# *The Crystal Structure of Bistetramethyldisilanilenedioxide $((CH_3)_4Si_2O)_2$*

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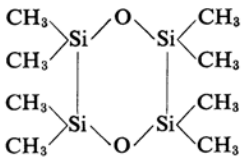
There have been many structural investigations of the bond angle and bond length of the Si–O–Si skeleton in various types of inorganic silicates. It would be of interest to extend these investigations in the field of organic silicon compounds. The crystal structures of various types of siloxanes have been studied by Frevel and Hunter[1], Roth and Harker[2], Peyronel[3] and Steinfink, Post and Fankuchen[4]. These structure analyses have shown that cyclic siloxanes have two configurations in the Si–O–Si rings, one planar and one puckered.

There has, however, been no study of the crystal structure of an organic silicon compound containing the Si–Si bond. It would be interesting, for instance, to determine the crystal structure of bistetramethyldisilanilenedioxide, which has a cyclic member which includes the Si–Si bond. From the results of chemical analysis, it was supposed that the molecule had following constitutional formula:



## Experimental

Crystals recrystallized several times from petroleum ether at 10°C are colorless, plate-like, and have no cleavage. The crystals very quickly sublime at room temperature, and are soluble in most organic solvents.

To prevent such sublimation of the specimen, the crystal was sealed in a thin-walled glass capillary. The quick sublimation and the low melting point made it impossible cut the crystal into a cylindrical specimen suitable for a X-ray photograph.

Oscillation and Weissenberg photographs were taken using Cu-$K_\alpha$ radiation filtered by nickel foil.

The cell dimensions and physical constants were determined to be as follows;

| | |
|---|---|
| $a=7.67\pm0.02$ Å | $D_{obs}=1.04$ g. cm$^{-3}$ |
| $b=6.64\pm0.02$ Å | $D_{calcd}=1.05$ g. cm$^{-3}$ |
| $c=17.39\pm0.03$ Å | m. p. $=42$°C |
| $\beta=111.0\pm0.2$° | mol. wt. $=264$ |
| $V=826.8$ Å$^3$ | $Z=2$ |

The reflections $(0\,k\,0)$ with $k$ odd and $(h\,0\,l)$ with $l$ odd were absent, the $(h\,k\,l)$ reflections showed no extinction rule. These extinction rules show that the corresponding space group is $C_{2h}^5-P2_1/c$. The oscillation photographs taken at $-50$°C did not show any transition within the temperature range, unlike that taken at room temperature. The exposure time was limited by the sublimation of the crystal, so it was very difficult to obtain three-dimentional intensity data. The equatorial Weissenberg photographs around the a and b axes were taken by using the multiple-film technique. The relative intensities of the observed reflections were estimated in terms of an arbitrary scale by visual comparison with an intensity scale. The observed structure factors were brought to an absolute scale by means of Wilson's method[5].

## Determination of the Configuration

The intensities of $(0\,k\,l)$ and $(h\,0\,l)$ reflections were corrected with the Lorentz and polarization factors. For the space group $P2_1/c$, two molecules in a unit cell have to be placed on the center of symmetry. This means that the molecule has a center of symmetry in itself. Therefore the asymmetric unit is a half of the molecule; two silicon atoms, one oxygen atom and four methyl groups. Consequently, twenty-one parameters, except for those of hydrogen atoms, should be determined in this structure analysis.

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, *Chem. Industr.*, **36**, 441 (1954).
4) H. Steinfink, B. Post and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1956).
5) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

First, an attempt was made to locate the silicon atoms by the Patterson function $P(xz)$ projection of the $(0\,l\,0)$ plane, because it is considered that overlapping of atoms were minimized in this projection (Fig. 1). All $(h\,0\,l)$ reflections which formed about two-thirds of the total number of unique $(h\,0\,l)$ reflections, were used to calculate the Patterson function. In the Patterson projection $P(xz)$, the silicon-silicon and silicon-oxygen vectors of adjacent molecules were fairly distinguishable. Thus, the coordinates of silicon and oxygen atoms could be approximately determined. The carbon atoms were not fixed by this Patterson projection. A probable structure model was made from the positions of the silicon and oxygen atoms derived from the Patterson projection and was corrected by structure factor refinements, referring to the covalent radii and tetrahedral angles about the silicon atoms[6].

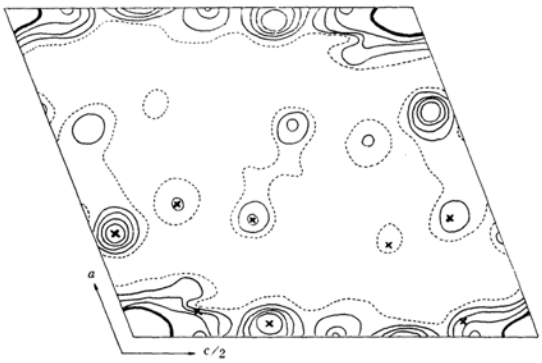



Fig. 1. Patterson function P($xz$) projected on the $(0\,l\,0)$ plane. Contours show equal intervals in an arbitrary scale. The intermolecular vectors between ring members are marked with crosses.

Although the results of the calculation of structure factors on the first model did not show a good agreement with the observed structure factors $F(h\,0\,l)$, even for the reflections with low indices, a two-dimensional Fourier synthesis on the $(h\,0\,l)$ plane was tried, using lower order reflections. The electron density map obtained here, however, indicated not only the outline of the molecule but also two silicon atoms, an oxygen atom and two carbon atoms. The structure factors were calculated, and several Fourier syntheses were made. After these procedures, the $(F_o-F_c)$ syntheses were applied for correcting the coordinates and temperature factors. The isotropic temperature factors for carbon atoms, oxygen atom and silicon atoms were $B_C=3.5$, $B_O=3.5$ and $B_{Si}=2.5$ Å$^2$ respectively at this step of the refinement.

6) L. C. Pauling, "The Nature of the Chemical Bond", Cornell University Rress, Ithaca, N. Y. (1960), p. 246.

On the other hand, an attempt to locate the $y$ parameters was calculating the Patterson function, $P(yz)$. The intensities of the $(0\,k\,l)$ reflections were generally weak because of the limitation of exposure time. The intensities of about one-third of the $(0\,k\,l)$ reflections observed were too weak to be measured. As has been mentioned before, no peaks corresponding to the intramolecular vectors could be resolved in this Patterson projection. Therefore, a special type of modified Patterson function[7] was calculated:

$$P'(yz)=\sum\sum|F(0\,k\,l)|^2(1-\exp(-\xi^2))\times\cos 2\pi ky\cos 2\pi lz$$

where $\xi=2\sin\theta$. This modified Patterson map was particularly effective in distinguishing the intramolecular vectors, as is shown in Fig. 2.

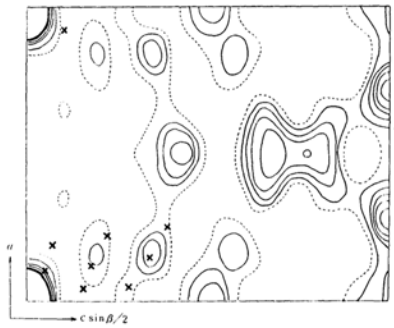



Fig. 2. A modified Patterson function projected on the $(l\,0\,0)$ plane. Contours are at equal intervals in an arbitrary scale. The intermolecular vectors between ring members are marked by crosses.

Using the $y$ parameters derived from this modified Patterson projection and the $z$ parameters obtained from the (0 1 0) projection, the structure factors of $(0\,k\,l)$ reflections were calculated. The usual successive refinements of atomic parameters were carried out. The isotropic temperature factors $B_C=9.0$ for carbon, $B_O=9.0$ for oxygen and $B_{Si}=5.0$ Å$^2$ were used in the calculations of $F(0\,k\,l)$. At this step of refinement, including the $(F_o-F_c)$ syntheses, the reliability factors, $R=\sum||F_o|-|F_c||/\sum|F_o|$, were 24.6% for $(0\,k\,l)$ and 21.2% for $(h\,0\,l)$.

The least square method was used in the next step of the refinement. Ten cycles of the refinement of positional and isotropic temperature factor parameters reduced the R factor from 24.6% to 20.1% for $(0\,k\,l)$ and from 21.2% to 13.5% for $(h\,0\,l)$, non-observed reflections being excluded.

The calculations of the structure factors and the least square refinements were carried

7) T. Watanabé and Y. Takaki, to be published.

TABLE I. ATOMIC PARAMETERS

| | $x$ | $y$ | $z$ | $B(\text{A}^2)$ $(h\,0\,l)$ | $B(\text{A}^2)$ $(0\,k\,l)$ |
|---|---|---|---|---|---|
| Si(1) | 0.1700 | 0.1262 | 0.0986 | 2.5 | 5.5 |
| (2) | 0.1400 | −0.0233 | −0.0716 | 3.1 | 6.6 |
| O | 0.2170 | 0.0845 | 0.0170 | 7.1 | 12.1 |
| C(1) | 0.2000 | 0.4000 | 0.1179 | 9.0 | 6.0 |
| (2) | 0.3397 | −0.0135 | 0.1894 | 4.6 | 6.5 |
| (3) | 0.1472 | 0.1500 | −0.1534 | 5.8 | 9.0 |
| (4) | 0.2800 | −0.2590 | −0.0777 | 8.4 | 6.4 |

out with a NEAC-2203 electronic computer, and the Fourier and Patterson functions, with a NEAC-2101 electronic computer. The least square calculations were performed using the program of Osaki[8]. The Hartree-Fock atomic scattering curves for carbon and oxygen atoms and Slater's for silicon atoms were employed throughout the calculations of the structure factors. In the computations of the structure factors, the contribution of hydrogen atoms was disregarded. The final atomic coordinates and isotropic temperature factors of each atom as obtained by the least square method are listed in Table I. The final electron density projections upon (1 0 0) and (0 1 0) are shown in Fig. 3 and Fig. 4 respectively. The observed and calculated structure factors are tabulated in Table II.

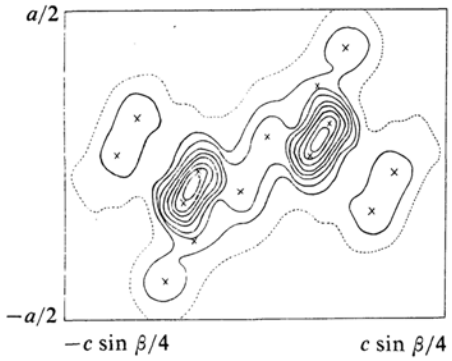



Fig. 3. Electron density projection of one molecule on the (1 0 0) plane. Atomic positions are marked by crosses. Contour intervals are 2 e Å$^{-2}$, the lowest contour (broken line) being at 2 e Å$^{-2}$.

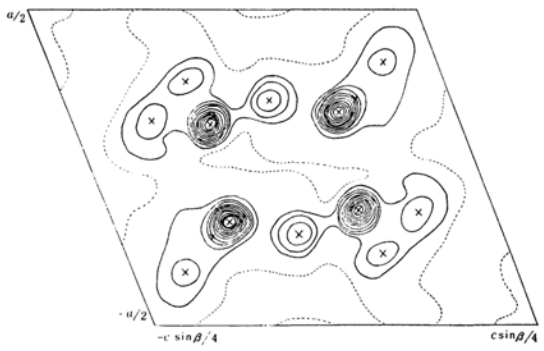



Fig. 4. Electron density projection of one molecule on the (0 1 0) plane. Atomic positions are marked by crosses. Contour intervals are 2 e Å$^{-2}$, the lowest contour (broken line) being at 2 e Å$^{-2}$.

8) K. Osaki, N3LSIMC (1961).

## Results and Discussion

Bond lengths and angles were obtained as given in Table III, and the arrangement of molecules in the unit cell, together with the

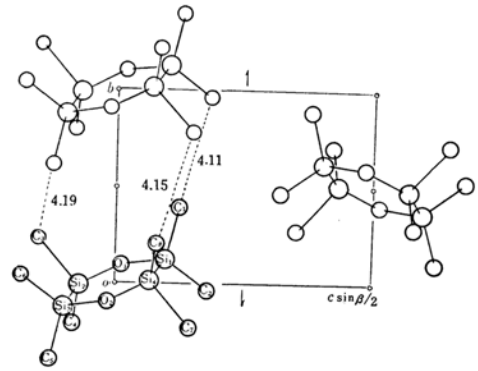



Fig. 5. Arrangement of the molecules projected on the (1 0 0) plane.

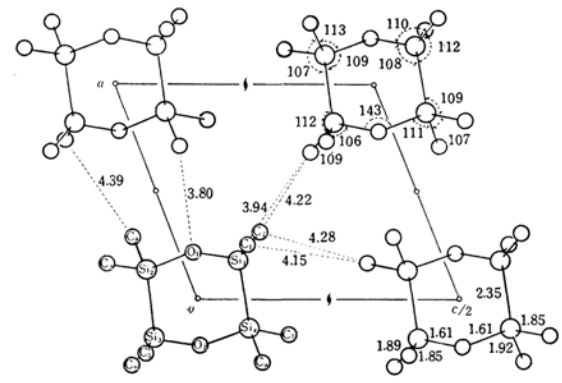



Fig. 6. Arrangement of the molecules projected on the (0 1 0) plane.

TABLE II. OBSERVED AND CALCULATED STRUCTURE FACTORS

| 0 k l | $\|F_o\|\times10$ | $F_c\times10$ | 0 k l | $\|F_o\|\times10$ | $F_c\times10$ | 0 k l | $\|F_o\|\times10$ | $F_c\times10$ | 0 k l | $\|F_o\|\times10$ | $F_c\times10$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 002 | 703 | 685 | 024 | 42 | 38 | 0312 | 48 | − 67 | 052 | 46 | − 6 |
| 4 | 550 | −573 | 5 | 294 | −266 | 13 | 34 | 38 | 3 | 0 | − 20 |
| 6 | 389 | −412 | 6 | 69 | − 62 | 14 | 34 | − 20 | 4 | 46 | − 41 |
| 8 | 163 | −147 | 7 | 137 | 137 | 15 | 95 | 88 | 5 | 0 | 27 |
| 10 | 262 | 236 | 8 | 139 | −133 | 16 | 66 | 19 | 6 | 71 | − 64 |
| 12 | 191 | 153 | 9 | 198 | 133 | 17 | 40 | 24 | 7 | 48 | − 36 |
| 14 | 0 | 11 | 10 | 0 | 20 | 040 | 60 | − 82 | 8 | 48 | − 46 |
| 011 | 1046 | 962 | 11 | 32 | − 46 | 1 | 60 | − 37 | 9 | 48 | − 60 |
| 2 | 468 | −512 | 12 | 32 | 24 | 2 | 0 | − 21 | 10 | 48 | 42 |
| 3 | 0 | 27 | 13 | 109 | −107 | 3 | 88 | −108 | 11 | 34 | − 26 |
| 4 | 510 | −520 | 14 | 71 | 35 | 4 | 105 | 127 | 12 | 67 | 69 |
| 5 | 48 | − 93 | 15 | 48 | − 31 | 5 | 85 | − 91 | 13 | 44 | 7 |
| 6 | 0 | 66 | 16 | 48 | 42 | 6 | 0 | − 9 | 14 | 42 | 9 |
| 7 | 298 | −292 | 17 | 42 | 31 | 7 | 44 | − 32 | 15 | 0 | 38 |
| 8 | 276 | 268 | 18 | 40 | − 5 | 8 | 149 | −199 | 060 | 0 | 32 |
| 9 | 38 | − 39 | 031 | 0 | 74 | 9 | 0 | 26 | 1 | 0 | 26 |
| 10 | 71 | 13 | 2 | 286 | −261 | 10 | 99 | − 97 | 2 | 0 | − 6 |
| 11 | 196 | 180 | 3 | 71 | 78 | 11 | 48 | 59 | 3 | 0 | 22 |
| 12 | 101 | − 97 | 4 | 212 | −215 | 12 | 34 | 20 | 5 | 0 | − 3 |
| 13 | 105 | 80 | 5 | 93 | 73 | 13 | 48 | 9 | 6 | 0 | − 20 |
| 14 | 71 | − 46 | 6 | 55 | 54 | 14 | 69 | 80 | 7 | 0 | − 7 |
| 15 | 0 | 5 | 7 | 125 | −166 | 15 | 46 | − 22 | 9 | 0 | − 39 |
| 020 | 425 | 444 | 8 | 123 | 100 | 16 | 38 | 50 | 10 | 0 | − 24 |
| 1 | 26 | − 44 | 9 | 131 | −141 | 17 | 40 | − 11 | 11 | 0 | − 6 |
| 2 | 69 | 132 | 10 | 0 | − 30 | 18 | 32 | − 17 | 12 | 38 | 39 |
| 3 | 306 | −332 | 11 | 46 | − 24 | 051 | 0 | 12 | 13 | 36 | 10 |
| 0 h l | $\|F_o\|\times10$ | $F_c\times10$ | 0 h l | $\|F_o\|\times10$ | $F_c\times10$ | 0 h l | $\|F_o\|\times10$ | $F_c\times10$ | 0 h l | $\|F_o\|\times10$ | $F_c\times10$ |
| 002 | 648 | 692 | 18 | 118 | 128 | −4 | 0 | 5 | −10 | 0 | 41 |
| 4 | 582 | −575 | −2 | 479 | −448 | −6 | 456 | 471 | −12 | 94 | 52 |
| 6 | 397 | −427 | −4 | 471 | 364 | −8 | 477 | 443 | −14 | 93 | − 13 |
| 8 | 158 | −177 | −6 | 172 | −209 | −10 | 153 | −165 | −16 | 65 | 19 |
| 10 | 278 | 300 | −8 | 244 | −240 | −12 | 469 | −400 | −18 | 107 | 64 |
| 12 | 259 | 248 | −10 | 107 | 109 | −12 | 265 | −231 | −20 | 94 | 86 |
| 14 | 50 | 35 | −12 | 252 | 262 | −16 | 65 | 76 | 700 | 145 | 163 |
| 16 | 0 | − 40 | −14 | 139 | 163 | −18 | 132 | 154 | 2 | 65 | − 57 |
| 100 | 675 | 675 | −16 | 132 | −125 | −20 | 59 | 26 | 4 | 113 | −140 |
| 2 | 118 | 173 | −18 | 185 | −189 | 500 | 132 | 105 | 6 | 59 | − 70 |
| 4 | 126 | −121 | −20 | 86 | − 69 | 2 | 118 | 63 | −2 | 252 | 260 |
| 6 | 126 | −103 | 300 | 629 | −736 | 4 | 166 | −136 | −4 | 0 | − 17 |
| 8 | 88 | 44 | 2 | 212 | −198 | 6 | 145 | −132 | −6 | 284 | −268 |
| 10 | 158 | −215 | 4 | 404 | 423 | 8 | 0 | − 5 | −8 | 332 | −285 |
| 12 | 225 | −255 | 6 | 364 | 374 | 10 | 113 | 144 | −10 | 93 | − 55 |
| 14 | 0 | − 23 | 8 | 0 | 8 | 12 | 113 | 143 | −12 | 231 | 240 |
| 16 | 94 | 86 | 10 | 153 | −145 | −2 | 107 | 71 | −14 | 206 | 159 |
| 18 | 99 | 125 | 12 | 132 | −162 | −4 | 93 | 85 | −16 | 0 | − 40 |
| −2 | 536 | 530 | 14 | 0 | 1 | −6 | 183 | 187 | −18 | 80 | − 74 |
| −4 | 490 | −495 | 16 | 99 | 84 | −8 | 364 | 368 | 800 | 0 | − 5 |
| −6 | 450 | −485 | −2 | 656 | −624 | −10 | 59 | 43 | 2 | 0 | 11 |
| −8 | 166 | −144 | −4 | 244 | 248 | −12 | 341 | −318 | 4 | 0 | 25 |
| −10 | 418 | 433 | −6 | 370 | 382 | −14 | 172 | −170 | −2 | 0 | 21 |
| −12 | 603 | 603 | −8 | 86 | −125 | −16 | 94 | 52 | −4 | 0 | 46 |
| −14 | 166 | 140 | −10 | 198 | −226 | −18 | 206 | 194 | −6 | 132 | −100 |
| −16 | 158 | −178 | −12 | 219 | −192 | −20 | 113 | 134 | −8 | 172 | −165 |
| −18 | 132 | −148 | −14 | 126 | − 70 | 600 | 337 | 316 | −10 | 0 | − 37 |
| −20 | 0 | − 40 | −16 | 0 | 51 | 2 | 132 | −102 | −12 | 126 | 134 |
| 200 | 868 | −898 | −18 | 65 | − 64 | 4 | 298 | −274 | −14 | 118 | 164 |
| 2 | 278 | −238 | −20 | 61 | − 61 | 6 | 172 | −174 | −16 | 0 | − 8 |
| 4 | 0 | 55 | 400 | 311 | −315 | 8 | 0 | 7 | −18 | 172 | −123 |
| 6 | 383 | 367 | 2 | 158 | 171 | 10 | 113 | 140 | 900 | 46 | − 71 |
| 8 | 107 | 88 | 4 | 364 | 336 | −2 | 319 | 282 | −2 | 73 | −107 |
| 10 | 305 | −361 | 6 | 59 | 52 | −4 | 0 | − 30 | −4 | 0 | − 3 |
| 12 | 279 | −326 | 8 | 0 | 4 | −6 | 158 | −156 | −6 | 99 | 79 |
| 14 | 0 | − 56 | −2 | 244 | −228 | −8 | 158 | −131 | −8 | 59 | 19 |
| 16 | 126 | 150 | | | | | | | | | |

TABLE III. BOND LENGTHS AND ANGLES

| | | | | |
|---|---|---|---|---|
| Si(1) | Si(2) | 2.35 Å | ∠C(1)Si(1)Si(4) | 111.9° |
| | O(1) | 1.61 | ∠C(2)Si(1)Si(4) | 111.6 |
| | C(1) | 1.85 | ∠C(3)Si(2)Si(3) | 109.5 |
| | C(2) | 1.89 | ∠C(4)Si(2)Si(3) | 107.3 |
| Si(2) | O(1) | 1.61 | ∠C(1)Si(1)O(1) | 106.1 |
| | C(3) | 1.85 | ∠C(2)Si(1)O(1) | 110.4 |
| | C(4) | 1.92 | ∠C(3)Si(2)O(1) | 111.0 |
| | | | ∠C(4)Si(2)O(1) | 113.3 |
| ∠O(1)Si(1)Si(4) | | 107.7° | | |
| ∠O(1)Si(2)Si(3) | | 108.6 | ∠C(1)Si(1)C(2) | 109.1 |
| | | | ∠C(1)Si(2)C(4) | 107.0 |
| ∠Si(1)O(1)Si(2) | | 143.2 | | |

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 |
|---|---|---|---|---|---|---|---|
| Bistetramethyl-disilanilenedioxide | 2.35 | 1.61 | 1.88 | 143 | — | 108 | 109 |
| Octamethylcyclo-tetrasiloxane | — | 1.65 | 1.92 | 142.5 | 109 | 106 | — |
| Hexamethylcyclo-trisiloxane | — | 1.614 | 1.929 | 136 | 104 | 106 | — |
| Spirosiloxane | — | 1.64 | 1.88 | 130 | 106 | 106 | — |
| Diethylsilanediol | — | 1.63 | 1.90 | — | 110 | 111 | — |
| Diallylsilanediol | — | 1.63 | 1.90 | — | 110 | 110 | — |

intermolecular bond lengths and angles as well as the intramolecular distances, are illustrated in Figs. 5 and 6.

The equation of a plane including the Si-O-Si triangle the ring member is:

$$6.63x-3.06y+z-62.5=0$$

and that including the four silicon atoms is:

$$3.06x-2.93y+z=0.$$

These two planes form an angle of 170°. Thus, the skeleton of the ring has a chair form. This shows that the configuration of the skeleton compensates for the energy of strain which may exist in the ring if it has a planar form.

The Si-Si bond distance, 2.35 Å, in the molecule is almost the same as that found in metallic silicon (2.34 Å). The Si-O bond length, 1.61 Å, is considerably shorter than the value (1.83 Å) which is the sum of the covalent radii of the silicon and oxygen atoms. This shrinkage of the bond length as known in silicates has already been reported also in organic silicon compounds[9-14]. The bond angle of Si-O-Si (143°) is greater than either the covalent $p$ orbital bond angle or the $sp^2$ and $sp^3$ hybrid orbital bond angle. This finding and the shrinkage of the Si-O bond length may indicate the presence of an ionic character in the Si-O-Si configuration, as was been suggested by Pauling[15]. The average bond length of the Si-C bond (1.88 Å) is almost in agreement with those of spirosiloxane, diethylsilanediol and diallylsilanediol. However, the deviations of the Si-C bond lengths from the average bond length are not small in this case. This may be caused by the overlapping of carbon atoms in the two-dimensional projections. The bond angles around the silicon atoms are almost regularly tetrahedral; their values agree with those of spirosiloxane, octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane, as is shown in Table IV. The intermolecular interaction seems to be somewhat weaker than the ordinary methyl-methyl interaction, because the crystal has an extremely large sublimation nature and a low melting point. In fact, the intermolecular distances of the crystal obtained in this study (Figs. 5 and 6) are longer than the ordinary van der Waals distance (4.0 Å) between methyl groups.

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9) L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945).
10) W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948).
11) G. Peyronel, *Chem.. Industr.*, **36**, 441 (1954).
12) H. Steinfink, B. Post and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1956).
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14) M. Kakudo and N. Kasai, This Bulletin, **27**, 605 (1954).
15) L. C. Pauling, "The Nature of the Chemical Bond", Cornell University Press, (1960), p. 321; *J. Phys. Chem.*, **56**, 361 (1952).

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