therefore that the S–O bond order may be lowered and the Ru–S bond order raised by overlap of empty antibonding π orbitals on the SO_2 ligand with the filled nonbonding d orbitals of the ruthenium. A molecular orbital treatment of the complex would be helpful in deciding the validity of this suggestion.

Acknowledgment.—This research was supported in part by the National Aeronautics and Space Administration. L. H. V. wishes to acknowledge the helpful suggestions of Drs. A. Zalkin and D. H. Templeton of the Lawrence Radiation Laboratory, University of California, Berkeley, with regard to the final structure refinement using their full-matrix program and the LRL IBM 7044 computer. The authors also wish to thank Dr. L. Vaska (Clarkson College of Technology, Potsdam, N. Y.) for informing us of his research on SO_2 complexes. Chemical analyses for N, H, and S were performed by Galbraith Laboratories and Schwarzkopf Microanalytical Laboratory.

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The System Trisulfur Dichloride and Methylamine. The Preparation of N,N'-Dimethylcyclohexasulfur-1,5-diimide[1]

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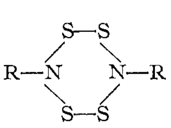
Received April 26, 1965

The reaction of trisulfur dichloride with methylamine has been investigated. Under conditions of high dilution using petroleum ether "B" as a solvent, a crystalline compound, $S_6(NCH_3)_2$, was prepared. Infrared and proton magnetic resonance spectra are reported in support of a 1,5 or symmetrical ring structure. A reaction mechanism for the formation of this eight-membered, cyclic imide is proposed.

Introduction

Various investigators have allowed S_2Cl_2 and SCl_2 to react with primary organic amines to form six- and eight-membered heterocyclic sulfur–nitrogen compounds.

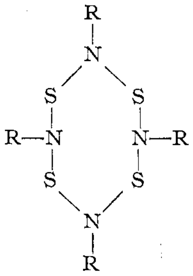
Becke-Goehring and Jenne[2,3] prepared a series of six-membered compounds by the reaction of S_2Cl_2 with primary amines. Configuration I was proposed for the primary product isolated



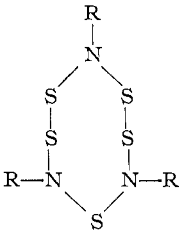
I

(R = ethyl, *n*-dodecyl, cyclohexyl, benzyl, and β-phenylethyl)

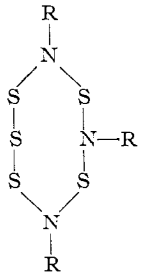
A series of eight-membered sulfur–nitrogen heterocycles, with proposed configurations II, III, and IV, have been prepared by the reaction of SCl_2 with primary amines. Stone and Nielsen[4,5] prepared the methyl analogs. Becke-Goehring and Schlotter[6] prepared the benzyl and β-phenylethyl analogs of II. Ross, Roscoe, and Pace[7] prepared the ethyl analog of II and the benzyl and β-phenylethyl analogs of III.



II



III



IV

II, R = methyl, ethyl, benzyl, β-phenylethyl
III, R = methyl, benzyl, β-phenylethyl
IV, R = methyl

No successful cyclizations of the polysulfur dichlorides (S_nCl_2, where $n > 2$) have been reported, although attempts have been implied.[8] Fehér, Naused, and Weber[9] have described the preparation and properties of the individual polysulfur dichlorides where n = 3, 4, 5, and 6.

Various open-chain condensations of S_3Cl_2 have been reported. Fehér and Kruse[10] have allowed S_3Cl_2 to react with a large excess of H_2S to prepare H_2S_5. Fehér and Weber[11] have prepared $RSO_2S_3SO_2R$ (where R = p-toluene) by the reaction of S_3Cl_2 with RSO_2Na.

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(2) M. Becke-Goehring and H. Jenne, *Angew. Chem.*, **70**, 399 (1958).
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(9) F. Fehér, K. Naused, and H. Weber, *Z. anorg. allgem. Chem.*, **290**, 303 (1957).
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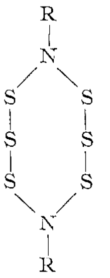
(11) F. Fehér and H. Weber, *Angew. Chem.*, **67**, 231 (1955).

Fehér, Krause, and Vogelbruch[12] have condensed C_2H_5SH with S_3Cl_2 to prepare $C_2H_5S_3C_2H_5$.

The present work reports investigations on cyclization condensation employing S_3Cl_2 and primary organic amines in attempts to prepare a molecule with configuration V. The hydrogen analog (R = H)



has been isolated from among the products of the reaction of NH_3 with S_2Cl_2.[13-15]

Experimental

Preparation of Sulfur Dichloride.—Sulfur dichloride was prepared by bubbling chlorine gas through S_2Cl_2 in the presence of dry iron powder according to the procedure of Jonas and Stohr as reported by Brauer.[16] Approximately 1500 ml. (2400 g.) of S_2Cl_2 (Eastman Kodak, Practical Grade) was used. The chlorine gas (The Matheson Co., Inc., Technical Grade) was dried by bubbling through H_2SO_4 and passing over P_2O_5. The product was distilled in the presence of 2 ml. of PCl_3 to inhibit decomposition. A Raschig ring-filled column 50 cm. long was employed in the fractionations. A few drops of PCl_3 were added to the receiver. The fraction boiling over the range from 55 to 62° was retained. Although bumping was excessive during the early stages of the distillation, boiling stones were not used due to their tendency to cause decomposition of the SCl_2.

It was possible to store the SCl_2 for months at 0° without significant decomposition if a few drops of PCl_3 were added. Immediately prior to each preparation of S_3Cl_2 (see below), the SCl_2 was redistilled except that no PCl_3 was added to the receiver and only the fraction boiling between 59 and 60° was retained.

Preparation of Trisulfur Dichloride.—Trisulfur dichloride was prepared by the reaction of H_2S with SCl_2 in a large excess of the latter as solvent according to the method of Fehér, Naused, and Weber.[9,16] Approximately 1400 ml. of freshly distilled SCl_2 was allowed to react with about 45 ml. of condensed (at −80°) H_2S (The Matheson Co., Inc., Technical Grade).

Although the reaction and distillation flasks and traps employed were patterned after those of Fehér, *et al.*, two modifications are recommended. The distillation flask used to remove the large excess of unreacted SCl_2 from the product was found to operate more successfully if equipped with a Claisen-type distillation head rather than the straight head described by Fehér. It was also found that the incorporation of ball-and-socket joints in the distillation system minimized breakage at two points, the inlet to the same distillation flask and at the SCl_2 siphon outlet tube on the first trap after the distillation flask. Maximum yields obtained by the present authors were 58% compared to 75% reported by Fehér.

Trisulfur dichloride was analyzed by iodometric determination of chlorine according to the method of Böhme and Schneider.[9,17] Approximately 0.3 g. of S_3Cl_2 was sealed in a thin-walled glass ampoule. The ampoule was shattered in a mixture of 10 ml. of CS_2 and 3 g. of KI in 20 ml. of water. The liberated iodine was titrated with 0.1 *N* $Na_2S_2O_3$. Chlorine results are reported for three samples analyzed by this procedure in terms of the S:Cl stoichiometry.

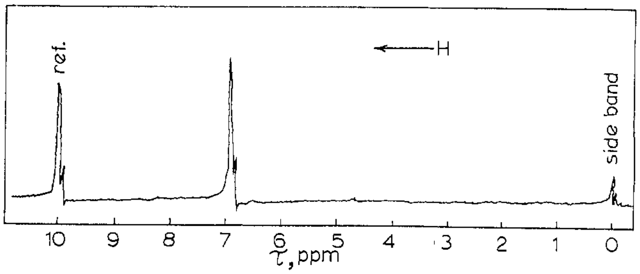


Figure 1.—The proton magnetic resonance spectrum of $S_6(NCH_3)_2$; 10% CS_2 solution with 1% $Si(CH_3)_4$ as an internal reference.

Anal. Calcd. for S_3Cl_2: S, 57.56; Cl, 42.44. Found: Cl, 42.40; 42.39; 42.60 (or $S_{2.01}Cl_2$; $S_{3.02}Cl_2$; $S_{2.99}Cl_2$).

Reaction of Trisulfur Dichloride with Methylamine.—Trisulfur dichloride and methylamine, CH_3NH_2, were allowed to react under conditions of very high dilution to favor the process of cyclization over chain polymerization. Three liters of petroleum ether "B" (boling range 60–70°), maintained at 0° throughout the reaction, served as the reaction medium. A solution of 75 ml. (43 g.) of S_3Cl_2 in 200 ml. of solvent was added dropwise with vigorous stirring to the reaction flask over a period of about 4 hr. After about 10 ml. of the S_3Cl_2 solution had been added, CH_3NH_2 (The Matheson Co. Inc., anhydrous) was bubbled into the reaction solvent at a rate of 50–60 ml./min. After addition of the S_3Cl_2 was complete, admission of the CH_3NH_2 was continued until the off-gases tested basic, at which time it was assumed that the reaction was complete.

Insoluble polymeric materials and $CH_3NH_2 \cdot HCl$ were removed by filtration. This mixture of insoluble solids was initially white but changed rapidly through yellow to a red-brown color. The faintly yellow filtrate was reduced in volume by means of a rotating evaporator under reduced pressure achieved by water aspirator. The evaporator flask was thermostated at 30°, a temperature which permitted a reasonable rate of evaporation without excessive thermal decomposition of the product. The volume was reduced to approximately 130 ml.

Column chromatography was found to be suitable as a means for isolating the reaction product. An absorption column 36 cm. long and 46 mm. in diameter was prepared with a packing of 680 g. of acid-washed alumina (Merck and Co., Inc.). This size and capacity of the column permits processing 60–65 ml. of the concentrate per run. The success of the column separation was found to be very dependent upon the thoroughness of the acid wash of the Al_2O_3. The column was eluted with petroleum ether "B." The first 2.5 l. of eluate contained the white crystalline product, $S_6(NCH_3)_2$. It was purified by repeated recrystallization from either petroleum ether "B" or acetone. It is worthy of note that the latter solvent would be unacceptable for the cyclic imide S_7NH due to decomposition (blue intermediate species being formed). The material was dissolved at room temperature and slowly cooled to 0°. Yellow, translucent, well-formed, rhombohedral crystals formed. If cooled rapidly to −80° fine, nearly white, needlelike crystals were formed. Yields ranged from 3.5 to 5.5% based on the total S_3Cl_2 used. The purified material melted in the range 72–77° with decomposition.

Anal. Calcd. for $S_6(NCH_3)_2$: C, 9.59; H, 2.41; N, 11.19; S, 76.81; mol. wt., 250.48. Found: C, 9.92; H, 2.43; N, 10.82, 11.19; S, 78.56, 75.98; mol. wt. (cryscopic in benzene), 260.7, 254.5.

Processing of succeeding eluted fractions yielded only a yellow oil. The oil rapidly decomposed into a red-brown tar even at reduced temperatures. The decomposition was accompanied by the evolution of methylamine, identifiable by its odor.

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TABLE I
INFRARED SPECTRA

Cm⁻¹	Intensity[a]	Cm.⁻¹	Intensity[a]
C–H stretch		C–N stretch	
2991	m	1148	w
2958	s	1117	s
2917	s	1053	vs
2881	s	S–N stretch	
		769	vs
2850	m		
2780	m		

[a] s, strong; m, medium; w, weak.

Infrared Spectrum.—Data derived from the infrared spectrum are found in Table I. A Perkin-Elmer Model 421 spectrophotometer was used. Assignments are those of Bellamy (C–H and C–N),[18] Crawford, Fenton, and Potts (C–H),[19] Heal (S–N),[15] and Lippincott and Tobin (S–N).[20] Carbon disulfide was employed as the solvent and measurements were made in a 129-μ cell.

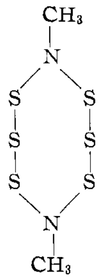
Proton Magnetic Resonance Spectrum.—The proton magnetic resonance spectrum was measured using a Varian DP-60 spectrometer with a 65.44-Mc. signal and 564.4-cycle side band. Measurements were made in a carbon disulfide solution approximately 10 vol. % in the cyclic imide and 1 vol. % in $Si(CH_3)_4$ as the internal reference. Line positions are given in terms of τ, the proton nuclear resonance shielding value, where[21]

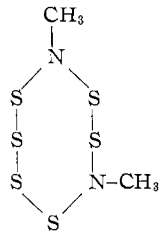
$$\tau \text{ (p.p.m.)} = 10 - \frac{\Delta[\mathrm{Si(CH_3)_4}] \times 10^6}{\text{oscillator frequency (c.p.s.)}}$$

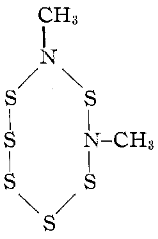
A single sharp peak was observed for the CH_3 group of $S_6(NCH_3)_2$ at a τ value of 6.88 p.p.m.

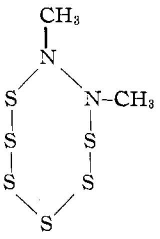
Discussion

Configuration V is proposed for the isomer of $S_6(NCH_3)_2$ isolated by the described procedure on the basis of its method of preparation and its physical properties. Other possible configurations are VI, VII, and VIII.

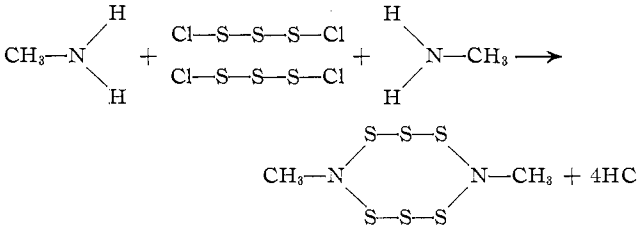

V


VI


VII


VIII

Configuration V would be expected to arise from a cyclization condensation in which the three-membered sulfur chains of S_3Cl_2 remain intact.



Such a cyclization is analogous to that proposed for the formation of $S_4(NR)_2$ (configuration I) (from S_2Cl_2 and RNH_2.[2,3] Configuration V is analogous to that determined for the 1,5- isomer of $S_6(NH)_2$ by X-ray crystallography.[14] The suggested name for configuration V is N,N′-dimethylcyclohexasulfur-1,5-diimide.

Configurations VI and VII might arise as the result of sulfur chain propagation and degradation. Their hydrogen analogs are known.[15] It is difficult to imagine how configuration VIII might arise; however work is continuing utilizing *sym*-dimethylhydrazine and S_2Cl_2 as well as S_3Cl_2 in attempts to prepare N–N members of the series. Replacement of CH_3NH_2 by $C_6H_5CH_2NH_2$ has as yet not produced a dibenzyl compound analogous to the dimethyl 1,5- isomer.

The infrared spectral data are consistent with configuration V. A single S–N stretching band is observed. The analogous 1,5- isomer of $S_6(NH)_2$ also shows a single S–N band. In contrast, the 1,4- and 1,3- isomers of $S_6(NH)_2$ show splittings of the S–N band.[5]

The proton magnetic resonance spectrum strongly supports configuration V. The single sharp resonance band would be expected from methyl protons symmetrically located. The symmetric molecule, $S_4(NCH_3)_4$, has also been shown to have a single peak in the same region. The nonsymmetric 1,3,5- and 1,4,6-isomers of $S_5(NCH_3)_3$ each show two peaks in the 7 p.p.m. region which are attributed to two types of chemical environment about the protons of each isomer.[5] It does not seem reasonable to predict different chemical environments about the protons of configurations VI or VII. Presumably, isomers with configurations V, VI, and VII would each show a single band which would differ from that of the other isomers in position only.

The melting point range (72–77°) suggests a possible mixture. We are of the opinion, however, that it is more reasonable to account for the range in terms of the thermal instability of the compound than as a result of a mixture. It was observed that the compound decomposes at a significant rate even at room temperature. The decomposition is accelerated as the temperature is elevated. The presence of decomposition products would increase the melting range and lower the observed melting point.

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