The Crystal Structure of Octamethyl Cyclotetrasiloxane*

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Octamethyl cyclotetrasiloxane, $[(CH_3)_2SiO]_4$, undergoes a solid-phase transition at $-16\cdot3°$ C. The crystal structure of the low-temperature modification has been determined. The unit cell is tetragonal, $a = 16\cdot10\pm0\cdot02$, $c = 6\cdot47\pm0\cdot01$ Å. The space group is $P4_2/n$ and there are four molecules per unit cell.

Bond lengths have been determined using electron-density projections and generalized projec-jections. The bond lengths and angles are Si–O = 1·65 Å, Si–C = 1·92 Å; Si–O–Si = 142·5°, O–Si–O = 109°, C–Si–C = 106°. The siloxane ring is puckered. The molecular packing is determined by the protruding methyl groups, the molecules being held together by van der Waals forces. The van der Waals radius of the non-bonded methyl group is 2·1 Å.
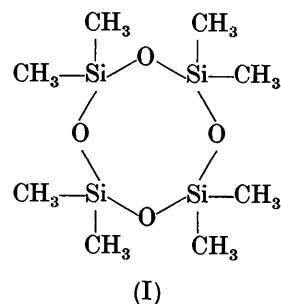
Above the transition temperature the space group changes to $I4_1/a$; the length of the a axis remains 16·10 Å but the c axis increases to 6·83 Å. The crystallographic evidence indicates that the transition involves a change from an ordered crystalline form to a disordered one in which each molecule may assume any of four alternative orientations.

Introduction

The wide interest in the chemistry of organosilicon compounds has led to the synthesis of many types of polymers of the form $-(R_1R_2)Si-O-Si(R_3R_4)-$. The substituent groups on the silicon atoms are, in most cases, halogen atoms or aliphatic or aromatic groups. The structures of the inorganic –Si–O–Si– chains found in the pyroxenes and in cyclic structures containing six or more alternate oxygen and silicon atoms in the form of polyvalent ions were determined many years ago by Bragg, Pauling, and others. However, very little is known of the crystal structures of the organic analogues of these compounds. There is considerable theoretical interest in the 'normal' valence angle of the oxygen atom in the –Si–O–Si– configuration and the limits of distortion that it can undergo. Such knowledge should be useful in efforts to predict the course of polymerization reactions and the conditions under which linear polymers can be terminated by ring formation.

In a preliminary note on the determination of the structures of cyclic siloxanes, Frevel & Hunter (1945) suggested that, with the exception of the trimeric cyclic siloxane, they contain puckered Si–O–Si rings. The recent determination of the structure of the cyclic trimer $[(CH_3)_2SiO]_3$ (Peyronel, 1954) showed that in this compound the Si–O–Si ring is planar; a planar ring configuration was also established for the structure of a related compound, octamethylspiro (5,5) pentasiloxane (Roth & Harker, 1948).

Octamethyl cyclotetrasiloxane, (I), is the simplest member of this series of siloxane molecules for which a puckered structure has been postulated.

$$
\begin{array}{ccc}
& CH_3 & & CH_3 & \\
& | & O & | & \\
CH_3{-}Si & & & Si{-}CH_3 \\
& & & & \\
O & & & & O \\
& & & & \\
CH_3{-}Si & & O & & Si{-}CH_3 \\
& | & & | & \\
& CH_3 & & CH_3 &
\end{array}
$$

(I)

The tetramer is liquid at room temperature (m.p. 17° C.) and undergoes a solid-phase transition at $-16\cdot3°$ C. (Hoffman, 1953). The crystal structure of the low-temperature modification is described in Part I of this paper; the high-temperature modification is discussed briefly in Part II.

1. The low-temperature modification

Experimental

Samples of octamethyl cyclotetrasiloxane, denoted hereafter as D_4, where D stands for the repeat unit '$(CH_3)_2SiO$' and the subscript denotes the number of units in the ring, were recrystallized several times, and small portions were sealed into thin-walled glass capillary tubes (0·3 mm. in diameter). Techniques for growing and maintaining single crystals of substances which are liquid or gaseous at room temperature have been described (Post, Schwartz & Fankuchen, 1951).

The technique has been adapted to the precession camera (Holtzberg, Post & Fankuchen, 1953). Crystals of D_4 always grew along what was later designated as the c axis of the unit cell, and it was found convenient to use both the Weissenberg and precession cameras to accumulate data in three dimensions.

The cyclic tetramer crystallizes in the tetragonal system. The unit-cell dimensions of the low-temperature modification (at $-50°\pm5°$ C.) are

$$a = 16\cdot10\pm0\cdot02, \quad c = 6\cdot47\pm0\cdot01 \text{ Å}.$$

There are four molecules per unit cell. The calculated X-ray density at $-50°$ C. is $1\cdot17$ g.cm.$^{-3}$, which compares with a measured density of $1\cdot06$ g.cm.$^{-3}$ (Hunter, Hyde, Warrick & Fletcher, 1946). The diffraction symmetry is $4/m$; the following types of reflections were systematically absent: $(hk0)$ with $h+k$ odd, $(00l)$ with l odd. The space group is therefore $P4_2/n$. Relative intensities of reflections were determined by visual comparison with calibrated intensity strips. Multiple-film techniques were used in the case of the Weissenberg diagrams, and precession diagrams were exposed for a series of fixed time intervals. The usual Lorentz and polarization corrections were applied to the measured intensities.

Structure determination

The centers of the four molecules in each unit cell are located at fourfold positions; four sets of such positions are listed in the *International Tables* for space group $P4_2/n$. $4(f)$ and $4(e)$ appeared unlikely choices since they require that the centers of adjacent molecules be separated by no more than half the length of the c axis (i.e. about $3\cdot2$ Å). $4(c)$ and $4(d)$, on the other hand, permit a staggered arrangement of the molecules and provide for relatively efficient packing of the four molecules in the unit cell. These two sets of positions are equivalent, the molecular centers being at centers of symmetry; $4(c)$ was chosen, since in this set one molecular center is at the cell origin (origin chosen at $\bar{1}$).

The asymmetric unit consists of half of one molecule (two silicon atoms, two oxygen atoms and four methyl groups). If hydrogen atoms are not considered, the structure determination is a 24-parameter problem. Since the center of each molecule is located at a center of symmetry, the four silicon atoms of each molecule must be coplanar; the same is true of the four oxygen atoms in the molecule.

It appeared probable, in view of the short c axis, that the (001) projection would show maximum resolution of the atoms. Examination of the $hk0$ Weissenberg diagram showed that the h and k indices of all prominent reflections were even. There were 64 independent reflections of this type. In addition, 29 extremely weak reflections, with odd h and k indices, were observed. The absence or the extreme weakness of $hk0$ reflections with odd h and k indices indicated that the four D_4 molecules must all present almost

the same appearance when viewed down the [001] direction. This will be the case if individual molecules show almost perfect fourfold symmetry in this projection. The operation of the fourfold symmetry axes on these 'fourfold' molecules will not alter their appearance appreciably in the projection. The intensities of the reflections having odd h and k indices are determined by the extent to which the molecules fall short of possessing fourfold symmetry in projection.

A Patterson (001) projection was computed and from it the orientation of the 'square' formed by the four silicon atoms in the ring of the molecule could be fixed relative to the a and b axes. This 'square' projection was then refined by successive Fourier syntheses (using only reflections with even h and k indices) until a stationary Fourier projection was obtained. The discrepancy factor for the $(hk0)$ reflections which were used in the refinement (h and k both even) was $16\cdot7\%$ at this stage of the structure determination.

A Patterson (010) projection and the Harker section $P(\frac{1}{2}, \frac{1}{2}, w)$ yielded some information about the z parameters of the atoms, and a (010) Fourier projection was computed. Since this was a projection along an axis $16\cdot1$ Å long, considerable overlap was encountered, and the Fourier refinement process did not bring the discrepancy factor for this zone under 21%.

In order to refine the structure further it was necessary to break away from a molecular model possessing fourfold symmetry in projection so that the $(hk0)$ structure factors with indices h and k both odd could be included in the summation. After many fruitless attempts, it became clear that the true atomic (x, y) parameters could not be observed from the $(hk0)$ data alone, since all the $(hk0)$ reflections which were due to the deviation of the molecule from fourfold symmetry in the (001) projection were extremely weak; it was later found that inclusion of these weak terms in the Fourier summation did not move the silicon and oxygen peaks from the positions of fourfold symmetry on the Fourier map. Actually, the existence of a significant shift of silicon and oxygen atoms from positions related by fourfold symmetry in the (001) projection necessarily implies that $(hk0)$ structure factors having odd h and k indices will, in general, all differ from zero. Presumably, if all these intensities could have been measured accurately and if the corresponding values of F_{hk0} were all included in the Fourier summation with the correct signs, the 'true' shift of the peaks would have been evident. However, because most of these reflections were too weak to be detected, the corresponding observed structure factors had to be assigned zero values; the remaining odd–odd terms which were used in the Fourier summation were not sufficient, in themselves, to cause the atomic peaks to shift from the 'fourfold' positions.

The limitations inherent in the use of the $(hk0)$ data are greatly reduced when reflections in an upper layer

of the reciprocal lattice are considered. Starting with the 'fourfold' (x, y) parameters and the z parameters obtained from the (010) projection, a generalized projection (Cochran & Dyer, 1952) was computed using 192 observed independent (hkl) structure factors. The functions

$$C_1(x, y) = \frac{1}{A} \sum_{hk} A_{hkl} \cos 2\pi(hx + ky),$$

$$S_1(x, y) = -\frac{1}{A} \sum_{hk} A_{hkl} \sin 2\pi(hx + ky)$$

and

$$|\varrho_1(x, y)| = [C_1^2(x, y) + S_1^2(x, y)]^{\frac{1}{2}}$$

were evaluated, and new x, y and z parameters (Clews & Cochran, 1949; Raeuchle & Rundle, 1952) were recovered which deviated significantly from the assumed model. A stationary generalized projection was obtained by the usual iterative Fourier refinement procedure; backshift corrections were applied; the final atomic locations are listed in Table 1.

Table 1. *Atomic parameters*

	x	y	z
Si_1	0.109_8	0.065_2	0.149
Si_2	0.067_7	-0.114_3	-0.007
O_1	0.018_3	0.109_5	0.145
O_2	0.113_5	-0.023_3	0.018
C_1	0.159_7	0.047_2	0.413
C_2	0.188_5	0.136_5	0.014
C_3	0.050_4	-0.164_3	0.265
C_4	0.142_3	-0.179_2	-0.168

The (001) electron-density map is shown in Fig. 1(a) and the (010) electron-density map in Fig. 1(b). The final positions of the atoms are marked by crosses. The values of the discrepancy coefficients for the final parameters, computed only for the observed reflections, are

$$R_{(hk0)} = 18.4\%, \quad R_{(h0l)} = 16.2\%, \quad R_{(hk1)} = 17.5\%,$$
$$R_{(hk2)} = 16.1\%.$$

For $(hk0)$ reflections with h and k indices both even, $R = 16.1\%$; the odd–odd $(hk0)$ reflections were all weak and difficult to measure accurately; for these reflections, $R = 55\%$.

The calculated structure factors were multiplied by an anisotropic temperature factor

$$\exp[-\beta(h^2 + k^2)/4a^2 - \gamma l^2/4c^2].$$

The values of β (3.2 Å^2) and γ (6.3 Å^2) were determined graphically. A list of some 500 observed and calculated structure factors is given in Table 2.*

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* Table 2 has been deposited as Document No. 4492 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
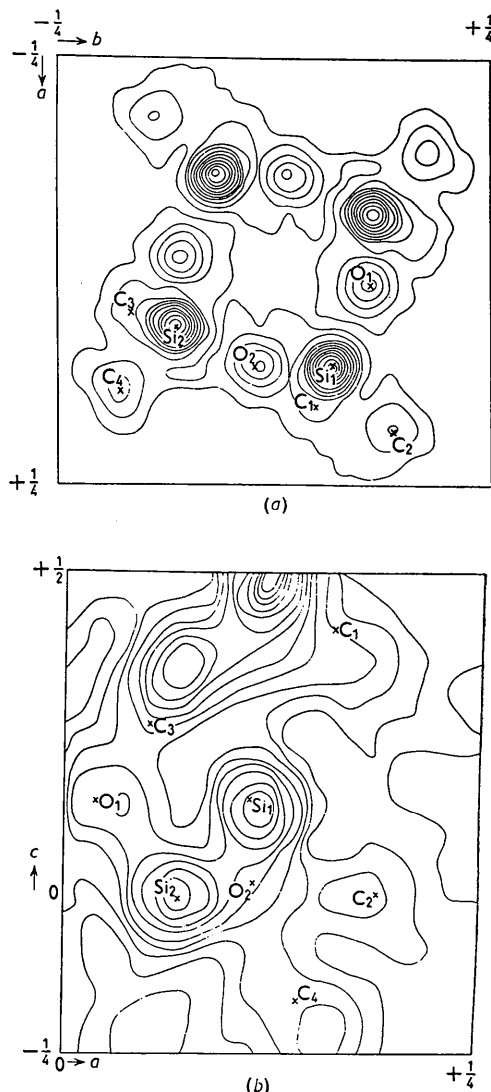

Fig. 1. (a) Electron-density projection of one molecule of octamethyl cyclotetrasiloxane on (001). Contours at intervals of approximately 2 e.Å^{-2}. Crosses mark positions of atomic centers.

(b) Electron-density projection on (010). Contours are at intervals of approximately 2 e.Å^{-2}. Crosses mark positions of atomic centers in one asymmetric unit.

Bond lengths and angles computed from the parameters listed in Table 1 are shown in Table 3.

Table 3. *Bond lengths and angles*

Bond lengths (Å)	Bond angles (°)
$Si_1–O_1 = 1.64$	$Si_1–O_2–Si_2 = 143.5$
$Si_1–O_2 = 1.66$	$Si_1–O_1–Si_2 = 141.5$
$Si_2–O_2 = 1.65$	$O_1–Si_1–O_2 = 105$
$Si_2–O_3 = 1.65$	$O_1–Si_2–O_2 = 113$
$Si_1–C_1 = 1.91$	$C_1–Si_1–C_2 = 102$
$Si_1–C_2 = 1.92$	$C_3–Si_2–C_4 = 110$
$Si_2–C_3 = 1.95$	
$Si_2–C_4 = 1.90$	

Estimation of accuracy

The standard deviations of the x and y parameters were estimated from the relationship (Cruickshank, 1949):

$$\sigma(x_i) = \frac{\frac{2\pi}{a_i A}\left[\Sigma m h_i^2 \Delta F^2\right]^{\frac{1}{2}}}{2p\varrho_0}.$$

Average values of p for the respective atoms were computed from the (001) projection (Fig. 1(a)) since it showed the best resolution of the atoms, and the ΔF values of the $(hk0)$ structure factors were used to estimate the standard deviations of the slopes, $\sigma(A_x)$ and $\sigma(A_y)$. The average value of $\sigma(x_i)$ for silicon is 0·01 Å, for oxygen 0·02 Å, and for carbon 0·04 Å. The application of Cruickshank's method to the $(h0l)$ reflections for the determination of $\sigma(z_i)$ is ruled out by the extensive overlapping of atoms which occurs in that projection. The anisotropic temperature factor indicates, however, that $\sigma(z_i)$ is approximately twice as great as $\sigma(x_i)$. The mean value of the standard deviations of the bond lengths for Si–O is 0·025 Å, and for Si–C is 0·07 Å, corresponding to probable errors in the bond lengths of 0·018 Å and 0·05 Å respectively.

An independent check of the mean positional error of the coordinates was obtained from a plot of $\bar{R}$ versus $\sin\theta$ (Luzzati, 1952). Values of $\bar{R}_{(\theta)} = ||F_o|-|F_c||\div|F_o|$ were determined, for intervals of $\sin\theta$ containing approximately equal numbers of $(hk0)$ structure factors. The mean error, $\overline{\Delta r}$, was found to be 0·045 Å. For the $(h0l)$ reflections, the mean error, $\overline{\Delta r}$, determined in the same way, was found to be 0·04 Å.

Both procedures for the estimation of errors yield values which are probably greater than the actual deviations. The results of determinations of the four independent Si–O and Si–C bond lengths are listed in Table 3; the mean Si–O bond length is 1·65 Å; that of Si–C is 1·92 Å. The standard deviations of single measurements are 0·01 Å for Si–O and 0·02 Å for Si–C.

Discussion of the structure

The crystal structures of two compounds similar to D_4 had been determined prior to this investigation (Roth & Harker, 1948; Peyronel, 1954). In both compounds, the siloxane ring is planar and has a Si–O–Si angle of about 130°. This angle would have had to increase to 160° to preserve the planarity of the ring in the structure of D_4. Apparently such a planar ring structure is too highly strained, and a puckered configuration is adopted; the Si–O–Si angle is only 142·5°. The equation of the plane of the four silicon atoms is

$$1·53x+y-1·56z = 0;$$

that of the four oxygen atoms is

$$x+3·00y-2·40z = 0;$$

the dihedral angle between these two planes is 30°. The configuration of the siloxane ring is illustrated in Fig. 2.

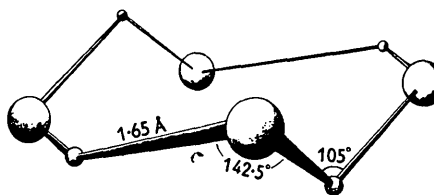It would be interesting to determine whether the Si–O–Si angle in larger-ring compounds has the same

Fig. 2. Configuration of Si–O–Si ring in octamethyl cyclotetrasiloxane.

value as in D_4. It is also possible that the configuration of the linear siloxane chains is such as to form a Si–O–Si angle of about 143°. Dipole-moment measurements on hexamethyl disiloxane have been interpreted by Sauer & Mead (1946) as indicating a Si–O–Si angle of 160°±15°; the lower limit of this range is close to the value found in this structure. The 142·5° oxygen angle obtained in this investigation is close to the value of 142° reported for α-quartz and 150° reported for α-cristobalite (Machatschki, 1936; Nieuwenkamp, 1937). The Si–O bond length found in this structure agrees well with the values for this bond reported by other investigators. Table 4 compares the bond lengths

Table 4. *Bond lengths and angles*

Molecule	Si–O	Si–C	Si–O–Si	O–Si–O	C–Si–C
D_4	1·65 Å	1·92 Å	142·5°	109°	106°
D_3	1·614	1·992	136	104	106
Spirosiloxane	1·64	1·88	130	106	106
α-Quartz	1·61	—	142	—	—
α-Cristobalite	1·59	—	150	—	—
SiC	—	1·93	—	—	—
Si(CH$_3$)$_3$Cl	—	1·89	—	—	—
Si(CH$_3$)$_2$Cl$_2$	—	1·83	—	—	—

found in D_4 with bond lengths found in related molecules.

The Si–C bond length is almost equal to the sum of the covalent radii of silicon and carbon: 1·94 Å; this bond, therefore, appears to be almost completely covalent in character. A progressive shortening of this bond with increasing substitution of highly electronegative atoms on silicon is evident from Table 4 (Livingston & Brockway, 1944, 1946).

The values 109° for the O–Si–O angle and 106° for the C–Si–C angle in D_4 agree with those reported for similar compounds (Table 4) and are near the tetrahedral angle (109° 28′).

The four molecules in the unit cell of D_4 are held together by van der Waals forces among the methyl groups. The molecular packing is such that a methyl group on one silicon atom fits into the space between two methyl groups bonded to two other silicon atoms. The distances between the centers of non-bonded

methyl groups range from 4·04 Å to 4·23 Å, corresponding to a van der Waals radius of about 2·1 Å.

2. The high-temperature modification

D_4 undergoes a solid-phase transformation at $-16\cdot3°$C. (Hoffman, 1953). Analysis of precession and Weissenberg diagrams of the high-temperature modification indicates that the space group changes from $P4_2/n$ below the transition temperature to $I4_1/a$ above the transition (the Laue symmetry remains $4/m$). The length of the a axis is unaffected by the transition, but the c axis increases from 6·47 Å to 6·83 Å.

The point symmetry of fourfold positions in $I4_1/a$ is $\bar{4}$. In the low-temperature modification the D_4 molecule does not possess this symmetry intrinsically. The energy of the transition appears to be far too small to involve a change in molecular configuration which would give the molecule $\bar{4}$ symmetry. It is necessary to postulate that each molecule possesses fourfold disorder, i.e. that each molecule can assume any of the four orientations achieved by rotating the molecule from its original, low-temperature orientation, about the c axis in 90° increments. The necessary point symmetry can also be achieved by assuming that individual molecules possess $4n$-fold disorder, where $n > 1$. This, however, would lead to Laue symmetry $4/mmm$; only fourfold orientational disorder appears adequate to give the required point symmetry without changing the Laue symmetry.

It is to be expected that disorder of this type will lead to an increase in the length of the c axis of the unit cell, as is observed. In the low-temperature modification, molecules aligned above one another in the c direction all possess the same orientation; in the high-temperature modification some are tilted one way, some another; steric interference increases, and the c axis must increase in length.

The structure factor expressions for $I4_1/a$ and $P4_2/n$ are identical for $F_{(hk0)}$ terms with h and k even. The X-ray diagrams of the $(hk0)$ zones of the high- and low-temperature modifications are strikingly similar, indicating that only minor shifts of the x and y parameters of the atoms occur in the transition (the length of the a axis does not change detectably in the transition). A detailed analysis of the crystal structure of the high-temperature modification is in progress.

It is interesting to speculate regarding the type of crystal structure that would have been reported if the melting point of octamethyltetrasiloxane had been 37° or 47° C. instead of 17° C. In that case the structure determination would undoubtedly have been based on data collected at room temperature (i.e. at some temperature between the transition temperature and the melting point). It is assumed that the existence of a low-temperature solid-state transformation would not be known to the investigators. The space group would then be $I4_1/a$, the point group symmetry of the molecule would be $\bar{4}$ and the molecule would be assigned a configuration consistent with that symmetry. Presumably the error in that assumption would become manifest during the course of a complete crystal-structure investigation; it is a warning, however, that determinations of molecular symmetry based on 'space-group evidence' alone should be accepted with considerable skepticism in the absence of evidence concerning possible transitions below the temperature at which the X-ray data were collected.

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