

portion of the clear liquid from each sample was removed and the boron determined by the carminic acid method.¹⁸

Nine samples analyzed by titration gave a value of quantum yield of decomposition of 0.22 ± 0.03 . Twelve samples analyzed by the carminic acid method gave values of 0.26 ± 0.03 . The difficulties involved in removing the small amount of reacted ma-

terial from the unreacted material and of accurately determining such small amounts of boron make a more accurate quantum yield determination very hard to obtain. Both methods agree within the limits of experimental error.

Mass Spectra. The mass spectra were obtained by using either a 60° sector-type mass spectrometer, or a Consolidated Electrodynamics Model 21-110B mass spectrometer. In either case, all samples were introduced *via* an all-glass inlet system operated at 230°. Exact mass determinations were made by electrical peak matching with the Consolidated Model 21-110B instrument.

(18) G. Charlot, "Colorimetric Determination of Elements," Elsevier Publishing Co., New York, N. Y., 1964, p 194.

Pentacoordinate Silicon. The Crystal Structure of Dimethylsilylamine Pentamer^{1a,b}

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Abstract: X-Ray diffraction crystal-structure analysis of dimethylsilylamine (DMSA) at -120° reveals that the unusual physical characteristics of this compound are due to the formation of ten-membered, nearly planar rings of alternating silicon and nitrogen atoms. Each silicon is pentacoordinated in a trigonal bipyramidal arrangement with two long Si-N bonds (of the order of 1.95 Å) in the apical directions and three hydrogen atoms at the corners of the triangular base. DMSA crystallizes in the monoclinic system, space group $P2_1/m$ (C_{2h}^2), $a = 6.37$ Å, $b = 19.53$ Å, $c = 9.52$ Å, and $\beta = 91.06^\circ$; there are ten formula units (two pentamers) per unit cell.

In 1954, Sujishi and Witz³ demonstrated that dimethylsilylamine (DMSA) differs considerably from other silylamine compounds. It was found that DMSA melts at $+3^\circ$, more than 100° higher than trisilylamine and methylsilylamine, and that it has an appreciably higher ΔH of sublimation. Recently it was shown that the infrared absorption spectrum of crystalline DMSA differs radically from that of the gas phase.⁴ These data were interpreted as indicating intermolecular association (of an unknown number of DMSA units) involving the nonbonding electrons on the nitrogen atom of one DMSA molecule and an empty silicon d orbital on an adjacent molecule. The present investigation was undertaken in an attempt to determine the crystal and molecular structure of crystalline DMSA.

The crystal data for $H_3SiN(CH_3)_2$ (mol wt 75.19) are: monoclinic, probable space group $P2_1/m$ (C_{2h}^2); $a = 6.37 \pm 0.3$ Å, $b = 19.53 \pm 0.10$ Å, $c = 9.52 \pm 0.05$ Å, $\beta = 91.06 \pm 0.10^\circ$; X-ray density = 1.054 g/cc for ten formula units/unit cell.

Experimental Section

DMSA was synthesized and purified according to the procedures described by Sujishi and Witz.³ A small amount of material was

condensed in an evacuated, thin-walled quartz tube of 0.3-mm diameter which was sealed and mounted on a precession camera. It was found that the presence of any impurities hindered single-crystal formation. Single crystals were grown from freshly purified samples using standard low-temperature X-ray diffraction techniques, and data were collected at -120° .

Zr-filtered Mo $K\alpha$ radiation was used to investigate 12 reciprocal lattice layers (hkl , $L = 0-4$; hkl , $K = 0-5$; and hkk). The intensities were obtained by visually comparing the spots on the film with a standard intensity strip. All data processing was done with local versions of standard crystallographic computer programs. Lorentz polarization factors were applied; the data were scaled using the Hamilton, Rollet, and Sparks algorithm for interlayer scaling;⁵ the over-all temperature factor and absolute scale factor were calculated; and E factors (normalized structure factors) were obtained.

The only systematically absent reflections were $0k0$, k odd, and the space group could be either $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2). Examination of the E factors indicated that the most probable space group is the centrosymmetric $P2_1/m$ (see below); this was subsequently verified by the structure determination.

	Theoretical ⁶		This investigation
	Centrosymmetric	Acentric	
$\langle E \rangle$	0.798	0.886	0.66
$\langle E^2 - 1 \rangle$	0.968	0.736	1.01

The signs of the observed structure factors were determined using SORTe,⁷ a computer program employing the Symbolic Addi-

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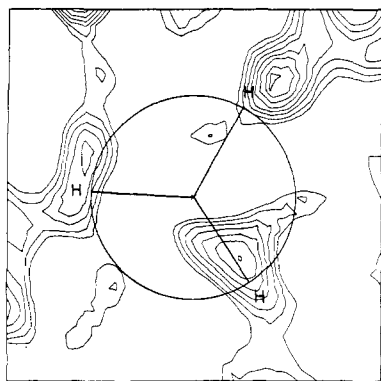


Figure 1. Difference Fourier through Si(3) in the plane perpendicular to the N(2)-N(3) vector. The Si(3) position is at the center of the circle of radius (=1.54 Å); maximum electron density = 0.6 e/Å³.

tion Method⁸ of direct determination of phases. The following initial signs and symbols were used [*hkl* (magnitude of *E* factor), sign or symbol]: 1.11.3 (3.19), +; 414 (2.96), +; 4.11.1 (2.45), +; 313 (2.84), *D*; 177 (3.09), *E*; and 2.12.4 (2.33), *F*. After two passes through the computer it was clear that $D = F \neq E$. Two *E* maps (Fourier maps using the *E* factors as amplitudes) were calculated using 283 *E* factors; a structure indicating a pentamer of DMSA with two and one-half molecules per asymmetric unit was found for $D = F = -, E = +$.

The fractional coordinates obtained from the *E* map were refined using a standard crystallographic least-squares program. The parameters listed in Table I are based on a refinement using 56 parameters (12 scale factors, 32 positional parameters, and 12

Table I. Parameters of Atoms in DMSA^a

Atom	<i>x</i> (σ _{<i>x</i>})	<i>y</i> (σ _{<i>y</i>})	<i>z</i> (σ _{<i>z</i>})	<i>B</i> (σ _{<i>B</i>})
Si(1)	8169 (10)	1151 (5)	6167 (7)	1.4 (0.2)
Si(2)	9526 (16)	2500 (..)	4364 (13)	1.4 (0.3)
Si(3)	5546 (10)	1672 (4)	8867 (7)	1.1 (0.2)
N(1)	9492 (25)	1489 (10)	4482 (20)	2.3 (0.5)
N(2)	4504 (46)	2500 (..)	9678 (33)	3.8 (0.9)
N(3)	6631 (27)	0843 (10)	7983 (19)	2.0 (0.5)
C(1)	8441 (30)	1218 (17)	3097 (23)	2.3 (0.6)
C(2)	5086 (44)	2500 (..)	1351 (36)	0.9 (0.8)
C(3)	4988 (31)	0344 (11)	7484 (24)	1.4 (0.5)
C(4)	1796 (25)	1270 (11)	4486 (20)	0.1 (0.4)
C(5)	8334 (30)	0537 (12)	8921 (21)	1.1 (0.5)
C(6)	2077 (43)	2500 (..)	9721 (33)	0.4 (0.7)

^a Fractional coordinates × 10⁴ and isotropic temperature factors (*B*) in Å². Estimated standard deviations are indicated in parentheses.

isotropic temperature factors) and 667 observations; 123 of the latter were duplicate reflections read on photographs of different layers; only the 544 unique terms were used in the Fourier summations.⁹ The discrepancy factor ($R = \sum |F_o - F_c| / \sum |F_o|$) is 0.131. The data were not of the highest quality; the attempted use of anisotropic temperature factors in the refinement resulted in "not positive-definitive" matrices, and even the isotropic temperature factors of the carbon atoms are unusually low. Of the original 283 *E*

(8) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963); **21**, 849 (1966).

(9) The table of observed and calculated structure factors has been submitted with the manuscript and has been deposited with the U. S. Library of Congress as Document No. 9512. Requests for copies should be addressed: Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting \$1.25 for microfilm or \$1.25 for electrostatic positive prints. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

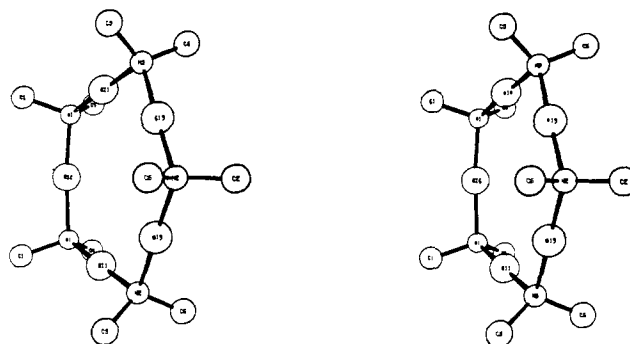


Figure 2. DMSA pentamer: stereo view. The hydrogen atoms are not shown but are probably trigonally arranged around each Si atom in a plane perpendicular to the N-Si-N bonds.

factors greater than 1.0, only the signs of two of the weakest were changed during the refinement.

A three-dimensional difference Fourier map was calculated in an attempt to determine the hydrogen atom positions. A large number of peaks of 0.5 to 0.8 e/Å³ were found; least-squares refinement of the coordinates of the peaks in the most reasonable positions was not conclusive in that the *R* value did not improve and the values for the coordinates of the hydrogen atoms did not converge even after eight cycles of refinement.

It seemed reasonable to assume that the hydrogen atoms attached to the silicon atoms were in the planes perpendicular to the nearly linear nitrogen-silicon-nitrogen bonds. Difference electron-density maps in these planes were calculated; the map obtained for the plane passing through Si(3) is shown in Figure 1 (also, see Description of Molecular Structure).

Finally, five cycles of refinement were carried out using the entire pentamer as the asymmetric unit and assuming space group P2₁. The refinement returned the coordinates to within one or two standard deviations of those obtained for the centrosymmetric structure, indicating that P2₁/m is the correct space group.

Description of Molecular and Crystal Structure

The crystal structure analysis confirms that intermolecular dative bonding is present in crystalline DMSA as suggested by previous investigators.^{3,4}

In the crystalline state DMSA is a pentamer consisting of ten-membered, slightly skewed rings formed by alternating silicon and nitrogen atoms. The nitrogen atoms lie at the corners of a nearly regular pentagon, while the silicon atoms are located midway along each side. Each of the five nitrogen atoms is tetrahedrally bonded to two carbon and two silicon atoms (Figure 2). (The tetrahedral angle of 109° 27' is nearly equal to the internal angle of a regular pentagon, 108°.) The hydrogen atoms attached to the silicons have not been accurately located (see Figure 1); it appears that they lie on planes perpendicular to each side of the pentagon and passing through the silicon atoms. Thus the silicon atoms are pentacoordinated in a trigonal bipyramidal arrangement. The infrared absorption spectrum of DMSA in the gas phase is the same both before and after solidification of the sample, indicating that the formation of the pentamer is reversible;⁴ the sample used in the present investigation was obtained from the same preparation as that used in the infrared study. Therefore, even though the heights of the hydrogen atom peaks were comparable to the noise level of the Fourier, there is little doubt that the compound is indeed DMSA.

Interatomic distances and angles are shown in Figures 3 and 4; the estimated standard deviations (esd) are 0.02 Å for the Si-N distances and 0.025 Å for the N-C

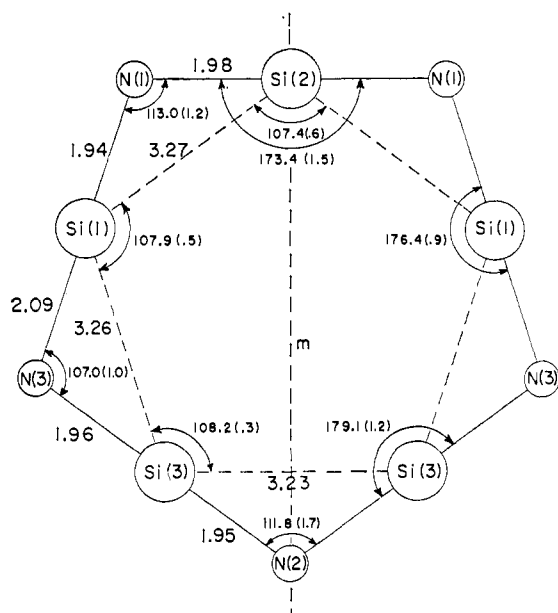


Figure 3. Interatomic distances and angles of the DMSA pentamer. A mirror plane (m) is perpendicular to the plane of the pentamer. The esd's of the interatomic distances are 0.02 Å; those of the angles are indicated in parentheses.

distances. The esd of the angles are indicated in the figures.

The least-squares equation for the ten-membered ring, which is bisected by the mirror plane and lies parallel to the b axis of the unit cell, is

$$5.402x + 4.893z = 7.364$$

where x and z are fractional coordinates. Examination of the deviations of the atoms from the plane (Table II) shows that the ring is not actually planar. A calculation of the least-squares plane through all the atoms except Si(3), N(2), and Si(3)' revealed that the deviation

Table II. Deviation of Atoms in Pentamer from Least-Squares Plane

Atom	Deviation, Å	
	a	b
Si(1), Si(1)'	+0.066	+0.025
Si(2)	-0.083	-0.031
Si(3), Si(3)'	-0.030	-0.218
N(1), N(1)'	-0.044	+0.003
N(2)	-0.152	-0.392
N(3), N(3)'	+0.124	-0.012

^a Least-squares plane defined by all atoms in ring: $5.402x + 4.893z = 7.364$. ^b Least-squares plane defined by all atoms except Si(3), N(2), and Si(3)': $5.557x + 4.497z = 7.288$.

of N(2) from this plane is 0.39 Å (Table II); the angle between the planes defined by N(3), Si(2), and N(3)' and by N(3), N(2), and N(3) is 169.8° with an esd of 1.0° . It is not unreasonable to assume that intermolecular packing forces could cause a distortion of this order of magnitude. The Fourier section of the plane defined by the above equation is shown in Figure 5; each contour line corresponds to $2 e/\text{Å}^3$. (Notice that the peak heights for N(2) and N(3), where the peak centers are 0.15 and 0.12 Å from the plane, are signifi-

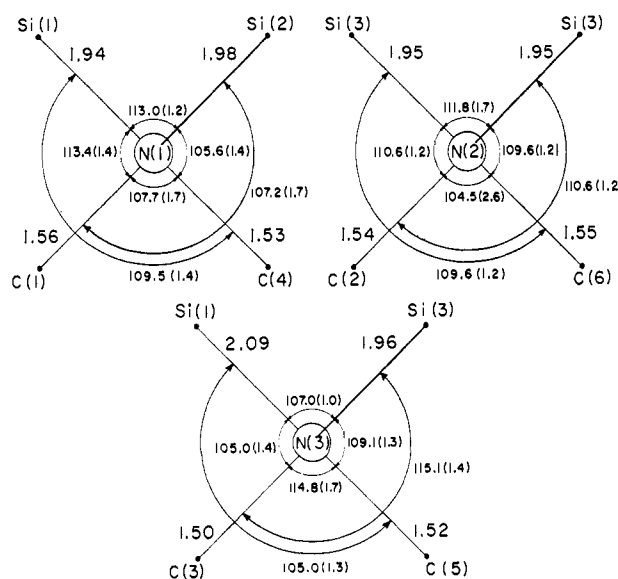


Figure 4. Bond lengths and angles around the three tetrahedral nitrogen atoms. The esd's of the bond lengths are 0.02 Å for Si-N and 0.025 Å for N-C; those of the angles are indicated in parenthesis.

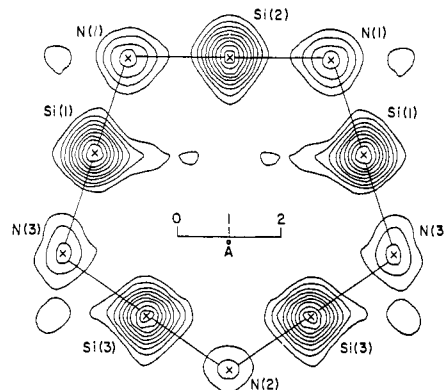


Figure 5. Fourier section through the DMSA pentamer. The equation of the plane is $5.402x + 4.893z = 7.364$. Each contour represents an electron density of $2e/\text{Å}^3$.

cantly less than those of N(1).) The coordination about the nitrogen atoms is normal, the average tetrahedral angle being 109.3° ($\sigma = 1.5^\circ$). The average N-C interatomic distance of 1.53 Å ($\sigma = 0.025$ Å) is comparable to those reported for some recently determined structures (1.48–1.49 Å,^{10–13} in the tetra-*n*-butyl ammonium ion: 1.523 Å ($\sigma = 0.016$ Å);¹⁴ bis(maleonitriledithiolato)iron(III): 1.56 Å ($\sigma = 0.02$ Å);¹⁵ tetramethylenedinitramine(diaquo)nickel(II): 1.571 Å ($\sigma = 0.016$ Å)¹⁶). Si-N interatomic distances have been determined by electron diffraction in hexamethylcyclotrisilazane¹⁷ (1.78

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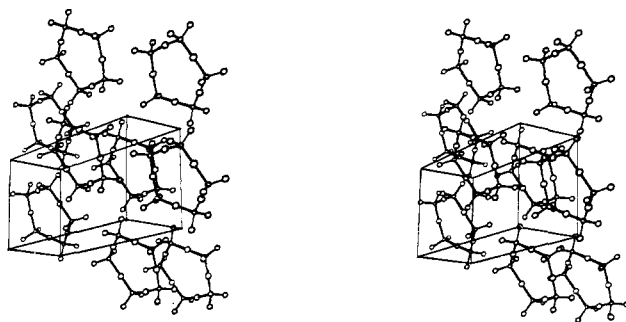


Figure 6. Packing diagram of crystalline DMSA: stereo view. The molecules pack in parallel planes.

± 0.03 Å) and trisilylamine¹⁸ (1.738 ± 0.020 Å) and by X-ray diffraction in octamethylcyclotetrasilazane.¹⁹ The values reported for the latter compound range from 1.687 to 1.750 Å with standard deviations of 0.010 Å; this compound contains puckered eight-membered rings of alternating Si-N atoms with two methyl groups attached to each silicon atom. However, all of these compounds contain tetrahedrally bonded silicon atoms and would be expected to have shorter Si-N bond lengths than crystalline DMSA, which consists of trigonal bipyramidal silicon atoms with the Si-N bonds in the apical directions.

The Si(1)-N(3) distance in DMSA appears to be significantly longer than the other Si-N distances. It was suspected that the parameters might have converged to a false minimum in the least-squares refinement. Positional coordinates of the N(3) atom were assigned values which would shorten this bond; five cycles of least-squares refinement returned the coordinates to the values previously obtained. We feel that this long bond is possibly indicative of the poor quality of the intensity data rather than of a physically real situation.

The DMSA molecules lie on planes parallel to the plane of the pentamers. A stereo view of the molecular packing is found in Figure 6.

Discussion

The crystal structure analysis reveals that the intermolecular dative bonding which occurs between monomers of DMSA is strong enough to result in a pentacoordinated silicon compound in which the identity of the monomer unit is lost.

Speculation about and chemical evidence for the existence of pentacoordinated silicon has appeared in the literature for a number of years. Pentacoordinate species have been suggested as intermediates in many displacement reactions occurring at silicon;²⁰ evidence

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has been presented for the existence of stable organic²¹⁻²⁵ and inorganic²⁶ anions containing pentavalent silicon; and, in at least one case, transannular dative bonding resulting in pentacoordinated silicon has been found.^{27,27a} In many of these cases it is claimed that the silicon atom is attached to a nitrogen by means of dative ($p \rightarrow d$)- π bonding. The present X-ray diffraction investigation provides the first unambiguous structural evidence for the formation of pentacoordinated silicon through ($p \rightarrow d$)- π bonding of the lone pair electrons on nitrogen and a d orbital of silicon. For sp^3d bonding, a square-planar pyramid is expected if the $d_{z^2-y^2}$ orbital is used, while a trigonal bipyramid is the most probable arrangement when the d_{z^2} orbital is involved.²⁸ On this basis it is evident that the sp^3 bonding of silicon in the gas phase of DMSA becomes $sp^3d_{z^2}$ bonding in the crystalline phase.

A detailed reassignment of the bonds in the infrared spectrum of crystalline DMSA^{4,29} does not seem possible in view of the large number of active fundamental vibrational frequencies of the pentamer unit. It is worth noting, however, that the two low-frequency broad, structured absorption bands centered at about 500 and 330 cm^{-1} can now be assigned with reasonable confidence to in-plane and out-of-plane ring-deformation modes, respectively. The absence of these strong bands in the argon matrix spectra, even at concentrations where distinct evidence of polymerization is observed,⁴ indicates that the associated species present under these conditions probably have open-chain rather than cyclic configurations.

In conclusion, it is noted that symmetry considerations and observed bond lengths prevent one from determining which of the adjacent nitrogen atoms was attached to a silicon atom in the monomeric gas phase. We would, therefore, predict that crystallization of a mixture of $D_3Si^{15}N(CH_3)_2$ and $H_3Si^{14}N(CH_3)_2$ would produce a solid that upon revaporization would yield a statistical distribution of the starting species, $D_3Si^{14}N(CH_3)_2$ and $H_3Si^{15}N(CH_3)_2$. An attempt to verify this prediction is planned for the near future.

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