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The Crystal and Molecular Structure of the Tricyclic Methyldisilanylenesiloxane, $((CH_3)_6Si_4O_3)_2$

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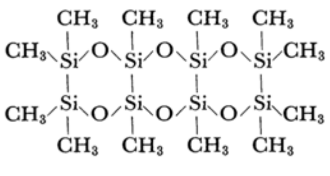
Tricyclic methyldisilanylenesiloxane, $((CH_3)_6Si_4O_3)_2$, crystallizes in the triclinic space group $P\bar{1}$ with the unit-cell dimensions $a=7.71$, $b=10.17$, $c=10.17$ Å, $\alpha=106.7°$, $\beta=109.6°$ and $\gamma=78.1°$ ($Dx=1.165\ \mathrm{g\cdot cm^{-3}}$ with $Z=1$ and $Dm=1.12\ \mathrm{g\cdot cm^{-3}}$). The phase problem was mainly solved by the Patterson function. The final atomic parameters were obtained by the least-squares refinement. The molecule consists of two seven-membered rings and one six-membered ring in the chair conformation with a center of symmetry, and the skeletons of those rings consist of Si-Si and Si-O bonds. The seven-membered ring is nearly planar, except for one oxygen atom. The six-membered ring has a chair form. The dihedral angle between these rings is about 109°. The whole molecule, approximately, has a non-crystallographic mirror plane perpendicular to the line connecting the mid-points of two Si-Si bonds in the six-membered ring. The lengths of the Si-Si bonds are 2.36 Å and 2.38 Å with e. s. d. 0.01 Å. The mean lengths of the Si-O bonds and the Si-C bonds are 1.65 Å and 1.91 Å respectively. The Si-O-Si bond angles are 148° for the seven-membered ring, and 133° for the six-membered ring. Most of the closest contacts between the molecules are either of the $CH_3\cdots CH_3$ type or of the $CH_3\cdots O$ type.

We have previously reported on the crystal and molecular structure of the dehydrated tetramer of 1, 2-dimethyldisilanetetraol, $(CH_3)_8Si_8O_8$ (I),[1] which is obtained from the acid hydrolyzates of 1, 1, 2, 2-tetraethoxydimethyldisilane, $(C_2H_5O)_2\cdot CH_3SiSiCH_3(OC_2H_5)_2$ (II). This study was of great interest in elucidating the cage-like conformation of the molecule, which contains the Si-Si bonds and two types of rings. As a continuation of our study on the crystal structures of this series of organosilicon compounds, the crystal and molecular structure of the tricyclic methyldisilanylenesiloxane, $((CH_3)_6Si_4O_3)_2$ (III), is studied by means of X-ray diffraction method. This new compound III, herein reported, was isolated by Kumada *et al.*[2] from the co-hydrolyzates of the compound II with 1, 2-diethoxytetramethyldisilane (IV). On the basis of the ready formation of the cubic compound I, these authors tentatively suggested that the tricyclic compound III might be composed of three six-membered bis(disilanylene) dioxide rings attached together through two Si-Si bonds as shown in the following molecular formula:



$$\begin{array}{ccccccccc}
 & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} & \\
 & | & & | & & | & & | & \\
\mathrm{CH_3}\diagdown & \mathrm{Si} & \diagup\mathrm{O}\diagdown & \mathrm{Si} & \diagup\mathrm{O}\diagdown & \mathrm{Si} & \diagup\mathrm{O}\diagdown & \mathrm{Si} & \diagup\mathrm{CH_3} \\
 & | & & | & & | & & | & \\
\mathrm{CH_3}\diagup & \mathrm{Si} & \diagdown\mathrm{O}\diagup & \mathrm{Si} & \diagdown\mathrm{O}\diagup & \mathrm{Si} & \diagdown\mathrm{O}\diagup & \mathrm{Si} & \diagdown\mathrm{CH_3} \\
 & | & & | & & | & & | & \\
 & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} &
\end{array}$$

Experimental

Specimens were kindly prepared and supplied by Professor Makoto Kumada of Kyoto University. They are soluble in most organic solvents and recrystallized several times from the solution in 90% ethanol. Crystals thus obtained are colorless and melt at 126°C, and their outlook suggests that the crystals belong to the triclinic system.

The unit cell dimensions, as determined from the oscillation and Weissenberg photographs taken with Cu$K\alpha$ radiation, are $a=7.71\pm0.02$ Å, $b=10.17\pm0.02$ Å, $c=10.17\pm0.02$ Å, $\alpha=106.7\pm0.2°$, $\beta=109.6\pm0.2°$ and $\gamma=78.1\pm0.2°$. There was no systematic absence of spectra in the X-ray photographs. The statistical method of Howells, Phillips and Rogers[3] indicated the presence of a center of symmetry, and consequently the space group C_i^1–$P\bar{1}$ was adopted for the crystal. Assuming one molecule in the unit cell, the density was calculated to be $1.165\ \mathrm{g\cdot cm^{-3}}$ in agreement with the measured density $1.12\ \mathrm{g\cdot cm^{-3}}$.

The intensities of spectra recorded on the equatorial and the 1st layer Weissenberg photographs around the *a*- *b*- and *c*-axes by means of the multiple-film technique were estimated visually and later corrected for Lorentz and polarization factors. The data on the 1st layer photographs were also corrected for the shape of spots.[4] They were converted to an absolute scale by means of Wilson's method.[5]

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1) T. Higuchi and A. Shimada, This Bulletin, **39**, 1316 (1966).

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

3) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

4) D. C. Phillips, *ibid.*, **7**, 746 (1954).

5) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

Structure Determination

Since the unit cell contains one molecule, the molecular center might coincide with a center of symmetry. The asymmetric unit consists of half a molecule, namely, four silicon atoms, three oxygen atoms and six methyl groups. The first attempt to get the approximate structure was based on the molecular model depicted in the preceding paragraph. If it is assumed that a molecule has three six-membered dioxide rings, the middle ring must have a chair form. Assuming the usual bond lengths and angles, the eight silicon atoms of a molecule may have the coplanar or the chair form. The former corresponds to the *trans* conformation of two methyl groups attached to a disilanylene bond in the middle ring with respect to that bond, and the latter to the *cis* conformation. This consideration gave several trial models to be tested. As for the orientation of a molecule in the crystal, some features of intensity data gave a promising clue. Thus, the extremely strong intensity of $\bar{1}01$ reflection indicates for the long axis of a molecule to lie approximately on the ($\bar{1}01$) plane. In this case the direction of the long axis is referred to that of the line connecting two mid-points of the outer Si–Si bonds. Moreover, the intensities of $0kl$ and $0lk$ spectra in Weissenberg photographs around the a axis were found to be nearly equal and this fact suggests that the long axis of a molecule lies approximately on either ($0\bar{1}1$) or (011) plane. The former might be probable due to the fact that the intensity of $0\bar{2}2$ reflection is very strong.

With the help of these clues, an attempt was made at first to obtain the positions of silicon atoms from the Patterson projection along the a axis, $P(VW)$. The highest peak on this map was readily identified as the multiple vector peaks between silicon atoms across oxygen atoms in the direction of the long axis of a molecule. There were no prominent peaks on the line connecting the origin and the highest peak, and hence it was supposed that the eight silicon atoms might have the chair form. Most of the other high Patterson peaks were explained by the vectors between silicon atoms of the molecule on the basis of its orientation proposed above. Although the peaks in this projection were much overlapped, the trial parameters of oxygen atoms as well as silicon atoms could be assumed. Then, the structure factors were calculated with these parameters, and electron-density projection along the a axis was synthesized. Some of methyl groups could be identified in this projection.

Then the Patterson projection along the b axis, $P(UW)$, was computed. Although many peaks in this map seemed to be closely approached, some informations about the x coordinates of silicon and oxygen atoms were laboriously obtained, with reference to the result in the projection along the a axis. The electron-density projection along this axis was prepared. Attempts were made to refine the structure by including methyl groups, but further refinement proved impossible by means of the successive Fourier method. Moreover, the atomic locations in electron-density projections along the a and b axes were displaced to be inconsistent with each other.

Therefore, the Patterson projection along the c axis, $P(UV)$, and the modified Patterson projection⁶⁾ along the a axis, $P'(VW)$, were computed. The latter is given by the following formula:

$$P'(VW) = \sum\sum|F(0kl)|^2 \times (1-\exp(-Q(\sin\theta/\lambda)^2))^2 \cos 2\pi(kV+lW)$$

where $Q=13$. In these projections, the peaks corresponding to the intramolecular vectors seemed to be fairly well resolved, and especially the Patterson projection $P(UV)$ clearly gave the vector peaks between two silicon atoms along the disilanylene bond to revise suitably the assumed direction of this bond, that is, the direction of the short axis of a molecule. With this new orientation of a molecule, the major Patterson peaks in projections along the three axes were explained effectively by the x, y and z coordinates of four silicon atoms of a molecule. Phases were calculated on this assumption and some of them were also checked by the inequality method at this stage. The electron-density projections along three axes gave the positions of oxygen atoms as well as those of silicon atoms. The methyl groups could also be found in the succeeding electron-density maps. The coordinates of all atoms except hydrogen atoms were then refined by the trial and error methods, and later by the successive Fourier syntheses. After these procedures, the difference syntheses were applied to further refining the coordinates of atoms and thier temperature factors. Although the R values were reduced to 0.302, 0.299 and 0.214 for $0kl$, $h0l$ and $hk0$ spectra respectively, the Si–O bond lengths and the Si–O–Si bond angles in the middle six-membered ring were particularly contrary to the conventional values. Moreover, the peaks due to the central ring were badly distorted in the electron-density maps.

At this stage, the usual and the partial difference maps of electron density were constructed in expectation that the assumptions regarding the configuration of the middle ring might be seriously in error. With aid of these maps, effort was made to fit the data by the trial and error variation of parameters, and it was concluded that the position of an oxygen atom in the middle ring had to be transferred to lead another trial structure.

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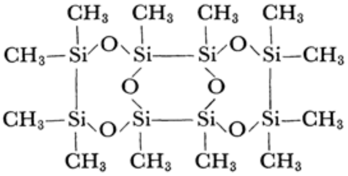
6) T. Watanabé and Y. Takaki, *Japan J. Appl. Phy.*, **3**, 783 (1964).

This new cyclic organosilicon structure contains two seven-membered rings, $(\text{–Si–O–Si–})_2\text{O}$,[*1] and one six-membered ring, $(\text{–Si–Si–O–})_2$, as shown in the following chemical formula:



The structure gave better agreement with observed intensities. After this difficulty had been overcome, the refinement proceeded normally, first by the successive Fourier syntheses and then by the difference syntheses until the R factors for $0kl$, $h0l$ and $hk0$ had dropped to 0.160, 0.227 and 0.188, respectively.

Final refinement was carried out on the 780 data of $0kl$, $h0l$, $hk0$ and $h1l$ reflections by means of the least-squares method with the programs7) written by Mr. Noritake Yasuoka for the OKITAC-5090D electronic computer and by Dr. Kazumi Nakatsu for the OKITAC-5090H electronic computer. The function minimized was $\sum w(F_o-F_c)^2$ and the weighting scheme for w was due to Hughes.8) After seven cycles, the reliability factor for the final parameters dropped to 0.122, only with 526 observed reflections. The value of F_o for the unobserved reflections (marked with asterisks in Table 2) is one half of the minimum observed structure amplitude and these values were included in the least-squares refinements.

Results and Discussion

The final atomic coordinates and the isotropic temperature factors are listed in Table 1. The observed and calculated structure factors are given in Table 2.[*2] Table 3 lists independent bond lengths, bond angles and non-bonded interatomic distances in a molecule. The final electron-density maps along the b- and c-axes are shown Figs. 1 and 2. The molecular arrangement in the crystal, together with intermolecular distances, may be seen in Fig. 3.

The configuration of a molecule is shown in Fig. 4. Figure 5 represents the intramolecular bond lengths and the bond angles. The relation of the eight silicons in a molecule is seen in Fig. 6. It is evident from the figures shown above that the molecule has, as a whole, a chair conformation with a center of symmetry and that, in very approximate terms, it has the symmetry $2/m$ along the line connecting the mid-points of two Si-Si bonds in the six-membered ring. The skeleton of a molecule consists of two seven-membered $(\text{–Si–O–Si–})_2\text{O}$ rings and one six-membered $(\text{–Si–Si–O–})_2$ ring. Every ring contains four silicon atoms. With six atoms in a plane and one atom deviated considerably from this plane, the seven-membered ring looks like an envelope. The six-membered ring has a chair form of $\bar{1}$ symmetry.

The four silicon atoms of the seven-membered ring form approximately a plane and this least-squares plane A, calculated by the program of

TABLE 1. ATOMIC PARAMETERS

Atomic parameters and estimated standard deviations

	x	$10^4\sigma(x)$	y	$10^4\sigma(y)$	z	$10^4\sigma(z)$	B	$10^2\sigma(B)$
Si(1)	0.3666	(6)	0.1992	(6)	0.3262	(4)	4.81	(13)
Si(2)	0.1686	(6)	0.3548	(5)	0.1881	(4)	4.85	(13)
Si(3)	0.2501	(5)	−0.0719	(5)	0.0919	(4)	3.97	(12)
Si(4)	0.0301	(5)	0.1272	(5)	−0.0964	(4)	3.85	(12)
O(1)	0.3375	(15)	0.0397	(14)	0.2428	(12)	5.75	(27)
O(2)	0.0799	(14)	0.2734	(13)	0.0201	(10)	5.02	(24)
O(3)	0.1931	(12)	0.0004	(12)	−0.0458	(9)	4.27	(22)
C(1)	0.6203	(25)	0.2214	(25)	0.3563	(20)	6.87	(46)
C(2)	0.3180	(27)	0.2313	(27)	0.5075	(21)	7.37	(50)
C(3)	0.3028	(23)	0.4956	(22)	0.1902	(17)	6.02	(41)
C(4)	−0.0377	(27)	0.4430	(25)	0.2553	(21)	7.38	(49)
C(5)	0.4312	(21)	−0.2174	(20)	0.0631	(16)	5.33	(36)
C(6)	0.0273	(21)	0.1410	(20)	−0.2810	(16)	5.36	(35)

[*1] The ready formation of the seven-membered ring structure has been demonstrated by Kumada *et al.* who obtained 2, 2, 4, 4, 5, 5, 7, 7-octamethyl-1, 3, 6-trioxa-2, 4, 5, 7-tetrasilacycloheptane, $(\text{–Si(CH}_3)_2\text{OSi(CH}_3)_2\text{–})_2\text{O}$, in good yield from the cohydrolysis of 1, 2-diethoxytetramethyldisilane with dimethyldichlorosilane.

7) N. Yasuoka and T. Mitsui, *Bull. Osaka Ind. Research Inst.*, **16**, 37 (1965).

8) E. W. Hughues, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

[*2] The complete data of the F_o-F_c table are kept as Document No. 6704 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥900 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

TABLE 3. BOND LENGTHS, BOND ANGLES AND NON-BONDED INTERATOMIC DISTANCES IN A MOLECULE
e. s. d. values in parenthesis

Bond lengths, Å

Si(1)	Si(2)	2.38	(0.01)
Si(3)	Si(4′)	2.36	(0.01)
Si(1)	O(1)	1.62	(0.02)
Si(2)	O(2)	1.65	(0.01)
Si(3)	O(1)	1.65	(0.02)
Si(3)	O(3)	1.66	(0.01)
Si(4)	O(2)	1.64	(0.02)
Si(4)	O(3)	1.67	(0.01)
Si(1)	C(1)	1.93	(0.02)
Si(1)	C(2)	1.93	(0.02)
Si(2)	C(3)	1.92	(0.02)
Si(2)	C(4)	1.90	(0.02)
Si(3)	C(5)	1.85	(0.02)
Si(4)	C(6)	1.92	(0.02)

Bond angles (°)

Si(1)	O(1)	Si(3)	148.2	(0.9)
Si(2)	O(2)	Si(4)	148.2	(0.8)
Si(3)	O(3)	Si(4)	132.7	(0.7)
Si(2)	Si(1)	O(1)	111.4	(0.5)
Si(1)	Si(2)	O(2)	111.2	(0.5)
Si(4′)	Si(3)	O(1)	109.1	(0.5)
Si(4′)	Si(3)	O(3)	105.6	(0.4)
Si(3′)	Si(4)	O(2)	109.5	(0.5)
Si(3′)	Si(4)	O(3)	106.0	(0.4)
C(1)	Si(1)	Si(2)	108.6	(0.7)
C(2)	Si(1)	Si(2)	111.3	(0.7)
C(3)	Si(2)	Si(1)	110.6	(0.6)
C(4)	Si(2)	Si(1)	112.7	(0.7)
C(5)	Si(3)	Si(4′)	116.8	(0.6)
C(6)	Si(4)	Si(3′)	114.1	(0.6)
O(1)	Si(3)	O(3)	110.1	(0.6)
O(3)	Si(4)	O(2)	109.0	(0.6)
C(1)	Si(1)	O(1)	107.7	(0.8)
C(2)	Si(1)	O(1)	107.3	(0.9)
C(3)	Si(2)	O(2)	108.5	(0.7)
C(4)	Si(2)	O(2)	105.5	(0.8)
C(5)	Si(3)	O(1)	108.7	(0.7)
C(5)	Si(3)	O(3)	106.5	(0.7)
C(6)	Si(4)	O(2)	108.9	(0.7)
C(6)	Si(4)	O(3)	109.2	(0.7)
C(1)	Si(1)	C(2)	110.5	(1.0)
C(3)	Si(2)	C(4)	108.2	(0.9)

Non-bonded interatomic distances, Å

Si(1)	Si(3)	3.15	(0.01)
Si(2)	Si(4)	3.16	(0.01)
Si(3)	Si(4)	3.05	(0.01)
Si(3)	Si(3′)	3.86	(0.01)
Si(4)	Si(4′)	3.84	(0.01)
Si(1)	Si(4)	4.15	(0.01)
Si(2)	Si(3)	4.13	(0.01)
Si(1)	O(3)	3.68	(0.01)
Si(2)	O(3)	3.71	(0.01)
Si(3)	O(2)	3.68	(0.01)
Si(4)	O(1)	3.70	(0.01)
Si(1)	O(2)	3.35	(0.01)
Si(2)	O(1)	3.33	(0.01)
Si(3)	O(3′)	3.24	(0.01)
Si(4)	O(3′)	3.23	(0.01)
Si(3)	O(2′)	3.29	(0.01)
Si(4)	O(1′)	3.29	(0.01)
O(1)	O(3)	2.71	(0.02)
O(2)	O(3)	2.69	(0.02)
O(1)	O(2)	3.58	(0.02)
O(3)	O(3′)	3.41	(0.01)
O(1)	O(3′)	3.95	(0.02)
O(2)	O(3′)	3.93	(0.01)
O(1)	C(6′)	3.83	(0.02)
C(1)	C(3)	3.71	(0.03)
C(2)	C(4)	3.84	(0.04)
C(4)	C(5′)	4.12	(0.03)

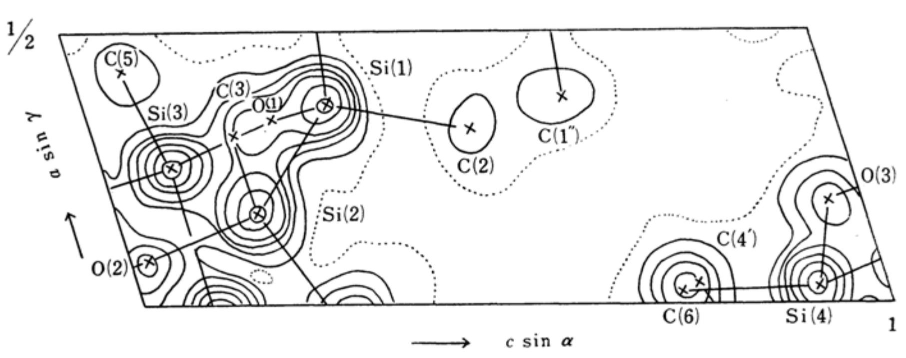


Fig. 1. Electron density projected along the *b* axis. Contours at intervals of 2e.Å^{-2} start with 2e.Å^{-2} contour (broken line), the interval being 4e.Å^{-2} after 10e.Å^{-2}.

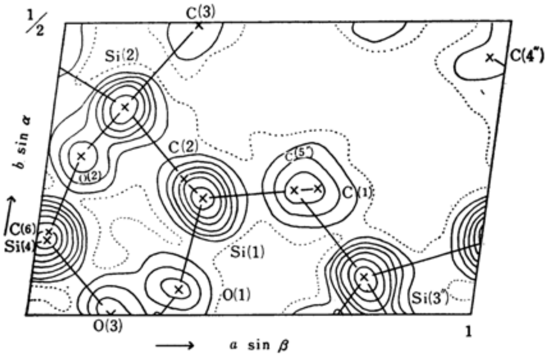


Fig. 2. Electron density projected along the *c* axis. Contours at intervals of 2e.Å^{-2} start with 2e.Å^{-2} contour (broken line), the interval being 4e.Å^{-2} after 10e.Å^{-2}.

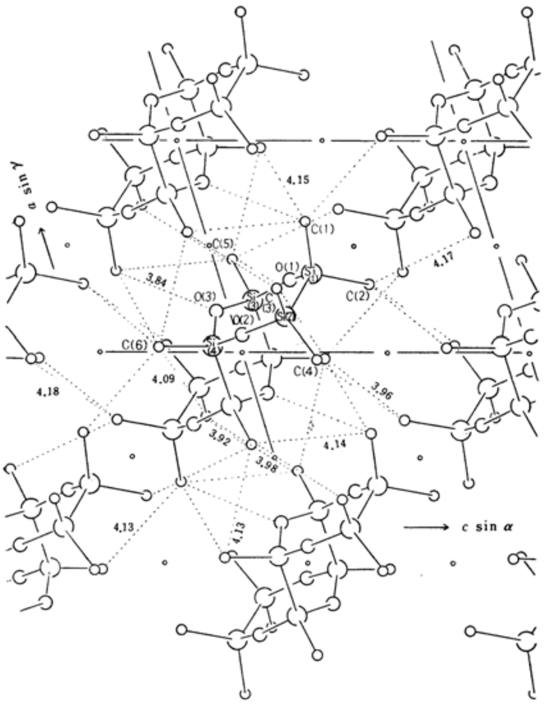


Fig. 3. Arrangement of the molecules projected along the *b* axis.

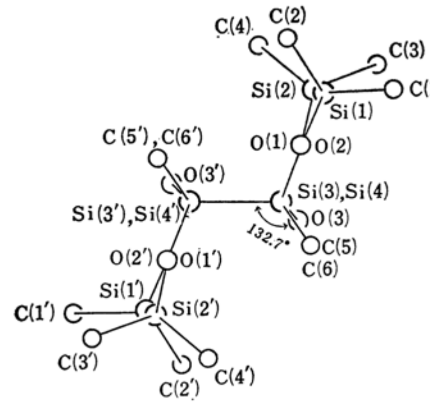


Fig. 4. Configuration of a molecule.

TABLE 4. DEVIATION OF ATOMS OF SEVEN-MEMBERED RING FROM THE PLANE A

Atom	Deviation, Å
Si(1)	−0.08
Si(2)	0.06
Si(3)	0.08
Si(4)	−0.06
O(1)	0.07
O(2)	−0.11
O(3)	−0.58

Miss. Y. Tsukuda for the OKITAC-5090H computer, has the following equation:

$$-2.783X - Y + 2.001Z + 4.014 = 0,$$

where *X*, *Y* and *Z* are expressed in Å with reference to the orthogonal axes *a'*, *b* and *c'*, such that the *bc* plane and the *bc'* plane are the same. Table 4 shows the deviation of atoms of this ring from the plane A. The dihedral angle between this plane and the plane through the Si(1), O(1) and Si(3) atoms is 9° and that between the plane A and the plane through the Si(2), O(2) and Si(4) atoms is 15°. The plane A makes an angle of 119° with the plane C through the Si(3), O(3) and Si(4) atoms.

The four silicon atoms of the six-membered ring form a complete plane B with the requirement of the symmetry and the equation of plane B is:

$$-0.030X - Y - 1.619Z = 0.$$

The skeleton of the six-membered ring has a chair form, the plane C being bent by 47° out of the plane B, with the O(3) atom displaced by 0.49 Å from the plane B. In comparison with this conformation of the ring, the corresponding rings in the compound I and bis(tetramethyldisilanylene) dioxide,[9] ($(CH_3)_4Si_2O)_2$ (V), have a boat form with the dihedral angle of 37° and a chair form with the dihedral angle of 10°, respectively. The plane A makes an angle of 109° with the plane B, and the plane C bisects nearly the angle between the plane A and the plane B.

The Si-Si bond distances, 2.36 Å and 2.38Å, in the molecule are almost the same as 2.35 Å and 2.36 Å in the related organosilicon compounds I and V. Every difference in non-equivalent Si-Si, Si-O and Si-C distances would not be probably significant, the mean values being 2.37 Å, 1.65 Å and 1.91 Å respectively, and these values agree well with those reported by other investigators. The bond angles around the silicon atoms are almost tetrahedral.

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

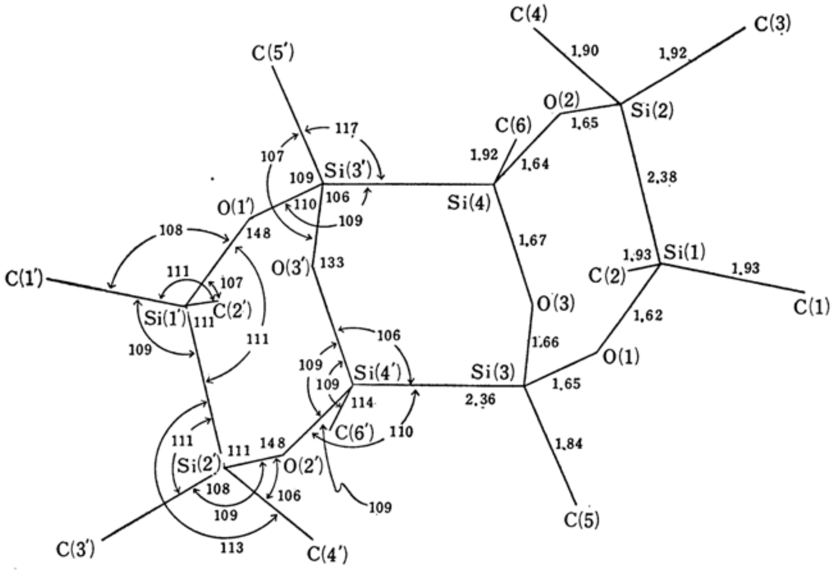

Fig. 5. Intramolecular bond lengths and bond angles.

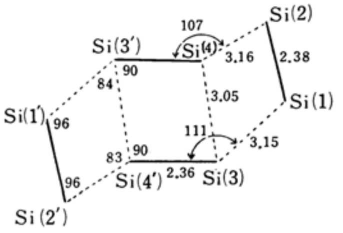

Fig. 6. Relations of the eight silicons in a molecule.

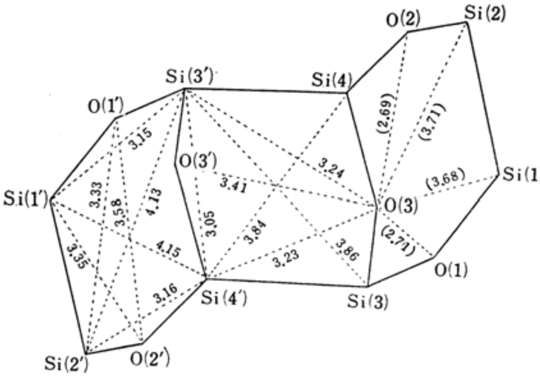

Fig. 7. Non-bonded interatomic distances in rings of a molecule.

The difference in the Si-O-Si bond angles of six-membered and seven-membered rings is 16° and this value may be significant, but these bond angles lie within the range of 130°—145°, those found in the other cyclic organosiloxane compounds. Hence, this distortion of the bond angles might be partly due to the interaction of non-bonding atoms in a molecule, although the situation of the strain differs considerably in two types of the rings. This environment will also be seen in the non-bonded interatomic distances in two types of the rings, as shown in Fig. 7. Thus, these distances for the seven-membered ring are longer by around 0.1 Å than the corresponding distances for the six-membered ring.

The significant differences between the temperature factors of the atoms in the inner and outer parts of molecule, as will be seen in Table 1, may suggest the thermal motion of the ellipsoidal molecule as a whole.

The mode of the packing of the ellipsoidal molecules in the crystal can be seen most clearly in Fig. 3. The molecules lie approximately on the $(\bar{1}01)$ plane, their long axes directing towards the [111] axis. Each molecule is effectively surrounded by the molecules in this plane and also by those below and above this plane. Most of the closest contacts are either of the $CH_3\cdots CH_3$ type or of the $CH_3\cdots O$ type, because the molecule possesses a surface comprised of twelve methyl groups.

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