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The Crystal and Molecular Structure of the Dehydrated Tetramer of 1, 2-Dimethyldisilanetetraol, $(CH_3)_8Si_8O_8$

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The crystal and molecular structure of $(CH_3)_8Si_8O_8$ has been determined by means of the Patterson projections and refined by the two-dimensional Fourier technique and the least-squares method. The space group is *P*4/*nnc*, with four molecules per unit cell. The unit cell constants are $a=11.73\pm0.02$ Å, and $c=17.17\pm0.02$ Å. The skeleton of a molecule consists of two "crown-shaped" $(\text{-Si-O-})_4$ rings which are crystallographically independent of each other and are connected by four Si–Si bonds along the *c* axis. The four six-membered $(\text{-Si-Si-O-})_2$ rings thus formed have boat forms. Hence, a molecule forms a cage-like conformation with an approximate symmetry of 4/*mmm*. Each molecule in the unit cell is surrounded by four adjacent molecules related with centers of symmetry; these molecules form, in a sense, a layer perpendicular to the c axis.

In structural investigations of cyclic organosilicon compounds, some interesting characteristics have been elucidated.[1-8] Thus, several types of rings have been reported to exist in those compounds containing Si–O, Si–Si, or Si–N bonds. Planar conformations are found in $(\text{-Si-O-})_3$ and $(\text{-Si-N-})_2$ skeletons,[3,7] and the $(\text{-Si-Si-O-})_2$ ring has a chair form close to a plane.[6] As for an eight-membered ring system, the $(\text{Si-O-})_4$ skeleton exists either in a puckered ring of a $\bar{1}$ symmetry[4] or in a "crown-shaped" ring,[5] while $(\text{-Si-N-})_4$ skeletons have "chair" and "cradle" forms.[8] In view of the strain associated with these ring conformations, the valence angle of the oxygen or nitrogen atom with two silicon atoms shows a wide range of variation; the former bond angle especially is reported to be larger than the corresponding angle in common organic compounds.

The dehydrated tetramer of 1, 2-dimethyldisilanetetraol, $(CH_3)_8Si_8O_8$ (I), herein reported on, was isolated by Kumada[9] from acid hydrolyzates of 1, 1, 2, 2-tetraethoxydimethyldisilane, $(C_2H_5O)_2CH_3SiSiCH_3(OC_2H_5)_2$. Purely chemical studies had suggested that this new compound has a cage-like configuration, as is shown in Fig. 1. This configuration may be considered to consist of two eight-membered $(\text{-Si-O-})_4$ rings and four six-membered $(\text{-Si-Si-O-})_2$ rings. In this respect, this molecule may be closely related to bistetramethyldisilanylenedioxide, $((CH_3)_4Si_2O)_2$,[6] and octa-(methylsilsesquioxane), $(CH_3SiO_{1.5})_8$ (III),[5] the molecular structures of which have already been established, by X-ray analyses, to be shown in Figs. 2(a) and (b).

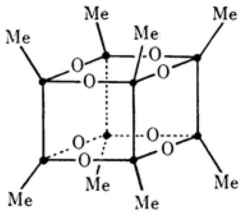

Fig. 1. Dehydrated tetramer of 1, 2-dimethyldisilanetetraol, $(CH_3)_8Si_8O_8$. Me: CH_3, ●: Si.

The present X-ray work was undertaken to confirm this molecular configuration, with the

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[1] L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945).

[2] W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948).

[3] G. Peyronel, *Chim. Industr.*, **36**, 441 (1954).

[4] H. Steinfink, B. Post and I. Fankuchen, *Acta Cryst.*, **8**, 430 (1956).

[5] K. Larrson, *Ark. Kemi*, **16**, 203 (1960).

[6] T. Takano, N. Kasai and M. Kakudo, This Bulletin, **36**, 585 (1963).

[7] P. J. Wheatley, *J. Chem. Soc.*, **1962**, 1721.

[8] G. S. Smith and L. E. Alexander, *Acta Cryst.*, **16**, 1015 (1963).

[9] M. Kumada, M. Ishikawa and B. Murai, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 37 (1963).

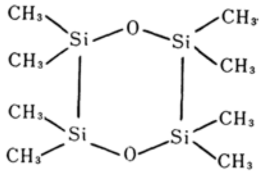

Fig. 2 (a). Bistetramethyldisilanilenedioxide, $((CH_3)_4Si_2O)_2$.

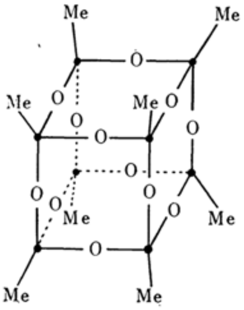

Fig. 2 (b). Octa-(methylsilsesquioxane), $(CH_3SiO_{1.5})_8$.
Me: CH_3, ●: Si.

hope that such information will contribute to the structural chemistry of organosilicon compounds in connection with the various problems mentioned above. The structural information regarding the silicon-oxygen configuration obtained by this work will also be useful in discussing the course of polymerization reactions and the conditions under which linear polymers can be terminated by ring formation.[10]

Experimental

The specimens were kindly prepared and supplied by Professor Makoto Kumada of Kyoto University.[9] They are soluble in most organic solvents and are recrystallized several times from the solution in chloroform. The crystals thus obtained were colorless cubes. They were decomposed so quickly because of the moisture that they were sealed into thin-walled glass capillary tubes.

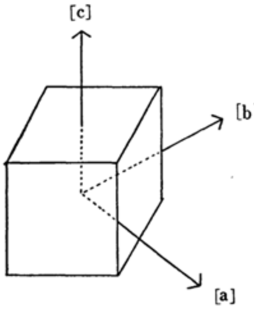

Fig. 3. The relation of principal axes to the crystal form.

Oscillation and Weissenberg photographs were taken with Cu$K\alpha$ radiation. These photographs indicate that the crystal has the Laue symmetry, $4/mmm$, and that the unit cell dimensions are $a=11.73\pm0.02$ Å and $c=17.17\pm0.02$ Å. The relation of principal axes to the crystal form is shown in Fig. 3.

There are four molecules per unit cell. The physical constants are found to be as follows: m. p. 320°C, mol. wt.$=473.0$, $D_{\mathrm{obs}}=1.30$ g. cm^{-3}, and $D_{\mathrm{calcd}}=1.33$g. cm^{-3}. The following types of reflections were systematically absent: $(hk0)$ with $h+k$ odd, $(h0l)$ with $h+l$ odd, and (hhl) with l odd. The corresponding space group is $P4/nnc$. The time of exposure was limited because of the decomposition of crystals, and it was very difficult to obtain three-dimensional intensity data. The equatorial and 1st-layer Weissenberg photographs around the b- and c-axes were taken by the multiple-film technique. The relative intensities of the reflections were measured by a visual comparison with calibrated intensity strips. The usual Lorentz and polarization corrections were applied to the measured intensities. No correction was made for absorption (the linear absorption coefficient for Cu$K\alpha$ radiation, $\mu=46.5$ cm^{-1}). The observed structure factors were brought to an absolute scale, primarily by means of Wilson's method.[11]

Structure Determination

Since the unit cell contains four molecules, the centers of the four molecules in each unit cell are located at fourfold positions; three sets of these positions are listed for the $P4/nnc$ space group, with reference to the origin at $\bar{1}$, in the *International Tables for X-ray Crystallography*. Positions $4(c)$ and $4(d)$ seem to be unwise choices, since they require that the centers of adjacent molecules be separated by half a length of the c axis, but no trains of peaks perpendicular to the c axis exist near at $U=0$ and $W=1/2$ of the Patterson map $P(UW)$. The $4(e)$ position, on the other hand, is suitable for the packing of molecules and it seems to explain the Patterson peaks; therefore, it was chosen for the center of a molecule. In this position the center of a molecule lies at the fourfold axis. The asymmetric unit consists of a quarter of one molecule, namely, two silicon atoms, two oxygen atoms and two methyl groups. Hence, eighteen parameters must be determined in this analysis, hydrogen atoms not being considered.

The first clue to the structure determination was obtained from the Patterson function, $P(UV)$, onto the (001) plane, which showed interatomic vectors between oxygen and silicon atoms as well as between silicon atoms. These vector peaks were easily interpreted with the aid of the fact that the molecule has a fourfold symmetry with conventional bond distances. These approximate positions of the $(\text{–Si–O–})_8$ skeleton gave a fairly

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[10] E. J. Lawton, W. T. Grubb and J. S. Balwit, *J. Polymer Sci.*, **19**, 455 (1956).

[11] A. J. C. Wilson, *Nature*, **150**, 152 (1942).

good agreement between calculated and observed structure factors.

The electron-density projection along c axis was then synthesized. It revealed the positions of four sets of silicon and oxygen atoms which are related by a fourfold axis and form squares respectively. Two methyl groups could also be found in the second electron-density projection. However, the heavy overlapping of all silicon and oxygen atoms prevented us from proceeding with a further refinement of this projection. A Patterson projection along the b axis gave some information about the z parameters of silicon and oxygen atoms, and the electron-density projection along the b axis was computed. This electron-density map along the b axis, together with the aid of the projection along the c axis, was sufficient to give all of the atomic positions except those of hydrogen atoms. The coordinates of the atoms were then refined by trial and error method, and later by successive Fourier syntheses. After these procedures, the (F_o-F_c) syntheses were applied in order to refine the coordinates and temperature factors further. At this stage of the structure determination, the reliability factors for $(hk0)$

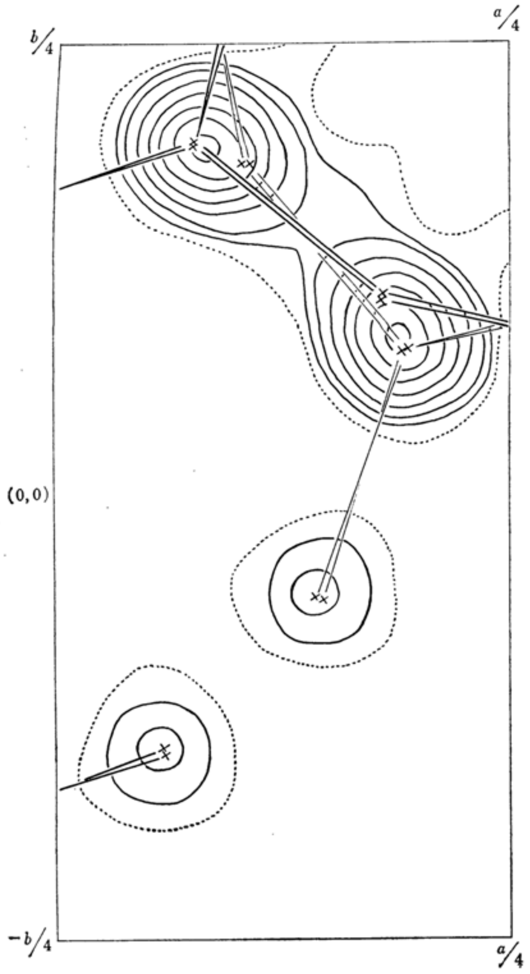

Fig. 4. Electron density projected on the (001). Contours at intervals of 4e. $Å^{-2}$ start with 2e. $Å^{-2}$ contour (broken line), the interval being 10e. $Å^{-2}$ after 10e. $Å^{-2}$.

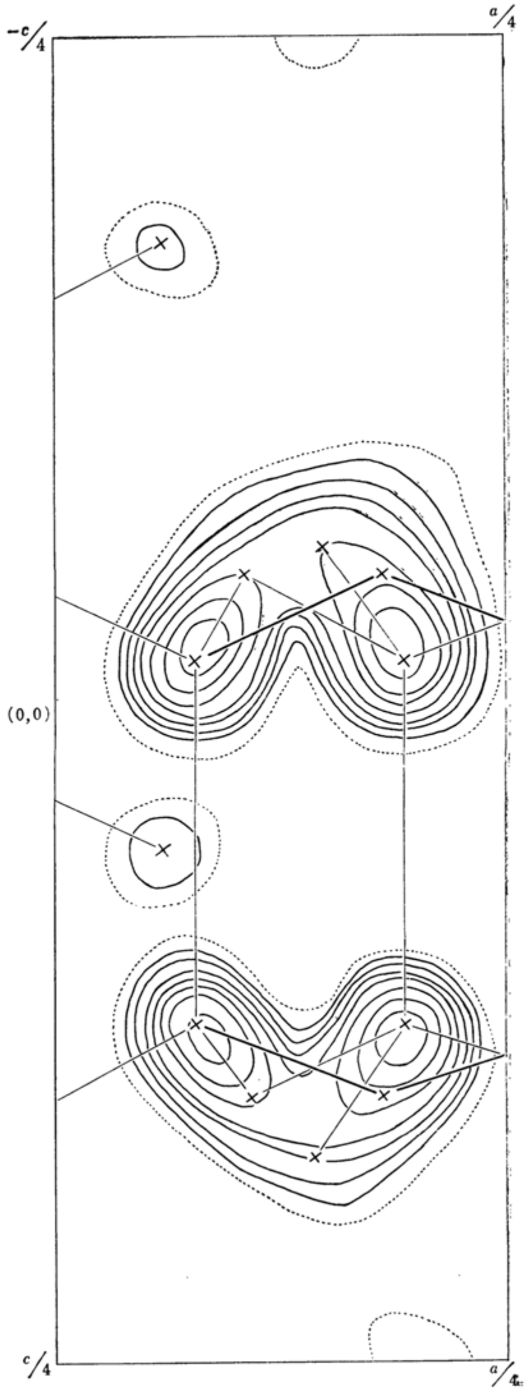

Fig. 5. Electron density projected on the (010). Contours at intervals of 2e. $Å^{-2}$ start with 2e. $Å^{-2}$ contour (broken line), the interval being 4e. $Å^{-2}$ after 10e. $Å^{-2}$.

Table I. Atomic parameters.

σ value in parenthesis.

	x	y	z	B (Å^2)
Si(1)	0.1914 (0.0009)	0.0767 (0.0010)	−0.0132 (0.0006)	2.54 (0.34)
Si(2)	0.1930 (0.0009)	0.0778 (0.0009)	0.1242 (0.0006)	2.60 (0.35)
O(1)	0.3202 (0.0023)	0.1039 (0.0027)	−0.0432 (0.0013)	2.83 (0.54)
O(2)	0.3196 (0.0019)	0.1083 (0.0022)	0.1509 (0.0012)	2.16 (0.48)
C(1)	0.1470 (0.0048)	−0.0596 (0.0041)	−0.0568 (0.0018)	3.97 (1.13)
C(2)	0.1438 (0.0049)	−0.0598 (0.0041)	0.1740 (0.0021)	4.05 (1.00)

Table II. Observed and calculated structure factors

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	2	0	67	43	12	6	0	25	26	* 3	0	11	6	18	8	0	4	13	2
	4		202	180		8		18	15			13	42	40			6	60	66
	6		33	32	13	1		25	26	*		15	6	15			8	101	106
	8		197	187		3		21	15	*		17	6	2			10	28	30
	10		73	83		5		11	10	*		19	6	4			12	22	23
	12		31	33	*	7		4	1	4	0	2	39	45	*		14	6	12
	14		6	1	14	2		25	21			4	12	19			16	28	40
1	1	0	276	268		4		16	18			6	34	50	9	0	1	53	52
2	2		212	210	0	0	2	267	291	*		8	5	5			3	31	39
3	1		126	131	*		4	3	60			10	54	45			5	92	94
	3		225	212			6	196	220	*		12	6	10			7	95	99
4	2		64	58			8	173	136	*		14	6	1	*		9	6	3
*	4		5	7			10	84	54	*		16	6	2	*		11	6	13
* 5	1		4	8			12	34	55	*		18	6	5			13	57	77
	3		92	79	*		14	6	17	*		20	6	6			15	48	52
	5		45	31			16	54	59	5	0	1	18	25	10	0	2	34	40
6	2		194	182			18	16	22			3	69	64	*		4	6	9
	4		64	50			20	19	19			5	91	81			6	26	34
	6		164	161	1	0	1	132	155			7	36	29			8	58	66
7	1		21	11			3	77	9	*		9	6	3	*		10	6	4
	3		148	138			5	303	292	*		11	6	11			12	15	20
	5		82	75			7	145	153			13	42	50	*		14	6	10
	7		92	90			9	26	6			15	36	38	*11	0	1	6	7
8	2		16	10			11	19	38	*		17	6	5	*		3	6	3
	4		75	64			13	98	80	*		19	5	3	*		5	6	14
	6		61	55			15	34	44	6	0	2	17	19	*		7	6	4
	8		64	48			17	6	6	*		4	5	0	*		9	6	5
9	1		146	137	*		19	6	7			6	13	11	*		11	6	6
	3		80	73			21	18	26			8	35	35	*		13	5	6
	5		42	36	2	0	2	7	24			10	15	20	12	0	2	14	19
	7		36	26			4	33	8	*		12	6	7	*		4	6	2
	9		97	95	*		6	3	18	*		14	6	2	*		6	6	12
*10	2		7	7			8	40	33	*		16	6	15			8	20	20
	4		20	22			10	13	7	*		18	5	1	*		10	5	4
	6		38	30	*		12	6	11	7	0	1	20	13	*		12	5	6
	8		49	42	*		14	6	6			3	11	16	*13	0	1	6	7
	10		20	25	*		16	6	2			5	17	22	*		3	6	7
*11	1		7	1	*		18	6	3			7	39	35			5	19	24
	3		71	61	*		20	5	1	*		9	6	1	*		7	5	7
	5		26	20	3	0	1	41	37	*		11	6	3	*		9	5	1
	7		21	18			3	34	21			13	18	30	*14	0	2	5	4
	9		14	3			5	77	72			15	16	24	*		4	5	4
12	2		43	39			7	58	59	*		17	6	5	*		6	4	2
*	4		7	5	*		9	5	3	8	0	2	94	88					

The value of index followed by an asterisk indicates reflection below the observable limit. The value of F_o in this case is minimumum observed value.

and $(h0l)$ reflections were found to be 12.9% and 22.8% respectively, the isotropic temperature factors being $B_C=3.5$, $B_O=3.5$ and $B_{Si}=3.0$ for carbon, oxygen and silicon atoms.

The least-squares method was applied in the next stage of the refinement. After nine cycles of the refinement of the positional and isotropic temperature factor parameters, the reliability factors for the final parameters dropped to 14.0%, with only observed reflections. The value of F_o listed for the unobserved reflections (marked with an asterisk in Table II) is $F_{\min}/2$; this value was used in the least-squares refinements. The calculations of the structure factors were made with an IBM 1401 computer. The least-squares refinements were carried out with the program written by Mr. Noritake Yasuoka[12] for an OKITAC-5090D electronic computer. In these calculations, the Hartree-Fock atomic scattering curves were used for carbon and oxygen atoms, and Slater's curve for silicon atoms, the contribution of hydrogen atoms being disregarded. The final atomic coordinates and isotropic temperature factors are listed in Table I. The final electron-density maps along the c and b axes are shown in Figs. 4 and 5, where the final positions of atoms are marked with crosses. The observed and calculated structure factors are given in Table II.

Results and Discussion

Some intersesting results were revealed in this structural work, although the poor experimental data resulting from the decomposition of crystals and the exclusion of many hydrogen atoms in the calculation of structure factors might not permit us to discuss the details of structural features. The conformation of a molecule and the molecular arrangement in the crystal, together with intermolecular distances, may be seen in Figs. 6 and 7, which represent the c and b axes projections for this crystal. Table III lists the independent bond lengths, the bond angles and the non-bonded interatomic distances in a molecule. Table IV compares the bond lengths and angles found in this analysis with those found in the related compounds.

TABLE III. BOND LENGTHS, BOND ANGLES AND NON-BONDED INTERATOMIC DISTANCES IN A MOLECULE

Bond lengths, Å

Si(1)	Si(2)	2.36	Si(2)	0(2‴)	1.63
Si(1)	O(1)	1.63	Si(1)	C(1)	1.84
Si(1)	O(1‴)	1.67	Si(2)	C(2)	1.92
Si(2)	O(2)	1.60			

Non-bonded interatomic distances, Å

Si(1)	Si(1′)	3.04	O(2)	O(2′)	2.62
Si(2)	Si(2′)	3.01	O(1)	O(1″)	3.80
Si(1)	Si(1″)	4.29	O(2)	O(2″)	3.70
Si(2)	Si(2″)	4.26	O(1)	O(2′)	3.33
O(1)	O(1′)	2.69			

Bond angles (°)

Si(2)	Si(1)	O(1)	107.9	O(2)	Si(2)	O(2‴)	108.8
Si(2)	Si(1)	O(1‴)	108.0	C(1)	Si(1)	Si(2)	114.4
Si(1)	Si(2)	O(2)	107.2	C(2)	Si(2)	Si(1)	116.1
Si(1)	Si(2)	O(2‴)	106.3	C(1)	Si(1)	O(1)	107.7
Si(1)	O(1)	Si(1′)	134.1	C(1)	Si(1)	O(1‴)	109.3
Si(2)	O(2)	Si(2′)	138.2	C(2)	Si(2)	O(2)	110.0
O(1)	Si(1)	O(1‴)	109.4	C(2)	Si(2)	O(2‴)	108.3

The skeleton of a molecule consists of two eight-membered (–Si–O–)$_4$ rings which are crystallographically independent of each other and which are connected by four Si–Si bonds along the c axis. Hence, the molecule forms a cage-like conformation with the approximate symmetry of $4/mmm$ predicted by chemical grounds. Two sets of four silicon atoms which are related by a fourfold axis form two square planes (3.04 Å × 3.04 Å, 3.01 Å × 3.01 Å) perpendicular to the c axis. Similarly, two sets of four oxygen atoms form two square planes, the sides of which are 2.69 Å and 2.62 Å. All of these planes are parallel to one another. The distance between two "silicon-square planes" is 2.36Å, while that between two "oxygen-square planes" is 3.33Å. The distances between the silicon-square plane and the oxygen-square plane are 0.52Å and 0.46Å respectively. Consequently, each of two (–Si–O–)$_4$ rings form a "crown-shaped" eight-membered ring. In this respect, the conformation of these rings is similar to that in octa-(methylsilsesquioxane) (III),[5] although the corresponding interplanar distance is 0.34Å in the latter. However, it differs from that in octamethylcyclotetrasiloxane (IV),[4] the puckered ring of $\bar{1}$ symmetry with a dihedral angle of 150° between the silicon- and oxygen-planes.

On the other hand, a set of the other four silicon atoms, Si(1), Si(1′), Si(2′) and Si(2), forms a plane approximately parallel to the c axis, and the best least-squares plane A, calculated by the program of Mr. Tsunehiro Takano for a NEAC 2101 computer, has the following equation:

$$0.4986x - y + 0.0061z - 0.2237 = 0$$

Table V shows the deviation of atoms from this plane, the individual atoms lying out of the plane by only insignificant amounts. The equation of a plane B through the Si(1), O(1), and Si(1′) atoms is:

$$0.4946x - y + 0.8315z - 0.0224 = 0$$

while that of a plane C through the Si(2), O(2), and Si(2′) atoms is:

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[12] N. Yasuoka and T. Mitsui, *Bull. Osaka Ind. Research Inst.*, **16**, 37 (1960).

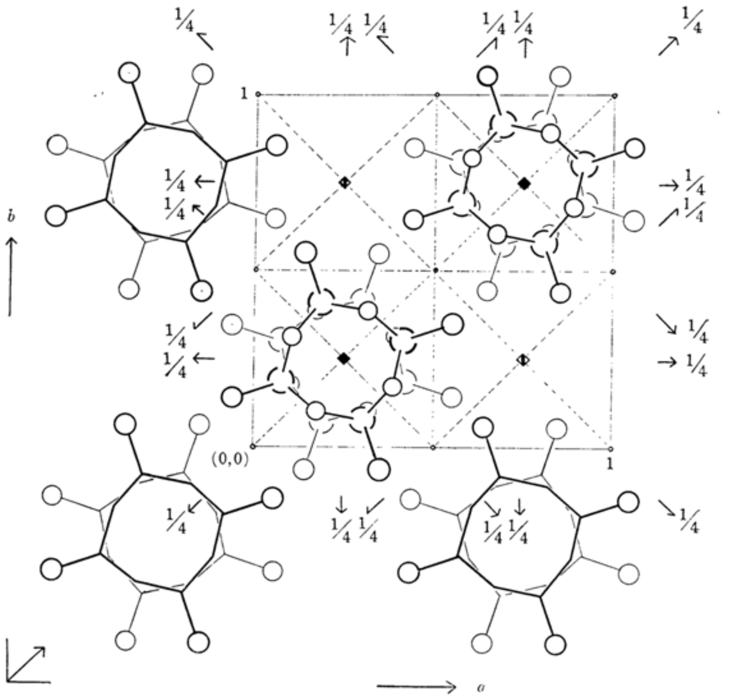

Fig. 6. Arrangement of the molecules projected on the (001).

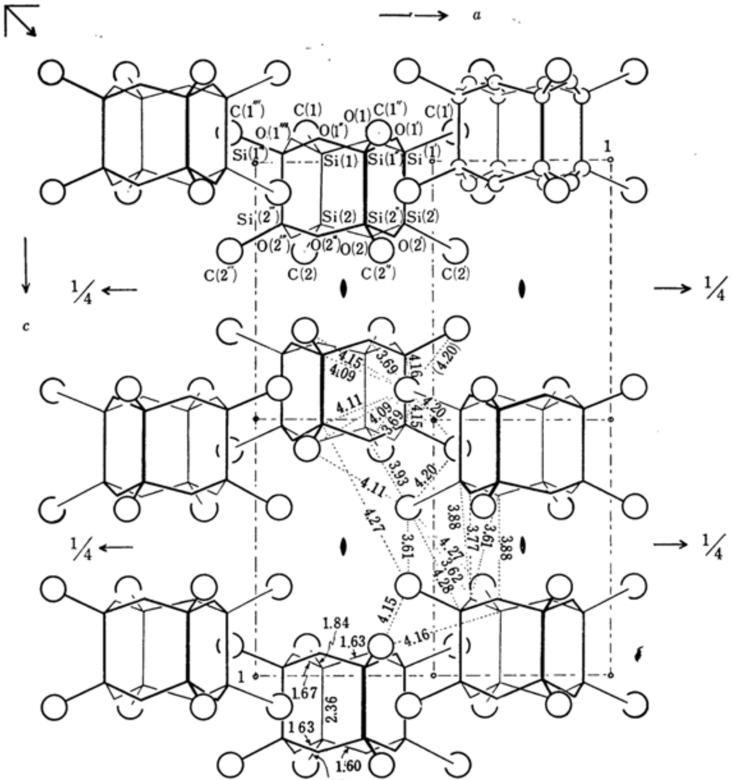

Fig. 7. Arrangement of the molecules projected on the (010).

TABLE IV. BOND LENGTHS AND ANGLES

Molecule		Si-Si	Si-O	Si-C	Si-O-Si	O-Si-O	C-Si-C	O-Si-Si
$(CH_3)_8Si_8O_8$	Dehydrated tetramer of 1, 2-dimethyldisilanetetraol	2.36	1.63	1.88	136	109	—	107
$(CH_3)_8Si_5O_6$	Spirosiloxane	—	1.64	1.88	130	106	106	—
$[(CH_3)_2SiO]_3$	Hexamethylcyclotrisiloxane	—	1.614	1.929	136	104	106	—
$[(CH_3]_2SiO]_4$	Octamethylcyclotetrasiloxane	—	1.65	1.92	142.5	109	106	—
$(CH_3SiO_{1.5})_8$	Octa-(methylsilsesquioxane)	—	1.61	1.90	145	111	—	—
$[(CH_3)_4Si_2O]_2$	Bistetramethyldi-silanylenedioxide	2.35	1.61	1.88	143	—	108	109
$[(CH_3)_3NSi(CH_3)_2]_2$	Tetramethyl-*N*, *N'*-bistri-methylsilylcyclodisilazane	—	—	1.876	—	—	107	—
$[(CH_3)_2SiNH]_4$	Octamethylcyclotetrasilazane	—	—	1.88	—	—	111	—

TABLE V. DEVIATION OF ATOMS FROM THE BEST PLANE (Si(1), Si(1′), Si(2′), Si(2))

Atom	Deviation, Å	Atom	Deviation, Å
Si(1)	−0.005	Si(2′)	−0.005
Si(1′)	0.005	O(1)	0.381
Si(2)	0.005	O(2)	0.350

$$0.5026x - y - 0.8479z + 1.5828 = 0$$

The dihedral angle between the two planes, A and B, is 144°, while that between the two planes, A and C, is 143°. Thus, the skeleton of the ring, Si(1), O(1), Si(1′), Si(2′), O(2) and Si(2), has a boat form, whereas the ring in compound II has a chair form, with a dihedral angle of 170°. The adoption of a crown-shaped conformation by eight-membered rings would necessitate these four six-membered rings having boat forms.

The Si-Si bond distance, 2.36Å, in the molecule is almost the same as the 2.34Å and 2.35Å distances found in metallic silicon and II. The differences in non-equivalent Si-O distances, Si–C distances and Si–O–Si bond angle would probably not be significant, the mean values being 1.63Å, 1.88Å and 136°. The mean Si-O bond lengths agree well with those reported by other investigators.1−6) The mean Si-C distance agrees with those found for II and spirosiloxane.2) The bond distances calculated from the sum of covalent radii with electronegativity13) corrections are Si–O=1.76Å and Si–C=1.88Å; the latter value is in good agreement with those found here, although the deviations of the Si-C bond lengths from the everage bond length are not small. The Si–O–Si bond angles are significantly smaller than those of II, III and IV, but they are the same as that in hexamethylcyclotrisiloxane. The corresponding angle in the spirosiloxane is 130°. The Si–N–Si angle of octamethylcyclotetrasilazane is 132°.8) These shorter bond lengths and the larger bond angles around the oxygen atoms might confirm that the Si–O–Si configuration is more flexible than the corresponding one in carbon compounds, probably due to the existence of an ionic character and the contribution of the *d*-orbital to Si–O bonds. The bond angles around the silicon atoms are almost tetrahedral.

Each molecule in the unit cell is surrounded by four adjacent molecules related by centers of symmetry; these molecules form, in a sense, a layer perpendicular to the *c* axis. They are held together in such a way that a methyl group on one silicon atom is located just upon the six-membered ring of an adjacent molecule. This molecular arrangement in a layer might suggest polar interaction between the methyl group and the oxygen atom. Each layer seems to be held together along the *c* axis by only van der Waals forces; this mode of molecular packing in the crystal is in good agreement with the fact that this crystal has a cleavage perpendicular to the *c* axis.

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