THE SULPHUR NITROGEN BOND

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1. Lewis Acid Adducts of Tetrasulphur Tetranitride

2. Reaction of Sulphur with dl-α-Methylbenzylamine

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SCOPE AND CONTENTS:

Adducts of aluminum chloride and aluminum bromide with tetrasulphur tetranitride have been prepared and characterized. The reaction of trimethylaluminum and triethylaluminum with tetrasulphur tetranitride has been studied. The reaction of sulphur with α-methylbenzylamine has been investigated, and the reaction mechanism proposed by Sasaki for benzylamine reacting with sulphur has been found to be consistent with the data, provided certain limitations are imposed.

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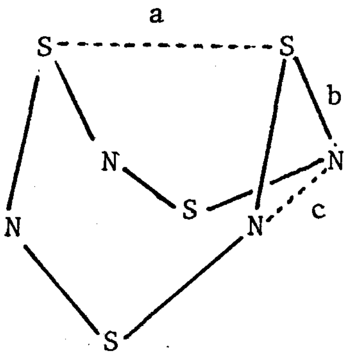
CHAPTER 1. INTRODUCTION

1. Tetrasulphur Tetranitride, S_4N_4, and Disulphur Dinitride, S_2N_2

Monomeric sulphur nitride or "THIAZYL", SN, is the sulphur analogue of nitric oxide and like nitric oxide is a radical. It has been detected in emission spectrum(1) and has been proposed as an intermediate in various reactions(2) of sulphur nitrogen compounds but has not been isolated. Three of the binary compounds between sulphur and nitrogen, S_4N_4(3), S_2N_2(4), and $(SN)_x$(5), can be regarded as polymers of the thiazyl radical. In these SN units are arranged "head to tail" without branching and with a delocalized system of multiple bonding. Other binary sulphur nitrogen compounds, including S_4N_2(3a), $S_{15}N_2$(1a), and $S_{16}N_2$(6), cannot be derived from SN. Of these tetrasulphur tetranitride is best known and has been most widely studied.

Tetrasulphur tetranitride is formed in small quantities in a great many reactions(1a). A standard method of preparation is to pass gaseous ammonia into a carbon tetrachloride solution of sulphur monochloride which has been saturated with elemental chlorine(3,7). Tetrasulphur tetranitride gives coloured monoclinic crystals(8) of density 2.23(1b). The colour changes from bright yellow at -190°C, through orange-yellow at room temperature, to orange-red at 100°C and to dark red at higher temperatures before decomposing at the melting point of 178°C. It is extremely insoluble in water but slightly soluble in many organic solvents$^{(9)}$. The molecular formula of tetrasulphur tetranitride has been thoroughly established by analysis and molecular weight determinations$^{(10,11)}$. The molecular structure is now known$^{(12)}$. In either the vapor or the solid state the molecule is a ring of alternating sulphur and nitrogen atoms bent into a bisphenoid (Fig. 1). The nitrogen atoms lie in a square plane with the sulphur atoms forming a slightly distorted tetrahedron.



a = 2.58 A

b = 1.62 A

c = 2.52 A

Fig. 1. Structure of S_4N_4

The sulphur nitrogen bond lengths within the ring are all equivalent and correspond to a bond order of roughly 1.5$^{(13)}$. The suggestion of a delocalized bonding system is supported by the abnormally high diamagnetic susceptibility which is thought to arise from a ring current $^{(14,15)}$. The S-S distances shown with dotted lines are 1.1 A shorter than the sum, 3.7 A, of two Van der Waal's radii for sulphur, implying considerable S-S bonding$^{(15)}$. It is not clear why the compound has a non-zero dipole moment$^{(16,17)}$.

Tetrasulphur tetranitride has an enthalpy of formation of 112±2 Kcal/mole$^{(18)}$. It occasionally undergoes violent decomposition, presumably to sulphur and nitrogen, on rapid heating or on grinding$^{(18)}$.

Thermal splitting of tetrasulphur tetranitride under high temperature and vacuum gives disulphur dinitride(3). Upon purification disulphur dinitride gives large colourless crystals which have a very repulsive smell and are prone to detonation. At room temperature this substance undergoes rapid polymerization(5). Disulphur dinitride is a planar 4-membered ring with alternating S-N atoms(19).

2. Reactions of S_4N_4 and S_2N_2

A. With Lewis Bases

In most cases nucleophiles appear to attack the more electropositive sulphur atoms of tetrasulphur tetranitride. In hydrolysis, for example, the nitrogen is converted to ammonia while sulphur forms a variety of oxyacids whose precise composition is dependent on the conditions(20).

Other Lewis bases which have been reacted with tetrasulphur tetranitride include amines(21,22), ammonia(23), diazomethane(24), Grignard reagents(25), phosphines(26,27), and cyanide ion(28). In many cases, the base attacks at sulphur (ammonia, secondary amines, Grignard reagents); although in some cases (triphenylphosphine and disubstituted diazomethane) both sulphur and nitrogen are proposed to undergo attack by the nucleophile. Ruff and Geisel(23) reported that tetrasulphur tetranitride and liquid ammonia gave a diammoniate of composition $S_4N_4 \cdot 2NH_3$ which, if correct, would be an acid-base adduct in which S_4N_4 functioned as the acid. Although this structure has not been completely investigated, the material has been reassigned as $S_2N_2 \cdot NH_3$ since it could also be prepared from S_2N_2 and ammonia and since careful sublimation gave back S_2N_2 and ammonia rather than S_4N_4 and ammonia(29). Diazomethanes and Grignard reagents cleave the S_4N_4 ring apparently with retention of a part of the S-N-S-N chain system(24,25), but structural evidence for the product is lacking. Cyanide ion and triphenylphosphine readily attack S_4N_4 in dimethyl formamide solution(27) removing one sulphur atom from the ring as thiocyanate and triphenylphosphine sulphide, respectively. In the latter case the other products have been isolated and shown to be $S_3N_4P(C_6H_5)_3$ and trithioformaldehyde$^{(26,30)}$. The structure of $S_3N_4P(C_6H_5)_3$ has recently been shown by Holt and Holt$^{(31)}$ to be a triphenyl phosphine group bonded through nitrogen to an S_3N_3 ring, five members of which are planar (see Fig. 2).

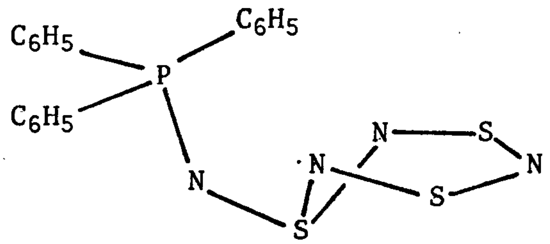
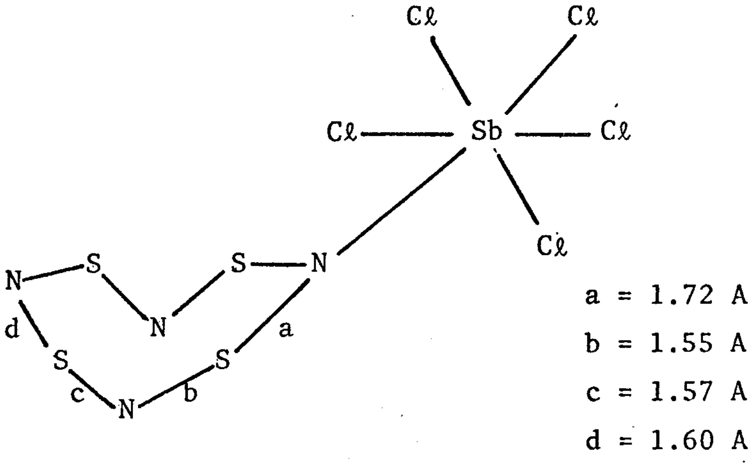


Fig. 2. Structure of $S_3N_4P(C_6H_5)_3$

In all of these cases, the original tetrasulphur tetranitride ring system was destroyed by the neucleophiles. Complexes in which S_4N_4 acts as a Lewis acid are not known.

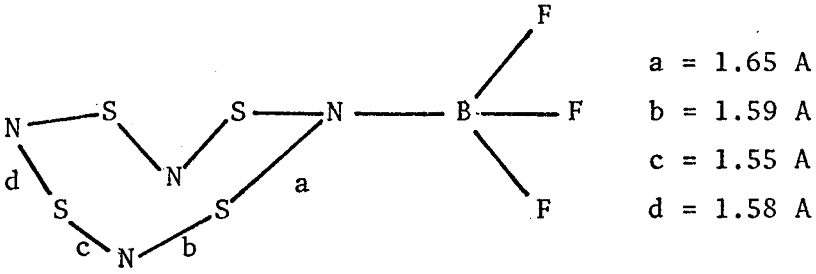
B. With Lewis Acids

With Lewis acids, tetrasulphur tetranitride forms a number of 1:1 adducts in which the nitrogen provides a lone pair of electrons. The best established adducts are $S_4N_4 \cdot SbC\ell_5$$^{(32)}$ and $S_4N_4 \cdot BF_3$$^{(33,34)}$. X-Ray crystallographic studies of these two adducts have shown that the sulphur nitrogen ring system undergoes a conformational change in forming the adduct. In both cases the four sulphur atoms are in a nearly square planar arrangement with two nitrogen atoms above and two below this plane (i.e., similar to S_4N_4 but with the S and N atoms interchanged). In the BF_3 adduct, the four atoms around the boron are approximately tetrahedral (Fig. 3 and Fig. 4).



a = 1.72 A
b = 1.55 A
c = 1.57 A
d = 1.60 A

Fig. 3. Structure of $S_4N_4SbC\ell_5$



a = 1.65 A
b = 1.59 A
c = 1.55 A
d = 1.58 A

Fig. 4. Structure of $S_4N_4 \cdot BF_3$

Other adducts reported include $S_4N_4 \cdot BC\ell_3$ (33), $S_4N_4 \cdot BBr_3$ (33), $S_4N_4 \cdot 4SbF_5$ (35), $S_4N_4 \cdot TiC\ell_4$ (36,37), $2S_4N_4 \cdot SnC\ell_4$ (36), and $S_4N_4 \cdot TeBr_4$ (38). In several of these adducts, the unusual stoichiometry suggests reinvestigation. If correct, the structure and bonding involved would be of interest. Recently, a number of transition metal halide complexes have been reported. These include $S_4N_4 \cdot VC\ell_4$ (36), $S_4N_4 \cdot WC\ell_4$ (36), $S_4N_4 \cdot MoC\ell_5$ (36), $S_4N_4 \cdot TiBr_4$, $S_4N_4 \cdot ZrC\ell_4$, $S_4N_4 \cdot NbC\ell_5$ and and $S_4N_4 \cdot TaC\ell_5$ (39). Banister, however, reacted S_4N_4 with similar transition metal halides using thionyl chloride as solvent and obtained adducts of different compositions$^{(40)}$. With S_4N_4, aluminum chloride and thionyl chloride, he obtained $S_5N_5^+A\ell C\ell_4^{-}$$^{(41)}$. The $S_5N_5^+$ ion was shown to be a nearly planar heart-shaped ten-membered ring of alternating nitrogens and sulphurs.

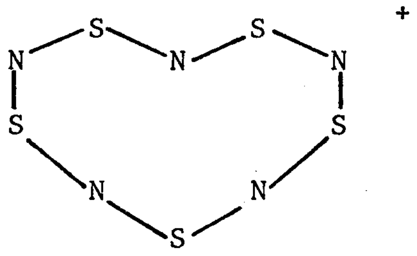
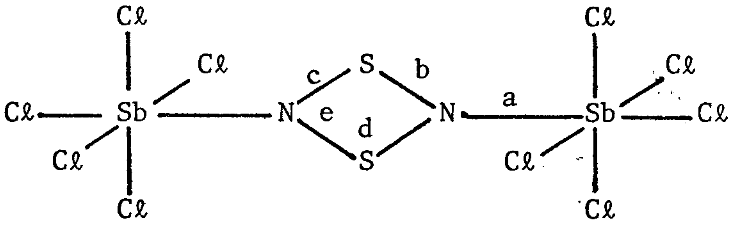


Fig. 5. Structure of the $S_5N_5^+$ ion

Jolly and Patton have recently reacted disulphur dinitride with several Lewis acids. Antimony pentachloride$^{(42)}$ and boron trihalides$^{(43)}$ were found to give adducts of composition $S_2N_2(SbC\ell_5)_2$, $S_2N_2 \cdot BC\ell_3$, $S_2N_2(BC\ell_3)_2$ and $(S_2N_2 \cdot BC\ell_3)_x$. A crystallographic study of $S_2N_2(SbC\ell_5)_2$$^{(44)}$ showed that the planar 4-membered S_2N_2 ring was intact with an $SbC\ell_5$ group bonded via the antimony atom to each nitrogen of the ring (Fig. 6).



a = 2.28 A
b = 1.62 A
c = 1.62 A
d = 84.8°
e = 95.4°

Fig. 6. Structure of $S_2N_2(SbC\ell_5)_2$

3. Aluminum Halides

Aluminum fluoride is very high melting, and its salt-like properties suggest it to be fairly ionic. It is insoluble in both polar and non-polar solvents. Chemically, it is rather inert especially compared with the other trihalides. Boiling sulphuric acid has no effect on it, and water at 400°C or fusion with potassium hydroxide decompose it only slowly$^{(45)}$.

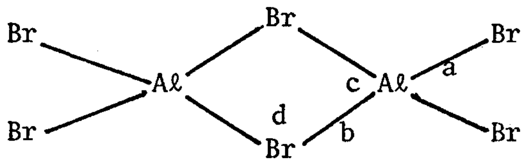
TABLE 1

Melting Points and Heat of Formation

of Aluminum Halides

	$A\ell F_3$	$A\ell C\ell_3$	$A\ell Br_3$	$A\ell I_3$
M.P. (°C)	1290	193	98	180
ΔH_f (cal/mole)		167	121	71

The other three halides are quite similar to each other but notably different from $A\ell F_3$. In the vapour near the boiling points, they are largely dimeric. At sufficiently high temperatures, dissociation into planar, triangular monomers, analogous to the boron trihalide, occurs. The structure of the dimer of aluminum bromide$^{(46)}$ is typical of the rest.



a = 2.21 A
b = 2.33 A
c = 93°
d = 87°

Fig. 7. Structure of $A\ell_2Br_6$

The configuration of halogen atoms about each metal is roughly tetrahedral. The formation of such dimers is attributable to the tendency of the metal atoms to complete their octets. They may be spilt by reaction with electron pair donors whereby complexes of the type $B:A\ell X_3$ are formed. The halides are extensively hydrolyzed in water.

With the exception of aluminum trifluoride the aluminum halides have long been used as catalysts in many electrophilic substitution reactions on organic and inorganic substrates. These reactions involve the generation of a very reactive carbonium-ion or highly polarized complex as an intermediate which leads to alkylation or acylation of the aromatic nuclei(47). Aluminum halides also form a number of 1:1 adducts with ketones, aldehydes, acid anhydrides and esters(48). Other Lewis bases which form adducts include nitrobenzene(49), phosphoryl chloride(50) and sulphuryl chloride(51). To date crystal structure work has not been reported for these adducts(48a).

In addition to forming adducts with oxygen-containing compounds, aluminum halides readily accept other electron pair donors such as olefins, nitrogen, sulphur, phosphorous and halogens(45). With alkali metal halides, stable salts of composition $M^+(A\ell X_4)^-$ are formed. Aluminum halides complex with ammonia to give aluminum halide ammoniates(52). In sulphur dioxide, Ruff(53) obtained a well-defined crystalline compound of formula $A\ell C\ell_3 \cdot SO_2$.

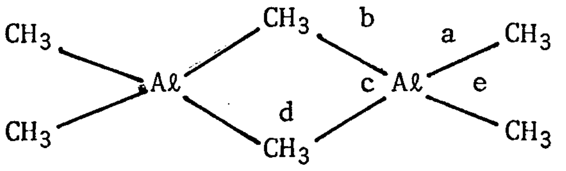
Karantassis(54) prepared $A\ell C\ell_3 \cdot 2HCN$ by adding hydrogen cyanide to aluminum chloride in a U-tube cooled in an ice and salt mixture.

4. Trimethyl and Triethyl Aluminum

A. General Properties and Reactions

Organic compounds of aluminum have attracted much attention as catalysts for the polymerization of olefins(55) and for use in the preparations of alkyl derivatives of other elements.

TRIMETHYLALUMINUM, mp. 15.0°C, bp. 126°C, is a clear mobile liquid at room temperature. It is very reactive towards nucleophiles, being explosively hydrolyzed to methane and aluminum hydroxide by cold water and taking fire instantly in air. The molecular weight, measured cryoscopically in benzene solution(56), corresponds to the dimeric formula $A\ell_2(CH_3)_6$, and a monomer-dimer equilibrium has been observed from 100°C to 160°C. The heat of dissociation to two moles of monomer is 20.2 Kcal/mole(57).



a = 1.99 A
b = 2.24 A
c = 110°
d = 70°
e = 124°

Fig. 8. Structure of $A\ell_2(CH_3)_6$

A bridged structure, analogous to that of diborane, is indicated by infrared spectra(58) and confirmed by X-ray crystal analysis(59). Recent evidence from IR and Raman spectroscopy raises the possibility of hydrogen participation in a three-center C-H-Aℓ bond in the bridging methyl group(60,61).

TRIETHYLALUMINUM, mp. -52.5°C, bp. 186.5°C, is also highly reactive and spontaneously inflammable. It is dimeric and dissociates more readily than the trimethyl derivative(57). Its properties are similar to those of trimethyl aluminum.

The characteristic reactions of organo-aluminum compounds may be grouped broadly into

(a) conversion into organoaluminums with a different degree of alkylation;

$$R_3A\ell + 2A\ell X_3 \longrightarrow 3RA\ell X_2$$

(b) isomerization;

$$(iso\text{-}C_3H_7)_3A\ell \longrightarrow (n\text{-}C_3H_7)_3A\ell$$

(c) complex formation with Lewis bases;

$$(CH_3)_3A\ell + N(CH_3)_3 \longrightarrow (CH_3)_3A\ell N(CH_3)_3$$

(d) exchange reactions with metal hydrides;

$$(C_2H_5)_2A\ell Br + LiH \longrightarrow (C_2H_5)_2A\ell H + LiBr$$

(e) conversion to other organometallic compounds;

$$R_3A\ell + 3HgX_2 \longrightarrow 3RHgX + A\ell X_3$$

(f) reactions with compounds containing active hydrogens;

$$R_3A\ell + R'OH \longrightarrow R_2A\ell OR' + RH$$

(g) oxidation;

$$R_3A\ell + 1\frac{1}{2}\,O_2 \longrightarrow A\ell(OR)_3$$

(h) reactions with the halogens, sulphur and selenium;

$$R_3A\ell + 3X_2 \longrightarrow 3RX + A\ell X_3$$

$$R_3A\ell + S \longrightarrow R_2A\ell SR$$

(i) reactions with allylethers, allylsulphides and allylamines;

$$R_3A\ell + CH_2{=}CH\text{-}CH_2NR'_2 \longrightarrow R_2A\ell\cdot NR'_2 + CH_2{=}CH\text{-}CH_2R$$

(j) reactions with compounds containing multiple bonds

(C=0, C=N, C≡N, S=0, etc.);

$$R_3A\ell + C{=}O \longrightarrow R\text{-}C\text{-}O\text{-}A\ell R_2$$

Owing to the considerable scope of this work, only those types of reactions which are relevant to the present work will be reviewed.

B. Complex Formation

Fully alkylated aliphatic organoaluminums tend to form complexes with molecules capable of donating a pair of electrons. These complexes are generally prepared by mixing equimolecular quantities of the reagents. Trimethylaluminum forms the following crystalline complexes with alkali metal fluorides(62).

TABLE 2

Melting Points of Trimethylaluminum Complexes

	M.P.
$(CH_3)_3A\ell NaF$	195°C
$[(CH_3)_3A\ell]_2NaF$	178°C
$(CH_3)_3A\ell KF$	145-150°C
$[(CH_3)_3A\ell]_2KF$	151-152°C

The following complexes of trimethylaluminum with compounds containing phosphorous, sulphur and other elements have been reported: (63,64,65,66): $(CH_3)_3A\ell N(CH_3)_3$, $(CH_3)_3A\ell P(CH_3)_3$, $(CH_3)_3A\ell O(CH_3)_2$, $(CH_3)_3A\ell S(CH_3)_2$, $(CH_3)_3A\ell Se(CH_3)_2$, $(CH_3)_3A\ell Te(CH_3)_2$. These were prepared by straight addition of the reactants. The trimethylamine trimethylaluminum complex is a white solid which melts at 105°C and the corresponding sulphide complex melts at -20°C. The stabilities of these complexes depends on the base and decrease in the order $Me_3N: > Me_3P: > Me_2O: > Me_2S:$(63,64).

C. Reactions with Compounds Containing Active Hydrogen

All organoaluminum compounds react vigorously with acids, water, alcohol, thiol, phenols and other compounds containing active hydrogen(67). All three alkyl groups are finally spilt off as hydrocarbons.

$$\begin{tikzcd} R_3A\ell + HOH \arrow[r] & R_2A\ell OH + RH \arrow[d, "H_2O"] \\ & A\ell(OH)_3 + 3RH \end{tikzcd}$$

D. Oxidation

Organoaluminum compounds are readily oxidized by oxygen; the lower aliphatic derivatives ignite spontaneously in air(68) to give products of uncertain compositions.

E. Reactions with the Halogens and Chalcogens

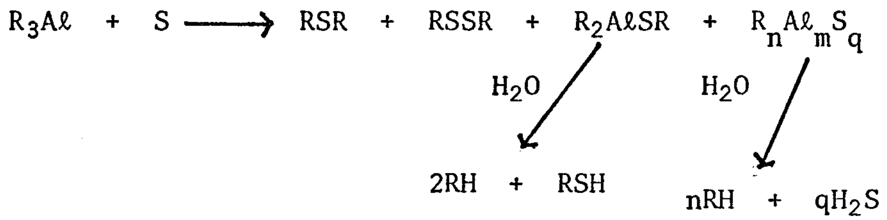
The reactions of halogens with trialkylaluminum give the corresponding alkyl halides(69).

$$R_3A\ell + 3X_2 \longrightarrow 3RX + A\ell X_3$$

The reaction of sulphur or selenium with trialkylaluminum leads to addition products such as $R_2A\ell SR$ or $R_2A\ell SeR$. These products may be distilled in vacuum without decomposition and hydrolyze rapidly with water to give the corresponding mercaptans(70).

$$R_3A\ell + S \longrightarrow R_2A\ell SR \xrightarrow{H_2O} RSH$$

Trialkylaluminum compounds react with two equivalents of sulphur to give mixtures that on distillation yield dialkylthioalkylaluminums, $R_2A\ell SR$, the corresponding mono and disulphides, R_2S and R_2S_2, and nondistillable residues(70). The residues give hydrocarbons and hydrogen sulphide on treatment with water.



5. Aims of the Present Work

Many adducts of S_4N_4 with Lewis acids have been prepared, and the structures of two of these adducts have been established. Among these Lewis acids and transition metal halides, noticeably missing members are the aluminum halides. In the one case where S_4N_4 and aluminum chloride were reacted, refluxing thionyl chloride was used as solvent and $S_5N_5^+A\ell C\ell_4^-$ obtained(41). Reactions between aluminum halides and S_4N_4 have not been investigated in organic solvents under mild conditions where possible 1:1 adducts might be stable. The reaction of tetrasulphur tetranitride with Lewis acids might also be extended to organometallic compounds although such reactions have not been reported.

The purpose of this work was to investigate the possible reactions of tetrasulphur tetranitride with aluminum halides and trialkylaluminums in organic solvents. Specifically, evidence for 1:1 complexes was sought.

CHAPTER 2. RESULTS

1. Adduct Between Tetrasulphur Tetranitride and Aluminum Chloride

A. Preliminary Observations

A series of preliminary reactions between tetrasulphur tetranitride and aluminum chloride suggested the formation of an air sensitive adduct of some sort. A red colour was observed immediately upon mixing, and a crude red solid product precipitated which gradually turned yellow on exposure to air. In order to obtain a pure sample of this material for characterization, it was necessary to carry out all reactions in an inert atmosphere. Glove bags were found to be inadequate, and the higher quality Vacuum Atmosphere Corporation's Dry Lab was consequently used for all future work.

Several solvents were investigated. Carbon tetrachloride was found to be unsatisfactory because of the low solubilities of both the product and the starting material. Methylene chloride was a good solvent for aluminum chloride, but the adduct was also quite soluble. Its low boiling point made crystallization procedures unsatisfactory. Chloroform behaved similarly to carbon tetrachloride. Ethylene dichloride appeared the most promising since it dissolved the adduct quite well, and with a bp. of 84°C provided opportunity for room temperature recrystallization.

The adduct which precipitated on mixing S_4N_4 and $A\ell C\ell_3$ was recrystallized from ethylene dichloride to give crystals which were uniformly dark red in appearance. These appeared to be both crystalline and homogeneous since an X-ray powder diagram gave a good diffraction pattern and elemental analyses were in good agreement with those calculated for a 1:1 adduct.

B. Composition of the Adduct

Analytical data for the complex are given in Table 3. The nitrogen and chlorine analyses were performed by Schwarzkoff Microanalytical Laboratory. Sulphur analyses from that laboratory were, however, consistently low by very nearly 25% of the total sulphur suspected to be present. Aluminum is known(71) to interfere with sulphur determination by the EDTA titration method used by Schwarzkoff. Since approximately one g atom of sulphur appeared to be missing for each g atom of aluminum presumed present, such interference was strongly suspected. Further inquiries into the method revealed that the sulphur was determined by back titration of excess barium chloride with standard EDTA solution

TABLE 3

Analytical Data for $S_4N_4 \cdot A\ell C\ell_3$

Element	Calcd.	Found
S	40.4	40.5
N	17.6	16.0
Cℓ	33.6	34.2
Aℓ	8.5	8.4
Total	100.1	99.1

using Erichrome Black T as indicator(72). This method is, however, a common procedure for the determination of aluminum(71). Therefore, its presence would obviously interfere with the back-titration of the barium chloride solution with EDTA. Each mole of $A\ell^{+++}$ present should mask 1 g atom of sulphur. This was verified in the laboratory, and consequently another method for determination of sulphur was sought.

Anderson(72a,73) precipitated sulphate as benzidine sulphate which was dissolved in dilute hydrochloric acid and analyzed spectrophotometrically at 250 mμ. This method was tried and found to be unsatisfactory. Applications to various known standards (thiourea, tetrasulphur tetranitride, sulphur) did not give consistent sets of calibration curves. Simple gravimetric analysis, although tedious and "old-fashion", nevertheless was found to give reliable and consistent results. A weighed sample was burned inside a combustion flask which had been flushed with oxygen and contained a small amount of hydrogen peroxide. All sulphur was thereby oxidized to SO_4^{--} ions. This was precipitated and weighed as barium sulphate in the usual manner(71). This method was run on S_4N_4 as a known standard and various quantities of $A\ell^{+++}$ were added. In all cases satisfactory results were obtained in both the absence and presence of $A\ell^{+++}$. $A\ell^{+++}$ to S ratios up to 1:1 were investigated. All sulphur analyses reported in this thesis are based on this method.

Aluminum determinations were carried out by neutron activation analysis using the McMaster rabbit system swimming pool reactor which has an available thermal neutron flux of about 10^{13} neutrons cm^{-2} s^{-1} at a reactor power of 2MW. The γ counts of $A\ell^{28}$ from the sample was compared with a standard, and the percentage of Aℓ in the sample thereby calculated. Once the analytical problems were solved, quite good agreement was obtained between the experimentally observed composition and that calculated based on a simple 1:1 adduct (see Table 3).

C. Decomposition to S_4N_4

The adduct was found to decompose slowly in air. A TLC of the decomposed product showed the presence of S_4N_4. Consequently, a quantitative decomposition was carried out to ascertain the amount of tetrasulphur tetranitride formed. This was done by exposing a weighed sample of adduct to the air for five days. The yellow product was then extracted repeatedly with benzene. The quantity of tetrasulphur tetranitride obtained on evaporation of the solvent gave the weight of S_4N_4 produced. In this manner 1 mmole of adduct was found to give 0.95 mmole of S_4N_4 or 95% of that expected for the 1:1 adduct required by the analysis. It therefore appears likely that the 8-membered S_4N_4 ring remains intact in the adduct. The other products of the decomposition were presumably aluminum hydroxide and hydrogen chloride.

At 100°C the adduct decomposed to a gummy material which appeared polymeric. Attempts to sublime either this product or the adduct were unsuccessful.

D. IR Spectrum and Structure of the Adduct

The vibrational spectra of tetrasulphur tetranitride have been studied by Bragin and Evans(74). Comparison of infrared and Raman frequencies with those from a valence force field calculation led them to an assignment of the 12 observed fundamentals, seven of which are infrared active. Of particular interest are the 6 N-S stretching fundamentals. Two of these (of A_1 and B_1 symmetry) are active in the Raman only, and a third (the A_2 band) is inactive both in infrared and Raman spectra. The remaining three bands are a strong B_2 vibration at 705 cm^{-1} and the vibrations of E symmetry at 766 cm^{-1} (very weak) and 938 cm^{-1} (strong). Of these the latter strong vibration at 938 cm^{-1} (925 cm^{-1} in solid) has historically been referred to as "the S-N stretch". The assignment of this band to an S-N stretch is in good agreement with the empirical criteria of Banister(75) et al who found a relationship between S-N stretching frequencies and S-N bond lengths. The S-N bond length in S_4N_4(8) is 1.616 A. Using Banister's empirical relationship

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

where μ_{SN} is wavelength in microns and r_{SN} is the bondlength in A, leads to a predicted stretching frequency of about 940 cm^{-1} for "the S-N bond".

An X-ray study on the complex of $SbC\ell_5$ with S_4N_4(32) indicated that the structure of S_4N_4 is changed rather considerably on co-ordination although the ring remains intact (see Fig. 3). The S-N distance for the co-ordinated nitrogen is 1.72 A suggesting (via the above equation) that an S-N stretching frequency at 780 cm^{-1} should appear in the $SbC\ell_5$ complex. A strong band is observed at about 785 cm^{-1}, and it seems quite reasonable to assign this to "the S-N stretching frequency" associated with the coordinated nitrogen. Similarly, strong bands at around 965 cm^{-1} to 1070 cm^{-1} are expected for the S-N stretching frequencies of the shorter S-N bonds of 1.60 A to 1.55 A. Bands are observed in this region in the $SbC\ell_5$ complex (see Table 4). Extending the same calculation to the $S_4N_4 \cdot BF_3$ adduct whose structure has also been crystallographically determined (see Fig. 4), there is also good agreement between the calculated stretching frequency (880 cm^{-1}) for the co-ordinated S-N bond and the observed band at 888 cm^{-1} (see Table 4).

In the IR spectrum of the aluminum chloride adduct (see Table 4 and Fig. 9) there are strong bands at 1045 cm^{-1}, 960 cm^{-1}, and 860 cm^{-1}. Based on the success of Banister's relationship between stretching frequencies and bond lengths in the $SbC\ell_5$ and BF_3 complexes where the bond lengths are known, these three bands might be assigned to S-N stretching absorptions which are very similar in character (i.e., bond lengths) to those in the $SbC\ell_5$ and BF_3 complexes. Thus, the band at 860 cm^{-1} could be assigned to the S-N stretching frequency of a co-ordinated nitrogen. The difference of 75 cm^{-1} compared to the S-N stretching in the $SbC\ell_5$ adduct corresponds to a decrease of about 0.08 A in N-S bond length, a result which is not unreasonable. Similarly, the bands at 1045 cm^{-1} and 960 cm^{-1} are most likely the N-S stretching frequencies associated with the shorter N-S bonds of the uncomplexed end of the molecule.

Further evidence for a nitrogen co-ordinated adduct is provided by a band at approximately 500 cm^{-1} in the spectra of $A\ell X_3 \cdot nNH_3$, where X = $C\ell$, Br, and I(76). This has been assigned to an N-$A\ell$ stretching vibration. A similar strong band at about 500 cm^{-1} occurs in the $A\ell C\ell_3$ adduct and can be similarly assigned.

It therefore appears quite likely that in the 1:1 adduct between aluminum chloride and tetrasulphur tetranitride, the Lewis acid is co-

TABLE 4

Infrared Spectra of Adducts of S_4N_4

S_4N_4 (74)		$S_4N_4 \cdot SbCl_5$ (33)	$S_4N_4 \cdot BF_3$ (33)	$S_4N_4 \cdot AlCl_3$	$S_4N_4 \cdot AlBr_3$
Solution	Solid				
		345 s		320 (w)	
		364 s			
				340 (w)	
	347 (s)	371 s			350 (w)
330 (m) b				360 (w)	
					380 (s)
		413 m		400 (s)	
			420 m-s		440 (w)
519.3(w) b	519.3 (w)				
	529.7 (w)			470 (s)(sh)	480 (s)
			490 wsh		
		513 ms	502 m		
	552.2 (s)				
556.5(m) b			527 s	500 (s)	
					515 (s)
			552 w	540 (w)(sh)	
			567 w	570 (w)(sh)	
		625 m	623 m-s		
				620 (m)	
			658 m-s		
			682 vw	675 (w)	
702 (m) s	701 (vs)		697 wv		
		705 w		700 (m)	715 (w)
705(vs) d					
	726 (s)		724 wv	720 (w)	
	760 (w)				
		765 wsh		750 (m)	
	766 (w)				770 (m)
		785 s			
	798 (w)				
		808 m			
		821 ms			830 (s)
				860 (s)	850 (s)
			888(s)		
			908 m		
	925 (s)			925 (m)	
938 (s) d			949 (s)	960 (s)	950 (s)
		978 ms			
				990 (m)	
	1007 (w)				
	1046 (w)			1045 (s)	1035 (s)
		1040 msh	1040 (vs)		
	1067 (w)	1060 (s)	1070 (s)		
			1117 (s)		

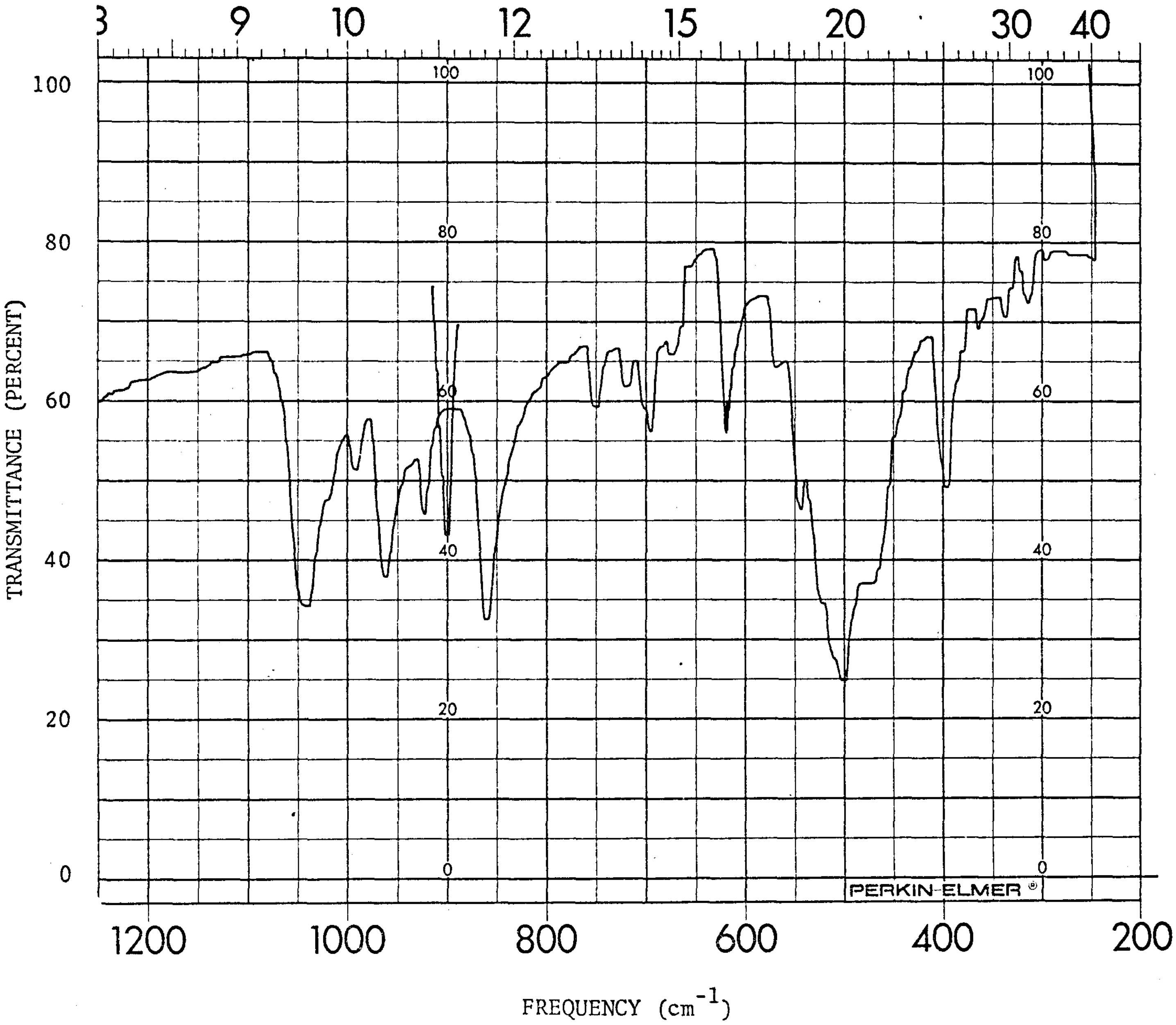


Figure 9. IR Spectrum of $S_4N_4AlCl_3$.

ordinated through the nitrogen giving a product whose structure as shown in Fig. 10 is very similar to those of the SbF_5 and BF_3 adducts.

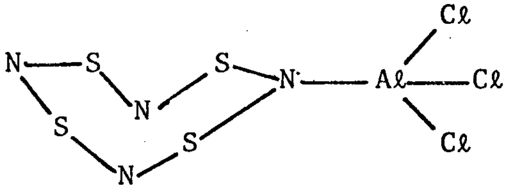


Fig. 10. Proposed structure of $S_4N_4 \cdot A\ell C\ell_3$

2. Adduct between Tetrasulphur Tetranitride and Aluminum Bromide

A. Halide Exchange with the Solvent

The reaction of S_4N_4 with aluminum bromide was expected to be similar to that with aluminum chloride. Addition of S_4N_4 to a solution of $A\ell Br_3$ in 1,2-dichloroethane did not lead to a similar product, however, but rather to one whose IR spectrum, X-ray powder diagram and sulphur analysis were identical to those of $S_4N_4 \cdot A\ell C\ell_3$. This result should probably not have been altogether unexpected since exchange of halide between $A\ell Br_3$ (free or in the adduct) and the chlorinated solvent might have been anticipated. A bromine containing adduct could be prepared when a brominated solvent was used. Thus, employment of 1,2-dibromoethane led to a product similar to, but different from, the 1:1 adduct described for the reaction with aluminum chloride.

The exchange of halides with the chlorinated solvent could have occurred before or after co-ordination of the S_4N_4. To established which, a sample of the bromide adduct was refluxed in ethylene dichloride for 36 hours. After removing the solvent, no chloride adduct was detected. Therefore, exchange of halide most likely occurs between the free aluminum halide and the solvent prior to complex formation.

B. Composition of the Adduct

The elemental analysis (Table 5) was in good agreement with that expected for a 1:1 adduct.

TABLE 5

Analytical Data for $S_4N_4A\ell Br_3$

	Calcd. %	Found %
S	28.3	28.4
N	12.4	12.0
Br	53.3	53.4
$A\ell$	6.0	5.6

C. Decomposition to S_4N_4

This adduct also decomposed slowly in air to give S_4N_4. A controlled quantitative decomposition of 0.382 mmole of this adduct gave 0.351 mmole of S_4N_4 representing a recovery of 92% of the total S_4N_4 present based on a 1:1 adduct. This again indicates that the sulphur nitride ring is intact and that the structure is probably similar to that of the chloride adduct. Like the chloride, the bromide hydrolyzes nearly instantaneously in water to give a more complex series of products which were not identified.

The decomposition temperature of the bromide was 125°C, and again there was some indication that the decomposed gummy product was polymeric.

D. IR Spectrum and Structure of the Adduct

The IR spectrum of this adduct had fewer bands than the corresponding chloride. However, as in the chloride, strong bands appear at 1035 cm^{-1}, 950 cm^{-1}, 850 cm^{-1} and around 480 cm^{-1} - 520 cm^{-1} (see Table 4 and Fig. 11). As in the chloride, these can be assigned to co-ordinated and not co-ordinated S-N stretching and to $A\ell$-N stretching

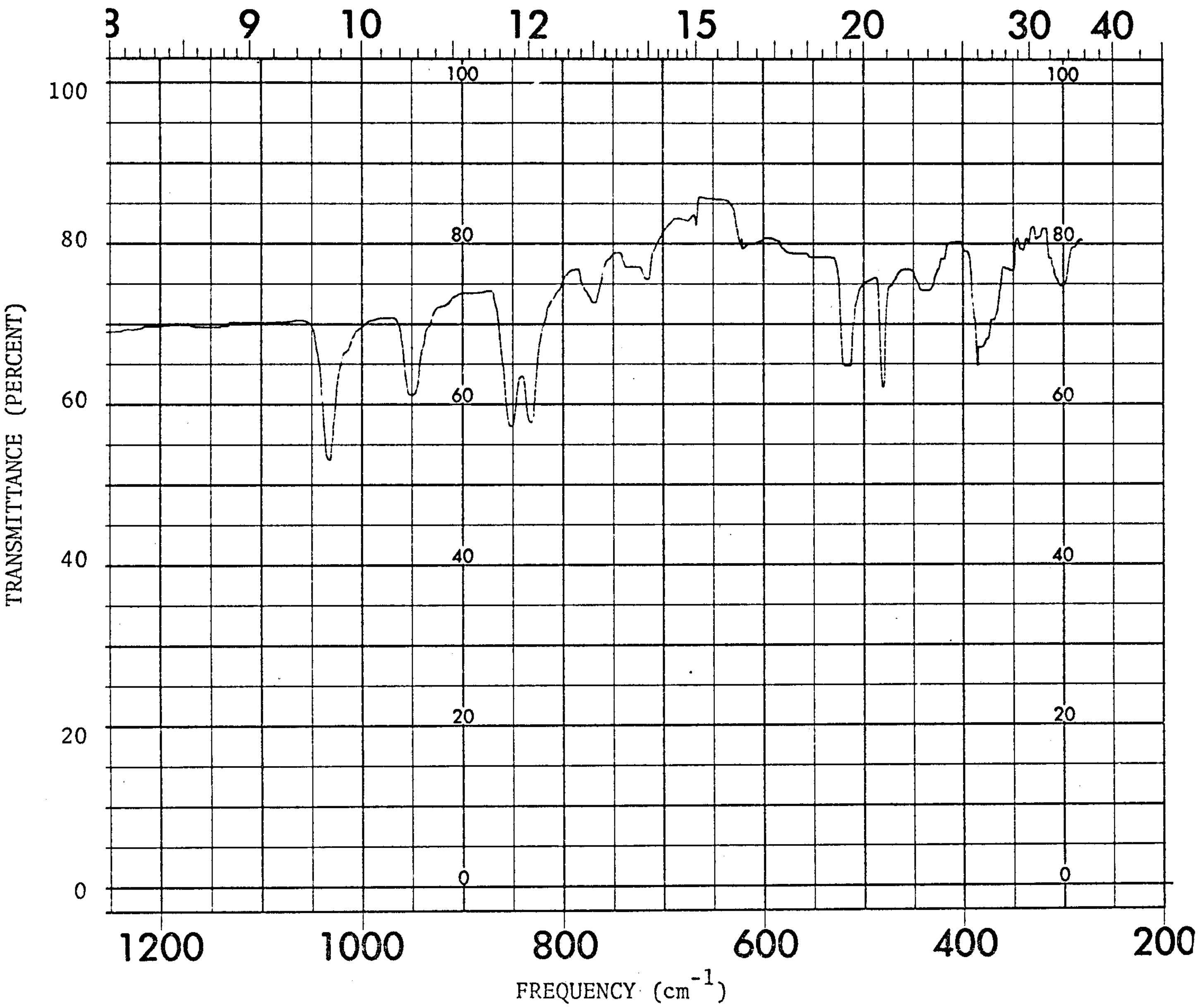


Figure 11. IR Spectrum of $S_4N_4AlBr_3$.

frequencies.

Therefore, it appears that both halides react similarly with S_4N_4 to give 1:1 adducts where the S_4N_4 ring is intact and coordination is through the nitrogen atom.

3. Reactions between Tetrasulphur Tetranitride and Trialkylaluminums

A. Composition of the Products

Because of the differences in reactivities of Aℓ-C and Aℓ-hal bonds and the extreme sensitivity of trialkylaluminum compounds to air, they might react towards tetrasulphur tetranitride in ways other than as simple Lewis acids. In fact the reactions of trimethyl and triethyl aluminum with tetrasulphur tetranitride did not give any products that could be identified as 1:1 adducts. The products isolated from these two reactions were quite similar (to each other) but were quite different from those isolated from reactions with the aluminum halides.

Elemental analysis (shown in Table 6) for the two products did not total 100%. Calculated empirical formulae from these compositions were not simple. For example, the trimethyl aluminum product (based on 1.0 for aluminum) has the composition $(S_{1.5}N_{1.9}A\ell_{1.0}C_{2.5}H_{8.2})$ and the triethyl aluminum product has the composition $(S_{2.6}N_{3.0}A\ell_{1.0}C_{3.1}H_{9.1})$. Note particularly that the S to N ratio is not 1:1 in either product, that the C to H ratios are not 1:3 and 2:5, respectively, and that the Aℓ:S and Aℓ:N ratios are not constant in the two cases.

The presence of oxygen in the products is a possibility although considerable care was taken to exclude it during the experiments. Perhaps a more logical explanation lies in the behaviour of the samples during the analytical procedure. The products have high melting points and explode when burned in a combustion flask leaving a white residue. The explosion probably leads to incomplete oxidation as the white

TABLE 6

Analytical Data for Reaction Products of S_4N_4 with $A\ell R_3$

	$A\ell(CH_3)_3$			$A\ell(C_2H_5)_3$		
	Calcd. Ratio $S_4N_4/A\ell R_3$		Found	Calcd. Ratio $S_4N_4/A\ell R_3$		Found
	1:1	1:2		1:1	1:2	
Aℓ	10.5	16.5	17.50	9.0	13.1	12.50
S	50.0	39.0	33.03	43.0	31.0	39.32
N	21.8	17.0	17.36	18.7	13.6	19.73
C	14.1	22.0	19.72	24.2	35.0	17.50
H	3.5	5.5	5.34	5.0	7.3	4.23
Total	99.9	100.0	92.95	99.9	100.0	94.28

residue is non-combustible. These factors could well contribute to an incomplete, inconsistent and meaningless analyses. In agreement, duplicate analysis for sulphur using progressively larger sample sizes led to progressively lower and lower apparent sulphur compositions. Another possible explanation for erratic analytical results lies in the purity of the products. They could have been mixtures of several products. Their low solubilities, high melting points and air sensitivities made purification processes very difficult. Samples of these materials did not give X-ray powder patterns. The products when prepared in ethylene dichloride were slightly different in appearance with those obtained from carbon tetrachloride although their apparent compositions and general properties were similar. Those prepared in ethylene dichloride were dark red solid masses and could be broken into small transparent granules. A small percentage of chloride, 1.5%, was detected by neutron activation analysis. When this product was ground into powder, it was no different in appearance than the yellow amorphous clay-like product obtained from carbon tetrachloride. Apparently, the solvent was trapped inside the substance and could not be easily removed even in vacuum. The possibility that the sample submitted to analysis was not homogeneous can also not be ruled out.

B. Decomposition Products

Both products obtained had very high melting points, well above 250°C and had very repugnant odours. On exposure to air, they decomposed slowly leaving a white residue. No S_4N_4 or S was formed in these reactions. With water they hydrolyzed violently, giving off ammonia, hydrogen sulphide and possibly other gases. In larger quantity they sometimes ignited spontaneously. Inside a combustion flask, the compounds exploded when burned leaving a white residue. Products from both the combustion and hydrolysis were insoluble in organic solvents and dilute acids and bases, but soluble in concentrated potassium hydroxide.

C. Spectra of the Products

The IR spectra of these reaction products were not well defined and showed only very broad absorptions. Apart from C-H stretches, no bands could be assigned. Their insolubilities prevented obtaining meaningful NMR spectra.

Although these substances were more or less crystalline in appearance, they failed to give a powder pattern when subjected to X-rays (see page 31).

Therefore, it appeared that S_4N_4 reacted with the trialkylaluminums in a very different manner than with the aluminum halides. The products did not appear to be simple adducts and their structures and compositions have not been defined. Inability to obtain reproducible and meaningful analytical data precluded further characterization of these "materials". It appears very likely, however, that the N-S ring system has been destroyed in the reaction.

CHAPTER 3. DISCUSSION

1. Aluminum Halide Adducts

The formation of 1:1 adducts between S_4N_4 and $A\ell X_3$ has been demonstrated. Their structures appear to be the same as those of several other Lewis acid adducts previously reported(16,6,7,8). These materials are quite different than those obtained by Banister(41) using thionyl chloride as solvent - i.e., $S_5N_5^+A\ell C\ell_4^-$. The presence of the tetrachloroaluminate anion in Banister's product suggests that S_4N_4 reacted with the thionyl chloride to form $S_5N_5^+C\ell^-$ and that the principle role of the $A\ell C\ell_3$ was to stabilize this product by complexing the chloride anion. This reaction may quite possibly involve no coordination in the Lewis acid-Lewis base sense other than stabilization of the chloride ion. In a separate publication(40) Banister also investigated other metal halides with tetrasulphur tetranitride in thionyl chloride and reported products of the types (a) $SNMC\ell_2$, (b) $S_2N_2MC\ell_n$ and (c) $S_3N_3SbC\ell_6$. No structural information on these compounds is available. Goehring(77) reacted nickel, cobalt and palladium with S_4N_4 in methyl and ethyl alcohol and obtained products which were formulated as simple 1:1 adducts of S_4N_4M. However, subsequent work by Piper(78), who reinvestigated the reaction of S_4N_4 with nickel chloride, has shown that they were actually mixtures of three compounds: $NiS_4N_4H_2$, NiS_5N_3H and NiS_6N_2. The following structure for $NiS_4N_4H_2$ was proposed:

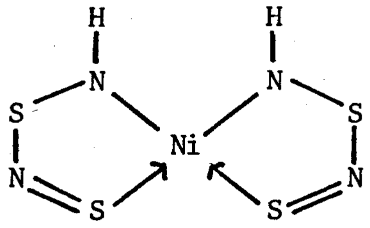


Fig. 12. Structure for $NiS_4N_4H_2$

The chemistry and properties of the aluminum halide adducts resemble to some extent the BF_3 adduct previously prepared by Wynne & Jolly(33). The boron trifluoride adduct was fairly labile decomposing reversibly to S_4N_4. The BF_3 in the adduct could be replaced by other Lewis acids such as $SbC\ell_5$ or $BC\ell_3$. This was a two-step reaction, however, with a yellow precipitate of $S_4N_4 \cdot BC\ell_3 \cdot SbC\ell_5$ formed as an intermediate. Vacuum pyrolysis of this mixed adduct led to loss of one of the ligands. A preliminary study of the displacement of $A\ell C\ell_3$ from $S_4N_4 \cdot A\ell C\ell_3$ by $SbC\ell_5$ indicated that a new mixed adduct was formed whose IR spectrum (Fig. 13) was different from both the $A\ell C\ell_3$ and $SbC\ell_5$ adducts. This material was formed either from $SbC\ell_5$ and $S_4N_4 \cdot A\ell C\ell_3$ or from $S_4N_4 \cdot SbC\ell_5$ and $A\ell C\ell_3$. Pyrolysis of the material formed from $S_4N_4 \cdot A\ell C\ell_3$ and $SbC\ell_5$, under high vacuum yielded some $S_4N_4 \cdot SbC\ell_5$ which was identified by IR spectroscopy. No $S_4N_4 \cdot A\ell C\ell_3$ was detected. Thus, it was likely that a similar diadduct of $S_4N_4 \cdot A\ell C\ell_3 \cdot SbC\ell_5$ had been formed.

The assignment of IR spectral bands in the aluminum chloride adduct (see Results) showed that there was a shift to higher energy of 75 cm^{-1} in the S-N stretch in going from 785 cm^{-1} to 860 cm^{-1}. The increase in the S-N stretching frequency of the co-ordinated nitrogen corresponds to a decrease of about 0.08 A in the N-S bond length compared to the

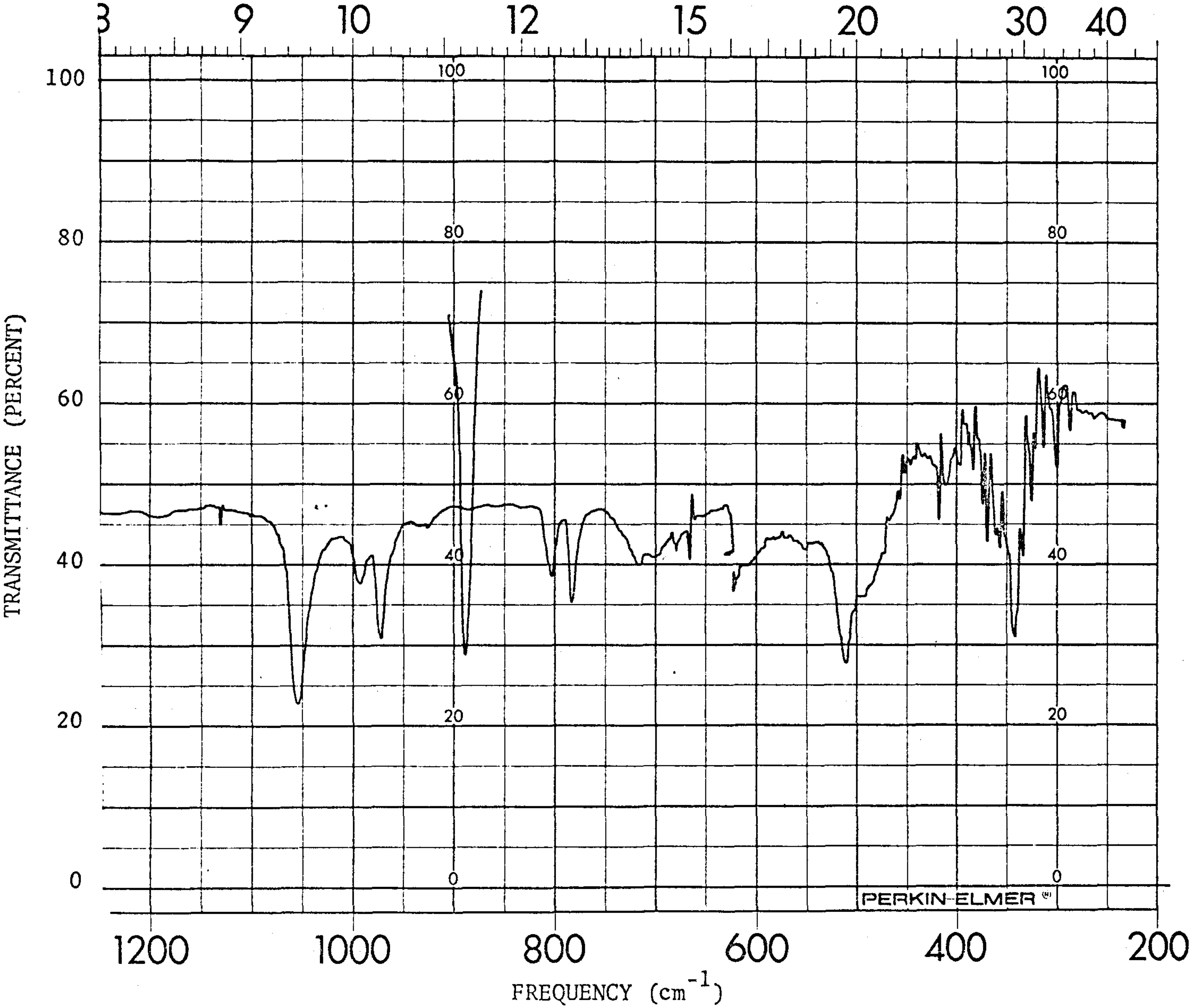


Figure 13. IR Spectrum of $S_4N_4AlCl_3SbCl_5$.

$SbC\ell_5$ complex.

The $S_4N_4 \cdot BF_3$ adduct decomposed reversibly to S_4N_4 and BF_3 under vacuum, but this was not the case with the aluminum halide adducts. An attempted high vacuum sublimation led to decomposition. Therefore, $S_4N_4 \cdot A\ell C\ell_3$ did not have an appreciable vapour pressure and the dissociation constant was quite small - i.e., the formation constant was appreciably higher than that for $S_4N_4 \cdot BF_3$. A high formation constant was also indicated by an experiment (page 19) which showed that $S_4N_4A\ell Br_3$ did not undergo halide exchange with ethylene dichloride even under reflux conditions. Since $A\ell Br_3$ was found to exchange completely with ethylene dichloride at room temperature, there can be very little free aluminum bromide present under these conditions. The first equilibrium below must lie very far to the left.

$$\begin{tikzcd}
S_4N_4A\ell Br_3 \arrow[r, shift left, harpoon] & S_4N_4 \arrow[l, shift left, harpoon] & + & A\ell Br_3 \arrow[d, shift left, harpoon] \arrow[d, phantom, "C_2H_4C\ell_2"' near start, shift right=4ex] \\
S_4N_4A\ell C\ell_3 \arrow[r, shift left, harpoon] & S_4N_4 \arrow[l, shift left, harpoon] & + & A\ell C\ell_3 \arrow[u, shift left, harpoon]
\end{tikzcd}$$

2. Trialkylaluminum Products

Tetrasulphur tetranitride and trialkylaluminum do not form any simple adducts similar to the aluminum halides although the actual products have not been identified. Lack of good analytical data was the main deterrent to further work.

Very little is known of the structure and nature of these products. Even without reliable analytical data, one point seems certain, the sulphur nitride ring has been cleaved. Whether the S-N-S-N chain system is retained as with Grignard reagents(25) and diazomethane(24) is not known. Both sulphur and nitrogen were present in the products.

The solids hydrolyzed violently in water to give ammonia, hydrogen sulphide, mercaptans and possibly other gases. These are similar to organoaluminum compounds to which sulphur has been added in so far as production of mercaptans are concerned. A possible explanation might be that they represent incomplete addition products similar to the dialkylthioalkylaluminum or perhaps "dialkylthioazylalkylaluminum". This is, of course, only a wild guess.

CHAPTER 4. EXPERIMENTAL SECTION

1. Instruments

A. Nuclear Magnetic Resonance Spectra

Proton NMR spectra were recorded on a Varian Associates, Model T-60 NMR spectrometer using reagent grade carbon tetrachloride as solvent and tetramethyl silane as an internal standard reference.

B. Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer IR 521 spectrophotometer. Samples were prepared as nujol or fluorolube mulls and run between Cesium Iodide plates.

C. X-Ray Powder Patterns

X-ray powder patterns were recorded on a cylindrical camera with diameter of 114.6 cm on a Phillip's generator with a Cu source. The films were exposed for 10 hrs with a nickel filter.

D. Elemental Analysis

Carbon, hydrogen, nitrogen, and halogen analyses were performed either by Schwarkzkopf Microanalytical Laboratory (56-19, 37th Avenue, Woodside, N.Y. 11377) or Alfred Bernhardt Mikroanalytisches Laboratorium (5251 Elbach uber Engelskirchen, Fritz-Pregl-Strasse 14-16, West Germany). Sulphur analyses were done in the laboratory by gravimetric analysis as barium sulphate (see page 51). Aluminum analyses were obtained by neutron activation analysis with the help of Mr. P. Y. Wong. About

10-20 mg of sample was accurately weighed and irradiated for 10 sec. The γ counts of the sample were compared with a standard and its aluminum content calculated. Under these conditions, the analysis was free of any chemical separation and by optimizing the irradiation time, the interferences of sulphur and chloride were eliminated(79). This type of analysis has a relative error of ±0.5%.

E. Melting Points

Melting points were measured on a Thomas Hoover capillary melting point apparatus in capillaries sealed under nitrogen and are uncorrected.

F. Dry Box

The handling of air-sensitive aluminum compounds was carried out in a Vacuum Atmosphere Corporation Dry Lab Model HE-43 equipped with Dry Train Model HE93B.

2. Reagents

A. Solvents

Reagent grade solvents were used throughout. Carbon tetrachloride and all other halogenated hydrocarbons were refluxed over phosphorous pentoxide for six hours and distilled prior to use. To prevent absorption of moisture, they were stored inside the dry box until used.

B. Tetrasulphur Tetranitride

Tetrasulphur tetranitride was prepared from sulphur monochloride and ammonia in the usual manner(5) with the slight modifications suggested by Sasaki(80). After recrystallization from benzene, the m.p. was 178° C *d*. Lit.(16) 179°C.

C. Aluminum Halides

Aluminum chloride and aluminum bromide were BDH reagent grade, and were purified by vacuum sublimation immediately prior to every reaction.

D. Trialkylaluminum

The neat trialkylaluminums were supplied by Alfa Inorganics Inc. in 225 gm cylinders. They were used without further purifications.

3. Chromatography

A. Thin Layer Chromatography

Glass plates coated with 0.25 mm layers of Silica Gel GF_{254} (E. Merck, Germany) were prepared in the usual manner(81). They were dried in air for at least 18 hours prior to use. The eluent used was methylene chloride with elution being allowed to proceed through a distance of 15 cm. The plates were examined under an ultraviolet lamp and were also developed by spraying with an aqueous solution of silver nitrate. As the activity of the plates varied slightly from day to day, a standard reference mixture consisting of S_8, S_7NH, $S_6N_2H_2$ and S_4N_4 was spotted on each plate along with the sample. R_f values were calculated in the usual manner(81).

B. Column Chromatography

Column chromatography was used to separate reaction mixtures. The absorbent used was silica gel (Grace 100-200 mesh). The ratio of absorbent to sample was in the range of 20:1 to 75:1. Eluents were hexane, benzene, ether, methanol and various mixtures of these.

Fractions of 100 ml were collected and solvents stripped on a rotary evaporator. Tared flasks were used so that the weight of each fraction could be determined.

4. Reaction of Tetrasulphur Tetranitride with Aluminum Chloride

Freshly sublimed aluminum chloride (0.88 gm, 6.4 mmole) was added to 50 ml of dry ethylene dichloride in a 100 ml round bottom flask. This solution was stirred at room temperature while tetrasulphur tetranitride (1.21 gm, 6.4 mmole) was added. The reaction mixture immediately turned dark red. After stirring for 5 hours, no undissolved tetrasulphur tetranitride remained. The solution was then filtered into another round bottom flask giving a clear dark solution. The flask was then taken out of the dry box and the volume of the solvent was reduced under vacuum until precipitation began. The flask was then heated on a steam bath under pressure (i.e., with an air tight screw cap) until all the crude product redissolved to give a clear dark red solution. The solution was allowed to stand overnight in the refrigerator whereupon dark red crystals were obtained. These were filtered inside the dry box and dried under vacuum. The product was a dark red crystalline material which decomposed at 100°C in a sealed tube.

On exposure to air, the adduct slowly turned yellow and became sticky. Extraction of this decomposed substance with benzene showed the presence of S_4N_4 ($R_f = 0.25$; CS_2 as eluent - R_f of authentic S_4N_4 is 0.25). On contact with water, the adduct hydrolyzed rapidly to give a dark green slime.

Elemental analysis are given in Table 3, (page 17), and IR data are in Table 4 (page 22) and Fig. 9 (page 23). The X-ray powder pattern was as follows:

d (A)	5.70	5.29	4.43	3.39	3.24	3.08	2.94	2.75
I	100	100	40	60	40	90	60	20

5. Reaction of Tetrasulphur Tetranitride with Aluminum Bromide in Ethylene Dichloride

Freshly sublimed aluminum bromide (3.14 gm, 11.8 mmole) was added to 50 ml of dry ethylene dichloride in a 100 ml round bottom flask. To this stirred solution was added 2.16 gm (11.8 mmole) of tetrasulphur tetranitride. The reaction mixture immediately turned dark red and was left stirring for 5 hours until no visible tetrasulphur tetranitride remained undissolved. The solution was then filtered into another flask giving a clear dark red solution. The work-up of the product was as described for the aluminum chloride reaction.

The product obtained was similar in appearance to that obtained from the aluminum chloride reaction and had a m.p. of 95°C. It contained 40.4% sulphur and the IR spectrum was identical to the aluminum chloride adduct.

6. Reaction of Tetrasulphur Tetranitride with Aluminum Bromide in Ethylene Dibromide

Freshly sublimed aluminum bromide (6.49 gm, 24.4 mmole) was added to 50 ml of dry ethylene dibromide in a 100 ml round bottom flask. To this stirred solution was added 4.53 gm (24.4 mmole) of tetrasulphur tetranitride. The reaction mixture slowly turned orange red and was left stirring overnight. The solution was then filtered into another round bottom flask giving a clear orange red solution. Work-up, as described for the chloride, led to orange crystals which were collected by filtration inside the dry box and dried under vacuum. The product was an orange red shiny powder which decomposed at 122±2°C. Elemental analyses are given in Table 5, page 26. On exposure to air, the adduct slowly turned yellow and became sticky. On extraction of this decomposed substance with benzene, S_4N_4 was obtained and identified by TLC ($R_f = 0.25$; CS_2 as eluent). On contact with water, the adduct hydrolyzed rapidly to give a dark green slime. The IR spectrum is given in Fig. 11, page 27 and Table 4, page 22. The X-ray powder pattern was as follows:

d (A)	7.40	5.70	4.81	4.33	3.30	3.10	2.85	2.66	2.01	1.84	1.76
I	10	10	40	40	20	100	20	10	10	10	10

7. Reaction of Tetrasulphur Tetranitride Aluminum Chloride with Antimony Pentachloride

Tetrasulphur tetranitride aluminum chloride (0.85 gm, 2.65 mmole) was weighed into 20 ml of dry carbon tetrachloride in a 50 ml round bottom flask. This solution was stirred at room temperature while 0.90 gm (3.0 mmole) of antimony pentachloride was added. After stirring for 5 hours, the solution was filtered, the product was thoroughly washed with fresh carbon tetrachloride to remove any excess or unreacted antimony pentachloride and dried under vacuum. The resulting product was a light brown powder whose IR spectrum is shown on page 35, Fig. 13. This light brown powder was placed in a sublimation apparatus and heated under vacuum to 120°C whereupon traces of $S_4N_4SbC\ell_5$ collected on the cold finger. The antimony pentachloride was identified by IR spectra. The decomposed residue was mainly S_4N_4 and some polymeric adduct of $S_4N_4A\ell C\ell_3$.

8. Reaction of Tetrasulphur Tetranitride Antimony Pentachloride with Aluminum Chloride

A sample of $S_4N_4SbC\ell_5$ was prepared according to the method described by Jolly et al (33). Aluminum chloride (0.50 gm, 3.17 mmole) and 1.50 gm (3.17 mmole) of $S_4N_4SbC\ell_5$ were mixed and stirred in 20 ml of dry carbon tetrachloride in a 50 ml round bottom flask for 5 hours. The solution was then filtered, and the product was collected, washed and dried under vacuum. The product obtained had the same appearance as that obtained from $S_4N_4A\ell C\ell_3$ and $SbC\ell_5$. The IR spectrum was found to be identical to that obtained from the previous experiment.

9. Reaction of Tetrasulphur Tetranitride with Trimethyl Aluminum

Tetrasulphur tetranitride (0.96 gm, 5.28 mmole) was added to 50 ml of dry ethylene dichloride in a 100 ml round bottom flask in the dry box. To this stirred mixture, trimethyl aluminum (1.0 ml, 10 mmole) was added dropwise. A violet colour was rapidly formed which lasted for a few seconds whereupon the solution returned to an orange red colour and in time complete solution of tetrasulphur tetranitride occurred. On further stirring a gelatinous precipitate gradually came out of solution. After 12 hours of stirring, the gelatinous precipitate was collected by filtration and washed thoroughly with fresh ethylene dichloride. After drying under vacuum this product became a red solid mass which when broken up gave small red orange granules. The material did not melt up to 250°C and was insoluble in carbon tetrachloride, chloroform, benzene and methylene chloride. The material decomposed slowly in air and had a repugnant odour. It reacted violently with water giving off ammonia, hydrogen sulphide and possibly other gases, and exploded when burned in oxygen leaving a white residue.

10. Reaction of Tetrasulphur Tetranitride with Triethyl Aluminum

Tetrasulphur tetranitride (0.97 gm, 5.28 mmole) was added to 50 ml of dry ethylene dichloride in a 100 ml round bottom flask. The solution was stirred and 1.4 ml (11.0 mmole) of triethylaluminum was added dropwise resulting in complete solution of the tetrasulphur tetranitride. A violet colour was observed but faded within seconds. On continued stirring, a gelatinous precipitate gradually came out of solution. After 12 hours, this was filtered off and washed thoroughly with fresh ethylene dichloride. After drying in vacuo, the product became a red solid mass, and on grinding, broke up into small dark granules. The material did not melt up to 250°C and was insoluble in carbon tetrachloride, chloroform, benzene and methylene chloride. It decomposed slowly in air and had a repugnant odour. It reacted violently with water giving off ammonia, hydrogen sulphide and possibly other gases and exploded when burned in oxygen leaving a white residue.

11. Quantitative Decomposition of $S_4N_4A\ell C\ell_3$

A 0.06075 gm sample of the reaction product from tetrasulphur tetranitride and aluminum chloride was carefully weighed onto a petri dish inside the dry box. After being transferred out of the dry box, the dish was allowed to stand open for five days. During this time it slowly turned yellow. The decomposed sample was extracted with boiling benzene and filtered. This was repeated until the benzene filtrate was colourless. All the benzene filtrates were collected in a pre-weighed round bottom flask and the volume reduced under vacuum until precipitation started to occur. Then the solution was left standing till all the benzene evaporated. The increase in weight, 0.3372 gm, of the flask was due solely to tetrasulphur tetranitride since a TLC of the benzene solution showed only one spot corresponding to the R_f and colour of tetrasulphur tetranitride. The weight of tetrasulphur tetranitride recovered corresponded to 95% of that expected based on a 1:1 adduct.

12. Quantitative Decomposition of $S_4N_4A\ell Br_3$

The procedure employed was identical to the one described for the quantitative decomposition of $S_4N_4 \cdot A\ell C\ell_3$. A 0.1724 gm sample of the reaction product from tetrasulphur tetranitride and aluminum bromide was used and 0.06461 gm of tetrasulphur tetranitride was recovered representing a recovery of 92% of the total S_4N_4 present based on a 1:1 adduct formulation.

13. Gravimetric Sulphur Analysis

The following procedure was used for all sulphur analyses reported in this thesis.

A 500 ml Erlenmeyer combustion flask, equipped with a ground glass stopper (ball and socket type) with a glass hook extending into the center of the flask, was charged with about 10 ml of distilled water and 3 ml of hydrogen peroxide. About 10-20 mg of sample was accurately weighed onto a black paper wrapper, folded carefully and tied with a platinum wire. The sample was quickly hung inside the combustion flask with the other end of the platinum wire on the hook. The flask was quickly flushed with oxygen and the stopper tightly clamped in place. The sample was ignited by irradiating the black wrapper with a high intensity IR lamp. As the sample burned, the oxide reacted with the hydrogen peroxide to form sulphuric acid. The flask was allowed to stand for $1\frac{1}{2}$ - 2 hours in order for oxidation and dissolution to reach completion. The contents of the flask were then transferred (filtered if necessary) to a beaker, and the sulphate precipitated by addition of 10 ml of a 10% barium chloride solution. The precipitate was digested for an hour on a hot plate with the solution brought to near boiling. After allowing the precipitate to settle overnight, the barium sulphate was filtered onto a pre-weighed porcelain filtering crucible which had been heated in a muffle furnace at 800°C to a constant weight. The crucible and the precipitates were then dried and heated in a muffle furnace at 800°C for $1\frac{1}{2}$ hours to a constant weight. The percentage of sulphur was calculated from the weight of barium sulphate and the weight of sample.

PART II. REACTIONS OF SULPHUR WITH dl-α-METHYLBENZYLAMINE

CHAPTER 1. INTRODUCTION

1. Reaction of Sulphur and Tetrasulphur Tetranitride with Amines

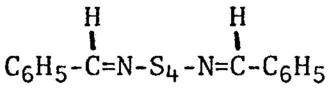
Sulphur dissolves readily in primary and secondary amines(82) to give alkylammonium polysulphides, but tertiary amines(83,84) do not react unless small amounts of impurities such as H_2S or SO_2 are present. The polysulphides are presumed responsible for the colours observed when sulphur is dissolved in an amine.

Levi(85) proposed the following scheme

$$2RR'NH + (x+1)S \longrightarrow RR'NS_xNRR' + H_2S$$

$$H_2S + 2RR'NH + yS \longrightarrow (RR'NH_2)_2S_{y+1}$$

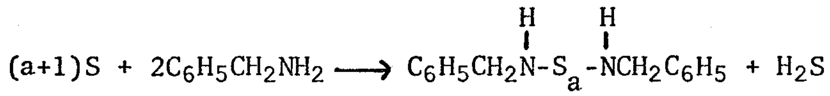
and successfully isolated piperidine trisulphide, dimethylamine and diethylamine tri- and disulphides from sulphur and the amine using lead oxide as a sulfide scavenger. With benzylamine and sulphur in the presence of lead oxide at room temperature, he obtained a yellow crystalline material which has been subsequently(22) shown to be benzylidenimine tetrasulphide [1].



$$C_6H_5\text{-}\overset{\displaystyle H}{\overset{|}{C}}\text{=N-}S_4\text{-N=}\overset{\displaystyle H}{\overset{|}{C}}\text{-}C_6H_5$$

[1]

In the absence of lead oxide, the reaction of sulphur with benzylamine gave different products, namely, benzylammonium polysulphide, ammonia, and N-benzylidene benzylamine(86). The following five step sequence involving benzylamine polysulphides and benzylidenimine polysulphides as intermediates has been established for the reaction.



$$(a+1)S + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2\overset{\overset{H}{|}}{N}\text{-}S_a\text{-}\overset{\overset{H}{|}}{N}CH_2C_6H_5 + H_2S \tag{1}$$

$$H_2S + (x-1)S + 2C_6H_5CH_2NH_2 \longrightarrow (C_6H_5CH_2NH_3^{+})_2S_x^{--} \tag{2}$$

$$\begin{aligned}3C_6H_5CH_2NH\text{-}S_a\text{-}NHCH_2C_6H_5 &\xrightarrow{[B]} 4C_6H_5CH_2NH_2\\ &+ C_6H_5CH{=}N\text{-}S_b\text{-}N{=}CHC_6H_5 + (3a-b)S\end{aligned} \tag{3}$$

$$\begin{aligned}C_6H_5CH{=}N\text{-}S_b\text{-}N{=}CHC_6H_5 + 2C_6H_5CH_2NH_2 &\xrightarrow{[S^{=}]} 2C_6H_5CH{=}NH\\ &+ C_6H_5CH_2NH\text{-}S_b\text{-}NHCH_2C_6H_5\end{aligned} \tag{4}$$

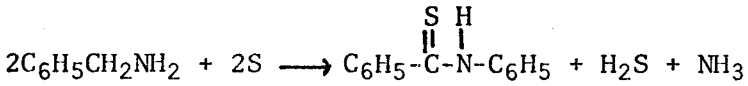
$$C_6H_5CH{=}NH + C_6H_5CH_2NH_2 \longrightarrow NH_3 + C_6H_5CH{=}N\text{-}CH_2C_6H_5 \tag{5}$$

In the presence of lead oxide (a hydrogen sulphide scavenger) the reaction becomes

$$(b+3)S + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}N\text{-}S_b\text{-}N{=}CHC_6H_5 + H_2S$$

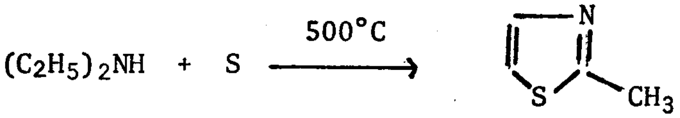
since step (4) which is apparently catalyzed by sulphide ion is blocked.

When sulphur is reacted with amines at elevated temperatures, different types of products, thioamides, are obtained. For example, when sulphur is refluxed in excess benzylamine, N-benzylthiobenzamide [2] is obtained in high yield$^{(87)}$. N-benzylidenimine benzylamine refluxed with sulphur also gives N-benzylthiobenzamide$^{(88)}$.



$$2C_6H_5CH_2NH_2 + 2S \longrightarrow C_6H_5\text{-}\overset{\overset{S}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}C_6H_5 + H_2S + NH_3 \tag*{[2]}$$

At higher temperatures, diethylamine and sulphur give thiazole [3](89). Reaction of benzylamine with tetrasulphur tetranitride at



[3]

an 8:1 molar ratio led to benzylidenimine polysulphides [4], ammonia, N-benzylidene benzylamine [5] and some free sulphur according to the equation. Other ring substituted benzylamines, *p*-chlorobenzylamine

$$S_4N_4 + 8C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}N\text{-}S_x\text{-}N{=}C_6H_5 \qquad [4]$$

$$+\ 3C_6H_5CH{=}N\text{-}CH_2C_6H_5 + (4-x)S + 7NH_3 \qquad [5]$$

and *p*-methoxybenzylamine, gave analogous arylamine polysulphides. However, α-methylbenzylamine did not lead to an analogous arylamine polysulphide while allylamine resulted in an apparent polymer(22). This reaction was, therefore, quite sensitive to small structural changes around the nitrogen atom.

2. Aim of Present Work

Sasaki reported that α-methylbenzylamine and tetrasulphur tetranitride did not give the corresponding arylidenimine polysulphide although he did not identify any products. This observation could suggest that either the mechanism he proposed was specific to ring substituted benzylamines or that the corresponding α-methylbenzylidenimine polysulphides were unstable and could not be isolated.

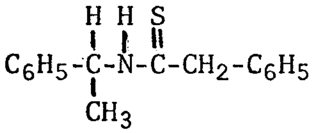
If α-methylbenzylidenimine polysulphide could be synthesized and studied, the information gathered could help to choose between these two possibilities and thus shed light on the reaction between tetrasulphur tetranitride and α-methylbenzylamine. Also, if the proposed reaction sequence for sulphur reacting with benzylamine holds for other primary amines, it would provide a convenient route for the conversion of amines to aldehydes and ketones since the arylidenimine polysulphides could be easily hydrolyzed.

The following work was undertaken with the aim of attempting to synthesize α-methylbenzylamine polysulphide and α-methylbenzylidenimine polysulphide to establish if the reaction of α-methylbenzylamine with sulphur followed the same mechanism as that of benzylamine with sulphur.

CHAPTER 2. RESULTS

Sulphur and α-methylbenzylamine reacted slowly *at room temperature* to give a red gummy precipitate which was identified as α-methylbenzylammonium polysulphide. The assignment of this structure was based on the following observations. When this substance was refluxed in methanol, it turned yellow and sulphur and another white material were obtained. This white material was very soluble in water and was later identified as α-methylbenzylammonium α-methylbenzylcarbamate, a reaction product between benzylamine and atmospheric carbon dioxide. Since polysulphide was formed, some sulphur had been reduced. Something must have been oxidized, but while there were traces of other products, none of these could be identified.

When sulphur was *refluxed* in α-methylbenzylamine under a nitrogen atmosphere, ammonia and hydrogen sulphide were evolved over the course of about six hours. The major product was characterized as the thiobenzamide, [6], based on the following evidence.



$$C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{N}-\overset{\overset{S}{\|}}{C}-CH_2-C_6H_5$$

[6]

The IR spectrum (Fig. 14) showed N-H adsorption at 3400 cm^{-1} and a C=S characteristic of the -NH-CS- linkage at 1150 cm^{-1}(90). The NMR spectrum (Fig. 15) showed four types of protons when run in carbon tetrachloride. They were at 7.20 ppm (phenyl), 5.70 ppm (quintet $-\underset{\underset{Me}{|}}{CH}-$), 3.96 ppm (singlet -$CH_2$-) and 1.50 ppm (doublet -CH_3). They were in the ratio

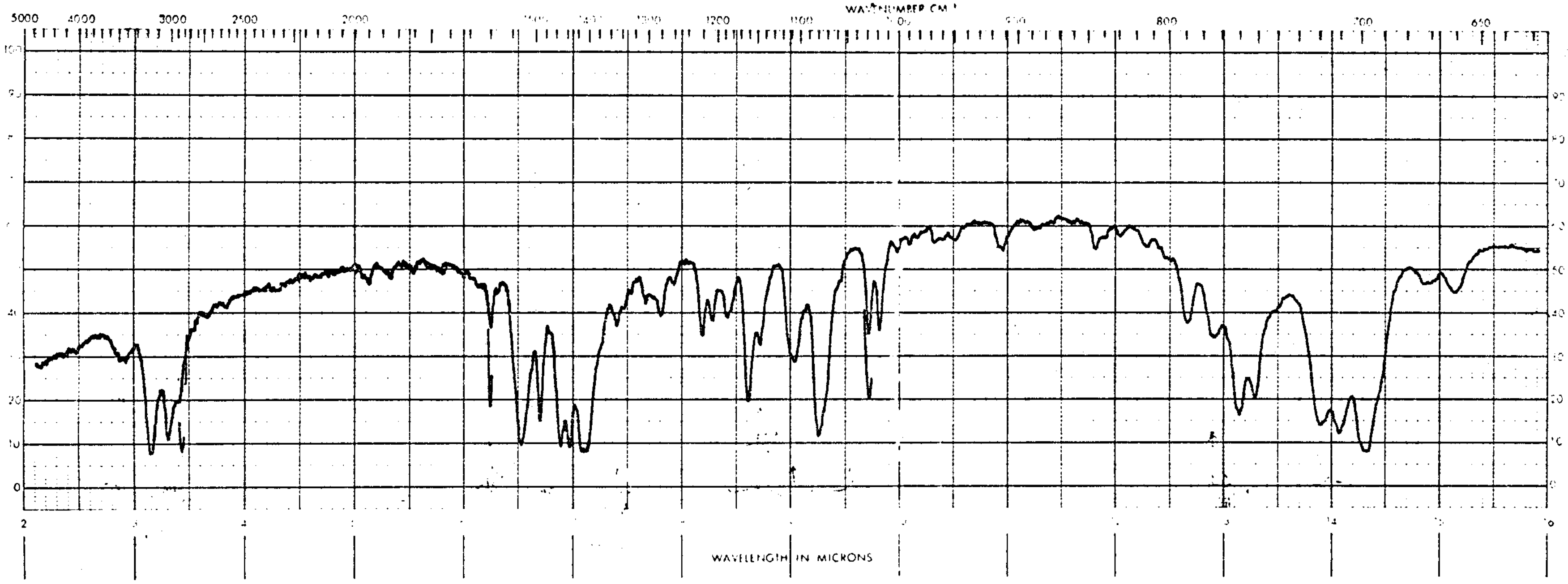


Figure 14. IR Spectrum of N-(α-Methylbenzyl)thiobenzamide.

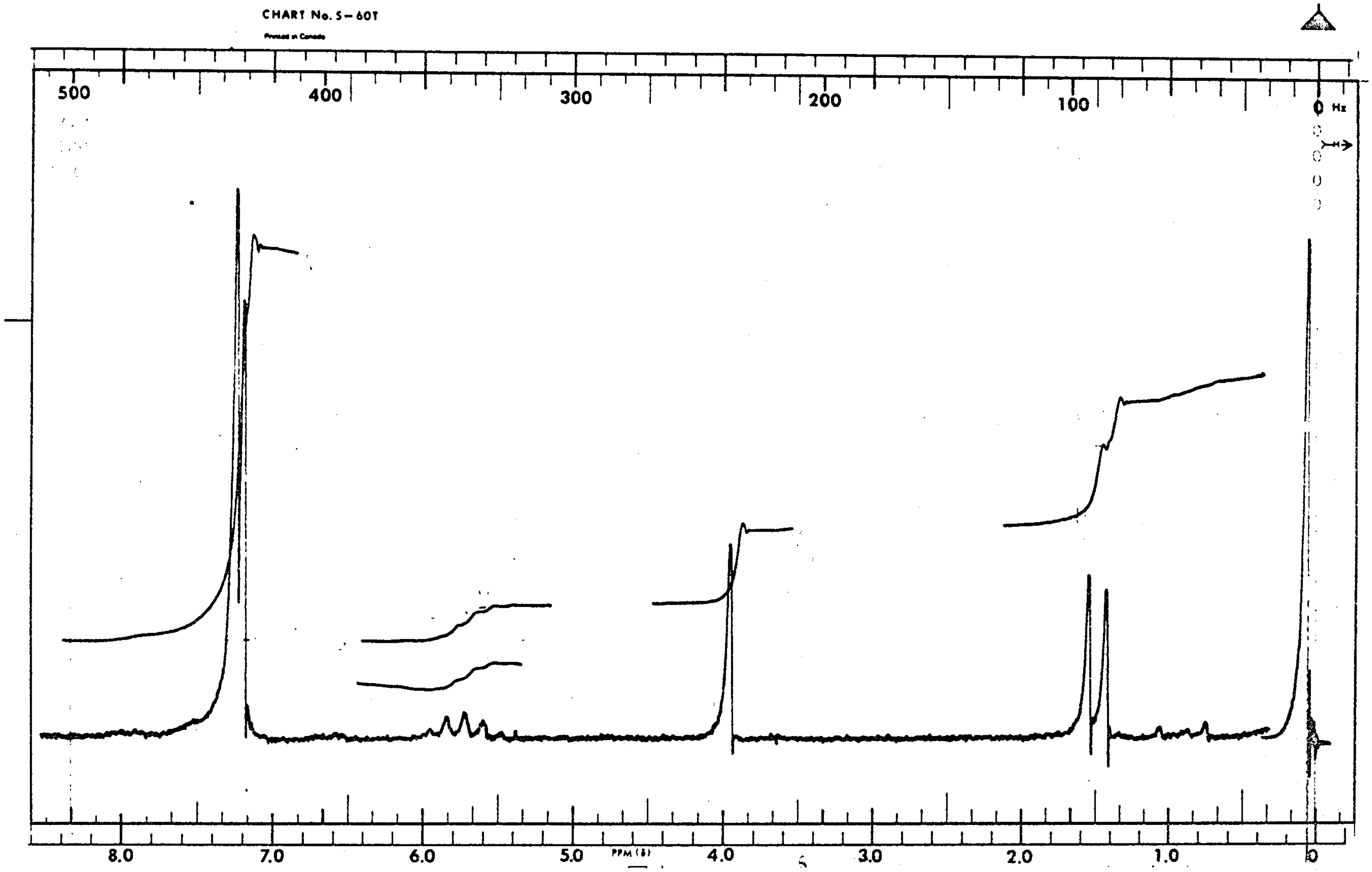


Figure 15. NMR Spectrum of N-(α-methylbenzyl)thiobenzamide in CCℓ₄.

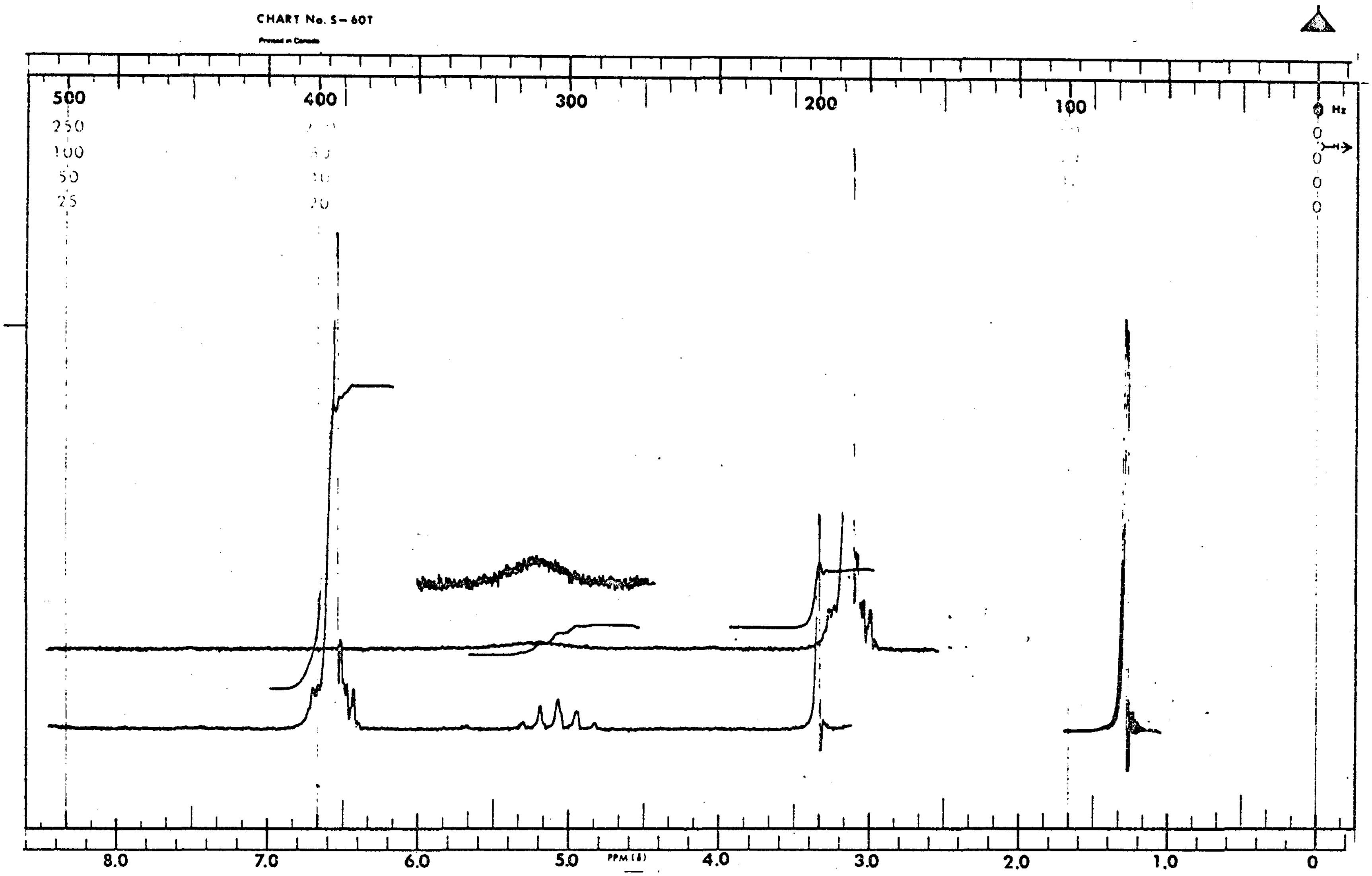
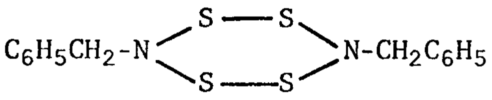


Figure 16. NMR Spectrum of N-(α-methylbenzyl)thiobenzamide in Acetone.

of 11:1:2:3, respectively. The N-H proton was not visible. However, when acetone was used as solvent, the N-H proton showed up clearly as a broad peak at 8.2 ppm (see Fig. 15 and Fig. 16). Elemental analysis was also in good agreement with that expected. Calcd. for $C_{16}H_{17}NS$: C, 75.2%; H, 6.76%; N, 5.5%; S, 12.5%. Found: C, 75.09%; H, 6.47%; N, 5.68%; S, 12.55%. This type of reaction has been previously reported by McMillan in 1948(87). He reacted sulphur with refluxing benzylamine and obtained the corresponding thiobenzamide.

In the presence of lead oxide with benzene as solvent, the reaction of sulphur with α-methylbenzylamine was slow, but eventually considerable quantities of lead sulphide were formed along with a yellow viscous liquid. The NMR of this viscous liquid (Fig. 18) showed 4 types of protons assignable to phenyl, $-\underset{\underset{CH_3}{|}}{C}-$, $-\underset{\underset{Me}{|}}{CH}-$ and NH- in the ratio of 5:3:1:1. The IR of this viscous liquid is shown in Fig. 17. The band at 3300 cm^{-1}, an N-H absorption, strongly suggested a structure of the methyl benzylamine polysulphide type rather than the expected imine polysulphide. All attempts to purify this substance by chromatography, distillation, or fractional recrystallization led to decomposition. Repetition of the reaction led to identical results, and consequently alternative syntheses of authentic α-methylbenzylamine polysulphide were undertaken.

Sasaki prepared benzylamine disulphide from benzylamine and sulphur monochloride(86). Goehring(91), however, obtained a six-membered dibenzyl tetrasulphur diimide [7] from the same reactants. Thus, this



[7]

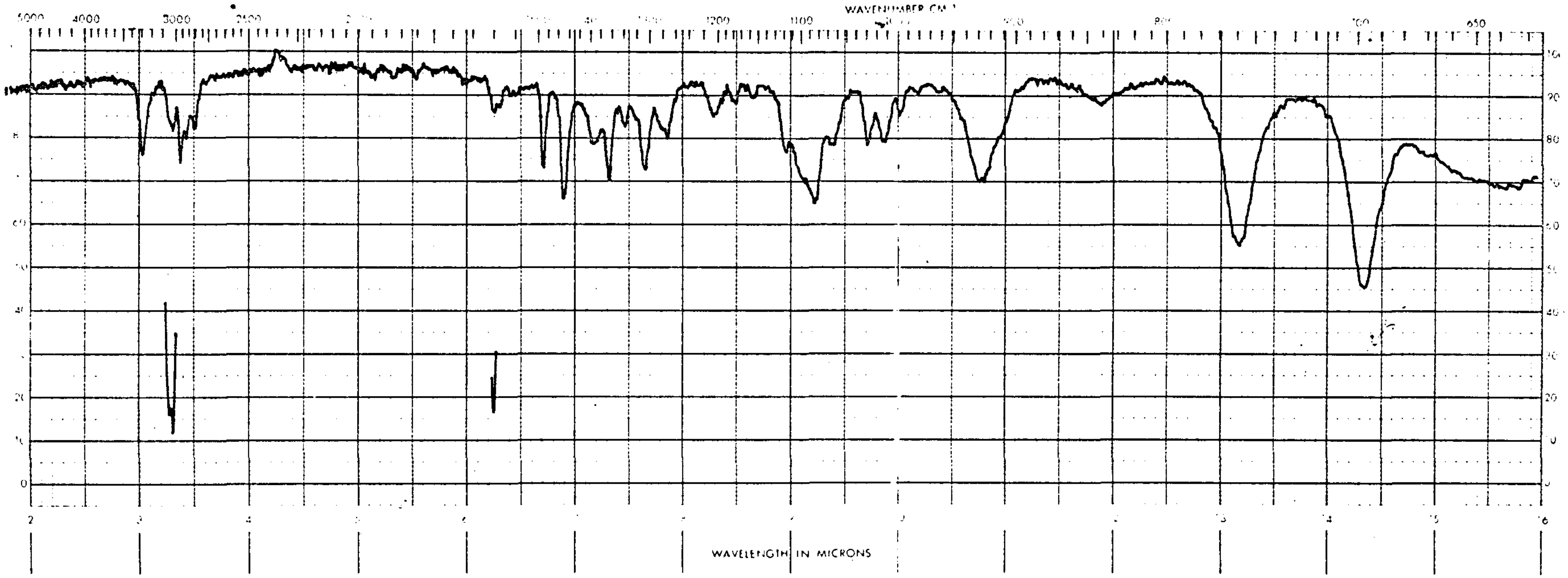


Figure 17. IR Spectrum of the Reaction Product of α-Methylbenzylamine with Sulphur.

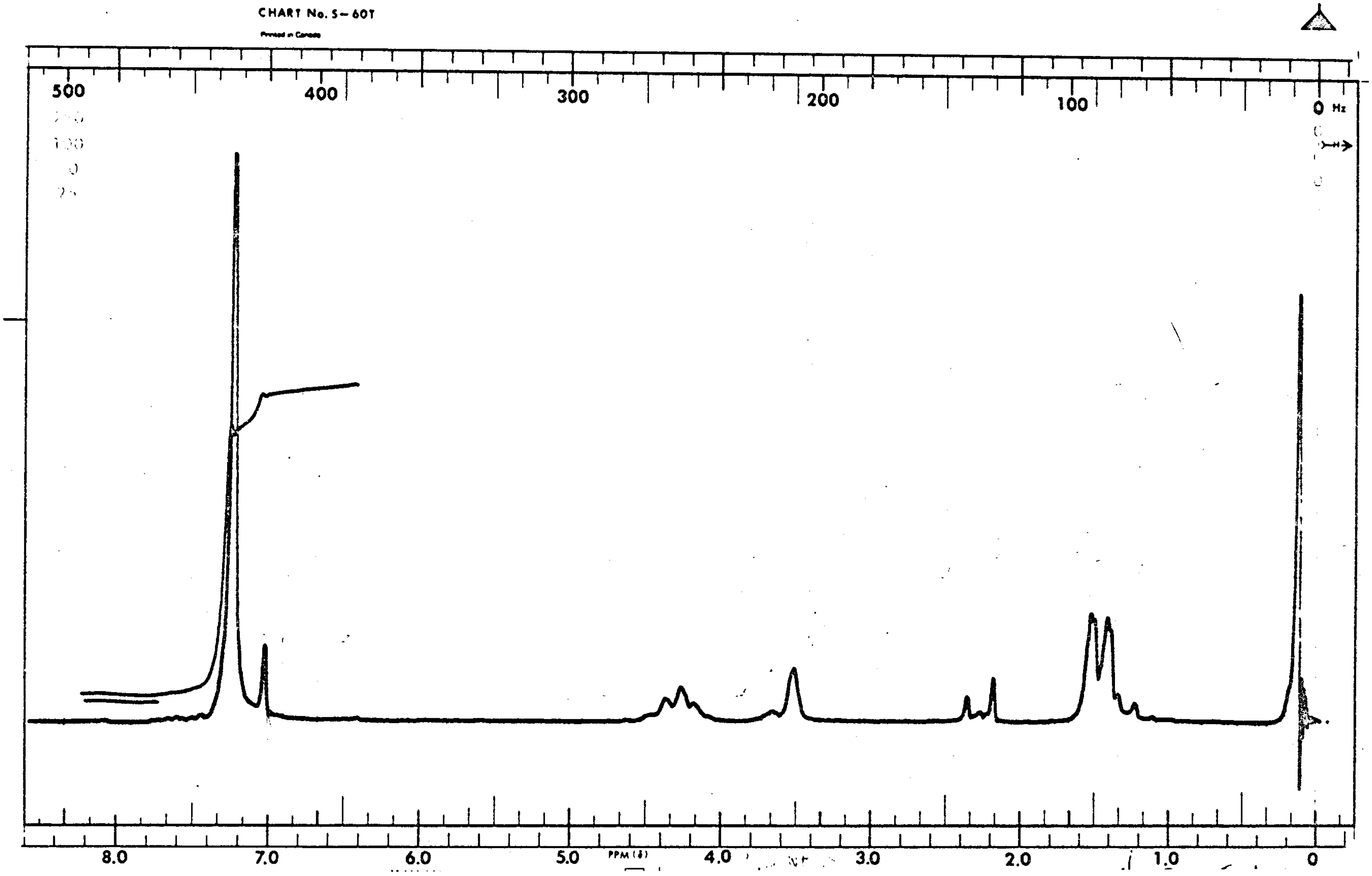


Figure 18. NMR Spectrum of the Reaction Product of α-Methylbenzylamine with Sulphur.

reaction can yield several products; however, the stoichiometries are different. The benzylamine disulphide reaction requires 4 moles of amine to 1 mole of sulphur monochloride, whereas the dibenzyl tetrasulphide diimide requires a 3:1 molar ratio. When α-methylbenzylamine and sulphur monochloride were reacted at ice temperature in a ratio of 4:1, a number of products were obtained. One of these was a crystalline material whose IR (Fig. 19) and NMR (Fig. 20) spectra suggested dibenzyl tetrasulphur diimide. The IR spectrum showed no N-H absorption, thus eliminating an arylamine disulphide. The NMR spectrum showed 3 types of proton at 7.35 ppm (phenyl, singlet), 5.70 ppm (-CH- quartet) and 1.70 ppm ($-CH_3$ doublet) in the ratio of 5:1:3. The elemental analysis was in agreement with the proposed structure. Calcd. for $C_{16}H_{18}N_2S_4$: C, 52.5%; H, 4.8%; N, 7.6%; S, 35.0%. Found: C, 52.25%; H, 5.01%; N, 7.84%; S, 35.21%. The other fraction was a yellow viscous liquid whose IR spectrum was identical to the material obtained from the reaction of α-methylbenzylamine with sulphur. Again, further manipulation of the liquid did not lead to either a pure or crystalline product. α-Methylbenzylamine polysulphide was probably present in both reactions but could not be purified. An attempted vacuum distillation of the liquid gave α-methylbenzylamine and a viscous gummy mass.

An attempt was also made to prepare α-methylbenzylidenimine polysulphide by an alternate route. Exner(92) prepared benzophenone imine disulphide from a ketimine derivative formed when phenyl magnesium bromide reacted with benzonitrile. The ketimine was then reacted with sulphur monochloride.

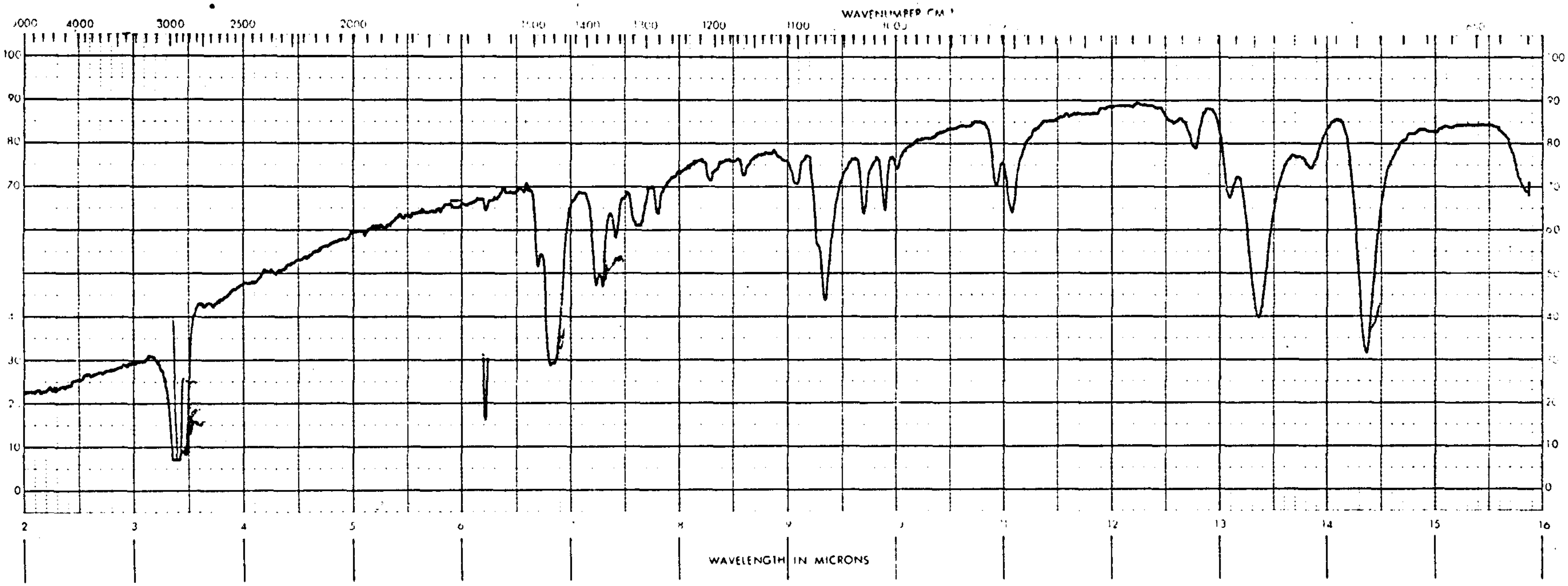


Figure 19. IR Spectrum of Cyclic Dibenzyl Tetrasulphide Diimide.

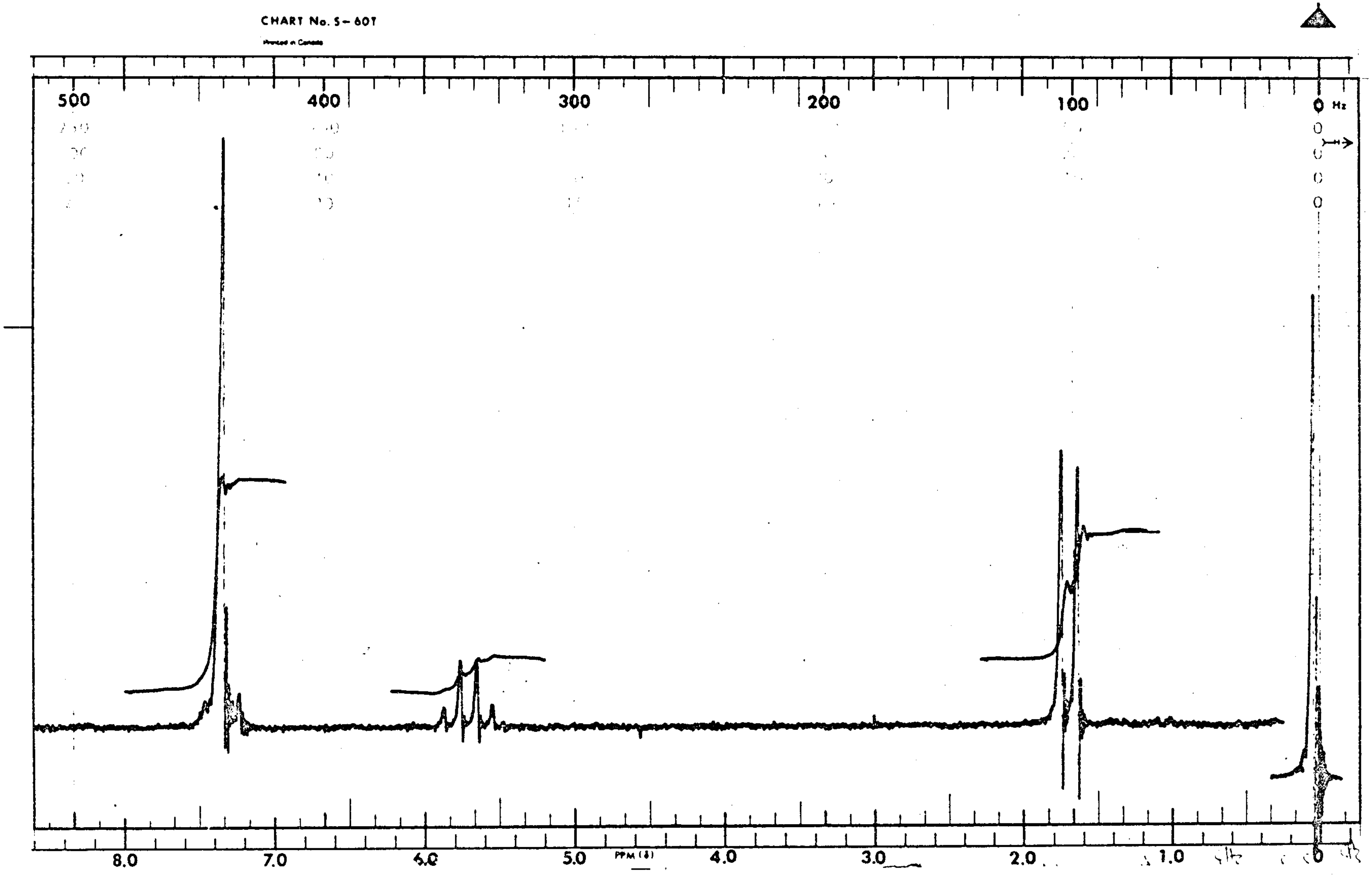


Figure 20. NMR Spectrum of Cyclic Dibenzyl Tetrasulphide Diimide.

$$C_6H_5\text{-}MgBr \quad + \quad C_6H_5CN \longrightarrow (C_6H_5)_2C{=}N^-MgBr^+$$

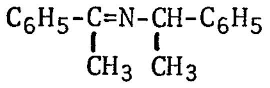
$$(C_6H_5)_2C{=}N^-MgBr^+ + S_2C\ell_2 \longrightarrow (C_6H_5)_2C{=}N\text{-}S\text{-}S\text{-}N{=}C\text{-}(C_6H_5)_2$$

This reaction should provide a route to the imine polysulphide of α-methylbenzylamine. Using phenyl magnesium bromide, acetonitrile and sulphur monochloride, however, no imine polysulphide was obtained. Instead, acetonitrile appeared to be polymerized by the Grignard reagent$^{(93)}$. The only products isolated were sulphur and biphenyl which presumably came from a coupling reaction of the Grignard. Changing the reactants to methyl magnesium iodide and benzonitrile did not help. The products isolated in this case were benzonitrile and dimethyl disulphide.

Since all efforts to prepare samples of both α-methylbenzylidenimine polysulphide and α-methyl benzylamine polysulphide were unsuccessful, this work was abandoned.

CHAPTER 3. DISCUSSION AND CONCLUSION

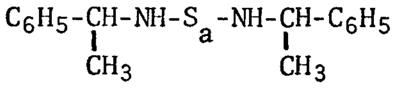
Reaction of sulphur and α-methylbenzylamine at room temperature was very slow with α-methylbenzylammonium polysulphide being the major product isolated. The N-(α-methylbenzylidene)α-methylbenzylamine, expected according to the reaction sequence proposed by Sasaki, was not obtained. This would be consistent with the equilibrium of



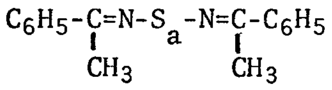
$$C_6H_5\text{-}\underset{CH_3}{C}\text{=}N\text{-}\underset{CH_3}{CH}\text{-}C_6H_5 \qquad [8]$$

step (1) (see page 53) lying fairly far to the left and the overall reaction stopping after steps (1) and (2).

Consistent with this idea, a reaction run in the presence of lead oxide appeared to give α-methylbenzylamine polysulphide [9]. This compound apparently does not undergo rapid disporportion to give the imine polysulphide as did benzylamine disulphide [10].



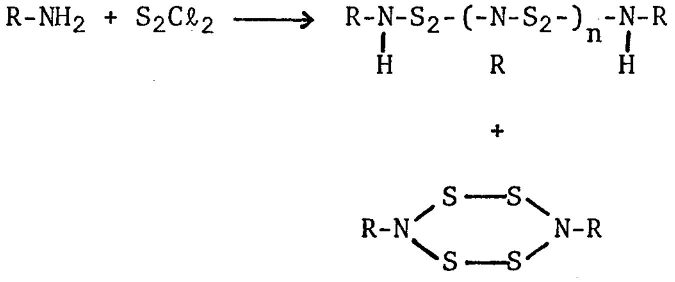
$$C_6H_5\text{-}\underset{CH_3}{CH}\text{-}NH\text{-}S_a\text{-}NH\text{-}\underset{CH_3}{CH}\text{-}C_6H_5 \qquad [9]$$



$$C_6H_5\text{-}\underset{CH_3}{C}\text{=}N\text{-}S_a\text{-}N\text{=}\underset{CH_3}{C}\text{-}C_6H_5 \qquad [10]$$

Under reflux conditions, sulphur and α-methylbenzylamine gave N-(α-methylbenzyl)-thiobenzamide. Thioamides are typical products of high temperature reactions of sulphur and amines. The mechanism of formation of this type of product is not well known but is not inconsistent with the formation and subsequent reaction of N-(α-methylbenzylidene)-α-methylbenzylamine. The analogous reaction on unsubstituted N-benzylidene benzylamine is known(88).

An alternate synthesis of α-methylbenzylamine disulphide via the reaction of α-methylbenzylamine and sulphur monochloride was not successful. Divalent sulphur chlorides react rapidly with primary amines, but primary amines are bifunctional with respect to these sulphur halides, <u>viz.</u>, both protons of the amine function are replaceable. As a result, polymeric sulphur imides(94) might be expected as products. The monomeric cyclic tetrasulphide diimides are also formed during the reaction, but the yield is generally low.



$$R\text{-}NH_2 + S_2C\ell_2 \longrightarrow R\text{-}\underset{H}{N}\text{-}S_2\text{-}(\text{-}\underset{R}{N}\text{-}S_2\text{-})_n\text{-}\underset{H}{N}\text{-}R$$

Thus, it is possible that the viscous oily products obtained contained some polymeric imides which caused difficulties in purification of this material. The IR spectrum of this material, however, shows fairly strong N-H absorption and the proton NMR spectrum indicates about one N-H per benzyl group. Thus, if the α-methylbenzylamine disulphide was contaminated with polymeric imides, the amount must have been fairly low. An alternate explanation for failure to obtain a crystalline product is that the α-methylbenzylamine used was a racemic d-l mixture. The product disulphide would then be a mixture of dd,ll, and dl in

1:1:2 ratios and might not be prone to crystallization.

It is therefore possible to apply Sasaki's sequence of reactions to explain the observations, provided that the first step is slow or reversible and that α-methylbenzylamine disulphide is a good deal more stable than benzylamine disulphide. It has been shown that the method of Grignard, nitrile and sulphur monochloride, is not a satisfactory use for the synthesis of the imine polysulphide. Apparently, the reaction is limited to symmetrical ketimines.

CHAPTER 4. EXPERIMENTAL SECTION

1. Reaction of Sulphur with d-1-α-Methylbenzylamine

Sulphur (1.24 gm, 38.8 mg atoms) and 8.2 gm (67.6 mmole) of α-methylbenzylamine were stirred in 30 ml of benzene in a 100 ml round bottom flask. The solution gradually turned red and after 48 hours was filtered to give a crude red product. This material when dissolved in boiling methanol gradually turned yellow and precipitated sulphur (identified by TLC and m.p.). The methanol solution upon standing gave white water soluble crystals of m.p. 140-143°C. A comparison of this material with an authentic sample of α-methylbenzylammonium α-methylbenzylcarbamate showed them to be identical. The benzene filtrate from the reaction showed several spots on TLC, but they were not identifiable.

2. Reaction of Sulphur with d-l-α-Methylbenzylamine under Reflux Conditions

Sulphur (3.70 gm, 116 mg atoms) and 14.0 gm (116 mmole) of α-methylbenzylamine were stirred in a 50 ml round bottom flask fitted with a condenser and heated in an oil bath at 110±5°C. Odours of sulphide and ammonia were noted. After six hours of reflux, when no more gases were given off, the dark gummy reaction product was thoroughly washed with ether from which some sulphur was recovered. The residue was then separated on a silica gel column. Sulphur was eluted by pure hexane followed by two small fractions which were not identified. The remaining major fraction, 5.8 gm, eluted by benzene, was recrystalized from hexane to give a white crystalline product of m.p. 89-91°C. A TLC with methylene dichloride as eluent gave an R_f of 0.32. The IR spectrum (Fig. 14) and NMR spectrum (Figs. 15, 16) were recorded. Elemental analysis (see page 60) and spectroscopic evidence showed this compound to be N-(α-methylbenzyl)thiobenzamide.

3. Reaction of Sulphur with d-l-α-Methylbenzylamine in the Presence of Lead Oxide

Sulphur (2.5 gm, 78 mg atoms), 7.8 gm (64 mmole) of α-methylbenzylamine and 11.2 gm (69 mmole) of lead oxide were added to 30 ml of dry benzene in a 50 ml round bottom flask and stirred for six days. The black lead sulphide formed was filtered off and thoroughly washed with ether. The ether-benzene mixture was evaporated on a rotatory evaporator to give 8.0 gm of a yellow viscous liquid. The IR and NMR spectra of this liquid are shown in Fig. 17 and Fig. 18, respectively. The presence of α-methylbenzylamine polysulphide was suspected. Any further manipulation of this yellow viscous liquid through crystallization, column chromatography, vacuum distillation and other techniques only led to decomposition.

4. Reaction of d-l-α-Methylbenzylamine and Sulphur Monochloride

α-Methylbenzylamine (19.4 gm, 160 mmole) was added to 120 ml of anhydrous ether in a 250 ml 3-necked round bottom flask, and then cooled in an ice bath. With continuous stirring, a dilute solution of sulphur monochloride (5.4 gm, 40 mmole) in 20 ml of anhydrous ether was added dropwise over $1\frac{1}{2}$ - 2 hours. The white amine hydrochloride salt formed was filtered off and washed thoroughly with ether. The ether filtrate was reduced in volume and 0.2 gm of a white crystalline product of m.p. 148-151°C was obtained. A TLC with carbon disulphide as eluent gave an R_f of 0.50. The IR and NMR spectra of this material are shown in Fig. 19 and Fig. 20, respectively. Elemental analyses (see page 63) were in good agreement with that expected for di(α-methylbenzyl)tetrasulphide diimide. The ether filtrate on evaporation gave 6.3 gm of a yellow viscous liquid whose IR spectrum was identical to that of the yellow viscous liquid obtained from the α-methylbenzylamine sulphur reaction (see page 60). All attempts to obtain a purer sample of this material only led to decomposition.

5. Reaction of Phenyl Magnesium Bromide, Acetonitrile and Sulphur Monochloride

A solution of phenyl magnesium bromide was prepared in a 250 ml 3-necked flask by adding 10 ml (98 mmoles) of bromobenzene to 2.4 gm (98 mmoles) of magnesium turnings in 50 ml of anhydrous ether. After all the magnesium had reacted, the flask was cooled in an ice bath and a dilute solution of acetonitrile (5.0 ml, 95 mmoles) in 10 ml of ether was added dropwise to the Grignard reagent with continuous stirring. The solution gradually turned from brownish to green and finally a viscous green layer separated. The reaction mixture was heated on a steam bath for ten minutes and then cooled in a methanol ice bath again. A dilute solution of sulphur monochloride, 4.0 ml (0.05 M) in 10 ml of ether, was added dropwise to the stirring mixture. After addition was complete, the ice bath was removed and stirring was continued for an hour. Then, any excess or unreacted Grignard reagent was decomposed by washing the solution with a dilute solution of ammonium chloride. After separation, the ether fraction was thoroughly washed with water and dried over anhydrous magnesium sulphate. After evaporating off the ether, the remaining residue was eluted on a silica gel column. Sulphur was eluted by pure hexane, followed by biphenyl with a 50:50 hexane-benzene solution. The biphenyl was identified by NMR and its m.p. of 66-68°C, Lit. 71°C. The rest of the fractions were mostly decomposed products and were not identifiable.

6. Reaction of Methyl Magnesium Iodide, Benzonitrile and Sulphur Monochloride

A solution of methyl magnesium iodide was prepared in a 250 ml 3-necked flask by adding 6.2 ml (0.105 M) of methyl iodide to 2.55 gm (0.105 M) of magnesium turnings in 50 ml of anhydrous ether. After all the magnesium had reacted, the flask was cooled in an ice bath and 10 ml (0.10 M) of benzonitrile was added dropwise to the Grignard with continuous stirring. The reaction mixture slowly turned green in colour. Then, the reaction mixture was heated on a steam bath for 10 minutes and cooled in a methanol ice bath again. A dilute solution of sulphur monochloride, 4.0 ml (0.05M) in 10 ml of anhydrous ether, was added slowly to the stirring mixture which gradually turned yellow. After addition was complete, the ice bath was removed and stirring was continued for an hour. Any excess or unreacted Grignard was decomposed by pouring the reaction mixture into a dilute solution of ammonium chloride. The ether layer was separated and washed with a dilute solution of thiosulphate to remove the iodine, then washed thoroughly with water and dried over anhydrous magnesium sulphate. After evaporating off the ether, the residue was eluted on a silica gel column and the dimethyl disulphide, identified by NMR and IR spectra, came off with hexane contaminated with traces of iodine. The next fraction was benzonitrile which was eluted by a mixture of 30:70 hexane:benzene solution. The benzonitrile was also identified by IR and NMR spectra. The rest of the fractions were not identifiable.

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