entgegengebracht hat, herzlich danken. Er legte der Akademie der Wissenschaften in Göttingen in der Sitzung vom 14 Februar 1947 eine kurze Mitteilung über die hier veröffentlichte Arbeit vor (Winkler, 1947 b).

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The Crystal Structure of Octamethylspiro [5·5] Pentasiloxane: Rotation about the Ionic Silicon–Oxygen Bond

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The crystal structure of octamethylspiro [5·5] pentasiloxane is reported. The Si–O distance is $1·64 \pm 0·03$ A. and the Si–CH₃ distance $1·88 \pm 0·03$ A. The $(SiO)_3$ ring is planar and the shape is determined by the tetrahedral silicon angles. Evidence is presented for the libration of methyl groups about siloxy bonds, and this is interpreted in terms of the ionic character of the Si–O bond. It is suggested that free rotation of CH₃ groups about siloxy bonds in the linear polymers is responsible for the small intermolecular forces characteristic of these compounds.

Introduction

Recent years have seen the development of the siloxanes, a new class of compounds with properties overlapping the organic and inorganic fields. The siloxanes may be considered organic compounds in which the carbon skeleton has been replaced by a –Si–O–Si–O–Si– skeleton. Dependent on the molecular weight, the presence of straight chain or ring structures, the type of substituents, and the number of cross linkages, the siloxanes range from gaseous compounds to solid high molecular polymers, including oils, resins, waxes and rubbers (Rochow, 1947).

The interpretation of siloxane chemistry in terms of carbon chemistry has met with considerable success in the synthetic fields, but the physical properties often appear anomalous. The major point of difference is summarized in the frequent statement that cohesive or van der Waals forces are reduced by the presence of siloxy (SiO) groups (Wilcock, 1946; Hunter, Warrick, Hyde & Currie, 1946).

In order better to understand these phenomena, it appeared desirable to determine the crystal structure of one of the siloxanes with the belief that a knowledge of the molecular structure and packing geometry would clarify the nature of the intermolecular interactions. There is presented here the result of an investigation of the crystal structure of octamethylspiro [5·5] pentasiloxane, hereinafter referred to as spirosiloxane.

Experimental

Approximately 0·5 g. of spirosiloxane was available from the preparation of Scott (1946). Ultimate analysis and the method of synthesis indicated the molecular formula:
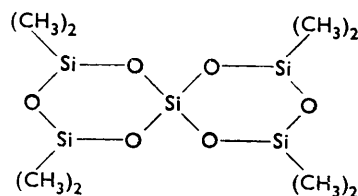
The spirosiloxane had been recrystallized from toluene as needle-like crystals about 1 mm. long and 0·1 mm. diameter.

Considerable difficulty was encountered in mounting the crystals for the X-ray work. The spirosiloxane sublimes at an appreciable rate at room temperature and is soluble in organic solvents and waxes. Limited success was attained by sealing the crystals in thin-walled Pyrex glass capillaries, but sublimation and recrystallization in other parts of the capillary occurred, and the

low scattering power required long exposures with attendant dark backgrounds. A successful mounting was developed, following techniques developed by V. Schaefer for preparing thin formvar films*.

A $0.5\,\mu$ thick film of formvar was formed by dipping a clean glass plate into a 2 % solution of formvar in ethylene dichloride, allowing it to drain and the solvent to evaporate. Squares 1 in. on a side were floated on to a water surface. A $0.5\,\mu$ film was picked up on a $\frac{3}{4}$ in. metal washer to which some rubber cement had been applied, and the film then built up to $1.0\,\mu$ by picking up a second square on the first, no adhesive being required. Two such washers were prepared and the crystal sealed between them merely by pressing the films together. Gentle blowing facilitated sealing by momentarily relaxing the films. The crystal in its formvar envelope was cut out with a cork-borer and mounted on a glass fibre with any convenient adhesive. The structure had considerable mechanical rigidity and crystals so mounted showed no sign of deterioration over a period of several months. The background scattering from the formvar (approximate formula, $C_5H_9O_2$) was extremely low. Dr J. S. Kasper of this laboratory has successfully applied the technique to the mounting of $B_{10}H_{14}$ crystals.

The diffraction data were obtained, using cobalt radiation. Laue photographs were taken in the conventional manner, using a flat cassette. Rotation and oscillation pictures were taken on Eastman Blue Brand film, using the Straumanis technique, in a cylindrical camera of 5 cm. radius, with Co $K\alpha$ radiation ($\lambda = 1.790$ A.) filtered through iron. Reflexions were indexed from sets of $22\frac{1}{2}°$ oscillation photographs ($7\frac{1}{2}°$ overlap) taken with a constant 4 hr. exposure. Intensities were measured on a scale of 1 to 100 by the visual comparison method, values less than 2 being considered doubtful. The observed intensities were corrected for the Lorentz and polarization factors and velocity factor (*Internationale Tabellen...*, 1935). The small crystals were completely bathed in the X-ray beam and absorption corrections were omitted. Cross comparison of intensities indicated an overall accuracy of about $\pm 30\%$.

A few powder photographs were taken of samples packed in thin-walled glass capillaries. These were used to measure the intensities of the very strong close-in reflexions.

The microscopic density of the spirosiloxane was determined by powdering a single crystal to minimize voids and adjusting the density of a $KCl\text{-}H_2O$ solution until the crystals neither rose nor sank. The density of the solution was then determined by conventional methods. The mean of several determinations gave d (25° C.) $= 1.180 \pm 0.002$ g.cm.$^{-3}$

Results. Laue photographs of a crystal mounted with the needle axis vertical showed a horizontal plane of symmetry and a vertical four-fold axis. To distinguish

between the Laue classes $4/m$ and $4/mmm$, photographs with the X-ray beam parallel to the needle axis were taken. These showed two symmetry planes at 45°, so the crystal is tetragonal and of Laue class $4/mmm$.

Rotation and oscillation photographs were taken about the **c** (needle), **a** and **a**+**b** directions. The reflexions were indexed by conventional reciprocal lattice methods on a tetragonal body centered lattice with $a = 14.09 \pm 0.03$ A. and $c = 10.18 \pm 0.03$ A. The complete reciprocal lattice out to $(\sin\theta)/\lambda = 0.53$ was covered. The experimental observations are summarized in Table 1. The intensities for {101}, {200}, {220}, {112}, {301} and {321} were taken from powder photographs to minimize the well-known errors encountered in measuring close-in single-crystal reflexions. The oscillation and powder data were reduced to the same intensity scale by averaging with the final set of calculated intensities. The data are reported as $F_{obs.} = (I_{obs.}.\tau/L)^{\frac{1}{2}}$ where $I_{obs.}$ is the observed intensity, L is the Lorentz-polarization factor and τ the velocity factor.

From the macroscopic density (1.180 g.cm.$^{-3}$) and the lattice parameters, there are four molecules in a unit cell:

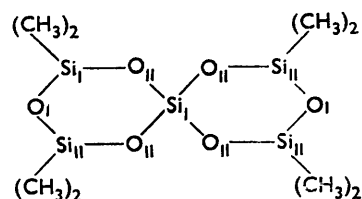$$n = (14.09)^2\,(10.18)\,(10^{-24})$$
$$\times\,(6.02 \times 10^{23})\,(1.180)/356.3 = 4.03.$$

Only those reflexions were found which obeyed the criteria:

$(hkl) \qquad h+k+l = 2n,$

$(hk0) \qquad h = 2n \qquad k = 2n,$

$(hhl) \qquad l = 2n \qquad 2h+l = 4n,$

$(h0l) \qquad h+l = 2n.$

Thus the probable space group is $D_{4h}^{19}\text{-}I4/amd$ (*Internationale Tabellen...*, 1935).

Designating the crystallographically different atoms as

the space group provides the following positions (*Internationale Tabellen...*, 1935), which were selected to conform with the assumed spiro configuration:

4 Si_I at 4(a),   8 O_I at 8(e),   16 Si_{II} at 16(h),

16 O_{II} at 16(h),   32 CH_3 at 32(i).

Thus, the Si_{II} and O_{II} atoms lie on mutually perpendicular vertical mirror planes and the Si_I atoms have the required point symmetry $\bar{4}2m$. The six membered Si–O rings are planar and the number of variable parameters is reduced to eight: $z(O_I)$, $x(Si_{II})$, $z(Si_{II})$, $x(O_{II})$, $z(O_{II})$, $x(CH_3)$, $y(CH_3)$ and $z(CH_3)$. The arrangement of molecules in the unit cell is shown schematically in Fig. 1.

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* Private communication from V. Schaefer of this laboratory.

There is a centre of symmetry at $0, \frac{1}{4}, \frac{1}{8}$. The structure factor is simplified by shifting the origin to the centre of symmetry, giving for the general positions

$$F(hkl) = 16 \cos 2\pi \{\tfrac{1}{4} (h + k + l)\}$$
$$\times f [\cos 2\pi hx \cos 2\pi ky \cos 2\pi \{\tfrac{1}{8} (2h + l) + lz\}$$
$$+ \cos 2\pi hy \cos 2\pi kx \cos 2\pi \{\tfrac{1}{8} (2h + l) - lz\}].$$

The following relations are derived from the structure factor for use in simplifying the calculation of the Fourier series:

$$F(hkl) = F(\bar{h}kl), \qquad F(hkl) = (-1)^k F(h\bar{k}l),$$
$$F(hkl) = (-1)^k F(h\bar{k}l), \qquad F(hkl) = (-1)^{\frac{1}{2}(h+k+l)} F(hk\bar{l}).$$

The resultant electron density map confirmed the general configuration of the molecule, but could not be used to evaluate parameters because the Si_{II} and O_{II} atoms projected to nearly the same point and the CH_3 groups were not resolved.

The $Si_{II}-O_{II}$ distance was obtained from a three-dimensional Patterson synthesis along $(0, 0, z)$. Fig. 2 shows this function: $P(0, 0, z) = \Sigma l \mid F(hkl) \mid^2 \cos 2\pi lz$. The peak at $z = 0·162$ gives the difference in the z coordinates of the Si_{II} and O_{II} atoms, and corresponds to 1·64 A. for the $Si_{II}-O_{II}$ bond length. The small peak at $z = 0·330$ is a composite of the Si_I-O_I and O_I-O_I (intermolecular) vectors. The function $P(x, 0, 0)$ was
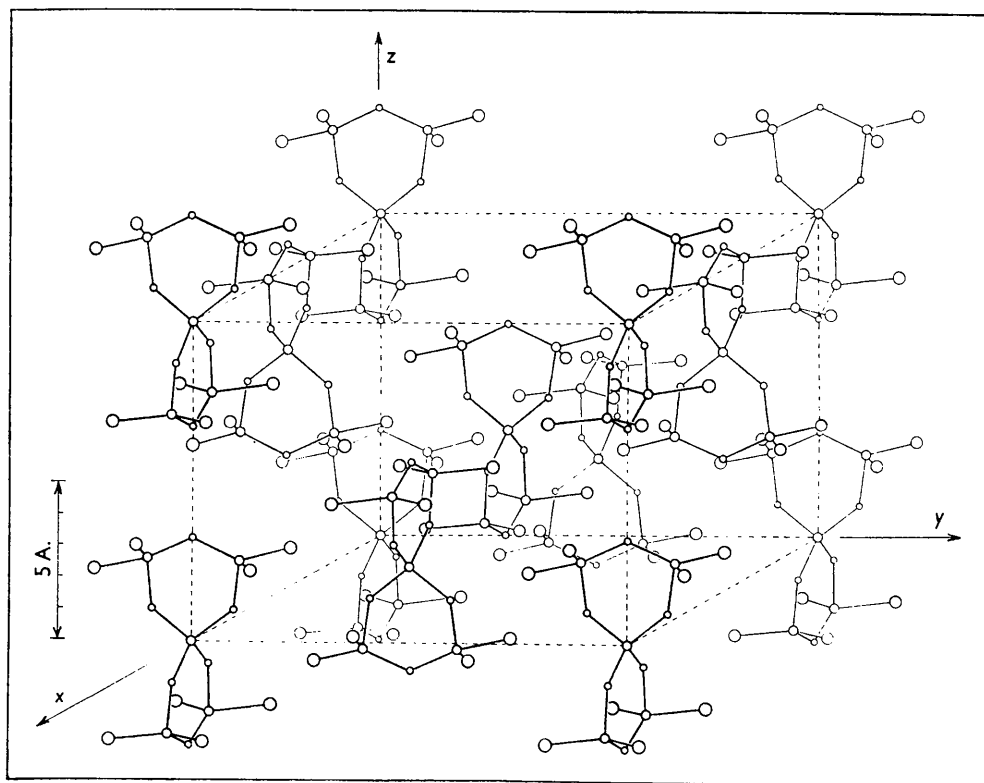
Fig. 1. Arrangement of spirosiloxane molecules in the unit cell

The atomic scattering factors for Si and O were taken from the *Internationale Tabellen...* (1935). The scattering factor for CH_3 was approximated by the iso-electronic F atom, the positions of H atoms being ignored.

Amplitudes of the $(hk0)$ reflexions were computed from the assumed structure, using covalent radii and assuming tetrahedral angles about the Si atoms (Pauling, 1940). There was encouraging agreement between observed and calculated intensities for close-in reflexions. Consequently, a projection of the content of the unit cell on the c face was computed:

$$\rho_z(x, y) = \Sigma h \Sigma k F(hk0) \cos 2\pi(hx + ky).$$

evaluated, but there was not sufficient resolution to separate the CH_3-CH_3 vector from the intermolecular O_I-O_I vector.

A complete set of $F(hkl)$'s was then computed, assuming the Si–O distances equivalent and equal to 1·67 A., the Si–C distance 1·94 A. and the Si angles tetrahedral (the use of 1·67 instead of 1·64 A. for the Si–O bond length resulted from the use of a c value which was later corrected). Comparison of calculated and observed $F(hkl)$ indicated agreement for most reflexions with small indices, but considerable disagreement for the higher orders. It appeared reasonable to believe that only slight refinement of parameters was required. Consequently, a projection on the b face of

the contents of the unit cell lying between $y = \frac{1}{4}$ and $y = \frac{1}{2}$ was made*. The quarter-cell synthesis projects a single molecule and should permit the evaluation of all the parameters. Again taking the origin at the centre of symmetry:

$$\rho_{\frac{1}{4}, y, \frac{1}{4}}(x, z) = \int_{\frac{1}{4}}^{\frac{1}{2}} \rho(x, y, z)\, dy$$

$$= \tfrac{1}{4} \Sigma h \Sigma l\, F(h0l) \cos 2\pi\, (hx + lz)$$

$$+ \Sigma h \Sigma k \Sigma l\, F(hkl)\, \{(\sin \tfrac{1}{4}\pi k)/k\} \cos 2\pi\, (hx + \tfrac{3}{8}k + lz).$$

The quarter-cell projection was evaluated using two-place Beevers-Lipson strips at 1/60 parameter intervals. The general features of the molecule were resolved, including the CH_3 groups. However, the siloxane ring was asymmetric (Si_I–O_{II} = 1·75 A., Si_{II}–O_{II} = 1·58 A., Si_{II}–O_I = 1·50 A.) and the CH_3 contours were badly distorted. There was no improvement between observed intensities and intensities calculated with parameters taken from this projection.
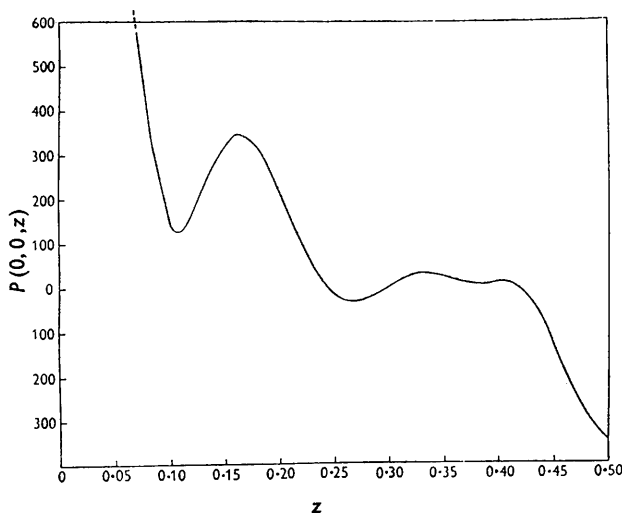

Fig. 2. Three-dimensional Patterson synthesis $P(0, 0, z)$ showing peak at $z = 0·162$ corresponding to Si_{II}–O_{II} distance of 1·64 A.

It appeared that the difficulty might be due to the fact that the projection utilized only a portion of the data and yet was required to show all features of the structure. Consequently, the electron density in a section through a mirror plane in the molecule was calculated: $\rho(0, y, z) = \Sigma h \Sigma k \Sigma l\, F(hkl) \cos 2\pi\, (ky + lz)$. The resultant map showed the expected six-membered ring, but again the molecule was distorted, although in a different manner than given by the projection (Si_I–O_{II} = 1·70 A., Si_{II}–O_{II} = 1·57 A., Si_{II}–O_I = 1·63 A.). The new parameters did not improve the agreement between observed and calculated intensities, and the changes in phase were not sufficient to alter the appearance of a second Fourier synthesis computed with corrected coefficients. To test the possibility that the assumptions regarding the positions of the CH_3 groups

* Private communication from Dr V. Schomaker.

might be seriously in error, a Fourier section through the CH_3 group:

$$\rho\,(x = 0·103, y, z)$$
$$= \Sigma h \Sigma k \Sigma l\, F(hkl) \cos 2\pi\, (0·103h + ky + lz)$$

was computed. The CH_3 parameters obtained were reasonably close to those assumed.

Concomittant with the Fourier synthesis, attempts were made to fit the data by trial-and-error variation of parameters. A methodical application of the method led to the conclusion that no values of the parameters reasonably close to the assumed ones could possibly fit the data. The original data were carefully checked, absorption corrections were made, intensities were computed with the empirical scattering factors for Si^{4+} and O^{2-} obtained by Bragg and West from their studies of the silicates, and the scattering factor of a CH_3 group was adjusted to approach that of carbon for large values of $(\sin \theta)/\lambda$. None of these changes improved the situation.

It was then noted that the contours of the CH_3 groups in the electron-density maps were distorted as though the CH_3 were librating with a large amplitude at a fixed distance from Si_{II}, thus sweeping through a large umbrella-like surface. It was decided to approximate the scattering function of a librating CH_3 group by considering the CH_3 to precess about its equilibrium position (Roth, 1947). The treatment is similar to that used to calculate the contribution of the freely rotating NO_3 group in $AgNO_3$ (Bijvoet & Ketelaar, 1932).

Consider the CH_3 group rotating in an orbit of radius r about the equilibrium position it would occupy if there were no precession. Let α be the angle between the plane of the orbit and the lattice plane of Bragg angle θ, and ϕ the angle describing the position of the CH_3 in the orbit. Then, the ratio of the amplitude scattered by the precessing CH_3 to the amplitude scattered by the equivalent group at its equilibrium position (taken as the origin) is

$$f'/f = \frac{1}{2\pi} \int_0^{2\pi} e^{4\pi i r \sin \phi \sin \theta \sin \alpha}\, d\phi$$

$$= J_0\, (4\pi\, (r/2) \sin \alpha \sin \theta),$$

where J_0 is the zero order Bessel function. The angle α is different, in general, for the different methyl groups. If X, Y, Z are the co-ordinates of the centre of the orbit of the CH_3 with respect to its bonded Si_{II} atom as origin, and d is the Si_{II}–CH_3 bond distance, then

$$\cos \alpha_{(XYZ)} = a\, (hX + kY + lZ)/d\, [h^2 + k^2 + (a/c)^2\, l^2]^{\frac{1}{2}}$$

and the total contribution of CH_3 groups is

$$F'_{CH_3}/F_{CH_3} = \tfrac{1}{8}\, [J_0\, (Q_1) + J_0\, (Q_2) + \ldots J_0\, (Q_8)],$$

where $Q_i = 4\pi\, (r/\lambda) \sin \alpha_i \sin \theta$, F_{CH_3} is the total contribution to the structure factor if all CH_3 groups are located at their equilibrium positions, and F'_{CH_3} is the contribution corrected for precession.

The precession radius r becomes a new independent parameter. Because of the semi-empirical nature of the precession concept, no attempt was made to determine
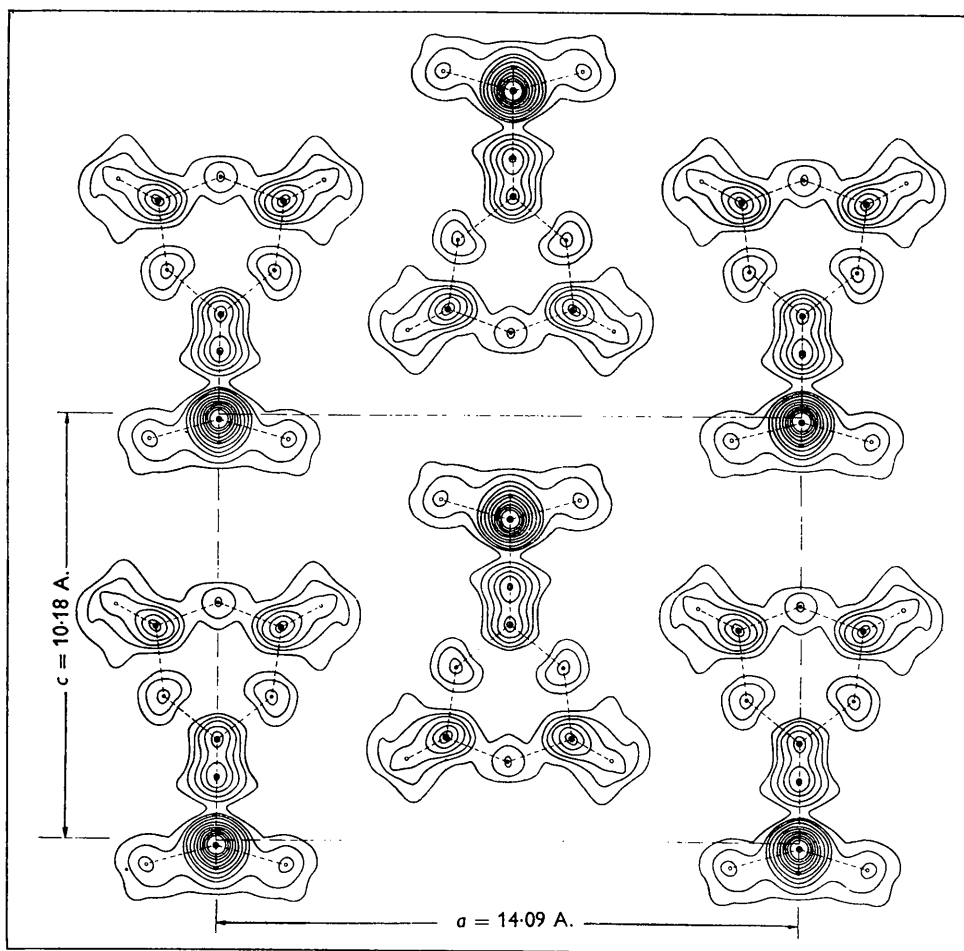
Fig. 3. The Fourier projection on the b face of the contents of the unit cell lying between $y = \frac{1}{4}$ and $y = \frac{1}{2}$. Contours are at equal intervals of electron density

an exact value for r. A selected portion of the data was investigated by varying r over the range from 0 to 0·7 A. It was found that $r = 0·6$ A. considerably improved the agreement between calculated and observed intensities.

A new set of phases was computed, assuming the original symmetrical model and including the pre-cessing CH_3 correction with $r = 0·6$ A. A quarter-cell projection (Fig. 3), a section through the molecule (Fig. 4), and two sections through the CH_3 group (Fig. 5) were computed. Reference to Fig. 1 shows the relation between these syntheses and the unit cell. Parameters taken from the sections were used to calculate a new set of phases, and, since the introduction of these phases into the Fourier syntheses resulted in negligible shifts of the atom positions, it was concluded that the limit of resolution with the available data had been attained.

The final parameters, referred to Si_I, are

$$x(Si_{II}) = 0·107, \quad z(Si_{II}) = 0·255; \quad z(O_I) = 0·326;$$

$$x(O_{II}) = 0·093; \quad z(O_{II}) = 0·098; \quad X(CH_3) = 0·107;$$

$$Y(CH_3) = 0·178; \quad Z(CH_3) = 0·307.$$
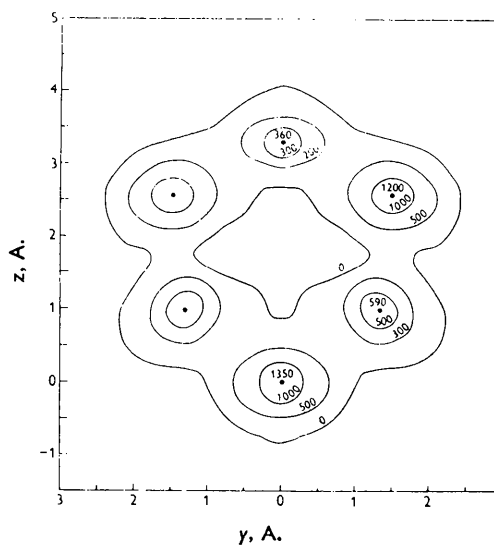
Fig. 4. Part of section through the three-dimensional Fourier series $\rho\,(x, y, z)$ at $x = 0$ showing $(SiO)_3$ ring

In Table 1 are summarized the observed and calculated values of F (hkl) for all reflexions to $(\sin \theta)/\lambda = 0.53$. Reflexions that were not observed are given as $\leqq 1$. Calculated amplitudes have been corrected for temperature motion by the factor $\exp\left[-B\left(\dfrac{\sin \theta}{\lambda}\right)^2\right]$ with $B = 4.92 \times 10^{-16}$ as obtained from a least-squares calculation. Inspection of the data shows that, while a high order of quantitative agreement has not been obtained, the observed amplitudes qualitatively follow the order predicted by the assumed structure. It is believed that the agreement is adequate to establish the correctness of the postulated structure.
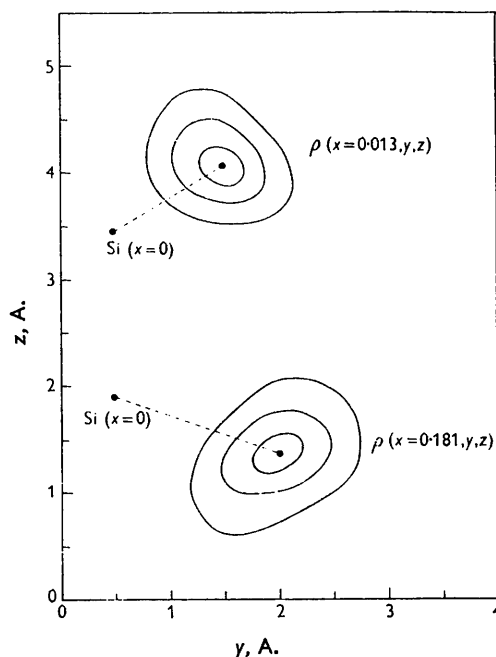
Fig. 5. Parts of sections parallel to a face of three-dimensional Fourier series ρ (x, y, z) at $x=0.103$ and $x=0.181$, showing cross-sections of methyl groups. (The origins of the two plots are arbitrary.)

A measure of the validity of the precession correction can be deduced from the following arguments. There were observed 129 reflexions with $5 \geqslant |F\ (hkl)| \geqq 1$. (Ten close-in reflexions with $|F(hkl)| > 5$ have been excluded because of the well-known errors involved; inclusion would not alter the conclusions, however.) The amplitude-weighted mean deviation*

$$\Sigma |F_{\text{obs.}}| (|F_{\text{obs.}}| - |F_{\text{calc.}}|)/\Sigma |F_{\text{obs.}}|$$

is 1.24 if the CH_3 groups are taken fixed at their equilibrium position. Including the correction for precession reduces the deviation to 0.75. Since the average $|F_{\text{obs.}}|$

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* An amplitude-weighted mean deviation was selected as an index of agreement between observed and calculated $F(hkl)$, because the percentage error in observed intensities decreases with increasing magnitude, and calculated amplitudes of small magnitude become uncertain, since they result either from the difference of several large terms or from trigonometric functions near their most sensitive region.

is 2.18, the mean deviation is 34%, about that estimated for the precision of the visual estimates of intensity. A second comparison is made by considering the calculated values for reflexions which were not observed, i.e. with $|F_{\text{obs.}}| \leqq 1$ (not including space-group absences). Out of a total of 57 unobserved reflexions, 17 are calculated to have $|F(hkl)| > 1$ (average $|F(hkl)| = 1.9$) assuming the CH_3 groups are stationary, whereas only 8 (average $|F(hkl)| = 1.4$) have computed values greater than unity if the CH_3 groups are assumed to precess.

The most convincing arguments are based on certain specific cases. For example, the forms {004} and {008} are both observed quite strong. Only the four z parameters are involved. It is found, however, that, if stationary CH_3 groups are assumed, {008} is calculated to be quite weak, the small amplitude resulting from the cancellation of strong contributions from Si atoms and CH_3 groups. Since these groups are contributing nearly their maximum to the structure factor, the intensity of {008} is insensitive to parameter changes (the oxygen contributions are relatively small regardless of their positions) and consequently it is not possible to obtain a resultant strong reflexion without radically altering the postulated structure. If the CH_3 contribution to $F(008)$ is decreased, by assuming its precession, this discrepancy disappears.

It does not appear reasonable to attempt a physical interpretation of the magnitude of r. Whereas the derivation treats r as the radius of a precession orbit, in reality it should be regarded merely as a parameter which increases the spread of electron density about the CH_3 group in certain preferred directions, i.e. an asymmetric temperature factor. Within the limits of the available data, the correction could probably be represented as a specific temperature factor applied to the CH_3 groups, i.e. $\exp\left[-B_{CH_3}\left(\dfrac{\sin \theta}{\lambda}\right)^2\right]$, but this would seem incorrect, since it implies abnormally large amplitudes for silicon methyl stretching vibrations.

The limits of precision indicated are believed to be due to two principal factors: the somewhat limited intensity data and the artificial concept of considering all the asymmetric thermal motion concentrated in the CH_3 groups. (It is interesting to note that the peaks in the electron-density maps are elongated in such a manner as to suggest that one of the principal thermal motions is a pivoting of the entire molecule about the central silicon atom.) An improved set of data undoubtedly could be obtained by increasing the exposure time past the 4 hr. used, and going to shorter wave-length radiation, but it is believed that measurements at low temperatures are indicated. It is doubtful that the available data warrant more refined correction for the motion of the CH_3 groups or the introduction of asymmetric temperature corrections for the other atoms in the structure.

Table 1. *Comparison of observed and calculated F(hkl)*

$F'_{calc.}$ is calculated on the basis of CH_3 groups occupying fixed equilibrium positions, and $F_{calc.}$ includes the correction for precession.

hkl	$F_{obs.}$	$F_{calc.}$	$F'_{calc.}$
200	13.2	15.9	15.8
220	11.8	-9.2	-9.0
400	0.9	0.4	-0.7
420	3.7	-3.6	-4.1
440	4.3	-4.3	-3.7
600	4.9	6.2	6.7
620	2.4	-3.1	-3.9
640	4.9	-5.9	-6.7
800	6.0	8.3	7.8
820	3.6	-4.7	-3.7
660	3.6	4.6	6.3
840	<1.0	1.5	2.4
860	<1.0	-1.7	-3.2
10.0.0	4.4	7.8	9.5
10.2.0	3.1	-4.8	4.1
10.4.0	2.0	1.6	1.1
880	1.4	3.0	1.7
10.6.0	1.0	-1.9	-2.8
12.0.0	1.7	-3.4	4.0
12.2.0	1.4	-1.9	-2.2
101	5.4	9.4	9.4
211	0.8	1.6	1.8
301	13.5	13.6	14.2
321	8.0	-5.6	-5.9
411	3.9	4.7	4.4
501	4.6	3.8	2.2
431	3.4	-5.4	-6.4
521	4.1	-4.8	-4.9
611	3.2	2.8	2.0
541	1.0	1.4	2.5
631	2.6	-3.1	-4.3
701	3.6	4.1	4.1
721	2.0	-1.5	-1.5
651	1.0	0	0.1
811	1.0	0.4	1.3
741	1.5	-2.1	-2.1
831	2.5	2.9	4.0
901	2.3	2.5	4.3
921	1.0	0.4	0.5
761	1.0	1.6	1.5

hkl	$F_{obs.}$	$F_{calc.}$	$F'_{calc.}$
851	1.9	-2.7	-2.6
941	1.7	-3.2	-4.2
10.1.1	1.7	-1.2	-0.8
10.3.1	2.2	3.1	4.1
871	<1.0	1.0	0.1
961	1.4	2.2	2.3
11.0.1	1.0	1.6	0.6
11.2.1	<1.0	-0.4	
10.5.1	1.7	-2.2	1.3
112	10.4	8.8	9.3
202	0.8	-1.6	-2.3
312	2.6	-3.3	-4.2
402	4.0	5.3	6.0
332	1.4	1.3	0.4
422	2.0	-0.5	
512	1.4	0.9	0.1
532	3.0	3.6	2.8
602	3.7	5.4	7.2
622	2.2	-1.6	-1.5
712	1.4	-7.3	-9.3
552	5.2	-0.8	1.8
642	1.4	1.4	1.4
732	1.7	-1.7	-1.7
802	<1.0	0	0
822	<1.0	-0.3	-2.3
752	2.6	-2.3	0.7
842	<1.0	-0.2	2.5
912	1.6	2.8	0.5
932	<1.0	-0.2	0.3
772	<1.0	0.3	0.6
862	<1.0	0.6	-0.8
10.0.2	<1.0	-0.1	0.4
10.2.2	<1.0	0.2	-0.4
952	<1.0	-0.4	0.6
10.4.2	<1.0	-0.7	2.2
11.1.2	1.0	1.1	1.4
11.3.2	1.4	0.6	
103	6.7	-8.1	-9.6
213	1.4	-0.3	0.5

hkl	$F_{obs.}$	$F_{calc.}$	$F'_{calc.}$
303	2.9	-2.5	-1.3
323	3.3	4.4	4.8
413	0.7	0.4	1.0
433	2.7	-2.8	-3.5
503	2.5	-3.1	-1.7
523	3.7	4.8	6.2
613	1.6	-2.1	-3.2
543	2.0	-2.2	-2.3
633	2.2	2.1	1.7
703	2.4	-2.5	-2.5
723	1.2	1.4	1.4
653	1.3	-1.5	0.1
813	1.3	-1.6	-0.6
743	1.0	-0.3	-0.3
833	2.3	3.2	3.5
903	1.7	-1.4	-2.5
923	1.0	0.1	-0.9
763	1.0	0.8	0.8
853	2.2	-3.4	-4.8
943	1.0	0.6	0.6
10.1.3	1.0	0	0
004	6.2	-6.3	-7.0
204	3.7	-3.4	-3.3
224	2.7	1.5	1.4
314	2.6	-3.0	-4.4
404	1.3	-0.8	-0.6
424	0.7	-0.5	-0.3
514	1.4	-0.8	-1.2
444	1.8	2.5	2.4
534	1.9	2.3	4.9
604	2.1	-1.9	-2.0
624	1.0	0.4	0.6
714	1.6	-1.2	-1.1
644	1.3	1.5	1.6
734	1.0	0.1	0.2
804	2.3	-3.4	-3.4
824	1.9	2.1	1.8
664	1.0	-0.6	-0.8
754	1.0	0.4	0.4
844	1.0	0.6	-0.8

hkl	$F_{obs.}$	$F_{calc.}$	$F'_{calc.}$
914	<1.0	-0.3	-2.0
934	<1.0	-0.8	-2.6
10.0.4	1.4	-2.7	-3.7
864	1.4	1.0	1.2
105	3.2	3.3	5.5
215	2.8	-2.2	-1.3
305	3.0	-3.4	-5.6
325	1.4	1.5	1.3
415	2.7	-2.8	-2.0
435	3.9	-0.2	0.1
505	3.1	-4.2	-5.2
525	2.1	2.8	1.6
615	1.6	-2.2	-3.0
545	1.6	-2.2	-2.5
635	1.9	-1.0	-1.0
705	1.7	-1.5	-1.5
725	1.7	0.7	0.7
655	<1.0	2.4	3.9
815	<1.0	-0.6	-0.1
745	2.0	0.2	0.2
835	2.4	-1.7	-1.6
905	<1.0	0.7	1.3
765	<1.0	0.3	0.3
925	1.7	-1.2	-0.3
855	1.7	2.4	1.0
116	3.7	-3.3	-2.4
206	1.2	1.0	2.6
316	<1.0	0.6	-0.6
406	1.0	1.3	1.3
336	3.2	-4.5	-4.5
426	1.3	1.0	1.0
516	1.9	2.5	2.7
536	4.1	-5.5	-6.1
606	<1.0	1.1	-1.2
626	<1.0	-0.6	-0.9
556	3.2	6.0	4.7
716	<1.0	0.1	0
646	<1.0	0.1	1.2
736	2.0	-2.5	-2.5

hkl	$F_{obs.}$	$F_{calc.}$	$F'_{calc.}$
806	<1.0	0.2	2.1
826	<1.0	0.2	-0.4
756	1.7	3.4	3.4
846	<1.0	-0.4	-1.5
916	1.4	-1.7	-1.9
107	1.9	1.1	1.8
217	<1.0	-0.4	-1.6
307	2.8	3.4	0.9
327	2.4	-1.6	-3.0
417	1.7	-2.4	-5.3
437	<1.0	0.6	2.5
507	3.5	3.7	2.2
527	2.6	-2.3	-0.5
617	1.4	-1.6	-1.2
547	<1.0	0.6	2.1
637	1.0	0.2	
707	1.4	2.1	
008	3.3	4.4	0.8
208	2.6	2.3	3.1
228	1.4	-1.0	-1.4
318	1.0	-0.1	-0.4
408	1.0	0.1	1.9
428	<1.0	0.6	1.4
518	<1.0	-0.5	0
448	1.3	-2.0	-2.5
109	1.4	0.2	0
219	1.3	-0.3	-0.9
309	1.8	1.8	1.2
329	1.3	-1.3	-0.8
419	<1.0	0.1	1.0
439	1.0	0.3	1.0
509	1.5	1.2	2.7
529	1.2	-1.3	-0.9
3.3.10	1.3	0.7	1.7
5.3.10	1.1	-0.3	0.2
1.0.11	0.6	-0.9	-0.3
3.0.11	0.9	-0.6	-0.9

A scale model of the molecule and its nearest neighbours is shown in Fig. 6. The final parameters correspond to the dimensions:

Si_I-O_{II} $= 1.64 \pm 0.03$ A. $\angle O_{II}Si_IO_{II}$ $= 105 \pm 4°$;
$Si_{II}-O_{II} = 1.61 \pm 0.03$ A. $\angle O_{II}Si_{II}O_I$ $= 108 \pm 4°$;
$Si_{II}-O_I$ $= 1.67 \pm 0.03$ A. $\angle CH_3Si_{II}CH_3 = 106 \pm 4°$;
$Si_{II}-CH_3 = 1.88 \pm 0.03$ A. $\angle Si_IO_{II}Si_{II}$ $= 134 \pm 4°$;
$\angle Si_{II}O_ISi_{II}$ $= 129 \pm 4°$.

Within the given limits of precision, all the Si–O distances are equivalent and equal to 1.64 ± 0.03 A., the Si angles tetrahedral ($109\frac{1}{2}°$), and the Si–O–Si angles 130°.
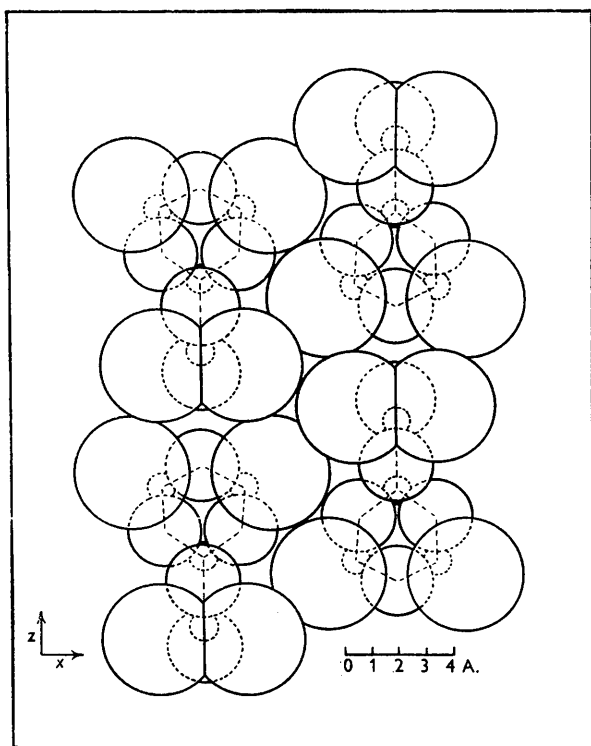
Fig. 6. Model of ideal molecule showing intermolecular contacts

Intermolecular contacts in the crystal are through methyl groups. The distances between centres of non-bonded methyl groups range from 4·1 to 4·3 A., corresponding to a van der Waals radius of about 2·1 A. This radius is slightly larger than the value 2·0 A. found in other crystals, in agreement with the postulated libration of methyl groups.

Discussion

The average Si–O bond distance in the spirosiloxane is 1·64 A., about the same as that observed in quartz and the silicates, but considerably shorter than the value 1·83 A. obtained from the sum of the covalent radii of silicon and oxygen. The central silicon atom is surrounded by four oxygen atoms in the tetrahedral arrangement characteristic of the SiO_4 groupings in inorganic compounds. Pauling considers the Si–O bond as covalent with about 50 % ionic character, and interprets the bond shortening as resulting from resonance between a variety of multiply bonded electronic structures (Pauling, 1940, §§ 30 and 46c). The ionic nature of the siloxane bond (Wright & Hunter, 1947) has been confirmed by the infra-red spectra of a series of cyclic and linear siloxane compounds.

On the other hand, methyl substituents are attached to silicon at the tetrahedral angle, and the Si–C distance 1·88 ± 0·03 A. is only slightly shorter than that predicted from the covalent radii (1·94 A.). This shortening may indicate some ionic contribution to the Si–C bond.

The precessing methyl concept is a useful mathematical device to reduce the scattering in certain directions, but consideration of the geometry involved shows that two methyl groups bonded to the same silicon atom could not be expected to librate independently of each other. The $Si(CH_3)_2$ assembly must be more or less rigid (except for the usual small distortions due to bending and stretching vibrations). The data consequently indicate a tendency of this grouping to pivot about the silicon atom, as though the silicon in O–Si–O were free to move as in a ball-and-socket joint. Complete rotation would not be expected because motion of the $Si(CH_3)_2$ is restricted by the planar siloxy ring. This relatively unhindered rotation of the silicon atom is in accord with the short siloxane bond distance, an ionic bond having no directional character other than that created by the Coulombic forces induced by the geometry of the environment. Movements of atoms in the ring undoubtedly occur, but are constrained by the strained planar structure.

According to this point of view, it is not surprising that the Si–O–Si angle is greater than that predicted between either covalent p bonds (90°) or sp^3 bonds ($109\frac{1}{2}°$). Since the spirosiloxane ring studied is planar and possibly under strain, an exact value for the free Si–O–Si angle cannot be derived. If the unstrained angle were less than 130°, strain in the ring could be relieved by puckering. Since the ring is planar, the unstrained angle would be equal to or greater than 130°. This is in agreement with the value 165° deduced from dipole moment measurements (Sauer & Mead, 1946). However, an alternative explanation can be developed in terms of resonance, the strain energy being compensated for by resonance between various double and non-bonded configurations. The facts that the silicon angles are tetrahedral, and there is no tendency toward the formation of equivalent 120° angles within the ring, militate against the latter hypothesis. A direct determination of the free Si–O–Si angle would aid in the differentiation of the two possibilities.

Many of the chemical and physical properties of the siloxane compounds can be interpreted in terms of these structural principles. (The ionic siloxane bond is readily cleaved by H^+ or OH^-, in contrast to the chemical stability of the C–O bond. The Si–CH$_3$ bond

is quite stable in accord with its covalent character.) The siloxanes, as a class, have 'abnormally' low boiling points and low temperature coefficients of viscosity. The seeming contradiction between the idea of a highly polar siloxane skeleton and the observed low intermolecular forces is resolved by assuming a low barrier to free rotation of CH_3 groups about siloxane bonds. The 'softness' of the bond angles, plus the favourable geometry reducing steric interactions of attached groups, should result in a negligible barrier to free rotation about the siloxane bonds in linear polymers. Consequently, the low boiling points and temperature coefficients of viscosity may be attributed to free rotation preventing chains from packing sufficiently closely for the short-range intermolecular forces to become strongly operative.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Rapid publication will be facilitated if the contributions are without illustrations.

The crystal structure of kalsilite.

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Kalsilite, the simplest of the three known polymorphous forms of $KAlSiO_4$, was isolated in minute quantities from volcanic rocks of S.W. Uganda in 1942 (Bannister & Hey, 1942) and synthesized in the laboratory for the first time in 1947 (Rigby & Richardson, 1947). Its unit-cell contents, dimensions and space group when determined by chemical analysis and single-crystal photographs revealed an obvious relationship to hexagonal tridymite, nepheline and kaliophilite (Bannister & Hey, 1931). In cell dimensions ($a = 5·17$, $c = 8·67$ A.) and space group ($C6_3 2$) kalsilite is, however, more closely related to $BaAl_2O_4$ ($a = 5·21$, $c = 8·76$ A.) (Wallmark & Westgren, 1937) which Nowacki (1942) pointed out is almost identical in crystal structure and parameter values with $KLiSO_4$ ($a = 5·13$, $c = 8·60$ A.) (Bradley, 1925; Ewald & Hermann, 1931).

Nagelschmidt recently sent us crystals of $KLiSO_4$ and also powder photographs of $KLiSO_4$ and artificial kalsilite showing the essential identity of their crystal structures. We have now obtained photometer records of our own powder photographs of kalsilite, $BaAl_2O_4$ and $KLiSO_4$ which confirm these suggestions of identity. The differences between the almost identical photometer curves for kalsilite and $KLiSO_4$ and the curve for $BaAl_2O_4$ can be attributed to the difference in the atomic scattering factors for the potassium and barium ions.

The comparison of calculated and estimated intensities for kalsilite establishes its structure type as $H2_8$ (Gottfried, 1940) and establishes parameter values. The (Si, Al)O_2 tetrahedral framework of kalsilite and the corresponding frameworks AlO_2 and LiO_2, SO_2 of $BaAl_2O_4$ and $KLiSO_4$ are derived from hexagonal tridymite, SiO_2, structure type $C10$. The (Si, Al)–O–(Si, Al) linkages between the tetrahedra along the c axis are straight as in tridymite. All other linkages, which in tridymite are also straight, have in kalsilite an approximately tetrahedral angle near to 109° 28′. The cavities in this modified tridymite structure are occupied by the large potassium ions.

Buerger (1946) has confirmed that the crystal structure of nepheline, $KNa_3Al_4Si_4O_{16}$, is based upon a tridymite-like framework, but the distortion is not confined to tetrahedral rotations in the c plane as in the $H2_8$ framework, and cavities of two sizes are developed which are occupied by the sodium and potassium ions respectively. The crystal structure of kaliophilite ($a = 26·94$, $c = 8·55$ A., space group $C6_3 2$) (Lukesh & Buerger, 1941), which has not yet been worked out in detail, is probably a multiple kalsilite structure. The c dimension is perceptibly less for kaliophilite than for kalsilite, possibly indicating slight flexing of the (Si, Al)–O–(Si, Al) linkages lying parallel to the c axis.