An Electron Diffraction Investigation of Hexamethylcyclotri- and Octamethylcyclotetrasilazanes

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The molecular structures of the vapors of hexamethylcyclotri- and octamethylcyclotetrasilazane were studied by the electron diffraction method. For the former the following data were obtained assuming $\angle CSiC$ to be $110°$: Si–N 1.78 ± 0.03 Å., Si–C 1.87 ± 0.05 Å., $\angle NSiN$ $111 \pm 5°$, $\angle SiNSi$ $117 \pm 4°$. For the latter, the assumption of the values of Si–N, Si–C, $\angle NSiN$ and $\angle CSiC$ obtained for the former lead to the result $\angle SiNSi = 123 \pm 4°$. The rings are both puckered, but the details of the shapes of the rings could not be determined.

For the purpose of determining the Si–N bond length and the SiNSi valence angle, the trimeric and tetrameric cyclic dimethylpolysilazanes of the general formula $[Si(CH_3)_2NH]_n$ were studied by electron diffraction.

Experimental

The trimer and tetramer were prepared after Brewer and Haber.[1] The benzene solution of dimethyldichlorosilane was treated with dry ammonia. After filtering out the ammonium chloride which separated, the product was subjected to fractional distillation (b.p.: trimer 185∼187°; tetramer, 223∼225°).

The electron diffraction photographs of the vapors were taken in a camera of the vertical type at a camera distance of 11 cm. and an electron wave length, as determined by calibration with gold foil, at about 0.06 Å. The liquid samples held at about 20° (trimer) or 80° (tetramer).

Results

The radial distribution functions and theoretical intensity curves were calculated according to the approximate formulas used by Spurr and Schomaker.[2] In the temperature factors $e^{-b_{ij}q^2}$ for the theoretical intensity curves, the b_{ij} were assumed to be zero for all bonded distances, 0.0001 for the

atom pairs of Si $\overset{/N\backslash}{\quad}$ Si, C $\overset{/Si\backslash}{\quad}$ C, N $\overset{/Si\backslash}{\quad}$ N, and Si $\overset{/C\backslash}{\quad}$ H

and 0.0002 or 0.0004 for other unbonded long distances. The C–H distance and the HCH angle were assumed to be 1.09 Å. and tetrahedral. For both compounds the parameters which determine the ratios of heavy-atom distances may be taken as the ratio of distances C–Si/N–Si, the valence angles $\angle SiNSi$, $\angle NSiN$ and $\angle CSiC$, and the form of the ring. The essential features of the pattern were fitted by adjusting the first three parameters.[3]

Hexamethylcyclotrisilazane.—The visual (V_1) and radial distribution (D_1) curves are shown in Fig. 1.[4] The peaks at 1.77 and 1.86 Å. of D_1 are due to bonded Si–N and Si–C and the peak at 2.99 Å. is supposed to be composed of unbonded Si···Si and C···N distances. Comparison of visual and theoretical curves was done mainly with models having the chair form of the (Si–N)₃ ring (the boat form was found to give essentially the

(1) S. D. Brewer and C. P. Haber, THIS JOURNAL, **70**, 3888 (1948).

(2) R. A. Spurr and V. Schomaker, *ibid.*, **64**, 2693 (1942).

(3) As N–H and < SiNH have no effect on the curve, they were not taken into consideration.

(4) Accurate determinations of maxima and minima in the range $q < 20$ were difficult on account of intense background. Therefore, the first and second maxima were omitted in the correlation treatments, although they were indicated in the visual curves in Fig. 1. Also some of the minima especially in the large q range could not be determined with sufficient accuracy.
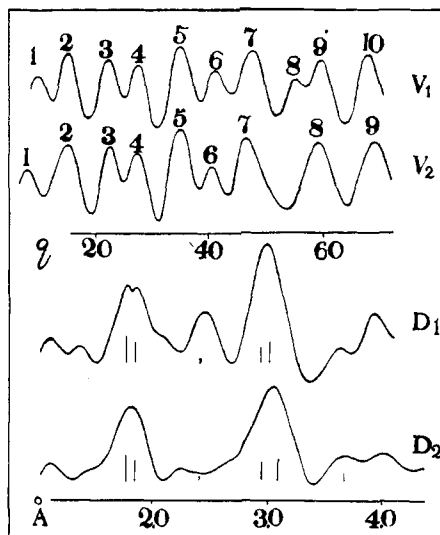
Fig. 1.—Visual and radial distribution curves for hexamethylcyclotrisilazane.

same curves) and the assumed value $110°$ for $\angle CSiC$. These curves are shown in Fig. 2. The vertical lines show the observed q values at maxima and minima of intensity.

The ratio of distances Si–C/Si–N was first taken to be $1.86/1.77 = 1.05$ as obtained from D_1, and various values of the valence angles $\angle SiNSi$ and $\angle NSiN$ were examined (curves A to I in Fig. 2). Then, $\angle NSiN$ was fixed at $111°$ and the values of $\angle SiNSi$ and Si–C/Si–N were changed (curves J to N in Fig. 2). The parameter values for each model are shown diagrammatically in Fig. 3. The observed maxima and minima are most satisfactorily reproduced by curve E. In the other curves, the relative positions of the 3rd, 4th, 6th, 8th, or 9th maxima to the 5th do not coincide with those of the visual curve.

Octamethylcyclotetrasilazane.—The visual and radial distribution curves are shown as V_2 and D_2 in Fig. 1. In D_2 the unresolved peak representing bonded Si–N and Si–C appears at 1.81 Å., and the peak which corresponds to 2.99 Å. in D_1 has its maximum at 3.04 Å. To interpret this feature of D_2, models which have the same values of Si–C/Si–N and of the silicon valence angles as the best model E of the trimer, but larger values of $\angle SiNSi$, were considered. Theoretical curves for such models with several different forms of the (Si–N)₄ ring are shown in Fig. 4.
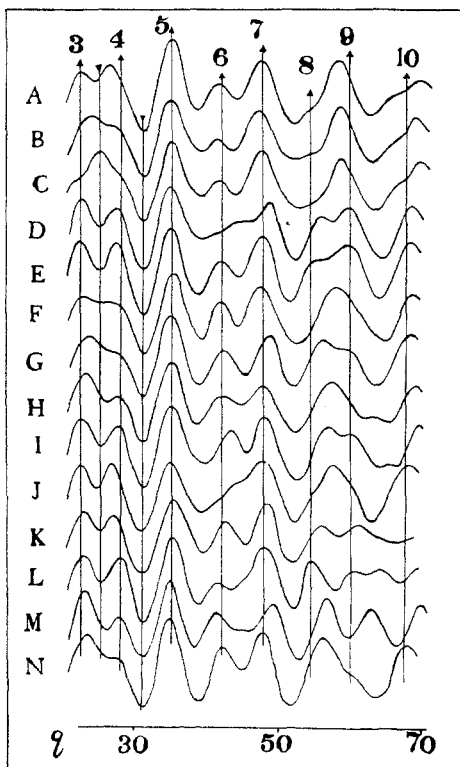
At $\angle SiNSi = 122°$, q for the 6th maximum is

Fig. 2.—Theoretical intensity curves for hexamethylcyclotrisilazane.

Fig. 3.
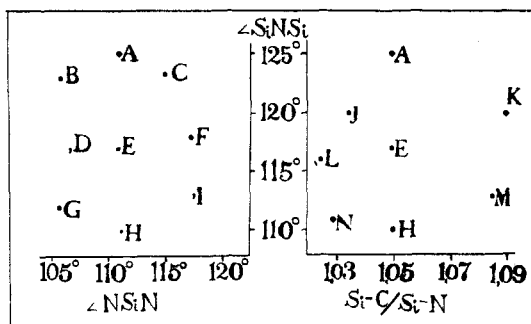
too great, except for curve B. The range of $\angle$ SiNSi which reproduces the visual intensity is 122 $\pm$ 3° for the cradle form and 125 $\pm$ 2° for the crown form. In other forms the effects of changing $\angle$ SiNSi resemble those in the crown form. The value of $\angle$ SiNSi thus deduced is 123 $\pm$ 4°. Even on the best curves, B and H, the 8th maximum has a shape which does not accord with the visual curve; this difficulty could probably be avoided by the use of much more severe temperature factors for the longer cross-ring distances.

Final Results and Discussion.—The quantitative comparisons of observed and calculated q values for the best curves are shown in Table I, and the final results are given in the Abstract.

The value 1.78 $\pm$ 0.03 Å. obtained for the bonded Si–N distance is in agreement with the value 1.80 Å, given by Schomaker and Stevenson's rule[5] within the limits of error.

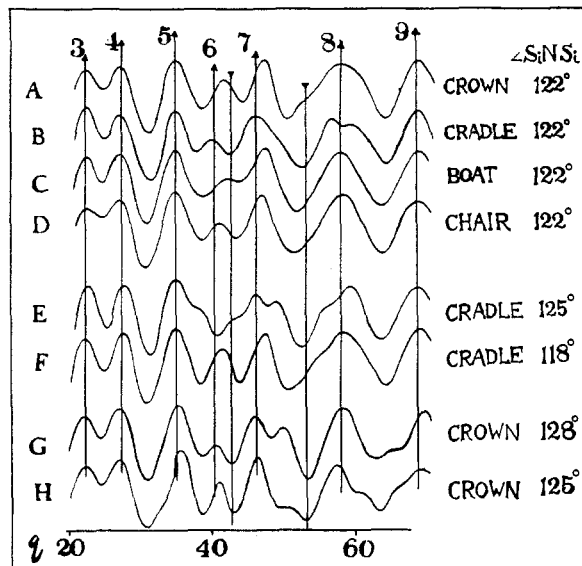(5) V. Schomaker and D. P. Stevenson, THIS JOURNAL, 63, 37 (1941).

Fig. 4.—Theoretical intensity curves for octamethylcyclotetrasilazane.

The valence angle of oxygen hitherto determined is 125 $\pm$ 5° for hexamethylcyclotrisiloxane[6] and about 140° for both octamethylcyclotetrasiloxane and tetra-(trimethylsiloxy)-silane,[7] while that of N is 117 $\pm$ 5° for hexamethylcyclotrisilazane and probably a little larger value for octamethylcyclotetrasilazane. As regards the shape of the ring, only hexamethylcyclotrisiloxane is planar, and the other three compounds are all puckered. The normal valence angle of oxygen in siloxanes is probably about 140° and this angle is easily deformed by the strain of the ring. In silazanes the normal valence angle of nitrogen is probably about 117° and the deformation observed for an eight-membered ring seems to be caused by the increase of mutual repulsion of methyl radicals with the increase of ring members. This difference of valence angles of O and N atoms may be correlated to the tendency of ring formation in siloxanes and silazanes shown

TABLE I

Max.	Min.	[(CH₃)₂SiNH]₃ q_{obs}	q_B/q_{obs}	[(CH₃)₂SiNH]₄ q_{obs}	q_B/q_{obs}	q_H/q_{obs}
3		22.3	1.026	22.4	1.035	1.017
	4	25.1	1.003	25.2	1.008	0.976
4		27.8	0.986	27.6	1.004	0.971
	5	31.1	1.006	31.0	1.000	0.986
5		35.4	1.002	35.1	0.991	1.013
	6	..	...	..	...	...
6		41.9	0.995	40.4	0.995	1.004
	7	..	...	42.8	0.994	1.000
7		47.7	1.002	46.3	1.007	0.997
	8	..	...	53.4	0.989	1.000
8		54.3	1.012	58.3	...	...
	9	..	...	..	...	...
9		60.0	0.992	69.1	0.995	0.994
	10	..	...	..	...	...
10		67.8	1.010	..	...	...
Av.			1.003		1.002	0.996
Av. dev.			0.008		0.009	0.012

(6) E. H. Aggarwal and S. H. Bauer, J. Chem. Phys., 18, 42 (1950).
(7) Unpublished data.

by Brewer and Haber,[1] who have studied the equilibria of linear and cyclic dimethylpolysilazanes at elevated temperatures and pressures and found that the tendency of ring formation is larger in the silazanes than in siloxanes.

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The Vibrational Spectra and Thermodynamic Functions of Lead Tetramethyl, Tin Tetramethyl and Germanium Tetramethyl

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The Raman and infrared spectra of $Pb(CH_3)_4$, $Sn(CH_3)_4$ and $Ge(CH_3)_4$ are given and compared with earlier investigations. The spectra have been used to make a detailed assignment of frequencies to the normal modes of vibration and to calculate values of C_p, $(H^0 - E_0^0)/T$, $-(F^0 - E_0^0)/T$, and S^1 from 300 to 1500 °K. Heat of combustion measurements were made on $Pb(CH_3)_4$ and $Sn(CH_3)_4$ and the results used to calculate the free energy of formation, the enthalpy of formation and entropy of formation at several temperatures for both compounds.

Introduction

While the tetramethyl compounds of the elements of the fourth group have come in for considerable spectroscopic study, there are still uncertainties in the assignments of their modes of vibration. These uncertainties stem in main from the facts that, one, the data in the literature are incomplete, and that, two, no one worker has carried through a complete study of a number of these compounds. The authors, having had at their disposal Raman spectrographs of high speed and resolving power, and infrared equipment covering a wide spectral range, felt that a re-examination of the infrared and Raman spectra of germanium, tin and lead tetramethyls would help to clear up some of the difficulties.[2-7]

The assignment of frequencies made from the spectra of these compounds was used to calculate their thermodynamic functions.

Preparations.—The sample of $Pb(CH_3)_4$ was supplied by Dr. Charles E. Waring of the Chemistry Department, University of Connecticut. After fractional distillation under vacuum, this sample had a b.p. 109° at 720 mm.

Tin tetramethyl was prepared by slowly adding $SnCl_4$ to CH_3MgI in ethyl ether solution. The product was fractionated with a simple Vigreux column, washed with NaF solution, then with cold water and then with concentrated H_2SO_4. After careful fractionation, the product boiled at 78.3° at 740 mm., $n^{21}D$ 1.4393, yield 45%.

Germanium tetramethyl was prepared by very slowly adding $GeCl_4$ to CH_3MgI in n-butyl ether solvent. The $Ge(CH_3)_4$ was distilled off, washed with cold, concentrated H_2SO_4, and fractionated in a good micro-column, b.p. 44.3° at 740 mm.; $n^{20}D$ 1.3882. An alternate preparation with ethyl ether solvent was found to give a 10% yield as compared with a 40% yield in n-butyl ether solvent.

Raman Spectra.—The Raman spectra of $Pb(CH_3)_4$ and $Sn(CH_3)_4$, in the liquid state, were obtained using a Zeiss 3-prism instrument in the spectroscopy laboratory at the

Massachusetts Institute of Technology. The instrument had a camera lens aperture of $F/4.5$, and a plate factor at 4500 Å. of 30 Å./mm. Excitation was accomplished using six General Electric AH-2 arcs filtered with 10 mm. of saturated $NaNO_2$ and Rhodamine DGN-extra (0.01 g./l.). The excitation unit has been described elsewhere.[8]

All Raman spectra were taken at 25°. Exposure times varied from 30 to 90 minutes. Semi-quantitative depolarization factors were determined by a single exposure method making use of a split polaroid and a half-wave plate. The split polaroid had the plane of polarization of one half perpendicular to that of the other half, and was used to split the Raman beam, which was excited by radiation from a given direction, into parallel and perpendicular components. The half-wave plate was placed behind that half of the polaroid which transmitted the parallel component. Its function was to rotate the plane of polarization of the parallel component into that of the perpendicular component. In this way, unequal polarization of one component over the other by the spectrograph was avoided.

Other Raman spectra of $Sn(CH_3)_4$, and Raman spectra of $Ge(CH_3)_4$, were obtained using a Hilger E 612 glass spectrograph at the University of Connecticut. This instrument had a camera aperture of $F/5.7$. Exposure times varied from 3 to 15 minutes. These short exposure times are to be attributed to the efficiency of the Hilger excitation unit, which has MgO reflectors.[9] The filters used were as described above. All spectra were taken on Kodak 103 aJ plates. The plates were read with a travelling microscope, and the lines converted to wave numbers with a calibration curve made from iron arc readings. The dimmer lines were read from an enlarged print made on Kodak Fast Projection Standard photographic paper. Finally, the positions of a few very dim lines were estimated, with the aid of a magnifier, by visually examining the plate against a diffusely lighted background.

The observed Raman spectra of $Pb(CH_3)_4$, $Sn(CH_3)_4$ and $Ge(CH_3)_4$, are given in Tables I, II and III, respectively, along with those reported by other workers.[1,5,6] Our spectra differ from those of previous workers in several respects. First, we observe lines not reported by other workers and, in some cases, do not observe lines reported by them as being strong. Second, we observe some lines in different positions than reported by previous workers. Third, we have resolved a number of lines reported as singlets, into doublets. The Raman spectra reported by us for $Pb(CH_3)_4$ differ from the data of Duncan and Murray, and Siebert, mainly in that we find a number of lines which they fail to observe, namely, the weak lines at 634, 700, 1019, 1300, 1400, 1544, and 1622 cm.$^{-1}$. The line observed at

(1) (a) Kansas State College; (b) University of Connecticut.

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(9) A. C. Menzies and J. Skinner, J. Sci. Instruments, **26**, 299 (1949).