peak at -3.04 ppm (relative to TMS at 0 ppm). An osmometric determination in benzene gave a molecular weight of 250 ± 2%. A mass spectrum gave the molecular weight as 250, agreeing with that expected for $S_6(NCH_3)_2$. Comparison with the osmometric molecular weight showed this to be the molecular ion peak. Consideration of the isotopic abundances of sulphur and nitrogen showed that this molecular ion group was consistent for six sulphur and two nitrogen atoms (Table 2).

Table 2

Relative Heights of Molecular Ion Peaks in $S_6(NCH_3)_2$

Mass	Relative Heights	
	Observed	Calculated
250	100	100
251	7	8
252	27	26
253	2	1
254	4	3

After the parent peak, that of highest mass number (157) corresponded to the grouping CH_3NS_4; measurable peaks also appeared for CH_3NS_3 (125), CH_3NS_2 (93), CH_3NS (61), and NS (46), as well as S_3 (96) and S_2 (64). The relative heights of the peaks appearing in the spectrum are shown in Figure 1.

From the above information, it was concluded that the compound was N,N'-dimethyl hexasulphur diimide, $S_6(NCH_3)_2$. After purification, the yield was 11%, based on the amount of hexasulphur diimide used. The R_f value on carbon disulphide/silica gel was 0.71 (relative to sulphur at 0.82).

The next compound eluted was a yellow oil with the vile smell typical of sulphane derivatives. On the TLC plate it formed a long streaky spot centred at 0.60. The infrared spectrum showed mainly carbon-hydrogen peaks, and the proton NMR spectrum indicated both methyl and ethyl groups. The chemical shifts (-2.58, -2,60, -2.64 ppm) for methyl, for example, were consistent with, though not conclusive proof of, the organic group residing on sulphur (27). Therefore this probably contained mixed polysulphanes formed by addition of ethyl lithium to sulphur-sulphur and/or sulphur-nitrogen bonds. Since this material did not contain the cyclic imide ring structure it was of little interest and was not further investigated.

A yellow solid, melting at 51.5-53°, was next obtained. This had an R_f value of 0.53. Its infrared spectrum (Table 9, carbon disulphide solution) showed N-H (3330 cm^{-1}), C-H (2990-2850 cm^{-1}) and C-N (1122, 1062 cm^{-1})

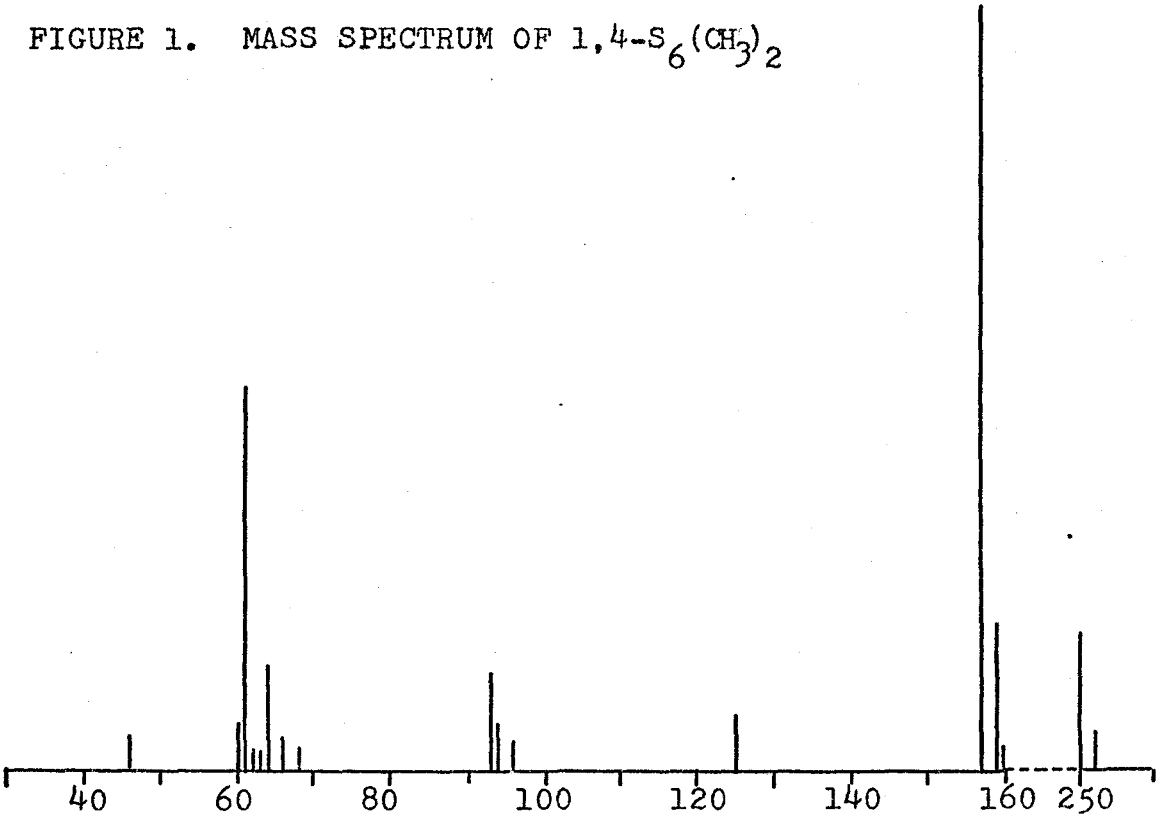
stretches, as well as two peaks which could be attributed to S-N groups (802, 745 cm^{-1}). The proton NMR spectrum showed a sharp peak at -3.10 ppm, and a broad peak centred at-3.76 ppm. Integration was poor due to the width of the lower peak but the ratio of the two was close to 3:1. It was therefore assumed that this was the monomethylated derivative, $S_6(NH)(NCH_3)$. This was confirmed by the mass spectrum, which gave a molecular weight of 236 (Figure 2). Again the parent ion grouping was consistent with the isotopic pattern expected for S_6N_2. In addition to all of the peaks mentioned above for N,N'-dimethyl hexasulphur diimide, peaks for S_4NH (143), S_3NH (111), S_2N (78), and SNH (47) were also present. A strong peak at 94 is difficult to explain except as the ion $S_5N_2^{++}$, or a rearranged species $S_2(CH_3)_2^{+}$. Yield of pure N-methyl hexasulphur diimide was 23% based on the starting imide used.

Finally, a quantity of light yellow solid, melting at 128-129°, was eluted. Its R_f value, 0.37, was identical to that of the starting material, 1,4-hexasulphur diimide, 27% being recovered.

(ii) Reaction with a 2:1 Molar Ratio of Ethyl Lithium

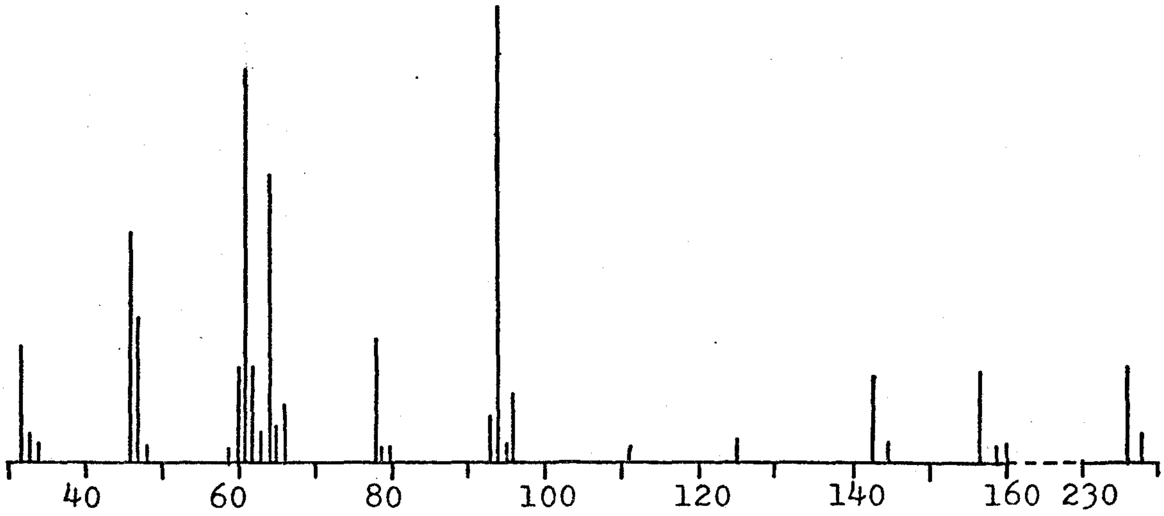
The reaction of 1,4-hexasulphur diimide was carried out as above, but using 2 moles of base per mole of imide. Again the presence of a highly coloured intermediate was noted. A thin layer chromatograph of the crude reaction

FIGURE 1. MASS SPECTRUM OF 1,4-$S_6(CH_3)_2$



(Note: In Figures 1-5, peaks less than 5% of the peak for mass number 61 are omitted)

FIGURE 2. MASS SPECTRUM OF 1,4-$S_6(NH)(NCH_3)$



mixture showed the same set of products as in the preceeding reaction. After a chromatographic separation, the yields of the relevant products were: N,N'-dimethyl hexasulphur diimide, 50%; N-methyl hexasulphur diimide, 6%; unreacted hexasulphur diimide, 6%. No significant change in the amount of dialkyl polysulphides was noted.

(iii) Reaction with a 2:1 Molar Ratio of Lithium Hydroxide

The reaction of 1,4-hexasulphur diimide with the weaker base, lithium hydroxide, was carried out using two moles of base per mole of imide. Generation of the coloured intermediate was considerably slower. The same series of products resulted; yields were: N,N'-dimethyl hexasulphur diimide, 38%; N-methyl hexasulphur diimide, 17%; unreacted hexasulphur diimide, 16%. Only trace amounts of sulphur and alkyl polysulphides were formed.

(b) Methylation of 1,5-Hexasulphur Diimide

When the 1,5 isomer of hexasulphur diimide was reacted with a 1:1 molar ratio of ethyl lithium, a similar coloured intermediate was formed and an analogous series of compounds resulted. A new N,N'-dimethyl hexasulphur diimide was obtained as a white solid, melting at 81.5-82°; the yield was 15%. The proton NMR spectrum showed a single peak at -3.15 ppm; the infrared spectrum (Table 7, carbon disulphide solution) again had C-H (2990-2783 cm^{-1}), N-C (1123, 1064, 1035 cm^{-1}) and S-N (775 cm^{-1}) bands, but none for N-H. The molecular weight, from the mass spectrum, was 250. Relative peak heights are found in Figure 3.

Open chain material was again formed, in comparable yield.

A new N-methyl hexasulphur diimide was formed in 27% yield. It was a yellow solid which when crystallized slowly formed long white needles melting at 100.5-102°. The proton NMR spectrum showed a broad peak at -4.02 ppm, assigned to N-H absorption, and a sharp peak at -3.12 ppm, assigned to N-CH_3; the areas were in the ratio 1:3. The infrared spectrum (Table 7, carbon disulphide solution) also fitted this structure, with N-H (3327 cm^{-1}), C-H (2990-2780 cm^{-1}), C-N (1123, 1062 cm^{-1}), and S-N (809, 766 cm^{-1}) peaks. The mass spectrum (Figure 4) gave a molecular weight of 236 and was similar to that of the previous N-methyl hexasulphur diimide. The peak at 94, attributed to $S_5N_2^{++}$ or $S_2(CH_3)_2^{+}$, was again present.

Of the original 1,5-hexasulphur diimide, 31% was recovered unchanged and identified from its infrared spectrum and melting point (146-146.5°).

R_f values for the above compounds on carbon disulphide/silica gel, relative to sulphur at 0.80, were: N,N'-dimethyl hexasulphur diimide, 0.68; N-methyl hexasulphur diimide, 0.57; 1,5-hexasulphur diimide, 0.23.

(c) Preparation of N,N'-Dimethyl Hexasulphur Diimide from Trisulphur Dichloride and Methylamine

The one alkyl derivative of hexasulphur diimide which

FIGURE 3. MASS SPECTRUM OF 1,5-$S_6(NCH_3)_2$

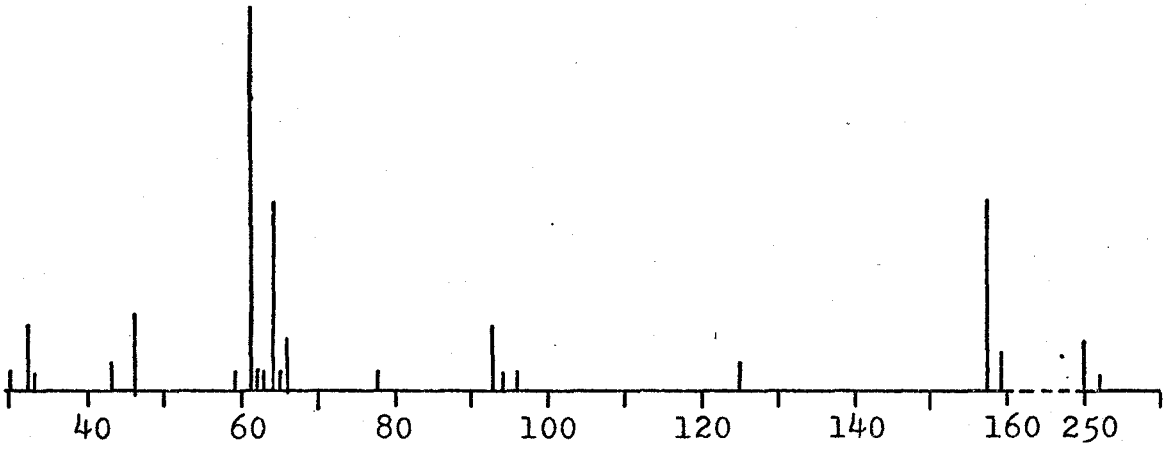
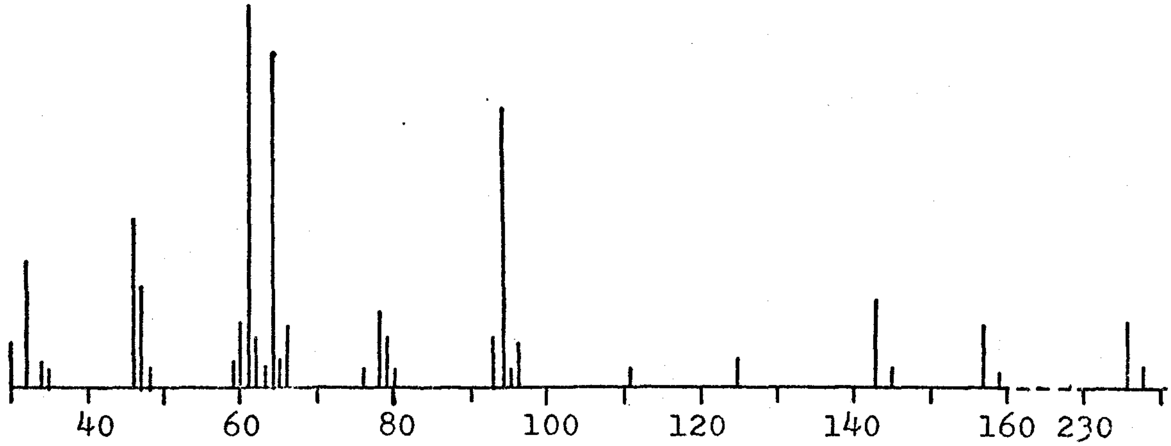


FIGURE 4. MASS SPECTRUM OF 1,5-$S_6(NH)(NCH_3)$



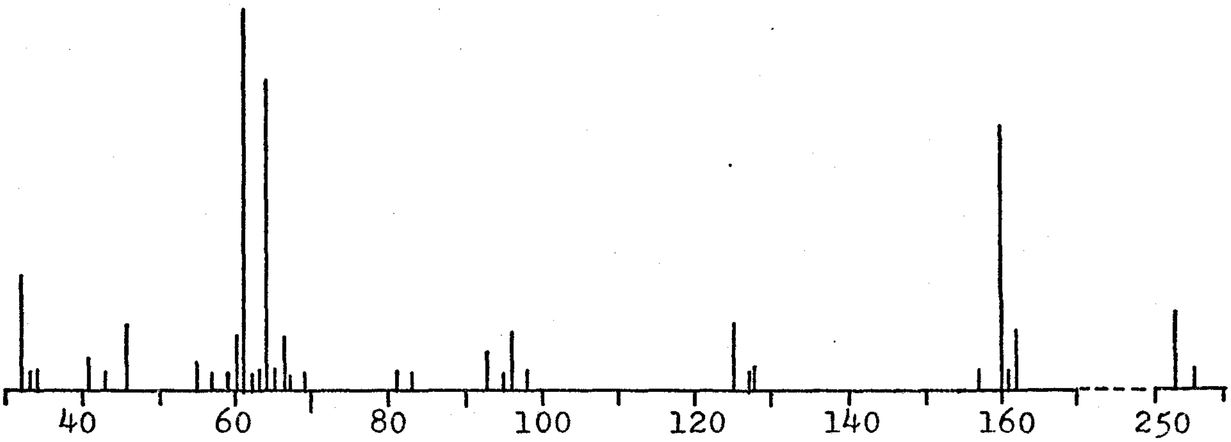
was previously reported (8) was a dimethyl compound, $S_6(NCH_3)_2$, prepared from trisulphur dichloride and methylamine and presumed to be the 1,5 isomer. The reported infrared spectrum was in reasonable agreement with that of the N,N'-dimethyl compound formed from the 1,5 isomer of hexasulphur diimide, as was the NMR spectrum, which consisted of a single line at -3.12 ppm (cf. -3.15). The reported melting point of 72-77° (the range being accounted for by the authors by the presence of decomposition products) was however somewhat lower (81.5-82°).

A sample of Brasted and Pond's dimethyl compound was consequently prepared from trisulphur dichloride and methylamine for comparison. It was found to be a white solid, melting between 80.5 and 81.5°, with a single sharp NMR peak at -3.15 ppm. The infrared spectrum was identical with that of N,N'-dimethyl hexasulphur diimide formed by alkylation of 1,5-hexasulphur diimide.

(d) Methylation of 1,3-Hexasulphur Diimide

The 1,3 isomer of hexasulphur diimide was treated with a 1:1 mole ratio of ethyl lithium followed by methyl iodide. Again the intense intermediate colour was noted. However, a thin layer chromatograph of the crude reaction products showed only two major components. These were purified as before by chromatography. After sulphur, the first product to be eluted was a yellow oil. The infrared and NMR spectra were identical with those of N-methyl heptasulphur imide; the NMR spectrum showed a single peak at -3.16 ppm. The R_f value was 0.75 (relative to sulphur at 0.82), and was the same as a sample of N-methyl heptasulphur imide spotted on the same plate. In addition, the mass spectrum (Figure 5) showed the molecular weight to be 253, correct for S_7NCH_3. Peaks for S_x (x = 1-6), SN, and S_xNCH_3 (x = 1-5) all appeared in the spectrum.

FIGURE 5. MASS SPECTRUM OF S_7NCH_3



(Note: Peaks also occurred at 189 (5%) and 192 (5%) and were assigned to S_5NCH_3 and S_6, respectively)

The major product was identified as alkyl polysulphides. The amount of unreacted hexasulphur diimide was negligible, and no products were obtained which could be identified as di- or mono-methylated derivatives.

2. INFRARED AND RAMAN SPECTRA

Both infrared and Raman data for the compounds heptasulphur imide, tetrasulphur tetraimide, and tetrasulphur tetranitride, were obtained. Infrared spectra only were recorded of the three isomers of hexasulphur diimide, as well as of the mono- and dimethyl derivatives of 1,5- and 1,4-hexasulphur diimide, and of N-methyl heptasulphur imide. This data is compiled in Tables 3 to 14 and Figures 6 to 11.

Table 3

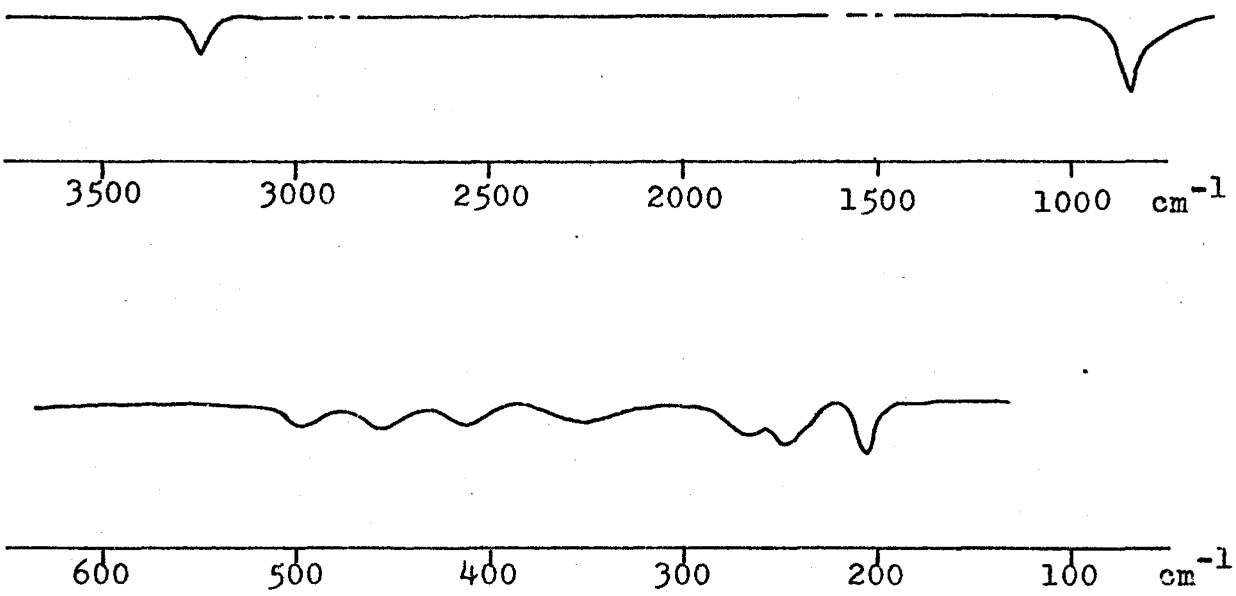
Infrared Spectra of Heptasulphur Imide (4000-69 cm^{-1})

Solid	Solution		
Nujol	CS_2	Benzene	THF
			3470 (w, br)
3255 (s)	3328 (s)	3295 (s)	3100 (vs, br)
	2455 (w)		
	1283 (w)		
812 (s)	802 (s)	803 (s)	805 (s)
497 (m)	493 (m)	509 (m)	
456 (m)	447 (m)	465 (m)	476 (m) 458 (sh)
426 (m)	. . .		
352 (m)	358 (w)	?	362 (m)
272 (m)	270 (m)	274 (br)	. . .
255 (m)	249 (w)	250 (br)	251 (w)
210 (m)	210 (sh)	206 (m)	212 (sh)
	204 (m)		206 (m)

(Note: In Tables 3-14, the following abbreviations have been used: s, strong; m, medium; w, weak; v, very, br, broad; . . ., region obscured by solvent band or not recorded.)

FIGURE 6. INFRARED SPECTRA OF HEPTASULPHUR IMIDE

A. Nujol



B. Solution

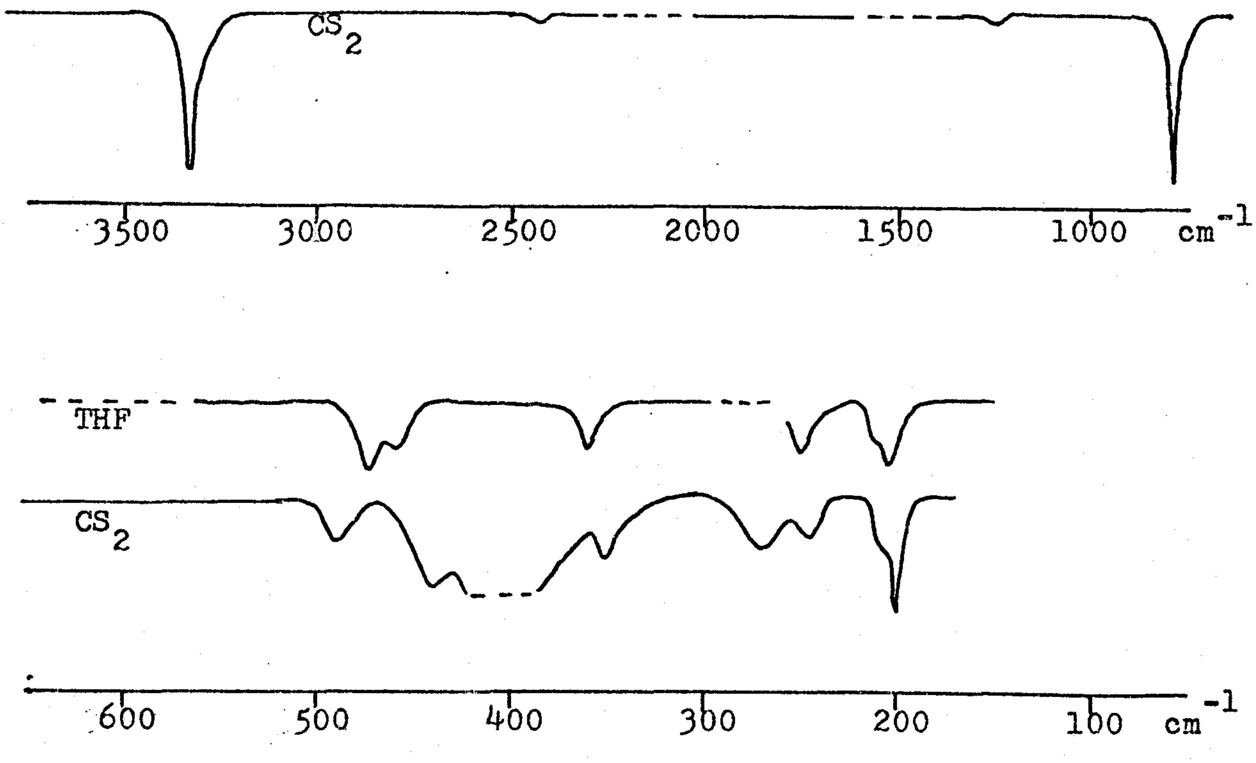


Table 4

Raman Spectra of Heptasulphur Imide

Solid	**Solution**	
	CS_2	Polarization in CS_2
3262 (w)		
1298 (vw)		
1278 (vw)		
888 (w)		
858 (w)		
723 (w)		
703 (w)		
499 (m)	494 (m)	0.71
480 (s)	480 (m)	0.14
461 (s)	459 (w)	0
441 (m)	441 (w)	0
288 (s)	280 (m)	0
266 (m)	253 (w)	0
251 (m)	249 (w)	0
220 (s)	212 (s) 163 (s)	
95 (s)		
80 (s)		
60 (s)		

Table 5

Infrared Spectra of N-Methyl Heptasulphur Imide

(4000-170 cm^{-1})

Thin Film	THF Solution
2980 (w)	•
2950 (w)	•
2910 (w)	•
2875 (w)	•
2838 (w)	•
2775 (w)	•
1449 (m)	•
1427 (w)	•
1396 (w)	•
1118 (w)	•
1062 (s)	•
759 (s)	•
579 (w)	583 (w)
471 (m)	476 (m)
449 (sh)	456 (sh)
365 (s)	366 (s)
284 (s)	282 (m)
251 (s)	253 (m)
210 (m)	211 (m)
190 (m)	188 (m)

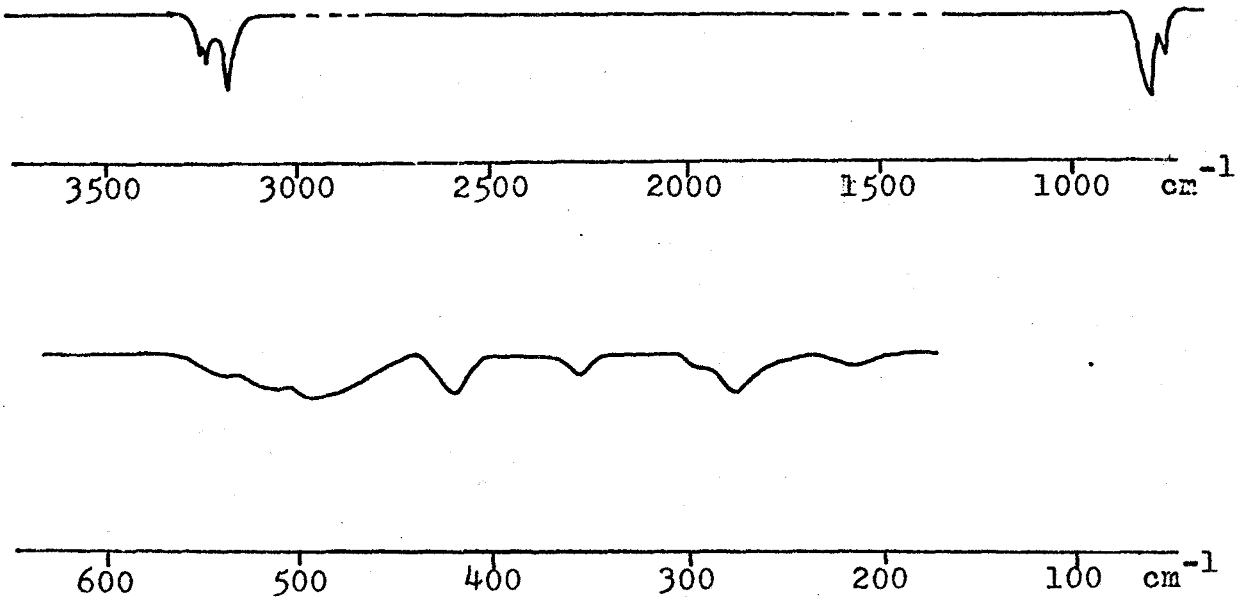
Table 6

Infrared Spectra of 1,5-Hexasulphur Diimide (4000-69 cm^{-1})

Solid	Solution		
Nujol	CS_2	Benzene	THF
			3565 (m,br)
			3500 (m,br)
3280 (sh)	3325 (s)	3305 (s)	
3267 (s)			
3228 (s)			3130 (vs,br)
812 (s)	812 (s)	814 (s)	811 (s)
720 (m)	775 (s)		
539 (sh)			
520 (sh)			
495 (m)		500 (m)	
	467 (m)	467 (sh)	476 (w)
			460 (m)
423 (m)	428 (m)	432 (m)	441 (m)
	. . .	401 (w)	389 (w)
360 (w)	. . .	360 (w)	362 (m)
294 (sh)			. . .
281 (m)	277 (w)	279 (m)	
		263 (w)	264 (w)
220 (w)		227 (w)?	
	212 (w)	214 (m)	215 (m)

FIGURE 7. INFRARED SPECTRA OF 1,5-HEXASULPHUR DIIMIDE

A. Nujol



B. Solution

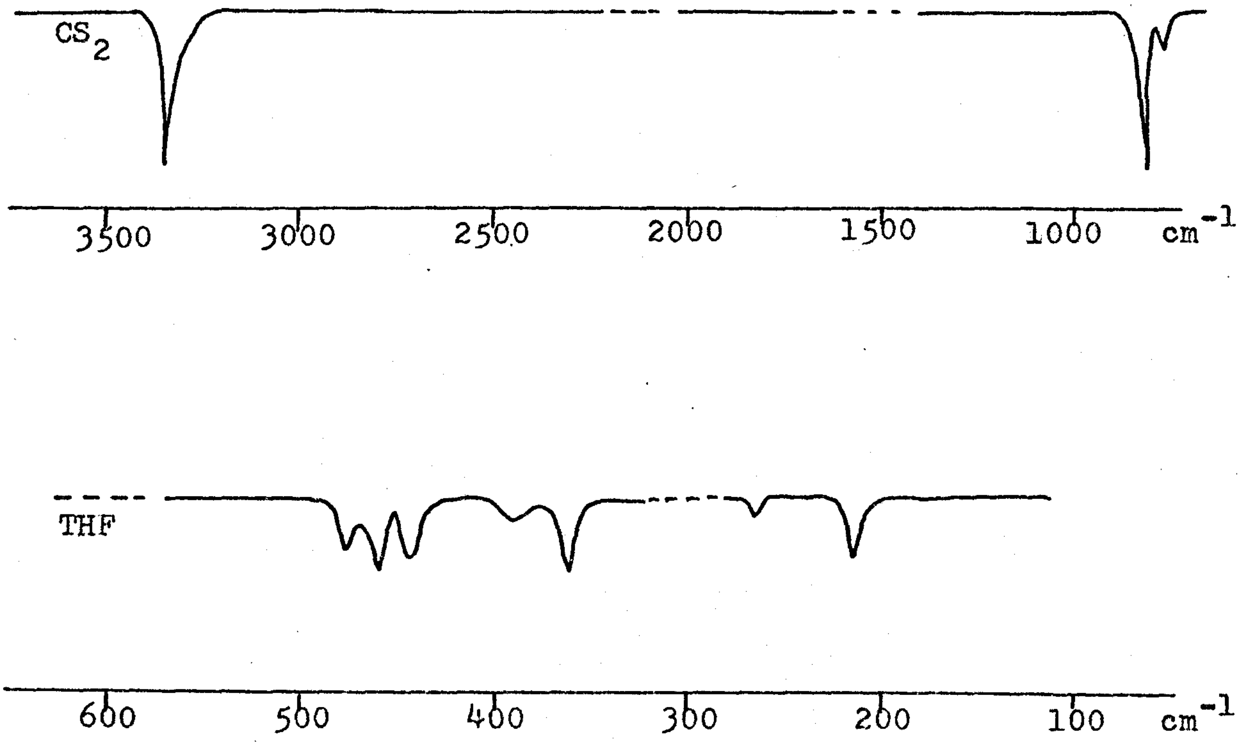


Table 7

Infrared Spectra of Alkylated 1,5-Hexasulphur Diimide

(4000-170 cm^{-1})

$1,5-S_6(NH)(NCH_3)$			$1,5-S_6(NCH_3)_2$		
Nujol	CS_2	Benzene	Nujol	CS_2	Benzene
3278 (s)	3327 (s)	3305 (s)			
.	2990 (w)		.	2990 (w)	
.	2960 (w)	2965 (w)	.	2960 (m)	2962 (m)
.	2920 (m)	2925 (m)	.	2920 (m)	2925 (m)
.	2883 (w)	2890 (w)	.	2883 (w)	2885 (w)
.	2852 (w)	2855 (w)	.	2850 (w)	2855 (w)
.	2780 (w)	2790 (w)?	.	2783 (w)	2785 (w)
		2585 (w)			
.		1518 (m)	.		
.		1455 (w)	.		1455 (m)
.	1430 (m)	1435 (m)	.	1430 (m)	1432 (s)
.	1416 (w)		.	1410 (w)	
.	1400 (w)		.	1402 (w)	
			1260 (w)	1259 (m)	1260 (m)
1118 (w)	1123 (w)	1124 (m)	1122 (m)	1123 (m)	1122 (m)
1061 (s)	1062 (s)	1062 (s)	1065 (s) 1052 (s)	1064 (m) 1035 (w)	1062 (s)
820 (s)	809 (s)	810 (s)			
764 (s)	766 (s)	768 (s)	775 (s)	775 (s)	776 (s)
			757 (m)		
			720 (m)		
	673 (m)	. . .		673 (s)	. . .

$1,5-S_6(NH)(NCH_3)$			$1,5-S_6(NCH_3)_2$		
Nujol	CS_2	Benzene	Nujol	CS_2	Benzene
			575 (m)	579 (w)	579 (w)
		520 (s)			
509 (m)	492 (m)				
465 (w)		471 (sh)		474 (w)	476 (w)
456 (w)	460 (m)	460 (m)		458 (w)	458 (w)
428 (w)	. . .	435 (m)	432 (w)	432 (w)	432 (w)
384 (m)	. . .	393 (m)	384 (w)	. . .	393 (m)
364 (m)	363 (m)	364 (m)			373 (m)
336 (sh)					
	287 (w)	288 (sh)	282 (w)		
270 (m)	273 (w)	276 (m)	273 (w)	280 (m)	281 (m)
	256 (w)	258 (w)		255 (w)	
200 (m)	195 (w)	195 (w)			
169 (m)	. . .				

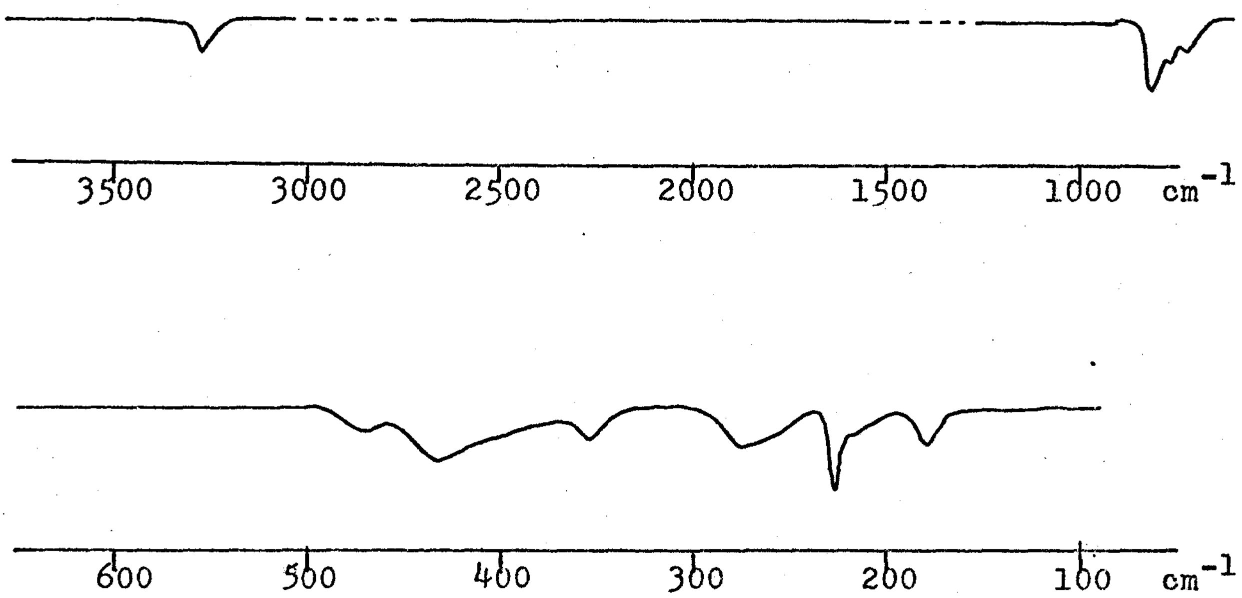
Table 8

Infrared Spectra of 1,4-Hexasulphur Diimide (4000-69 cm^{-1})

Solid		Solution	
Nujol	CS_2	Benzene	THF
			3460 (w, br)
3275 (s)	3328 (s)	3303 (s)	3125 (s, vbr)
814 (s)	815 (s)	818 (s)	818 (s)
770 (sh)	775 (sh)	778 (sh)	780 (sh)
725 (sh)			
469 (br)	460 (br)	468 (s,br)	467 (m)
430 (br)	. . .		439 (w)
355 (m)	355 (m)	360 (m)	369 (m)
273 (br)	273 (s)	273 (m)	.
226 (s)	218 (s)	218 (s)	.
179 (m)		179 (w)	.
	. . .	166 (w)	.

FIGURE 8. INFRARED SPECTRA OF 1,4-HEXASULPHUR DIIMIDE

A. Nujol



B. Solution

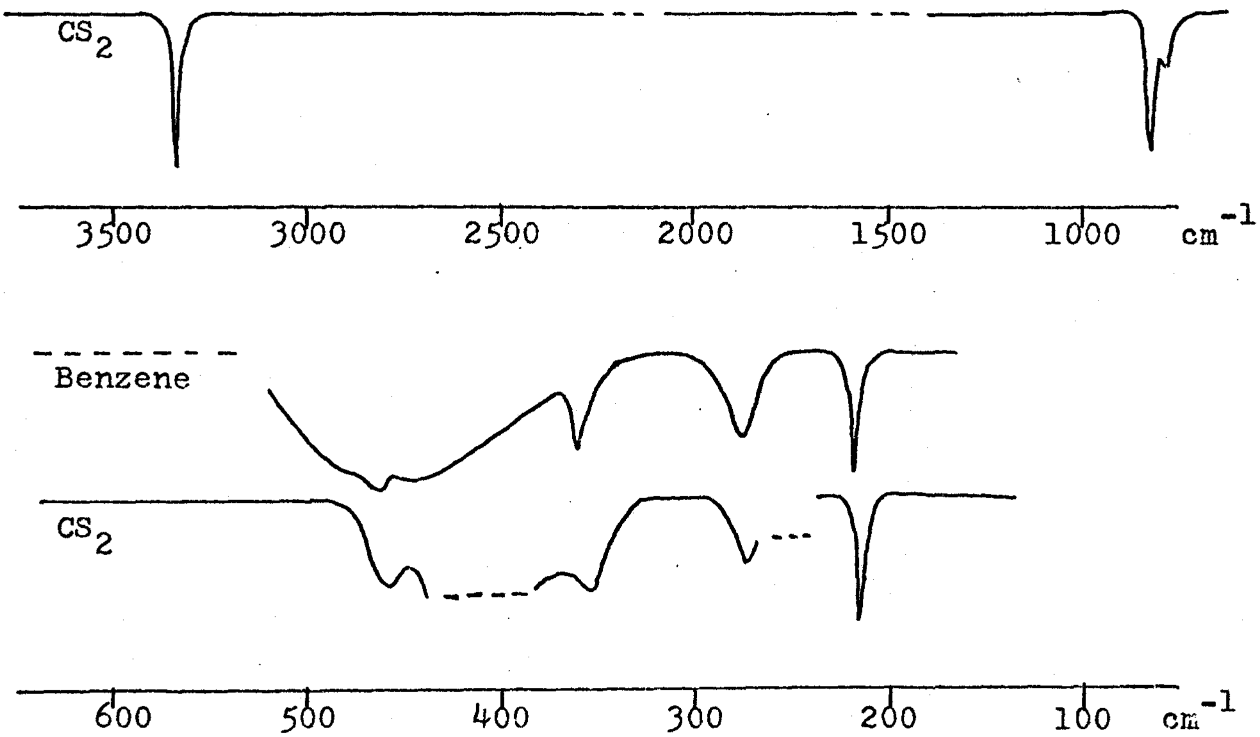


Table 9

Infrared Spectra of Alkylated 1,4-Hexasulphur Diimide

(4000-170 cm^{-1})

$1,4-S_6(NH)(NCH_3)$			$1,4-S_6(NCH_3)_2$		
Nujol	CS_2	Benzene	ThinFilm	CS_2	Benzene
3295 (w)	3330 (s)	3305 (s)			
•	2990 (w)			2988 (w)	
•	2958 (w)	2965 (w)	2965 (s)	2955 (m)	2960 (m)
•	2920 (m)	2927 (w)	2920 (s)	2918 (m)	2923 (m)
•					2895 (w)
•	2882 (w)	2890 (w)		2880 (w)	2880 (w)
•	2850 (w)	2855 (w)	2850 (s)	2850 (w)	2855 (m)
•	2780 (w)?			2778 (w)	
•	2540 (w)?				
				1950 (w)	
				1808 (w)	
			1462 (w)		
			1454 (w)		1452 (m)
	1428 (m)	1432 (m)	1427 (m)	1426 (m)	1432 (m)
	1409 (w)	. . .	1415 (sh)		
	1400 (w)		1400 (sh)	1398 (w)	
			1377 (w)		
1283 (w)			1260 (s)		1250 (m)
1155 (w)					
1130 (m)	1122 (w)	1121 (w)	1094 (s)	1122 (m)	1120 (m)

1,4-$S_6(NH)(NCH_3)$			1,4-$S_6(NCH_3)_2$		
Nujol	CS_2	Benzene	ThinFilm	CS_2	Benzene
1066 (s)	1062 (s)	1062 (m)	1058 (s)	1060 (s)	1059 (s)
		1028 (m)	1019 (s)	1033 (w)	. . .
				1012 (w)	
			864 (m)		846 (m)
					820 (sh)
808 (s)	802 (s)	803 (s)	798 (s)	772 (s)	775 (s)
756 (s)	745 (m)	745 (m)		732 (m)	732 (w)
			672 (w)	672 (s)	. . .
			572 (w)	572 (w)	570 (w)
492 (m)	491 (m)	502 (m)			
				479 (w)	
460 (w)	461 (m)	467 (m)	467 (w)	465 (w)	465 (w)
419 (br)	. . .				
			383 (m)	. . .	381 (m)
368 (br)	. . .	364 (m)			371 (sh)
					358 (sh)
		291 (w)?			
276 (br)	271 (m)	275 (m)	281 (m)	281 (m)	282 (m)
	260 (m)				
205 (w)		204 (w)	198 (w)	198 (w)	198 (w)
200 (w)		200 (w)			

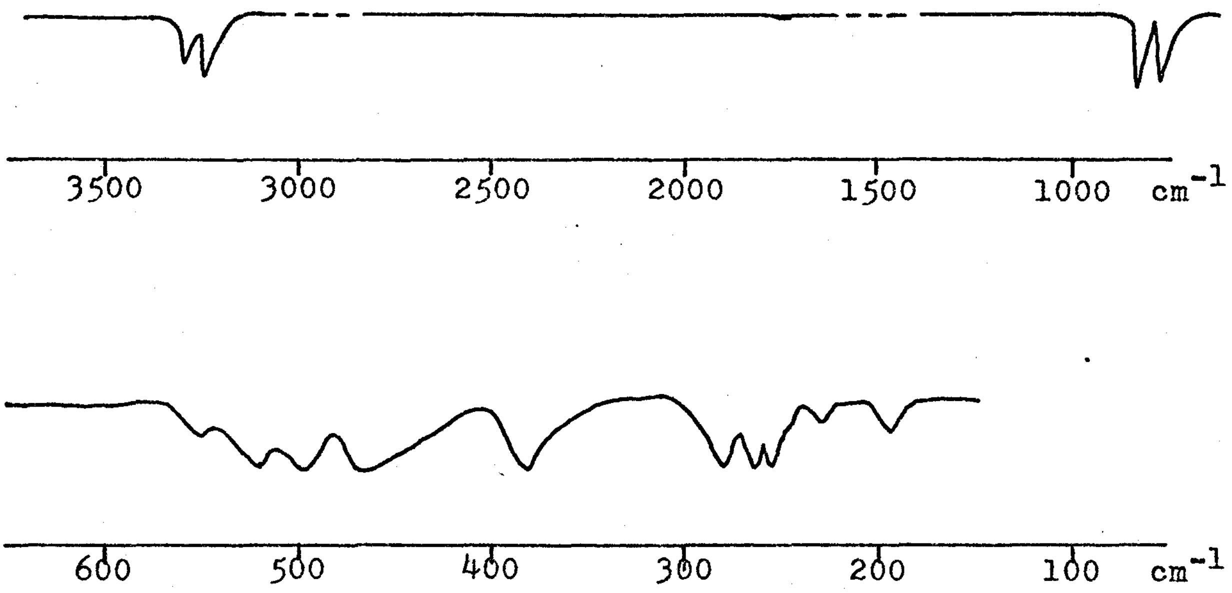
Table 10

Infrared Spectra of 1,3-Hexasulphur Diimide (4000-69 cm^{-1})

Solid	Solution		
Nujol	CS_2	Benzene	THF
			3580 (w,br)
			3500 (w,br)
3302 (m)	3335 (s)	3320 (s)	
3252 (m)			3175 (vs,br)
	2920 (w)?		
835 (s)	835 (s)	835 (s)	833 (s)
773 (s)	773 (s)	776 (s)	776 (s)
550 (m)	544 (sh)	541 (w)	539 (w)
524 (s)	520 (sh)	522 (w)	
498 (s)	498 (m)	489 (w)	495 (w)
	480 (m)		476 (m)
469 (s)	464 (m)	467 (m)	
	454 (m)	456 (sh)	456 (sh)
	. . .	401 (m)	403 (m)
384 (s)			
	331 (w)		
282 (s)	286 (m)	291 (m,br)	293 (m)
264 (m)		261 (s)	262 (m)
259 (m)	. . .		
228 (m)	220 (w)	220 (m)	221 (m)
196 (m)	. . .		. . .
		172 (w)	

FIGURE 9. INFRARED SPECTRA OF 1,3-HEXASULPHUR DIIMIDE

A. Nujol



B. Solution

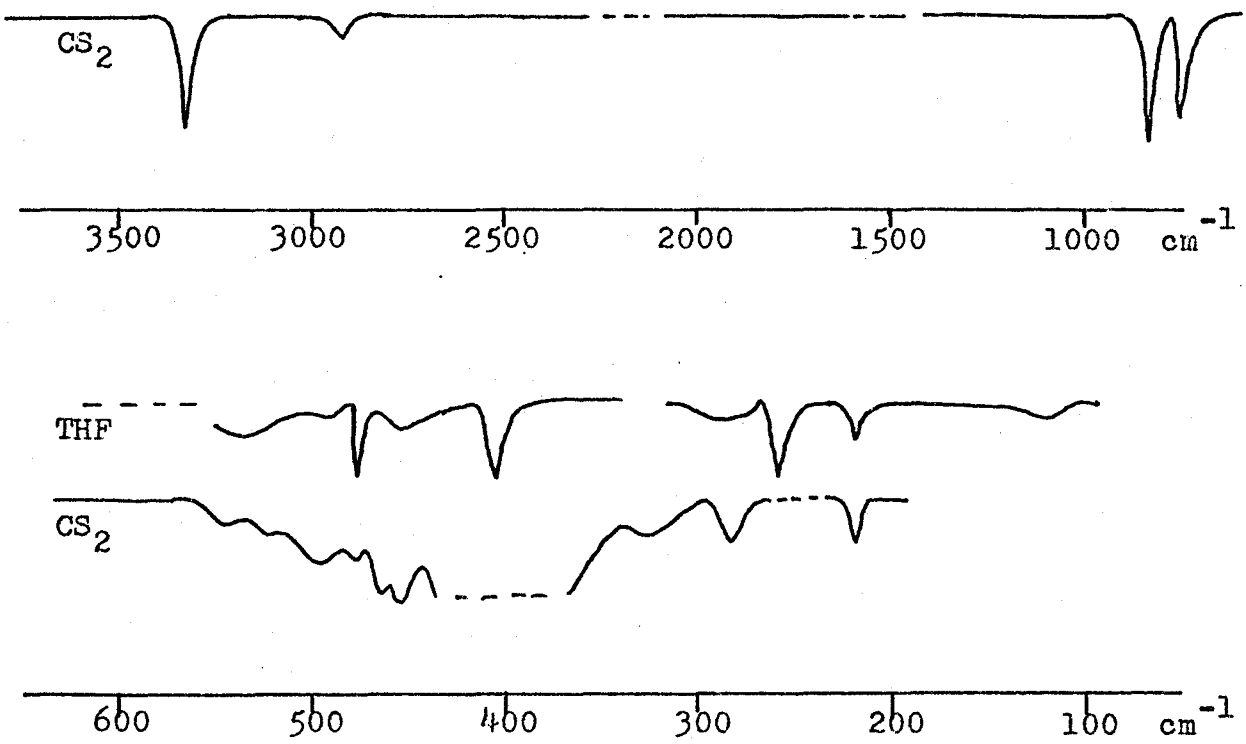


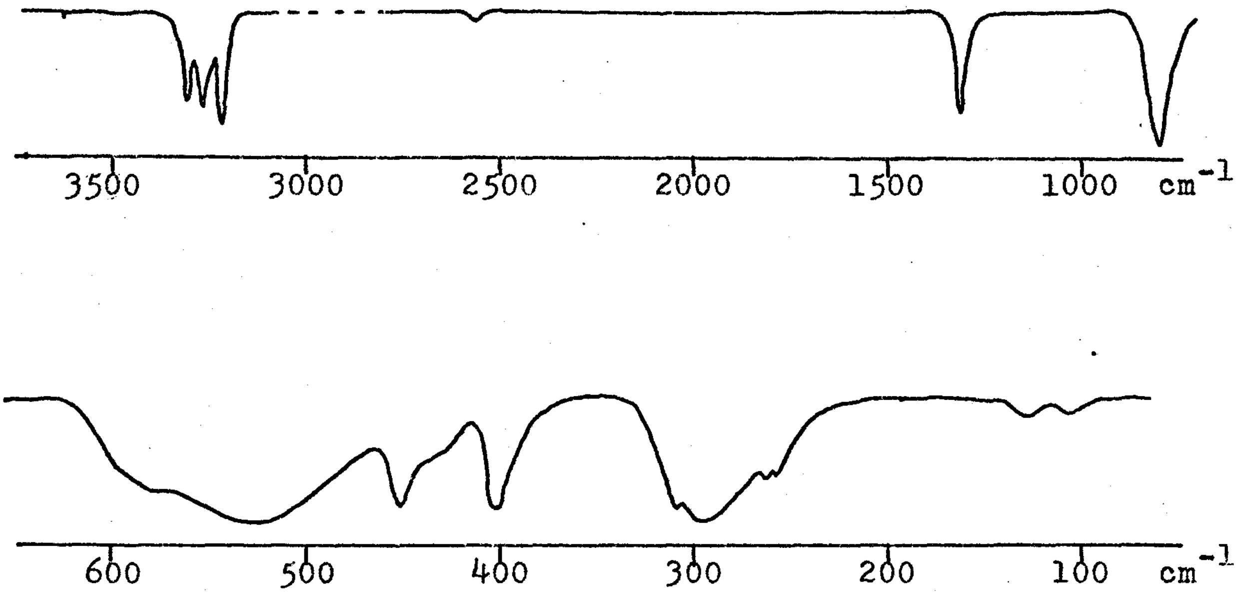
Table 11

Infrared Spectra of Tetrasulphur Tetraimide (4000-69 cm^{-1})

Solid		Solution	
Nujol	THF	Acetone	Pyridine
		3550 (br)	
3310 (s)			
3285 (s)	3250 (s)	3280 (s,br)	3130 (s)
3220 (s)			3050 (sh)
2575 (w)		2650 (br)	2730 (br)
1295 (m)			
820 (vs)	821 (s)	825 (s)	821 (s)
584 (sh)	597 (v.br)	•	
523 (br)		•	• • •
	486 (m)	•	
452 (s)	453 (s)	•	454 (m)
437 (sh)		•	
402 (s)	400 (s)	•	
309 (sh)	•		
300 (s,br)	•	293 (s)	293 (s)
258 (sh)	•		
256 (sh)	•		
127 (w)		•	•
106 (w)		•	•

FIGURE 10. INFRARED SPECTRA OF TETRASULPHUR TETRAIMIDE

A. Nujol



B. Solution

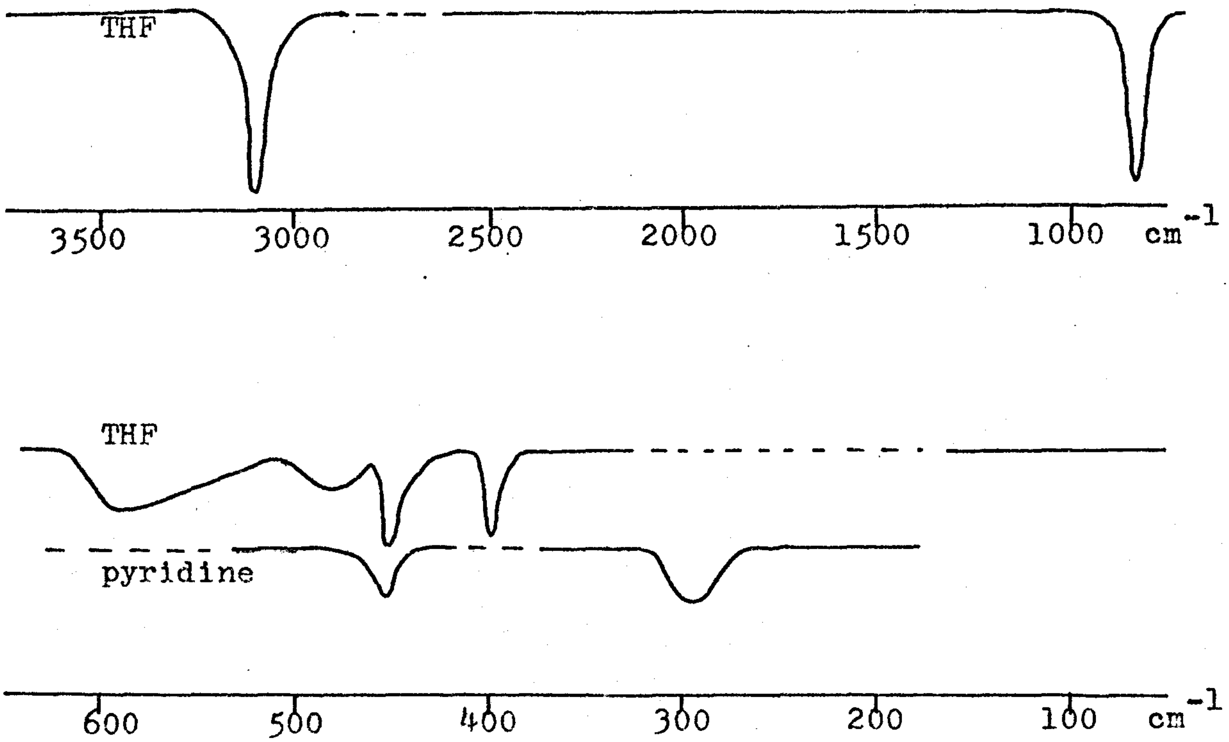


Table 12

Raman Spectrum of Tetrasulphur Tetraimide

Solid

3317 (m)
3293 (m)
3229 (m)
1330 (w)
1309 (w)
1267 (w)
863 (w)
836 (w)
753 (sh)
725 (m)
546 (w)
506 (m)
468 (m)
409 (w)
334 (w)
314 (w)
264 (s)
220 (s)
143 (m)
131 (m)
109 (m)
84 (s)
65 (sh)
48 (m)
40 (m)

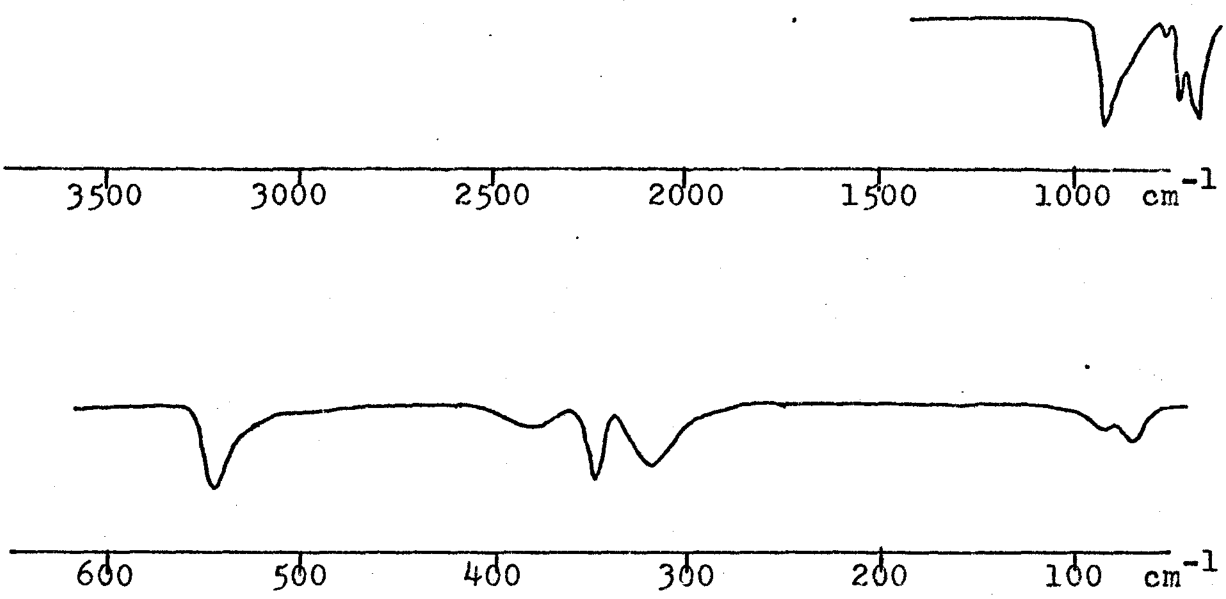
Table 13

Infrared Spectra of Tetrasulphur Tetranitride (4000-69 cm^{-1})

Solid	Solution		
Nujol	CS_2	Benzene	Dioxane
925 (s)	939 (s)	936 (s)	937 (s)
765 (w)			
725 (m)			
697 (s)	705 (s)		702 (s)
548 (s)	552 (s)	543 (s)	545 (s)
384 (w)	• • •		
343 (s)			•
322 (s)	325 (m)	320 (m)	•
78 (w)	•		•
75 (w)	•		•

FIGURE 11. INFRARED SPECTRA OF TETRASULPHUR TETRANITRIDE

A. Nujol



B. Solution

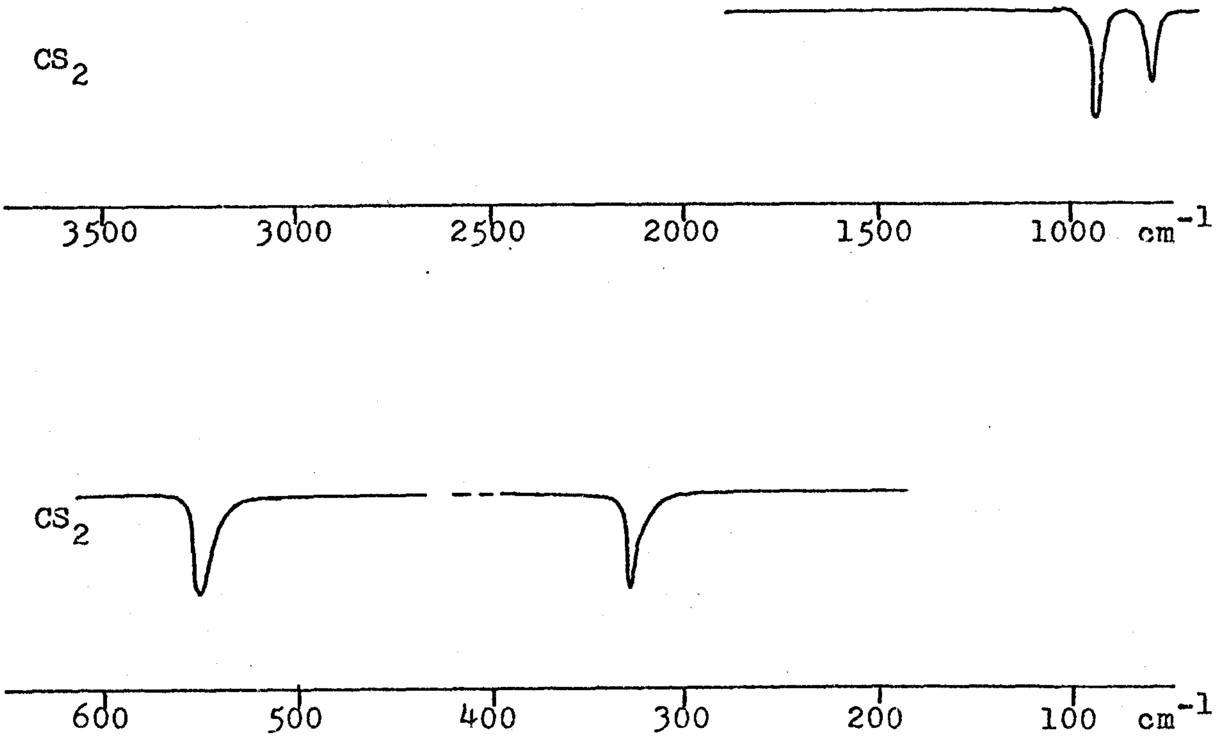


Table 14

Raman Spectra of Tetrasulphur tetranitride

Solid	**Solution**		
	CS_2	Dioxane	Polarization in Dioxane
	960 (w)?		
	942 (w)?		
	920 (w)?		
770 (w)		773 (vw)	?
725 (w)		729 (w)	0
708 (w)			
564 (s)	571 (w)	582 (m)	0
525 (w)			
350 (m)		355 (w)?	?
222 (s)	215 (s)	224 (s)	0.26
200 (s)		188 (s)	0.61
99 (m)			
82 (w)			
73 (w)			
60 (s)			
53 (s)			

DISCUSSION

1. PREPARATION OF ORGANIC DERIVATIVES

The synthesis of alkylated derivatives of the hexasulphur diimides under basic conditions was successfully carried out. The compounds 1,4-dimethyl hexasulphur diimide, 1,4-monomethyl hexasulphur diimide, 1,5-dimethyl hexasulphur diimide, and 1,5-monomethyl hexasulphur diimide were prepared and characterized. However it was not possible to alkylate the 1,3 isomer of hexasulphur diimide under the conditions used.

(a) Methylation of 1,4-Hexasulphur Diimide

This reaction was successfully carried out under several sets of conditions. The reaction with a 1:1 molar ratio of base resulted in the formation of a substantial amount of the expected monomethyl derivative, but a significant amount of dimethylated imide was also formed. This may be due to an equilibrium disproportionation between two singly charged ions:

$$S_6N_2H^- + S_6N_2H^- \rightleftharpoons S_6N_2^{2-} + S_6(NH)_2$$

or perhaps to proton abstraction on the initially formed monomethyl derivative by a mole of anion:

$$S_6(NH)(NCH_3) + S_6N_2H^- \rightleftharpoons S_6N_2CH_3^- + S_6(NH)_2$$

As required by either of these schemes, there was a significant amount of unreacted hexasulphur diimide remaining at the end of the reaction.

An addition reaction of the base to the sulphur-nitrogen skeleton (to either sulphur-sulphur or sulphur-nitrogen bonds or both) occurred in competition with the proton abstraction, resulting in the formation of sulphur and (eventually) dialkyl sulphanes.

The amount of dimethyl diimide was substantially increased (from 11 to 50%) by the use of a 2:1 molar ratio of base. There was no significant increase in the amount of dialkyl polysulphide material formed. Unreacted starting material, while much less, was nevertheless present, indicating that significant amounts of base must be consumed in degradation of the imide to polysulphides.

The use of the weaker (less nucleophilic) base, lithium hydroxide, resulted in less degradation of the sulphur imide due to attack on the S-N skeleton. Proton abstraction by lithium hydroxide was slower (partly due to lower solubility of the hydroxide in tetrahydrofuran) than that by ethyl lithium; but the fact that the reaction succeeded at all demonstrates a considerably greater acidity for the imide protons than has been generally accepted.

Although lithium hydroxide dissolves slowly and gives substantially reduced colour in the resulting solutions, it still leads to appreciable amounts of dimethylated species. The total yield of recoverable imide (71%) is slightly higher than in either of the previous two cases (61 and 62%). This is expected from the reduced yields of polysulphides.

(b) Methylation of 1,5-Hexasulphur Diimide

The reaction of 1,5-hexasulphur diimide with a 1:1 molar ratio of base resulted in both N,N'-dimethyl and N-methyl hexasulphur diimides, and again unreacted hexasulphur diimide remained. The ratio of dimethyl : monomethyl : unreacted diimide was essentially identical to that in the previous case. The sample of N,N'-dimethyl hexasulphur diimide prepared from trisulphur dichloride and methylamine proved to be identical to the N,N'-dimethyl hexasulphur diimide prepared from 1,5-hexasulphur diimide.

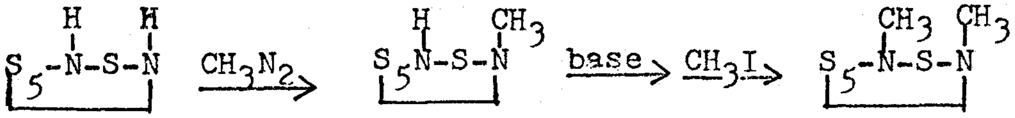
The possibility of rearrangement of the imides during the reaction is considered to be very unlikely. Evidence in support of this statement lies predominantly in the finding of three unique sets of products from the three imides. Rearrangement would be expected to occur only if some one set of products were substantially more stable than another. If this were the case, at least two of the isomeric imides--if not all three--should have resulted in a common product. Since this did not occur, the two series of mono- and dimethyl products obtained must possess the same atomic arrangement of sulphur and nitrogen atoms as the starting imides. Therefore the alkylation reaction provides an unambiguous link between the structures of the 1,4 and 1,5 hexasulphur diimides and the corresponding mono- and dimethyl hexasulphur diimides.

The established geometry of the 1,5-hexasulphur diimide (50, 52) and hence of the N,N'-1,5-dimethyl hexasulphur diimide, provides firm support to the proposed 1,5 structure of the compound prepared by Brasted and Pond (8).

(c) Methylation of 1,3-Hexasulphur Diimide

An attempt to methylate the 1,3 isomer resulted in formation of N-methyl heptasulphur imide and open chain sulphanes. Since the other two isomers could be successfully alkylated, it appears that the instability of the 1,3 isomer in the presence of base must arise through the proximity of the two N-H groups. Either the proximity of the two nitrogens favours addition of base over proton abstraction, or the ions break down after they have formed. Since the proton NMR spectrum shows only methyl, and not ethyl, groups (which would indicate addition), the latter possibility is favoured. Either the $-\overset{H}{N}-S-\overset{-}{N}-$ or the $-\overset{-}{N}-S-\overset{-}{N}-$ group must be unstable. If the $-\overset{H}{N}-S-\overset{-}{N}-$ link is dissociating, it is unlikely that any useful chemistry can be carried out of the 1,3 isomer. However, if it is only on formation on the doubly charged ion that dissociation occurs, a reaction involving abstraction of only one proton should be successful.

A possible means of distinguishing between the two possibilities is the series of reactions:



$$\underbrace{S_5-\overset{H}{N}-S-\overset{H}{N}}_{5} \xrightarrow{CH_3N_2} \underbrace{S_5\overset{H}{N}-S-\overset{CH_3}{N}}_{5} \xrightarrow{base} \xrightarrow{CH_3I} \underbrace{S_5-\overset{CH_3}{N}-S-\overset{CH_3}{N}}_{5}$$

The presence of N-methyl heptasulphur imide among the reaction products is difficult to explain. Obviously both ring cleavage (breaking of sulphur-nitrogen bonds) and chain lengthening (formation and destruction of sulphur-sulphur bonds) must be occurring under the basic conditions employed.

Since these conditions approximate those used in the preparation of the imides (9b) (THF rather than DMF and imide anions rather than ammonia as base) it appears quite likely that similar facile making and breaking of bonds would occur under both conditions. The complete absence of tetrasulphur tetraimide, the low yields of the pentasulphur triimides (32), and the low yield of 1,3-hexasulphur diimide in the latter reaction (31) find an explanation in these results. If these imides (as anions) were formed they would rearrange to the heptasulphur imide anion.

(d) Probable Scope of This Reaction

The synthetic method used to make methyl derivatives of the hexasulphur diimides is undoubtedly also suitable for other organic derivatives. In addition, it should be possible to make mixed derivatives of the type $S_6(NR)(NR')$ by isolating the monomethyl compound and reacting it further. It does not seem likely, however, that the method will prove suitable for use with the pentasulphur triimides, or for tetrasulphur tetraimide, since these all contain the $-\overset{H}{N}-S-\overset{H}{N}-$ linkage found in 1,3-hexasulphur diimide.

2. NMR, MASS SPECTRA AND INFRARED SPECTRA

(a) Proton NMR Spectra

The NMR spectra of the methylated derivatives of 1,5 and 1,4-hexasulphur diimide, and heptasulphur imide, are summarized in Table 15.

Table 15

Chemical Shifts for Methylated Imides

Compound	Chemical Shift for N-CH_3
1,4-$S_6(NCH_3)_2$	-3.04
1,4-$S_6(NH)(NCH_3)$	-3.10
1,5-$S_6(NH)(NCH_3)$	-3.12
1,5-$S_6(NCH_3)_2$	-3.15
S_7NCH_3	-3.16

The overall range in the position of the N-CH_3 protons is only 0.12 ppm; although there does seem to be a discernible trend in the direction of decreasing (absolute) chemical shift with decreasing distance between adjacent nitrogen atoms, the magnitude of the change is too small to be of much use in correlating the structures. Thus, while the NMR spectra were useful for differentiating between mono- and disubstituted derivatives, they are not useful as a means of assigning the isomeric ring structure on which a compound is based.

(b) Mass Spectra

The mass spectra of the 1,4- and 1,5-dimethyl hexasulphur diimides (Figures 1 and 3) were very similar both in positions of peaks and their relative heights, with the exception of the peak at mass number 157, which was much higher in the spectrum of the 1,4 isomer. This peak corresponds to the fragment S_4NCH_3, and could arise from cleavage of two sulphur-nitrogen bonds. However, though its intensity is reduced, the same fragment arises from 1,5-hexasulphur diimide, although no chain of four sulphur atoms is present in this compound. The spectra of the isomeric monomethyl hexasulphur diimides (Figures 2 and 4) are also nearly superimposable, even with respect to the 157 peak. Therefore, bonds must be broken in a way which makes the isomeric structures indistinguishable.

Although mass spectra do not appear to be useful for identifying the arrangement of sulphur and nitrogen atoms in the eight-membered ring, they do provide much useful information about the constitution of the organic derivatives, and it seems surprising that other workers have not utilized them. Low temperatures and the direct inlet method are required, because of the instability of these compounds at normal operating temperatures (around 200°). However, once these precautions have been taken, useful spectra can be obtained. These provide the molecular weight, and since S^{34} is present in 4.4% abundance, the parent ion group can be used to check the proposed formula. In the case of the monomethyl derivatives, S_xNH fragments supplemented the S_x and S_xNCH_3 fragments found in the dimethyl derivatives and were useful as a further proof of structure.

(c) Infrared Spectra

Two types of information were sought from the infrared spectra. The assignment of bands where possible was attempted; and the use of the spectra as a qualitative tool both for distinguishing between the isomeric imides, and relating the alkyl derivatives to their imides, was considered.

(i) Assignments

The agreement between the theoretical and observed spectra for the sulphur imides and tetrasulphur tetranitride is summarized in Table 16. (Vibrations below 100 cm^{-1} which are probably due to lattice vibrations are not included in the number of observed bands.)

For heptasulphur imide and the three isomeric hexasulphur imides, the agreement between the theoretical and observed spectra is too poor, and the symmetry of the compounds too low, to make an attempt to assign any bands other than the N-H and N-S stretches (around 3350-3200, and 835-800, cm^{-1}, respectively).

For tetrasulphur tetranitride, a complete vibrational assignment has been carried out (35), and the tetrasulphur

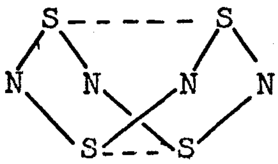
Table 16

Theoretical and Observed Spectra of the Sulphur Imides

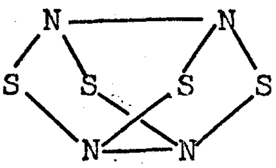
Compound	Symmetry	Theoretical Fundamentals		Observed Bands	
		Infrared	Raman	Infrared	Raman
S_7NH	C_s	21: 12A'+9A"	21: 12A'+9A"	11	15
1,5-$S_6(NH)_2$	C_{2v}	19: $8A_1+6B_1$ $+5B_2$	24: $8A_1+5A_2+$ $6B_1+5B_2$	13	
1,4-$S_6(NH)_2$	C_2	24: 13A+11B	24: 13A+11B	10	
1,3-$S_6(NH)_2$	C_s	24: 13A'+11A"	24: 13A'+11A"	14	
$S_4(NH)_4$	C_{4v}	12: $5A_1+7E$	21: $5A_1+5B_1+$ $4B_2+7E$	17	21
S_4N_4	D_{2d}	7: $3B_2+4E$	12: $3A_1+2B_1+$ $3B_2+4E$	8	8

tetraimide spectrum has also been considered with respect to the tetrasulphur tetranitride assignments. Unfortunately, the normal coordinate analysis is based on an incorrect structure . While it might be argued that the structures differ in the solid and in solution, this is unlikely since the spectra are very similar in the two phases (Tables 13, 14, and Figure 11).

The two structures are shown below (XXV a,b).



XXVa



XXVb

The crystallographically correct structure (XXVa) features coplanar nitrogen atoms with a sulphur-nitrogen bond order of about 1.3 and a partial sulphur-sulphur bond (bond order about 0.48-0.36) (46,49). In comparison, the structure on which the infrared interpretation was based features coplanar sulphur atoms, two full nitrogen-nitrogen bonds across the ring, and sulphur nitrogen bonds of bond order 1.00. Formally, the two structures are related by the interchanging of the sulphur and nitrogen atoms; both have D_{2d} symmetry.

The frequencies of torsional bending modes will not be much changed by interchanging sulphur and nitrogen atoms, since the same total mass will be involved, although details of the assignments may differ. However, modes involving changed N-N distance, and assigned by the authors to bands at 934 cm^{-1} in the infrared, and 888 cm^{-1} in the Raman spectrum (by comparison with hydrazine) would become changes in S-S distance, and would be expected to occur at substantially lower wavenumbers. Since the S-N bond order is greater than one (i.e., the force constant is larger), the frequency assigned to the S-N stretch should be a higher wavenumber.

The band which appears at 939 cm^{-1} in the infrared spectrum (which was previously assigned to an N-N stretch of B_2 symmetry) could be of either B_2 or E symmetry and is probably the S-N bond stretching frequency. From the empirical relation (6):

$$r_{SN} = 0.0483(\mu SN) + 1.099$$

a value of r = 1.613 A is predicted by an S-N stretch at 939 cm^{-1}; this is in very good agreement with the experimental value of 1.616.

The Raman spectrum in dioxane solution shows three polarized (and therefore totally symmetric) bands which must be assigned to A_1 vibrations (see Table 14). The highest of these, at 729 cm^{-1}, is probably also due to S-N stretching. This band was previously assigned as a composite of the 939 cm^{-1} band and a calculated bending mode at 177 cm^{-1} which could not be observed; however, such a combination would not be polarized. Bands of A_1 symmetry are forbidden in the infrared, and no band appears here in solution. A band at 725 cm^{-1} is observed in the infrared of the solid; however, this is allowed by the site symmetry. (The space group of tetrasulphur tetranitride is $P2_1/n$ (C^5_{2h}); only one of its subgroups, C_i, forbids totally symmetric bands in the infrared. This is not a possible site symmetry in this case, because the molecule itself does not have a centre of symmetry.)

The other two polarized bands, at 582 and 224 cm^{-1}, do not appear at all in the infrared. The first of these (previously assigned as an N-S stretch of E symmetry) is more probably the totally symmetric stretch involving mainly changes in S-S distance. The final polarized band at 224 cm^{-1} was previously assigned to angle bendings of both B_1 and E symmetry (overlapping); it probably involves instead totally symmetric changes in SSN angles. Speculation on further assignments does not appear profitable.

Reduction of tetrasulphur tetranitride with alcoholic tin (II) chloride gives tetrasulphur tetraimide (53). Three major structural changes accompany this reduction. First, both S-S bonds are broken; second, the N-S bond order is reduced to 1.00; and third, the bisphenoid D_{2d} structure opens to a crown-like (α-sulphur) structure of C_{4v} symmetry. Such major changes do not lend themselves to convincing arguments based on analogy, and the only useful observation to be made is that the N-S stretching frequency decreases from 939 cm^{-1} to 820 cm^{-1} in tetrasulphur tetraimide (both are infrared and Raman active in both compounds) as required for the reduction in N-S bond order. This band is present in all of the remaining sulphur imides, the range being from 835 cm^{-1} in 1,3-hexasulphur diimide to 803 cm^{-1} in heptasulphur imide. The new bands near 3300 cm^{-1} are obviously the N-H stretch.

(ii) Qualitative Observations

While definite assignments cannot be made for the sulphur imides, their spectra are of considerable value as a means of identification. The infrared spectra of the solids have a series of broad, almost indistinguishable bands. However, there are enough differences in the solution spectra, particularly in the region 600-200 cm^{-1}, to allow differentiation between any of the imides whose spectra have been recorded (see Figures 6-11).

The reliability of this method may be compared to other possible means of identifying the isomers. The melting points of the three imides span approximately 30°, but the reported melting points of any one isomer span up to 15°. Mass spectra fragmentation patterns in both the monomethyl and dimethyl derivatives are very similar for the isomers. The proton NMR spectra of the N-CH_3 protons in these derivatives differ by perhaps 0.1 ppm at most. Infrared spectra in the region 4000-600 cm^{-1} for the three imides consist of the N-H stretch near 3300 cm^{-1} and the N-S stretch near 835 cm^{-1}.

These bands shift as much from solvent to solvent as they do between isomers. Thus there has been no single reproducible property to be quoted as a guide for distinguishing isomers. The infrared spectra in the region 600 to 200 cm^{-1} provide this characteristic and reproducible property. This is their chief value.

A possible further use of the spectra might be in identifying derivatives of various imides as belonging to a particular sulphur-nitrogen skeletal arrangement. To do so, patterns must be found which are relatively invariant to changes in substituent. If these exist, it is in the far infrared region, since the effect of organic substituents is to add peaks in the region 3500-700cm^{-1}, and to shift the S-N peak. However, vibrations which are mainly skeletal deformations would be expected to be less sensitive to changes in substituent. For the rather limited number of compounds available, it appears that the introduction of substitients alters the spectra in a way which obscures any patterns observed for the imides themselves.

EXPERIMENTAL

1. INSTRUMENTAL

(a) Infrared and Raman Spectra

Infrared Spectra for routine product identification were recorded in the region 4000-600 cm^{-1} on a Beckman IR-5 spectrophotometer. Samples were prepared as Nujol mulls or thin films between sodium chloride plates, or in carbon disulphide solution in 0.1 mm sodium chloride or cesium iodide cells.

Infrared spectra of heptasulphur imide, the three isomers of hexasulphur diimide, tetrasulphur tetraimide, and tetrasulphur tetranitride were also recorded over the range 4000-69 cm^{-1}, as were spectra of the methylated species N-methyl heptasulphur imide, and 1,5- and 1,4-dimethyl hexasulphur diimide and 1,5- and 1,4-monomethyl hexasulphur diimide. In addition, Raman spectra of heptasulphur imide, tetrasulphur tetraimide, and tetrasulphur tetranitride were obtained.

These infrared spectra in the range 4000-600 cm^{-1} were recorded on a Perkin Elmer 521 grating instrument. Nujol mulls and thin films were pressed between sodium chloride plates; solutions were held in 0.1 mm sodium chloride or cesium iodide cells. A polystyrene strip was used for calibration.

A Perkin Elmer 301, equipped with Globar and mercury sources, was used in the region 670-69 cm^{-1}. The instrument was flushed with nitrogen (liquid nitrogen and a heating element) before use, to prevent interference from the water vapour lines found in this region. Nujol mulls and thin films were pressed between polyethylene plates; solutions were recorded in 0.1 mm cesium iodide cells, or 0.5 mm when solubility was low. Below 170 cm^{-1}, solutions were sealed in polyethylene cells made by soldering two 1-inch circles together with an annular ring of polyethylene as a spacer. The instrument was calibrated using the peaks of the water vapour spectrum (7).

Raman spectra were obtained with a Spex Industries Model 1400 spectrometer employing a Spectra Physics Model 125 helium/neon laser source at 6328 A, a double monochromator and a phototube detector with an electrometer amplifier and recorder. Both solid and solution samples were sealed in melting point capillaries.

(b) Proton NMR

Proton magnetic resonance spectra were obtained on a Varian A-60 or H-100 instrument using carbon disulphide or carbon tetrachloride as solvents. Blank spectra were run to check for solvent impurities. Tetra-methyl silane was used as an internal reference; chemical shifts are reported as parts per million upfield from the reference.

(c) Mass Spectra

Samples for mass spectra were introduced at room temperature by direct inlet into a Perkin Elmer Hitachi Model RMU-6A instrument. An ionizing potential of 80 eV was used. Counting was based on the carbon (12), nitrogen (28), and sulphur (32) peaks.

(d) Molecular Weights

Molecular weight determinations were done on a Mechrolab Model 301A Vapour Pressure Osmometer, with benzene as solvent. The calibration curve was based on heptasulphur imide.

(e) Melting Points

These were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected.

2. SOLVENTS

Reagent grade solvents were used in all cases except hexane and dimethylformamide, which were technical grade. No special purification was undertaken unless specified.

3. CHROMATOGRAPHY

Column chromatography on silica gel adsorbent (Grace Davison Chemical, mesh size 100-200) was used to separate reaction mixtures. Column packing varied from 70 to 500 g adsorbent; however, a minimal ratio of adsorbent to sample of 50:1 (by weight) was maintained. As eluent, either carbon disulphide, or hexane with a varying percentage of benzene, was used. Fractions of 100 ml, or 50 ml for the smaller columns, were collected and solvents stripped on a rotary evaporator. Tared flasks were used so that the weight of each fraction could be determined directly.

Thin layer chromatography was the usual method of checking the column separation and was also one criterion for identification of sulphur imides and for sample homogeneity and purity.

Silica Gel GF_{254} (acc. to Stahl, E. Merck, Darmstadt, Germany) and water were slurried in a ratio of 1:2 and applied to the plates in a 0.25 mm layer. This was allowed to dry overnight in air. After the plates had been spotted with sample, they were eluted a distance of 15 cm with carbon disulphide and were either examined under an ultraviolet lamp or developed with an aqueous solution of silver nitrate. Since plate conditions vary slightly, R_f values are quoted with sulphur as a standard. (R_f value is defined as $\frac{\text{distance moved by substance}}{\text{distance moved by solvent}}$.)

In cases where preparative scale thin layer chromatography was used for separation, the plates were prepared as above, but with a 1 mm coating of silica gel. Samples of about 40 mg were streaked in a line parallel to the bottom of the plate, and eluted as often as plate size permitted. The position of the sample was determined using an ultraviolet lamp; the silica gel was scraped off and slurried with ether, and the sample recovered by filtration and evaporation.

4. PREPARATION OF THE SULPHUR IMIDES

With a few modifications, heptasulphur imide was prepared according to the method of Becke-Goehring, Jenne and Fluck (20) as reported by Brauer (9b). About 3 l. of dimethylformamide was introduced into a 5 l., 3-neck flask with a low temperature thermometer, gas inlet tube and mechanical stirrer, and cooled to 0-5° with a methanol/dry ice bath. Ammonia (Matheson, anhydrous) was bubbled through the solvent at a rate of 10 cubic feet per hour; after 20 minutes, the addition of 250 ml of sulphur monochloride (Matheson, Coleman, and Bell, practical) in 5 ml aliquots was begun. The temperature was allowed to return to 0° after each addition. When addition was complete, the reaction flask was allowed to stand at 0° for 1-2 hours; the mixture was then poured into 6-7 gallons of ice cold 1% hydrochloric acid and neutralized with cold 10% hydrochloric acid. After standing several hours to allow the solids to settle, the supernatant liquid was decanted, and the solids taken up in 2 l. of ether. This was dried with saturated sodium chloride and anhydrous sodium sulphate and removed *in vacuo*. The solids were recrystallized from boiling benzene to give plate-like crystals of heptasulphur imide.

The mother liquor, which was enriched in the lower sulphur imides, was concentrated and transferred to a

500 g silica gel column. This was eluted with hexane/benzene to effect a preliminary separation (i.e., mixtures of heptasulphur imide and 1,4-hexasulphur diimide, or 1,4- and 1,5 hexasulphur diimide, etc., were obtained). For further purification, appropriate fractions were combined and separated on smaller columns eluted with carbon disulphide. Fractions from these columns containing only 1,5- and 1,3-hexasulphur diimides were separated using preparative scale thin layer chromatography.

After all stages of purification, samples of four imides were obtained which showed no impurities by thin layer chromatography. Their R_f values and melting points are compared with reported values in Table 17.

Table 17

Observed and Reported Properties of the Sulphur Imides

Imide	R_f		Melting Point	
	Observed	Literature	Observed	Literature
S_7NH	0.57	0.58 (31)	112.0-112.5°	113° (48)
1,4-$S_6(NH)_2$	0.35	0.34 (31)	128-129°	130° (50) 133° (31)
1,5-$S_6(NH)_2$	0.23	0.24 (31)	144-145°	153° (50) 155° (31)
1,3-$S_6(NH)_2$	0.19	0.22 (31)	119-120°	120° (14) 123° (50) 130° (31)

Although thin layer chromatography of the crude reaction mixture indicated the presence of the penta-sulphur isomers, none was found after workup and chromatography.

5. ALKYLATION OF SULPHUR IMIDES

(a) Reactions of 1,4-Hexasulphur Diimide

(i) 1:1 Molar Ethyl Lithium

In a typical alkylation reaction, 371 mg of 1,4-hexasulphur diimide (obtained as described previously) and a magnetic stirring bar were placed in a 100 ml round-bottom flask, and 60 ml of dry tetrahydrofuran, which had been refluxed over and freshly distilled from lithium aluminum hydride, was added. The flask was fitted with a rubber septum. It was then cooled to 0° in an ice bath, with stirring, and 1.3 ml of ethyl lithium solution (Alfa Inorganics, Inc., 1.3 molar in benzene) was added using a hypodermic syringe. The solution quickly turned dark green, then dark blue. After ten minutes, an excess (about 0.5 ml) of methyl iodide (Fisher Scientific) was added. The solution slowly turned orange. After standing overnight, the solvent was stripped off, leaving a red oil. This was dissolved in 10 ml of carbon disulphide and transferred to a column containing 70 g of silica gel, which was then eluted with hexane. As the percentage of benzene in the eluent was gradually increased from 0 to 20%, products were eluted in the order given in Table 18; R_f values are for carbon disulphide/silica gel.

Table 18

Reaction of 1,4-$S_6(NH)_2$ with a 1:1 Molar Ratio of CH_3CH_2Li

R_f	Amount	Description
0.82	10 mg	sulphur
0.71	49 mg	colourless oil which hardened to a white solid; m.p. 24.5-25.5°
0.60	33 mg	yellow oil
0.53	89 mg	yellow oil which hardened to a yellow solid; m.p. 51.5-53°
0.37	101 mg	pale yellow solid, m.p. 128-129°

These products were identifed from infrared, NMR, and mass spectral data, as described in the "Results" section.

(ii) 2:1 Molar Ethyl Lithium

The reaction was carried out according to the above procedure, with 341 mg of 1,4-hexasulphur diimide, 2.4 ml of 1.3 M ethyl lithium, and 0.75 ml of methyl iodide. The R_f values and amounts of the products obtained are listed in Table 19.

(iii) 2:1 Molar Lithium Hydroxide

Lithium hydroxide (British Drug Houses, reagent) was dried *in vacuo* at 100° over phosphorus pentoxide for 48 hours. It was added to the 1,4-hexasulphur diimide in tetrahydrofuran solution by briefly removing the septum. Since the reaction seemed quite slow, a period of 3½ hours was allowed to elapse before the methyl iodide was added. Other details were unchanged. The products obtained from 300 mg of hexasulphur diimide, 73 mg of lithium hydroxide, and 0.7 ml of methyl iodide are listed in Table 19.

Table 19

Reaction of 1,4-$S_6(NH)_2$ with a 2:1 Molar Ratio of Base

R_f	Amount of Material		Identification
	CH_3CH_2Li	LiOH	
0.82	25 mg	20 mg	sulphur
0.71	193 mg	128 mg	dimethyl hexasulphur diimide
0.60	20 mg	trace	alkyl polysulphides
0.53	20 mg	54 mg	monomethyl hexasulphur diimide
0.37	20 mg	48 mg	unreacted hexasulphur diimide

(b) Reaction of 1,5-Hexasulphur Diimide with a 1:1 Molar Ratio of Ethyl Lithium

The procedure was that given in Section 5 (a) (i). Quantities used were 273 mg of diimide, 1 ml of 1.3 M ethyl lithium solution, and 0.5 ml of methyl iodide. The products obtained after purification are listed in Table 20.

Table 20

Reaction of 1,5-$S_6(NH)_2$ with a 1:1 Molar Ratio of CH_3CH_2Li

R_f	Amount	Description
0.80	6 mg	sulphur
0.68	46 mg	white solid, m.p. 81.5-82°
0.67	21 mg	yellow oil
0.51	77 mg	yellow solid, m.p. 100.5-102°
0.23	84 mg	white solid, m.p. 146-146.5°

Identification of these fractions is described in the

"Results" section.

(c) Reaction of 1,3-Hexasulphur Diimide with a 1:1 Molar Ratio of Ethyl Lithium

The procedure followed is given in Section 5 (a) (i). The quantities used were 284 mg of imide, 1 ml of 1.3 M ethyl lithium, and 0.5 ml of methyl iodide. The products obtained after purification are listed in Table 21.

Table 21

Reaction of $1,3\text{-}S_6(NH)_2$ with a 1:1 Molar Ratio of CH_3GH_2Li

R_f	Amount	Description
0.82	19 mg	sulphur
0.75	51 mg	yellow oil
0.67	77 mg	yellow oil plus solid; vile smell
0.15	15 mg	white solid

Identification of these fractions is described in the "Results" section.

(d) Reaction of Heptasulphur Imide with Ethyl Lithium

Following the above procedure, 262 mg of heptasulphur imide was reacted with 0.85 ml of 1.3 M ethyl lithium and 0.3 ml of methyl iodide. After purification, 157 mg of yellow oil, identifiable as N-methyl heptasulphur imide by its R_f value, infrared and NMR spectra, was obtained (41).

6. PREPARATION OF TRISULPHUR DICHLORIDE

Trisulphur dichloride was prepared by the reaction of sulphur dichloride and hydrogen sulphide at -80°, as described by Brauer (9a). Sulphur dichloride served as the solvent for the reaction:

$$\mathrm{Cl\text{-}S}[\mathrm{Cl} + \mathrm{H}]\mathrm{S}[\mathrm{H} + \mathrm{Cl}]\mathrm{S\text{-}Cl} \longrightarrow \mathrm{S_3Cl_2} + \mathrm{2HCl}$$

The sulphur dichloride was technical grade, supplied by Matheson, Coleman, and Bell, and was twice distilled, once immediately before use. Hydrogen sulphide was used as supplied by Matheson. The procedure differs from that given by Brauer on two points. A more efficient method of introducing the hydrogen sulphide was to condense the required volume in a pressure-equalizing, graduated separatory funnel topped by a methanol/dry ice condenser with drying tube. The liquid hydrogen sulphide was then allowed to drop into the reaction flask, and any which volatilized was recondensed and recycled. It was also found more convenient, in distilling off the bulk of the solvent, to use large flasks rather than Brauer's siphoning apparatus.

7. REACTION OF TRISULPHUR DICHLORIDE AND METHYLAMINE

The procedure is outlined by Brasted and Pond (8). In a 5 l., 3-neck flask, 2½ l. of hexane (cf. ref 8, petroleum ether "B", boiling range 60-70°) was cooled to 0° with stirring. The trisulphur dichloride from the preparation above, dissolved in hexane, was added dropwise; after 25 ml of solution had been added, passage of monomethylamine (Matheson) at a rate of 0.1 cubic feet per hour was begun. After addition of chlorosulphane was complete, the flow of methylamine was continued until the off-gases tested basic. The precipitate (methyl ammonium chloride and insoluble polymeric materials) was filtered off and the filtrate concentrated under aspirator vacuum. It was then chromatographed on a 500 g silica gel column and eluted with hexane. First off the column was a yellow oil (R_f = 0.77 vs. 0.82 for sulphur) identified as N-methyl heptasulphur imide. This was followed by the white crystals identified by Brasted and Pond as 1,5-dimethyl hexasulphur diimide; they melted at 80.5-81.5° (lit. 72-77°) and had an R_f value of 0.68. There were no other products identifiable as methyl-substituted sulphur imides; TLC of the filtrate showed a series of spots near the origin, presumably polymers of varying chain length.

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