crystals. These crystals were spread out on a towel and, after a day, were pressed down and spread again on a new dry towel. After two more days of such treatment these crystals, m.p. 33–34°, were analyzed.

Anal. Calcd. for $C_{20}H_{18}Pb$: C, 51.59; H, 3.90. Found: C, 51.58; H, 4.07.

Diphenyldivinyllead.—The procedure was, in general, the same as that in the preparation of triphenylvinyllead except that diphenyllead dichloride was used instead of triphenyllead chloride. The Grignard reagent was prepared from 3.17 g. of magnesium (0.130 mole) and 14.0 g. of vinyl bromide (0.130 mole) in 120 ml. of tetrahydrofuran. To the Grignard solution, 28.18 g. of diphenyllead dichloride and 120 ml. of tetrahydrofuran were added. The procedure for isolation was the same, except that petroleum ether, b.p. 30–60°, was used instead of hexane for the extraction, and the pot temperature during the molecular distillation was 120–155°. The yield was 13.69 g. (50.1%) of pale yellow liquid. This was redistilled in a molecular still, and a middle fraction analyzed.

Anal. Calcd. for $C_{16}H_{16}Pb$: C, 46.25; H, 3.88; Pb, 49.87. Found: C, 46.10; H, 3.89; Pb, 49.48.

Trivinyllead Acetate.—Tetravinyllead (1.000 g. or 0.00318 mole) prepared from vinylmagnesium bromide, 0.1962 g. glacial acetic acid (0.00318 mole + 3% excess) and a piece of silica gel as catalyst were mixed. A gas was evolved, and after 20 minutes the mixture solidified to a white crystalline mass. This solid was heated on a steam-bath for 1/2 hour to complete the reaction. The precipitate was washed several times with petroleum ether, leaving 0.89 g. (81% yield) of product, m.p. 168–170°. The product was sublimed at 100° (1 mm.) to obtain the analytical sample, m.p. 168–170°. (The solid can be crystallized from benzene.)

Anal. Calcd. for $C_8H_{12}O_2Pb$: C, 27.66; H, 3.48. Found: C, 27.50; H, 3.70.

A sample of trivinyllead acetate prepared in 84% yield from tetravinyllead from vinylmagnesium chloride melted at 169–170°. The mixture melting point of this sample with some of the analytical sample above was 168–170°.

Trivinyllead Chloride.—Tetravinyllead (1.00 g. or 0.00318 mole) prepared from vinylmagnesium bromide was dissolved in 10 ml. of hexane. Dry hydrogen chloride was passed through the solution. The precipitate was filtered and washed with hexane, and the filtrate was treated with more hydrogen chloride. The process was repeated until a precipitate was obtained which did not melt when heated up to 200°. Four fractions were obtained, melting at 114–118°, 117–120°, 120–122° and 120–122°. Later fractions, which did not melt below 200°, were discarded. The combined solids weighed 0.31 g. (30.3% yield). A portion was sublimed at 90° (1 mm.) to give a white solid, m.p. 119–121°, which was analyzed.

Anal. Calcd. for C_6H_9ClPb: C, 22.25; H, 2.80. Found: C, 22.35; H, 2.90.

A sample of trivinyllead chloride was prepared from the tetravinyllead from vinylmagnesium chloride. This sample was sublimed at 90° (1 mm.) to give a product melting at 120–122°. The mixture melting point of this sample with some of the analytical sample above was 120–122°.

Trivinyllead Trichloroacetate.—Tetravinyllead (1.000 g. or 0.00318 mole) prepared from vinylmagnesium bromide was mixed slowly (caution) with 0.536 g. trichloroacetic acid (0.00318 mole + 3% excess) and a piece of silica gel as catalyst. A violent exothermic reaction occurred, leaving a solid product with a brown tint. The product was washed several times with petroleum ether to remove unreacted starting materials. The product was sublimed at 180–195° (1 mm.) to obtain the analytical sample which did not melt below 300°. The crude product weighed 1.06 g. (74% yield).

Anal. Calcd. for $C_8H_9Cl_3O_2Pb$: C, 21.32; H, 2.01. Found: C, 21.01; H, 1.76.

Divinyllead Dichloride.—A saturated solution of chlorine in acetic acid was added to 1.00 g. of tetravinyllead until the yellow color persisted. The white precipitate which formed was filtered, and more chlorine in acetic acid was added to the filtrate, which was allowed to stand overnight. The additional solids which deposited from the filtrate were collected and combined with the original white solid. The combined dry product weighed 0.7664 g. (72% yield). Dithizone analysis showed the product to contain 92% divinyllead salt, a slight amount of trivinyllead salt and no inorganic lead salts. The product was recrystallized from methanol and water to give white crystals which were dried at 100° (20 mm.) for 2 hours for analysis.

Anal. Calcd. for $C_4H_6Cl_2Pb$: C, 14.46; H, 1.82. Found: C, 14.31; H, 1.80.

This sample showed the presence of trace amounts of ethyllead compounds by infrared analysis. Another sample of divinyllead dichloride prepared from the tetravinyllead from vinylmagnesium chloride possessed the same spectrum, except that there was no evidence for ethyllead contaminants.

Infrared spectra were obtained on all of the above vinyllead salts. The presence of the vinyl group was confirmed by an absorption peak at 6.3 μ. Infrared spectra of the trivinyllead salts indicate no ethyl-to-lead bonds (8.6 μ).

Acknowledgments.—The authors are indebted to R. A. Ashby, R. P. Curry, William J. Easley, W. W. Parker, G. Z. Smith and especially to S. R. Henderson, for analytical information.

BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL COMPANY]

The Reaction of Sulfur Dichloride with Methylamine[1]

BY BOB D. STONE AND MORRIS L. NIELSEN

RECEIVED OCTOBER 30, 1958

The reaction of sulfur dichloride with methylamine in hexane solution has been investigated and found to produce an amorphous polymer of approximate composition $(CH_3NS)x$, crystalline $(CH_3NS)_4$ and two crystalline isomers of molecular formula $(CH_3N)_3S_5$. Possible structures and a reaction mechanism are proposed.

Formation of cyclic S_4N_4 by the action of NH_3 on SCl_2 or S_2Cl_2 has long been known.[2,3] Goehring and Weis[4] have reported that SCl_4 and n-$C_4H_9NH_2$ at −60° gave (A), a yellow oil stable only below 50°. Levi[5] obtained a crystalline compound (B) by action of S_2Cl_2 on $C_2H_5NH_2$. Becke-Goehring and Jenne[6] have repeated Levi's work recently and extended it to other amines. Lengfeld and Stieglitz,[7] on treatment of SCl_2 with $C_2H_5NH_2$ in hexane,

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[1] Presented at the 134th meeting of the American Chemical Society, Chicago, Illinois, September 7-12, 1958.

[2] R. Schenck, *Ann. Chem. Liebigs*, **290**, 171 (1896).

[3] M. Goehring, "Ergebnisse und Probleme der Chemie die Schwefelstickstoffverbindungen," Akademie-Verlag, Berlin, 1957, pp. 1-26.

[4] M. Goehring and G. Weis, *Angew. Chem.*, **68**, 678 (1956).

[5] T. G. Levi, *Gazz. chim. ital.*, **61**, 294 (1931).

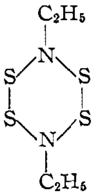
[6] M. Becke-Goehring and H. Jenne, *Angew. Chem.*, **70**, 399 (1958).

[7] F. Lengfeld and J. Stieglitz, *Ber.*, **28**, 2742 (1895).

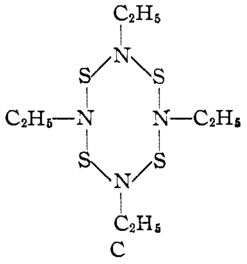
obtained an unstable yellow oil to which they assigned the structure C. Meuwsen and Holch[8] have duplicated these results.

$C_4H_9N{=}S{=}NC_4H_9$

A



B



C

We have investigated the reaction of SCl_2 with CH_3NH_2 in hexane. This paper reports an extension of work described in an earlier preliminary communication.[9]

Experimental[10]

Reagents.—Technical grade SCl_2 (Matheson Co., Inc.) was twice distilled in the presence of a small amount of PCl_3 through a 12″ Vigreux column as prescribed by Brauer.[11] The fraction boiling between 55 and 61° was redistilled in the presence of a trace of PCl_3, retaining that boiling between 58 and 61°. The function of PCl_3 in this distillation apparently is to inhibit the decomposition of SCl_2

$$2SCl_2 \rightleftarrows S_2Cl_2 + Cl_2$$

Lowry and Jessop[12] have shown that this equilibrium is 16–18% toward the right at room temperature. The appearance of an absorption peak at 266 mμ (characteristic of S_2Cl_2[12]) in freshly-distilled SCl_2 was followed with time. Qualitatively, this showed that the decomposition reaction proceeds to approximately $^1/_4$ of its equilibrium value in one hour at room temperature even in the presence of 1% PCl_3. Thus, while PCl_3 inhibits the decomposition of SCl_2 sufficiently to allow distillation, it does not prevent decomposition over long periods of time. Consequently, SCl_2 was used as quickly as possible after distillation.

Methylamine (Matheson Co., Inc.) was taken from a half-used 50-lb. cylinder. Levels of NH_3, $(CH_3)_2NH$ and $(CH_3)_3N$ were shown to be no more than 0.1, 0.5 and 0.5%, respectively, by vapor-chromatography on a substrate of 1 part polypropylene glycol "2025" (Carbide and Carbon Chemicals Co.) and 5 parts silicone "DC-550" (Dow Corning Corp.) on firebrick (Fisher Scientific Co.) which had been neutralized with methanolic NaOH.[13]

Skellysolve B, a petroleum fraction with a boiling-point range of 60–70° and consisting principally of hexanes was used as a medium for the SCl_2–CH_3NH_2 reaction and as the eluting solvent in the chromatography experiments.

Alumina used in the chromatographic separation was either acid-washed Al_2O_3 from Merck and Co., Inc., or type "H" chromatographic Al_2O_3 from Peter Spence and Sons, Ltd.

Reaction of SCl_2 with CH_3NH_2.—Gaseous CH_3NH_2 was passed into a stirred solution of 45 g. of SCl_2 in 850 ml. of hexane at the rate of about 300 ml./min. until the reaction mixture turned pink and the off-gases were basic. The temperature of the reaction mixture was held below 15° by an ice-bath. The slurry was filtered, and the filter cake was washed repeatedly with methanol to remove $CH_3NH_2 \cdot HCl$. The plastic residue was dissolved in chloroform and reprecipitated by pouring the solution into excess ethanol. After the ethanol was decanted, the sticky product (11 g.) was dried in a vacuum desiccator over calcium chloride.

The product was a low polymer of variable composition, but its formula approximated $(CH_3NS)x$. Analyses of a typical sample are given.

Anal. Calcd. for CH_3NS: C, 19.65; H, 4.95; N, 22.92; S, 52.48. Found: C, 19.53, 20.03; H, 4.22, 4.95; N, 21.15, 20.25; S, 50.32, 51.43.

A sample of polymer prepared by this method was fractionated by dissolving 10 g. of it in 50 g. of dry benzene and adding hexane gradually to precipitate fractions of varying molecular weights.

Hexane added, g.	Wt. (g.) from 10 g. of polymer	State	Sp. visc. (1% in benzene)
50	2.6	Brittle solid	0.070
90	1.7	Brittle solid	.070
180	1.5	Gum	.052
330	0.5	Gum	.052
..	3.7 (in soln.)	Oil	.022

By pulling slowly, the lower molecular weight material could be stretched in long threads; but when stretched rapidly, it fractured cleanly. When struck sharply, it shattered.

The polymer was unstable: it decomposed slowly on standing a few weeks at room temperature and decomposed violently at 80–100°. The temperature at which this violent decomposition occurred was not reproducible. Products of the decomposition were NH_3 (identified as NH_4Cl), sulfur and an unidentified red oil.

On evaporating hexane from the original filtrate, a reddish-yellow oil resembling Lengfeld and Stieglitz' product remained. This oil was extremely unstable, usually decomposing suddenly after standing a few hours at room temperature. It caused an explosion on attempted distillation at 15 mm.

Chromatography on an Al_2O_3 column using hexane as the eluting solvent showed that this oil contained at least two crystalline compounds. These were not obtained in sufficient quantity in this experiment to allow complete characterization, but they were shown to be $(CH_3NS)_4$ and $(CH_3N)_3S_5$ (I) (described below) by their X-ray diffraction patterns. The bulk of the mixture was an unstable oil which decomposed before it could be analyzed, but was presumably low polymer.

Preparation and Separation of Crystalline Compounds.—Since the crystalline compounds described above are probably cyclic, conditions of extreme dilution were expected to favor their formation over that of the polymer. Consequently, the experiment was repeated with the reactants being maintained at low concentrations. To 2.5 liters of hexane, a solution of 208 g. of SCl_2 in a liter of hexane was added through a constant-flow dropping funnel over a period of 36 hours. At the beginning, 30 ml. of the SCl_2 solution was added so that this reactant would be in slight excess at all times. Simultaneously, CH_3NH_2 was bubbled into the reaction flask at 70–80 ml./min. The temperature was maintained between 2 and 5° throughout the run. After SCl_2 addition was complete, passage of CH_3NH_2 was continued until the off-gas tested basic. The solids which had separated contained 34 g. of hexane-insoluble polymer in addition to by-product $CH_3NH_2 \cdot HCl$.

The hexane filtrate was evaporated to 300 ml. and put on a column (95 mm. i.d. × 25 cm. long) of 1300 g. Al_2O_3 (total column volume, 750 ml.) and the column was eluted with hexane. The first 1.5 column volumes of solution contained 10.5 g. of a white solid which crystallized in long flat needles. It was recrystallized from methanol by dissolving at room temperature, then slowly cooling to −78°. Recrystallization was repeated until a product of constant melting point and constant X-ray diffraction pattern was obtained. The purified material melted at 54–55°, decomposing at 190°. This compound will be referred to as $(CH_3N)_3S_5$ (I).

Anal. Calcd. for $(CH_3N)_3S_5$: C, 14.56; H, 3.67; N, 16.98; S, 64.79; mol. wt., 247.5. Found: C, 14.39; H, 3.73; N, 16.42; S, 65.78; mol. wt. (cryoscopic in benzene), 249.

The next column volume contained 2.1 g. of a second compound which also crystallized as flat needles. Material

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(8) A. Meuwsen and H. Holch, *Ber.*, **64**, 2301 (1931).

(9) B. D. Stone and M. L. Nielsen, THIS JOURNAL, **79**, 1264 (1957).

(10) We are indebted to Mrs. W. Harden and Mr. R. Knotts for C, H and N analyses; to Mrs. G. Kratzer and Mr. J. Weis for S analyses; to Mr. J. Pustinger and Mr. R. Coffey for infrared and Raman spectra measurements; to Mr. W. Coakley and Mr. R. Eckstein for n.m.r. measurements; and to Mr. R. Ferguson for XRD patterns.

(11) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 288.

(12) T. M. Lowry and G. Jessop, *J. Chem. Soc.*, 1421 (1929).

(13) A. T. James, A. J. P. Martin and G. H. Smith, *Biochem. J.*, **52**, 238 (1952).

purified by repeated recrystallizations from methanol, as described above, melted at 44–46.5°. This substance will be referred to as $(CH_3N)_3S_5$ (II).

Anal. Calcd. for $(CH_3N)_3S_5$: C, 14.56; H, 3.67; N, 16.98; S, 64.79; mol. wt., 247.5. Found: C, 14.80; H, 3.56; N, 16.63; S, 65.16; mol. wt. (cryoscopic in benzene), 239, 247.

A third crystalline compound began to appear in the third column volume of eluting solvent, but a total of 14 column volumes was necessary to remove completely the 35.5 g. of this substance. After recrystallization from hexane, this compound melted at 126–126.5° and decomposed at 190°. The crystals were long, thin needles, a mass giving the appearance of cotton. Slow crystallization gave needles as long as 2.5 cm.

Anal. Calcd. for $(CH_3NS)_4$: C, 19.65, H, 4.95; N, 22.92; S, 52.48; mol. wt., 244.4. Found: C, 19.92; H, 4.84; N, 23.61; S, 52.27; mol. wt. (cryoscopic in benzene), 243.

A colored oil which remained on the column could not be eluted with hexane and decomposed on the column before it could be eluted with other solvents. Presumably, it was low polymer.

Attempted Hydrolysis of $(CH_3NS)_4$ and $(CH_3N)_3S_5$ (I).—To 0.6728 g. of $(CH_3NS)_4$ dissolved in 100 ml. of methanol, 2.2 g. of NaOH (5 moles/g. atom sulfur) in 12 ml. of H_2O was added, and the solution was refluxed for 2 hours. After cooling, 0.5727 g. of unchanged $(CH_3NS)_4$ (85% of original) was recovered by precipitation with a large excess of H_2O. The recovered material was identified by its X-ray diffraction pattern.

In a similar experiment on $(CH_3N)_3S_5$ (I), 0.4087 g. of an original 0.5728-g. sample was recovered after refluxing for 2 hours with 5 mole equivalents of NaOH in a 10:1 methanol–water solution. This recovered material was identified as unchanged $(CH_3N)_3S_5$(I) by its X-ray diffraction pattern. Thus it was shown that these substances are quite resistant to hydrolysis in dilute alkali. This is consistent with the fact that dilute alkali attacks $H_4S_4N_4$ only slowly.

Infrared Spectra.—The infrared spectra summarized in Table I were measured using Baird Model B (NaCl optics) and Beckman IR-4 (NaCl and KBr optics) instruments. The spectra of the crystalline compounds were obtained from mulls in Nujol and hexachlorobutadiene, while the spectrum of the polymer was obtained in carbon disulfide and carbon tetrachloride solutions. The position of the various absorption peaks is given by the wave number (cm.$^{-1}$) and their relative intensities (within each spectrum) are indicated by the small letters.

TABLE I

INFRARED SPECTRA

(s) strong; (m) medium; (w) weak; (v) variable; (sh) shoulder; (bw) broad weak.

$(CH_3NS)_x$ polymer	$(CH_3NS)_4$	$(CH_3N)_3S_5$ (I)	$(CH_3N)_3S_5$ (II)
2900(m)	2950(m)	2850(m)	2900(m)
1435(m)	1450(m)	1440(m)	1430(m)
1220(v)	1400(v)	1155(v)	1155(v)
1160(v)	1155(v)	1115(m)	1120(m)
1120(v)	1120(m)	1075(sh)	1070(s)
1070(s)	1070(s)	1065(s)	805(m)
945(s)	780(s)	785(s)	778(s)
760(sh)	605(w)	770(s)	717(m)
715(s)	583(v)	583(sh)	593(sh)
	453(m)	570(w)	581(w)
		470(bw)	470(w)

Raman Spectra.—The Raman spectra of $(CH_3N)_3S_5$ (I) and $(CH_3N)_3S_5$ (II) were measured in cyclohexane solution, using a Cary Spectrophotometer Model No. 81. Excitation was by the Hg line at 4358 Å. and the filter solution was prepared by dissolving 1.75 g. of ethyl violet in 125 ml. of nitrotoluene and diluting to 3000 ml. with isopropyl alcohol. The spectra were complicated by an intense background radiation scatter, possibly due to fluorescence or photodecomposition. With both materials, however, Raman shifts were observed at $\Delta\nu$ values of 480–490 cm.$^{-1}$, which agrees with that reported for the S–S grouping.[14]

Nuclear Magnetic Resonance Spectra.—The nuclear magnetic resonance spectra of the protons in the polymer and the three crystalline compounds were measured using a Varian Associates Nuclear Magnetic Resonance Spectrometer with a 12 in. electromagnet and a 40 MC. signal. Measurements were made in carbon tetrachloride solution in a 5 mm. tube using H_2O as an external reference according to the method of Zimmerman and Foster.[15] Chemical shifts were calculated from the equation

$$\text{Shift(p.p.m.)} = (H - H_R)/H_R$$

where H = magnetic field strength of sample at the nucleus; and H_R = magnetic field strength of reference material at the nucleus.

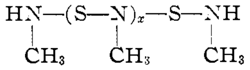
Two samples of polymer were examined by a high resolution technique. The sample of very low molecular weight gave one peak at 1.5 p.p.m., assigned to protons on the CH_3–N group and another at 2.7 p.p.m. assigned to terminal H–N protons.[16] The sample of apparently higher molecular weight gave a single peak at 1.4 p.p.m.

The crystalline compounds were examined by an ultra high resolution technique. A single peak at 1.02 p.p.m. was observed for $(CH_3NS)_4$, while $(CH_3N)_3S_5$(I) gave peaks at 1.45 and 1.66 p.p.m. (area ratio 1:0.91); and $(CH_3N)_3S_5$(II) gave peaks at 1.15 and 1.31 p.p.m. (area ratio 1:1.93).

X-Ray Powder Diffraction Patterns.—X-Ray powder data were determined with a General Electric XRD-3 Diffractometer using nickel-filtered copper radiation (λ 1.5418 Å.). Each of the crystalline substances has a characteristic powder pattern. Detailed data on these patterns are reported elsewhere.[17]

Discussion

From the method of preparation and its physical properties, we propose a linear structure such as D for the polymeric material.



$$\underset{CH_3}{\underset{|}{HN}}\text{—}(S\text{—}\underset{CH_3}{\underset{|}{N}})_x\text{—}S\text{—}\underset{CH_3}{\underset{|}{NH}}$$

D

This is favored over possible linked-ring structures because linking through ring-nitrogens is not possible (due to methyl groups), and linking through ring-sulfur would involve oxidation of sulfur. The solubility of the polymer in solvents such as benzene, chloroform and pyridine indicates that cross-linking is not appreciable. Since some S_2Cl_2 undoubtedly is formed in the SCl_2 during the time required for the reaction, some –NSSN– groups may be present. Nuclear magnetic resonance measurements on low polymer show two types of hydrogens, indicating a terminal H–N group.

The indefinite composition of this material can probably be explained by difficulty in freeing it from solvent and by its instability. (It decomposed slowly even at room temperature.) Samples for analyses were held under vacuum at room temperature for several hours, but were not heated for fear of accelerating decomposition.

We propose the structures shown for the crystalline compounds $(CH_3NS)_4$, $(CH_3N)_3S_5$ (I)

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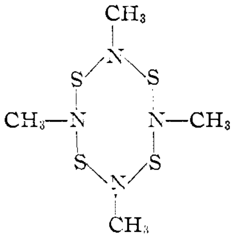
(14) J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publ. Corp., New York, N. Y., 1939, pp. 258–9.

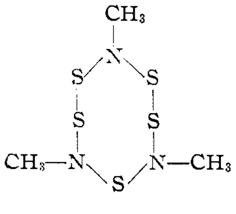
(15) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

(16) J. E. Wertz, *Chem. Revs.*, **55**, 853 (1955).

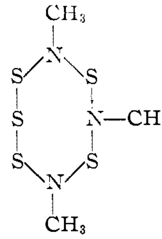
(17) This material has been deposited as Document No. 5810 with the American Documentation Institute Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document No. and by remitting (in advance) $1.25 for photoprints or for 35 mm. microfilm. Make checks payable to Chief, Photoduplication Service, Library of Congress.



$(CH_3NS)_4$



$(CH_3N)_3S_5$ (I)



$(CH_3N)_3S_5$ (II)

and $(CH_3N)_3S_5$ (II), respectively. Suggested names for these are: $(CH_3NS)_4$,N,N',N'',N'''-tetramethylcyclotetrasulfur-1,3,5,7-tetraimide or, alternatively, N,N',N'',N'''-tetramethyltetrathia-1,3,5.7-tetrazacyclooctate; $(CH_3N)_3S_5$ (I), N,N,N''-trimethylcyclopentasulfur 1,3,6-triimide or, alternatively, N,-N',N''-trimethylpentathia-1,3,6-triazacyclooctane; and $(CH_3N)_3S_5$ (II), N,N',N'' trimethylcyclopentasulfur-1,3,5-triimide or, alternatively, N,N',N''-trimethylpentathia-1,3,5-triazacyclooctane.

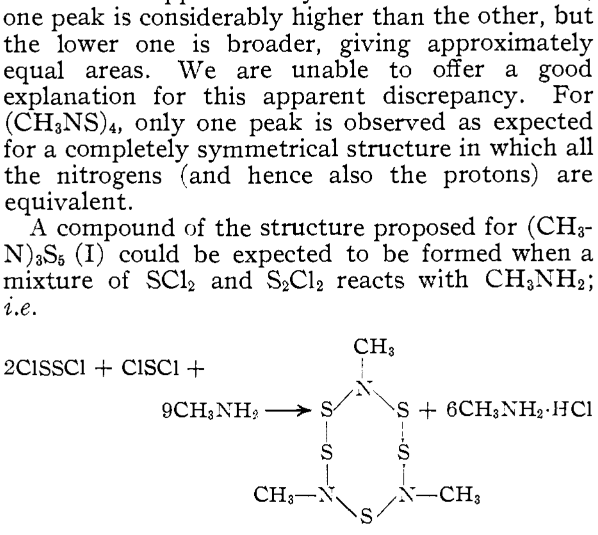
The structure suggested for $(CH_3NS)_4$ is analogous to the proved structure for $H_4S_4N_4$[18] and also to the structure which Lengfeld and Stieglitz assigned to the tetraethyl derivative. By analogy with the SCl_2–NH_3 reaction, such a compound would be expected from reaction of pure SCl_2 with CH_3NH_2. This symmetrical structure is also consistent with the fact that only one type of proton was revealed by nuclear magnetic resonance analysis.

Proof that compounds $(CH_3N)_3S_5$ (I) and (II) are different molecular species is provided by their different X-ray diffraction patterns, their different n.m.r. spectra, their different infrared spectra, depression in mixed melting points, and differences in stability, I undergoing no appreciable decomposition on standing for several months at room temperature whereas II shows considerable decomposition in a few weeks.

The fact that both I and II have two chemical shifts in their proton nuclear magnetic resonance spectra indicates two types of chemical environments for protons. However, with both compounds the shifts are very close together, indicating that the differences are very small. Our interpretation of these spectra is that all the protons are on methyl groups attached to nitrogen and that differences in surroundings of the nitrogens account for the slight differences in shifts for some of the protons involved.

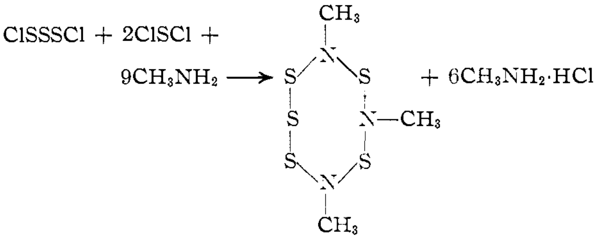
The n.m.r. spectrum of II is in good agreement with the proposed structure, but that for I agrees only qualitatively. In both structures, one of the two peaks should be twice as large as the other, since in each case two nitrogens are identical while the third is different. In the case of II, the area ratio of the two peaks is approximately 2:1, but for I the ratio is approximately 1:1. In the latter case, one peak is considerably higher than the other, but the lower one is broader, giving approximately equal areas. We are unable to offer a good explanation for this apparent discrepancy. For $(CH_3NS)_4$, only one peak is observed as expected for a completely symmetrical structure in which all the nitrogens (and hence also the protons) are equivalent.

A compound of the structure proposed for $(CH_3N)_3S_5$ (I) could be expected to be formed when a mixture of SCl_2 and S_2Cl_2 reacts with CH_3NH_2; *i.e.*



Since we have shown qualitatively that the decomposition of SCl_2 into S_2Cl_2 and Cl_2 proceeds well toward equilibrium in the time required for our reaction, it appears that sufficient S_2Cl_2 is present to account for the formation of this product. Furthermore, the Raman spectrum indicates that the compound contains –S–S– groups.

Formation of the $(CH_3N)_3S_5$ (II) structure by a scheme similar to that postulated above for I requires the presence of S_3Cl_2 as a reacting species



Although S_3Cl_2 has not been isolated directly from the SCl_2–S_2Cl_2 system, it has been suggested as a decomposition product of S_2Cl_2.[19]

Feher and his co-workers[20] have synthesized it by the action of H_2S on excess SCl_2. Feher and

$$ClSCl + HSH + ClSCl \longrightarrow ClSSSCl + 2HCl$$

Baudler[21] also have produced lower chlorides of sulfur by a heat treatment of S_2Cl_2. The formation of the cyclic S_7NH in the reaction of S_2Cl_2 with NH_3[22] can possibly be explained by an analogous mechanism.[23]

We have assigned the above structures to $(CH_3N)_3S_5$ (I) and (II), respectively, for two reasons: (1) the quantity of S_2Cl_2 formed from SCl_2 is probably greater than that of S_3Cl_2 and hence I would be expected to occur in greater quantities than II; and (2) structure II would be expected to

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be less stable than I. These assumptions are consistent with the relative yields and stabilities observed for the two compounds.

The structure proposed for $(CH_3N)_3S_5$ (I) is somewhat similar to B which Levi[5] and Becke-Goehring and Jenne[6] obtained from S_2Cl_2 and $C_2H_5NH_2$. The –SSSN– grouping in the structure proposed for $(CH_3N)_3S_5$ (II) has been suggested as a possible form of the $-S_3N-$ ligand in $Ni(S_3N)_2$. Piper[24] isolated this latter compound from the reaction of S_4N_4 with $NiCl_2$.

Although we have not examined the analogous reaction of SCl_2 with $C_2H_5NH_2$, our results raise some doubt that the unstable oil obtained by Lengfeld and Stieglitz was a single molecular species.

(24) T. S. Piper, THIS JOURNAL, **80**, 30 (1958).

DAYTON, OHIO

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Molecular Structure of Pivalonitrile by Electron Diffraction[1]

BY R. L. LIVINGSTON AND C. N. RAMACHANDRA RAO[2]

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The molecular structure of pivalonitrile has been studied by the sector-microphotometer method of electron diffraction. The central C–C distance has been found to be 1.46 ± 0.020 Å. The other parameters are: C–C = 1.540 ± 0.010 Å., C–N = 1.160 ± 0.007 Å. and ∠C–C–CN = 109.5 ± 1.5°.

Electron diffraction and microwave investigations of CH_3CN,[3,4] CF_3CN[3,5] and CH_3CH_2CN[6] have shown that there is a considerable contraction in the central C–C distances in these molecules; such contractions have been regarded as evidence for hyperconjugation. It seemed worth while to investigate the molecular structure of pivalonitrile (α,α-dimethylpropanenitrile) in order to determine whether there is similar contraction of the C–C in this compound.

Experimental

The sample of pivalonitrile was obtained from the du Pont Company. After a few vacuum distillations, the sample was found to be at least 99% pure by a cooling curve analysis.

Several electron diffraction patterns were taken with an r^3-sector at two camera distances, employing electrons of wave length 0.05452 Å. Kodak Lantern Slide Contrast Plates were used with camera distances of 10.19 and 25.10 cm. Microphotometer traces of four of the best plates were taken using a Leeds and Northrup microphotometer. The transmittancies were converted to arbitrary intensity units[7] and the results at each camera distance were averaged. The total range of data extended from $q = 16$ to $q = 112$.

The radial distribution procedure was employed by calculation of curves by the equation[8]

$$rD(r) = \sum_{q=1,2,\ldots}^{q_{\max}} I_m(q)\exp(-bq^2)\sin\frac{\pi qr}{10} \qquad (1)$$

where $rD(r)$ is the radial distribution function, r is the internuclear separation and $\exp(-bq^2) = 0.10$ at $q = q_{\max}$.

For the radial distribution calculations, the intensity data between $q = 0$ and $q = 15$ were taken from a theoretical scattering curve calculated by[8]

$$I_m(q) = \sum_i \sum_j \frac{Z_iZ_j}{r_{ij}}\exp(-b_{ij}q^2)\sin\frac{\pi qr_{ij}}{10} \qquad (2)$$

The initial radial distribution curve showed some extraneous features. By treating these extraneous features as intensity data by means of equation 1, an estimate was obtained of the changes to be made in the background line. The second and final radial distribution curve is shown in Fig. 1 and the final experimental intensity curve is shown in Fig. 2.

Results and Discussion

The radial distribution curve did not give directly any of the parameters of pivalonitrile. It showed five peaks and two were resolved by the procedures of Karle and Karle.[9] The first peak was decomposed to give the C–H and the C–N distances. The second peak at 1.52_3 Å. was decomposed to give two types of C–C distances. The areas of these decomposed peaks are in good agreement with the calculated nZ_iZ_j/r_{ij} values (Table I). The third and fourth peaks are each due to the contributions from a number of distances and no attempt was made to decompose them. The fifth peak is rather small and represents a non-bonded N–H distance. The position of this peak is not reliable since small oscillations in the zero line of the radial distribution curve can change the shape of such a peak considerably. The radial distribution curve gives the C–C and the central C–C bonds as 1.54 and 1.46 Å., respectively. The C–H and the C–N distances are found to be 1.09 and 1.16 Å. The radial distribution curve does not, however, provide any information about the C–C–CN angle (α). The relevant results from the radial distribution curve are summarized in Table I. The table also lists the root mean square amplitudes of vibration, Δr_{ij}, obtained by the Karle's method.[7,10]

TABLE I

RESULTS OF THE RADIAL DISTRIBUTION CURVE FOR PIVALONITRILE

Distance	r_{ij}	Δr_{ij}	Area	nZ_iZ_j/r_{ij}
C–H	1.09	0.075	88.4	88.6
C–N	1.16	.00	49.8	51.4
C–C(central)	1.46	.05	34.4	35.7
C–C	1.54	.05	100	100

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[1] Contains material from the doctoral dissertation of C. N. R. Rao. Presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

[2] Purdue Research Foundation Fellow in Chemistry, 1956–1957; Standard Oil Foundation Fellow in Chemistry, 1957–1958.

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