Electron Diffraction Investigation on the Molecular Structures of Some Organosilicon Compounds. I

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Introduction

Those organosilicon polymers, which have bonds between silicon and organic radicals, possess various properties of practical importance, i. e., low boiling points, small temperature coefficients of viscosity, high thermal stability, etc. These characteristic properties are closely related to their molecular structures. The knowledge of bond lengths and valence angles of low-molecular compounds provides the basis for consideration of the structures of polymers. The present study deals with the electron diffraction experiments on the vapors of several low-molecular organosilicon compounds. Organosilicon compounds which have so far been investigated by electron diffraction are mainly the derivatives of silane containing methyl groups and halogen atoms as substituents. In the present study, hexamethyldisiloxane, tetra-(trimethylsiloxy)-silane, octamethylcyclotetrasiloxane, and the two lowest members of dimethylcyclopolysilazanes and dimethylcyclopolysilthianes were investigated in order to determine the bond lengths of Si-O, Si-N and Si-S as well as the valence angles of O, N, S and Si atoms. In addition to the results on these compounds, data are also presented on several methyl, ethyl and phenyl derivatives of silane and halogenosilane.

Experimental

Method and Apparatus.—The electron diffraction apparatus used in this study has been described by Kimura[1]. The photographs taken were studied visually. The radial distribution curves and the theoretical intensity curves were calculated accorcing to the approximate formula used by Spurr and Schomaker[2]. In the temperature factors, $\exp(-b_{ij}q^2)$, for the theoretical intensity curves, b_{ij} was assumed to be equal to zero for all bonded distances, 0.0001 or 0.0002 for the atom pairs $\overset{\mathrm{Si}}{\widehat{\mathrm{O\cdots C}}}$, $\overset{\mathrm{Si}}{\widehat{\mathrm{C\cdots C}}}$, $\overset{\mathrm{Si}}{\widehat{\mathrm{Cl\cdots Cl}}}$, $\overset{\mathrm{O}}{\widehat{\mathrm{Si\cdots Si}}}$, etc., and 0.0004 or larger values for other nonbonded long distances. As the compounds used in this study constained relatively large numbers of parameters concerning their molecular structures, it was very difficult to derive unique conclusions from the observed intensity data unless some reasonable assumptions were made. Therefore the C-H distance and the valence angle of carbon in aliphatic organic radicals were assumed to be 1.09 Å and 109.5°, respectively. For particularly complicated compounds such as $((CH_3)_2SiS)_3$ and $((CH_3)_2SiO)_4$, the bond lengths well resolved in the radial distribution curves were used to evaluate the valence angles. The results thus obtained gave one of the models which could reproduce the observed intensity data, but other possibilities could not entirely be ruled out.

Compounds Studied.—(1) *Methylbromosilanes.*—Monomethyltribromosilane and dimethyldibromosilane were prepared by passing methyl bromide over heated silicon containing copper at 350°[3]. The product was fractionated. The boiling point of $(CH_3)SiBr_3$ was 130-134° and that of $(CH_3)_2SiBr_2$ was 112-113°. Trimethylmonobromosilane was prepared by passing the mixture of methyl bromide and dimethyldibromosilane over aluminum heated at 350°[4]. It boiled at 80°.

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[1] M. Kimura, *Chem. Researches* (*Japan*), **9**. 53 (1951).

[2] R.A.Spurr and V.Schomaker, *J. Am. Chem. Soc.*, **64**, 2693 (1942).

[3] E.G.Rochow, *J. Am. Chem. Soc.*,, **67**, 963 (1945).

[4] D.T. Hurd, ibid., **67**, 1545 (1945).

TABLE I

Compounds	Si-Br (Å)	Si-C (Å)	∠Br-Si-Br	∠C-Si-C
$(CH_3)SiBr_3$	2.17 ± 0.03	1.93 (assumed)	$109.5\pm2°$	—
$(CH_3)_2SiBr_2$	2.21 ± 0.03	1.92 ± 0.06	$109.5\pm2°$	109.5° (assumed)
$(CH_3)_3SiBr$	2.21 ± 0.03	1.86 ± 0.05	—	$114\pm4°$

(2) *Tetramethylorthosilicate.*—This compound was prepared by the reaction of silicon tetrachloride with methanol[5]. Its boiling point and melting point were 118-120° and 1-2°, respectively.

(3) *Hexachlorodisiloxane.* — This compound was prepared by passing the mixture of oxygen and chlorine over heated silicon[6] and fractionating the product. Its boiling point was 136-138°.

(4) *Hexamethylcyclotrisilazane and Octamethylcyclotetrasilazane.*—These compounds were prepared after Brewer and Haber[7]. The solution of dimethyldichlorosilane in benzene was treated with ammonia. After ammonium chloride was separated by filtration the filtrate was subjected to fractional distillation. The boiling point of the trimer was 185-187° and that of the tetramer was 223-225°.

(5) *Tetramethylcyclodisilthiane and Hexamethylcyclotrisilthiane.*—The trimer was prepared by the method of Champetier et al. who prepared its ethyl homologue[9]. The dimer was prepared by the thermal rearrangement of the trimer at 200° in a stream of hydrogen sulfide[8]. The boiling point of the dimer was 172-173°, and that of the trimer was 151.5-153.5°/38 mmHg.

(6) *Ethyltrichlorosilane, α- and β-chloroethyltrichlorosilane, tetraphenylsilane, phenyltrichlorosilane, octamethylcyclotetrasiloxane and tetra-(trimethylsiloxy)-silane* were furnished by Mr. M. Murata of the Osaka Municipal Technical Research Institute. Hexachlorodisilmethylene and hexamethyldisiloxane were given to the present writer by Dr. M. Kumata of Osaka City University and Mr. I. Hizawa of Sumitomo Chemical Co., respectively.

Results

(1) **Methylbromosilanes**[10].—The molecular structures of these compounds as revealed by electron diffraction experiments at 20-30° are shown in Table I. Calculations were based on the following: 1) C-H distance equal to 1.09 Å, 2) ∠H-C-Si equal to 109.5°, and 3) staggered relative positions of Br and H in a CH_3 radical with respect to a Si-C bond.

(2) **Ethyltrichlorosilane ($(C_2H_5)SiCl_3$), α-Chloroethyltrichlorosilane ($CH_3\cdot CHCl\cdot SiCl_3$), β-Chloroethyltrichlorosilane ($Cl CH_2\cdot CH_2\cdot SiCl_3$) and Hexachlorodisilmethylene ($Cl_3Si\cdot CH_2\cdot SiCl_3$)** These compounds were studied to obtain data on the structure of $SiCl_3$ radical as well as on rotation about Si-C bond. The structure of $SiCl_3$ remains unchanged throughout these compounds, that is Si-Cl$=2.00\pm0.02$ Å, and ∠Cl-Si-Cl$=109.5\pm2°$. Ethyl, chloroethyl, and disilmethylene radicals contribute little to intensity curves and therefore it was necessary to assume the structure of these radicals, i. e., C-C 1.54 Å, C-Cl 1.76 Å, Si-C 1.88 Å, and the valence angles of carbon 109.5°. Under these assumptions, the value of about 3 kcal./mol. was deduced for the potential barrier of the hindered rotation about Si-C bond in α-chloroethyltrichlorosilane. For hexachlorodisilmethylene, almost free rotation about Si-C bond was found to exist.

(3) **Tetraphenylsilane and Phenyltrichlorosilane**[12].—Two compounds, $Si(C_6H_5)_4$ and $(C_6H_5)SiCl_3$, were studied to determine the bond lengths between silicon and aromatic carbon and to get some information on the rotation about the Si-C bond. For tetraphenylsilane, the interatomic distance Si-C$=1.87\pm0.03$Å was obtained. Rotation about the bond between the silicon atom and the phenyl group was found to be restricted. The equilibrium position of four phenyl groups was the same as that of four nitro groups of tetranitromethane studied by stosick[13]. Model B in Fig. 1 is a sketch of the equilibrium configuration of the molecule in which all groups are rotated through the same angle 30° about Si-C bond from the positions of A in Fig. 1. In phenyltrichlorosilane, the contribution of phenyl group to the total scattering curve was so small that no data could be obtained except the following structure of the $SiCl_3$ radical; Si-Cl$=2.00$ ±0.02 Å, ∠Cl-Si-Cl$=109.5\pm2°$.

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[5] E.G.Rochow, ibid., **70**, 2170 (1945).

[6] L. Troost and P. Hautefeuille, *Bull. Soc. Chim. France*, **13**, 213 (1870), ibid., **35**, 360 (1881).

[7] S.D.Brewer and C.P.Haber, *J. Am., Chem. Soc.*, **70**, 3888 (1948).

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[11] C.Iida, M Yokoi, and K.Yamasaki, *J. Chem. Soc. Japan*, (*Pure Chem.Sect.*), **73**, 882 (1952).

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[13] A.J. Stosick, *J. Am. Chem. Soc.*, **61**, 1127 (1937).

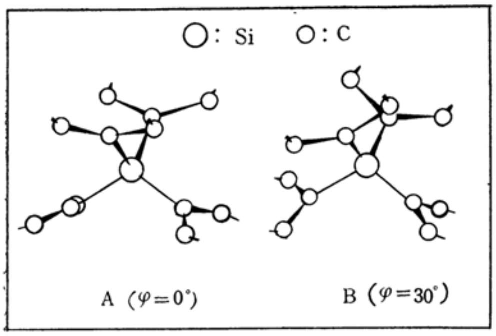

Fig. 1

(4) Tetramethylorthosilicate Si$(OCH_3)_4$[14].—The bond lengths and valence angles obtained were Si–O=1.64±0.03 Å, C–O=1.42±0.04 Å, and ∠Si–O–C=113±2°. A carbon atom in a methoxy group had a staggered configuration relative to the oxygen atoms in the other groups.

(5) Hexamethyltrisilazane $((CH_3)_2SiNH)_3$ and Octamethylcyclotetrasilazane $((CH_3)_2SiNH)_4$[15]. — Trimeric and tetrameric cyclic dimethylpolysilazane were studied for the purpose of evaluating the Si–N bond length and the Si–N–Si valence angle. For the trimer, the following data were obtained assuming ∠C–Si–C to be 110°; Si–N=1.78±0.03 Å, Si–C=1.87±0.05 Å, ∠N–Si–N=111±5° and ∠Si–N–Si=117±4°. For the tetramer, by assuming the values of Si–N, Si–C, ∠N–Si–N and ∠C–Si–C to be the same as those in the trimer, the valence angle of nitrogen was found to be 123±4°. The rings of these two compounds are puckered, although detailed shapes of the rings could not be determined.

(6) Tetramethylcyclodisilthiane and Hexamethylcyclotrisilthiane[16]. — Two compounds, $((CH_3)_2SiS)_2$ and $((CH_3)_2SiS)_3$, were studied to determine the Si–S bond length and the Si–S–Si valence angle. The Si–S bond length was found to be 2.18±0.03 Å in the former compound and 2.15±0.03 Å in the latter. Assuming ∠C–Si–C to be 110°, estimated bond agles were ∠Si–S–Si=75° and ∠S–Si–S=105° for the disilthiane, and ∠Si–S–Si=110° and ∠S–Si–S=115° for the trisilthiane.

(7) Hexamethyldisiloxane$(CH_3)_3SiOSi(CH_3)_3$.—The visual curve (V) and the radial distribution curve (R) are shown in Fig. 2. In (R), two maxima at 1.63 and 1.88 Å correspond to Si–O and Si–C bond lengths. The maxima at 2.84 and 3.12 Å are supposed to correspond to $\overset{\text{Si}}{\text{O}\cdots\text{C}}$ and $\overset{\text{Si}}{\text{C}\cdots\text{C}}$ respectively. As the values 2.84 and 3.10 Å are obtained to $\overset{\text{Si}}{\textbf{O}\cdots\text{C}}$ and $\overset{\text{Si}}{\text{C}\cdots\text{C}}$ respectively by assuming Si–O 1.63Å, Si–C 1.88 Å and ∠O–Si–C 108°, this choice seems to be adequate. The distance Si···Si seems to be masked by these two maxima. If this distance overlaps on the maximum at 3.12 or 2.84 Å, the corresponding valence angle of oxygen would be about 150 or 120°.

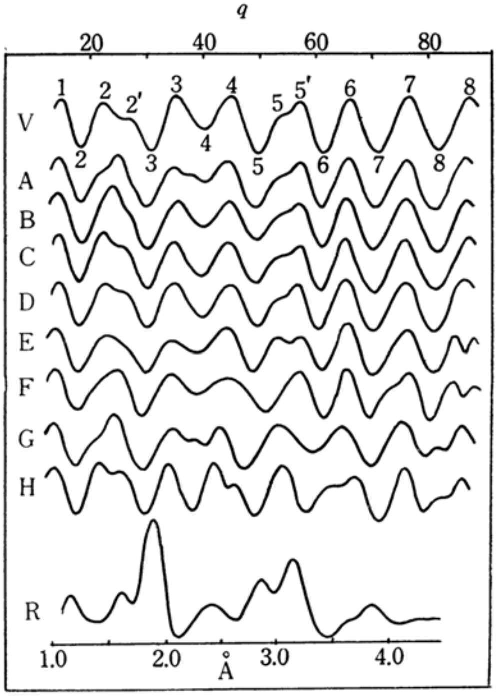

Fig. 2. Visual infensity, theoretical intensity and radial distribution curves of hexamethyldisiloxane.

To estimate Si–O–Si angle and to determine the accuracy of values of Si–O and Si–C bond lengths and O–Si–C angle, the theoretical intensity curves of several models, the bond lengths and the valence angles of which are listed in Table II, were compared with the visual curve in Fig. 2. The configuration of two trimethylsilyl groups was assumed to be the one as illustrated in Fig. 3 throughout these models. Since the relative contribution of long atomic distances to the total intensity was small, and moreover large temperature factors were adopted for the long

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[14] K. Yamasaki, A. Kotera, M. Yokoi and Y. Ueda. *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **72**, 544 (1951); *J. Chem. Phys.*, **18**, 1414 (1950).

[15] M. Yokoi and K. Yamasaki, *J. Am. Chem. Soc.*, **75**, 4139 (1953).

[16] M. Yokoi, T. Nomura, and K. Yamasaki, *J. Am. Chem. Soc.*, **77**, 4484 (1955).

distances, a change in the configuration gave little change in the theoretical intensity curves. The shapes and the q-values of 2nd and 2nd′ maxima of the theoretical intensity curves vary with the change of Si–O–Si angle. The best qualitative fit was obtained by curve C, the Si–O–Si angle of the model being equal to 130°. In the range of q larger than 40, theoretical curves A–D are consistent with the visual curve. The deviations of O–Si–C angle from 108° gave the change of the q-values of 4th and 5th maxima (G and H), while the change of Si–O/Si–C caused the disagreement in the shapes and the q-values of 5th and 5th′ maxima (E and F). The observed and the calculated q-values of curve C are compared quantitatively Table IV. The final results obtained are: Si–O=1.63±0.05 Å, Si–C=1.88±0.03 Å, ∠Si–O–Si=130±10° and ∠O–Si–C=108±4°.

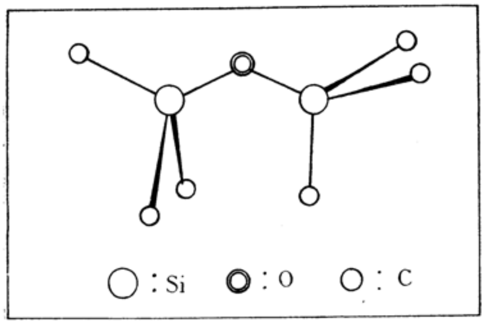

Fig. 3

TABLE II

Model	Si–O (Å)	Si–C (Å)	∠Si–O–Si	∠O–Si–C
A	1.63	1.88	114°	108°
B	1.63	1.88	120	108
C	1.63	1.88	130	108
D	1.63	1.88	140	108
E	1.59	1.92	130	108
F	1.69	1.86	130	108
G	1.63	1.88	130	102
H	1.63	1.88	130	112

(8) **Hexachlorodisiloxane** (**$Cl_3SiOSiCl_3$**).—In this compound the change of Si–O–Si angle had little effect on the over-all scattering intensity. Therefore the Si–O–Si angle was assumed to be 130°. Several theoretical curves are compared with the visual curve (V) in Fig. 4. The bond lengths and the valence angle ∠Cl–Si–Cl of each model are listed in Table III.

TABLE III

Model	Si-O (Å)	Si-Cl (Å)	∠Cl-Si-Cl
A	1.64	2.02	109.5°
B	1.64	2.02	109.5
C	1.68	2.01	109.5
D	1.58	2.03	109.5
E	1.64	2.02	112
F	1.64	2.02	107

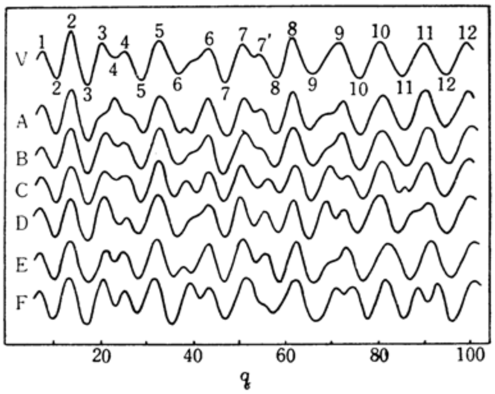

Fig. 4. Visual and theoretical intensity curves of hexachlorodisiloxane.

TABLE IV

Max.	Min.	$((CH_3)_3Si)_2O$ $q_{obs.}$	$q_C/q_{obs.}$	$(Cl_3Si)_2O$ $q_{obs.}$	$q_B/q_{obs.}$
1		15.2	0.974	8.0	1.013
	2	18.5	1.030	10.7	0.973
2		21.9	1.072	14.2	0.972
2′		27.1	0.996	—	—
	3	30.5	1.015	17.3	1.000
3		34.9	1.005	20.3	1.024
	4	40.5	0.970	23.1	—
4		45.1	0.980	25.4	1.000
	5	49.5	0.990	28.8	0.993
5		53.8	0.991	32.2	0.991
5′		57.3	1.007	—	—
	6	61.3	1.000	36.5	0.982
6		65.8	1.000	43.2	0.991
	7	70.9	0.994	46.7	1.000
7		76.8	0.994	50.2	1.007
7′		—	—	54.4	1.000
	8	82.3	1.000	57.8	1.011
8		87.4	0.999	61.9	1.001
	9			66.7	0.988
9				71.8	—
	10			76.2	1.012
10				80.9	1.002
	11			86.1	0.994
11				90.1	1.018
Mean			1.001		0.999
Mean deviation			0.015		0.010

When two $SiCl_3$ radicals were fixed in a certain relative position, the interference of long Cl···Cl had some effect on 3rd and 4th maxima as shown in the curve A of Fig. 4. The most satisfactory model (curve B) was the free rotation model. Approximate curves were calculated ignoring the effect of long distances which vary by rotation. Curves C–F were calculated also with the omission of long distances. The change of Cl–Si–Cl angle from tetrahedral angle to 112° gave a small maximum between 5th and 6th maxima, while for ∠Cl–Si–Cl equal to 107°, 7th′ maximum disappeared and the shape and the position of 6th maximum were not in accord with those of the visual curve (E and F). The shapes and the q-values of 7th' and 9th maxima of the model, Si–O/Si–Cl in which is 1.58/2.03 or 1.68/2.01, were not in accord with the visual curve (C and D). With these qualitative considerations and the quantitative comparisons given in Table IV, the final results obtained are: Si–Cl=2.02±0.02 Å, Si–O=1.64±0.05 Å and ∠Cl–Si–Cl=109.5±2°.

(9) **Tetra-(trimethylsiloxy)-silane ($\mathbf{Si(OSi(CH_3)_3)_4}$).**—The radial distribution curve calculated from the visual curve is shown in Fig. 5 together with that of octamethylcyclotetrasiloxane. Maxima at 1.63, 1.88 and 3.06 Å appear on both curves. Maxima at 1.63 and 1.88 Å are due to bonded Si–O and Si–C distances, respectively, which are consistent with values determined for hexamethyldisiloxane. In the vicinity of 3 Å in the curves, maxima corresponding to non-bonded $\overset{\text{Si}}{\widehat{\text{O}\cdots\text{C}}}$ and $\overset{\text{O}}{\widehat{\text{Si}\cdots\text{Si}}}$ distances should appear. If Si–O–Si angle is larger than O–Si–C, and the maximum at 3.06 Å is due to $\overset{\text{O}}{\widehat{\text{Si}\cdots\text{Si}}}$, then Si–O–Si angle should be 140°. To clarify this point, comparisons were made of theoretical intensity curves with the visual intensity curve, for models having various valence angles, Si–O and Si–C bond lengths being assumed to be 1.63 and 1.88 Å respectively as obtained from the radial distribution curve. The valence angle of central silicon atom was assumed to be

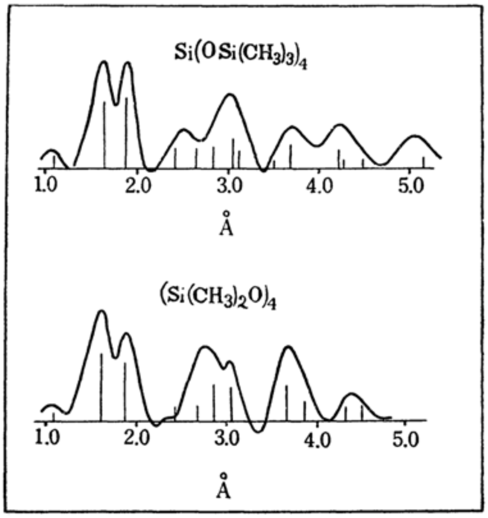

Fig. 5. Radial distribution curves of tetra-(trimethylsiloxy)-silane and octamethylcyclotetrasiloxane.

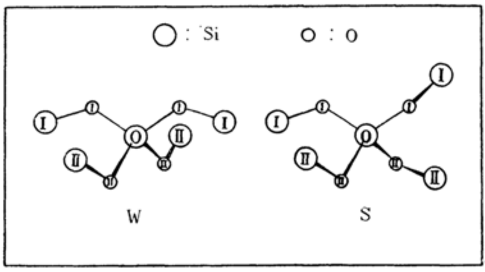

Fig. 6

W: The two Si atoms, the two O atoms designated by I (or II) and the central Si atom are coplanar, forming W-shaped chain.

S: One Si atom at the end of each chain is twisted through 60° about Si-O bond from the position of the W-form.

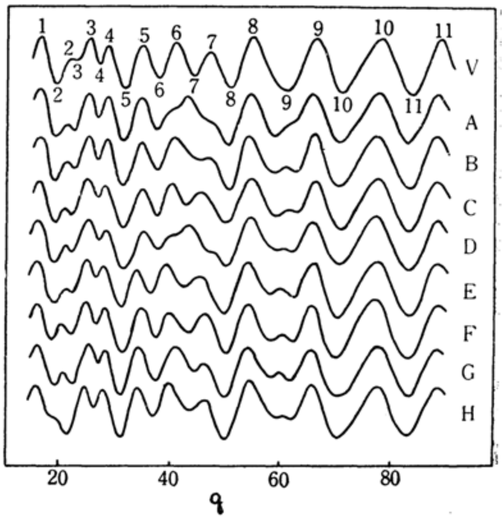

Fig. 7. Visual and theoretical intensity curves of tetra-(trimethylsiloxy)-silane.

tetrahedral. These curves are shown in Fig. 7 with the visual curve (V). The valence angles of each model are listed in Table V. The relative positions of four trimethylsiloxy groups were assumed to take either W- or S-form as shown in Fig. 6. In the theoretical curves of models of W-form (for example, curve H in Fig. 7), the second maximum was near the first maximum and was not consistent with the visual curve. Therefore models having W-form were rejected. For models of S-form (curves A–G), good agreement was obtained for the second maximum. The features of the theoretical intensity curve, which are sensitive to the change of Si–O–Si and O–Si–C angles are the shapes and the *q*-values of 5th and 6th and 7th maxima. Curve B corresponding to the model in which Si–O–Si and O–Si–C angles are 140° and 107° respectively, well reproduces the features of the visual intensity curve. The variation of Si_0–O and Si_I–O in the vicinity of 1.63 Å gave curve F and G, in which the *q*-values of 6th maxima are not consitent with the visual curve. From these considerations the values of ∠Si–O–Si and ∠O–Si–C which well reproduce the visual intensity curve, were found to be 140±5° and 107±3° respectively.

TABLE V

Model	Si_0-O(Å)	Si_I-O(Å)	∠Si-O-Si	∠O-Si-C
A	1.63	1.63	140°	110°
B	1.63	1.63	140	107
C	1.63	1.63	140	104
D	1.63	1.63	135	107
E	1.63	1.63	145	107
F	1.60	1.65	140	107
G	1.65	1.60	140	107
H	1.63	1.63	140	107

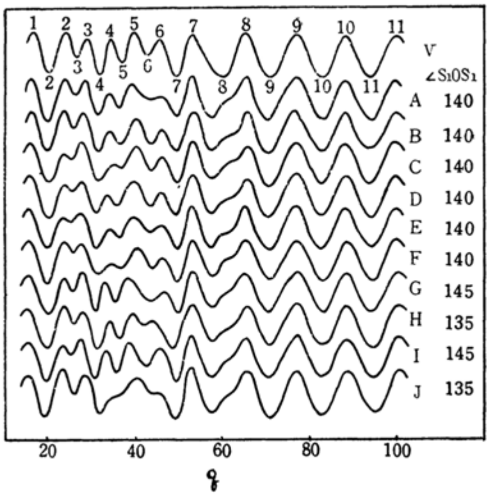

Fig. 8. Visual and theoretical intensity curves of octamethylcyclotetrasiloxane.

(10) Octamethylcyclotetrasiloxane **($((CH_3)_2SiO)_4$).**—Theoretical intensity curves for models assuming the tetrahedral angle of silicon atom are shown in Fig. 8 together with the visual curve (V). There are several conceivable forms of an eight-membered ring of $(Si–O)_4$ as shown in Fig. 9. The variation of the form caused minor changes in the shapes and the *q*-values of 2nd and 3rd maxima. This is a natural consequence of large temperatur factors used for long distances. The

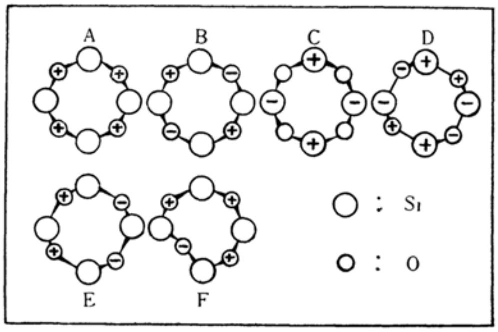

Fig. 9

TABLE VI

Max.	Min.	$Si(OSi(CH_3)_3)_4$ $q_{obs.}$	$Si(OSi(CH_3)_3)_4$ $q_B/q_{obs.}$	$((CH_3)_2SiO)_4$ $q_{obs.}$	$((CH_3)_2SiO)_4$ $q_B/q_{obs.}$
1		16.2	(0.950)	16.1	0.975
	2	18.6	1.000	20.1	1.009
2		20.8	0.981	23.4	1.000
	3	22.2	0.972	26.1	0.976
3		24.7	0.979	28.6	0.973
	4	26.4	0.992	31.2	0.987
4		27.9	0.993	33.8	0.994
	5	31.0	1.006	36.5	0.994
5		34.2	1.002	39.1	1.006
	6	37.0	1.011	43.0	0.986
6		40.2	0.997	46.1	0.982
	7	43.2	1.027	49.5	0.988
7		46.4	0.991	52.9	1.012
	8	50.0	0.989	60.4	—
8		54.0	0.989	65.4	1.017
	9	60.7	—	71.2	0.995
9		65.6	1.011	77.3	0.993
	10	69.7	1.012	83.4	0.991
10		77.7	0.998	88.8	1.000
	11	83.4	0.993	95.2	0.990
11		88.4	0.982	100.3	0.998
Mean			0.994		0.994
Mean deviation			0.011		0.009

variation of the Si–O–Si angle of a symmetrical crown form considerably affects the relative positions of 4th, 5th and 6th maxima as indicated by curves G and H. The same is true for a cradle form (cf. curves I and J). In this case, too, the best agreement with the visual curve was obtained with models in which the Si–O–Si angle was 140°. The quantitative comparison of the observed *q*-values with the calculated ones for the best models of tetra-(trimethylsiloxy)-silane and octamethylcyclotetrasiloxane is shown in Table VI. For the latter compound, the curve of cradle form (B in Fig. 8) was found to be better than those of other forms. The distances appearing in the best curve are shown schematically in Fig. 5. The distances ranging from 2.4 to 2.9 Å in the distribution curve are not consistent with the distances appearing in the best model.

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