

Fig. 5. Plot of the unit-cell volume of the monoclinic modification and half the unit-cell volume of the orthorhombic modification of *N*-methylurea-oxalic acid (2:1) against temperature.

view, and may be due to differences in hydrogen bonding in the different compounds.

From Figs. 1 and 3 we see that the crystal structures of the orthorhombic and monoclinic modifications in the planes are very much alike. The monoclinic modification has a crystallographic inversion centre at the C-C bond in oxalic acid. This does not apply to the orthorhombic modification, although the atomic positions are almost in agreement with an inversion centre at the same place. Other differences between the crystal structures are: the orientation of the methyl group, the distance between two parallel layers (3.21 and 3.24 Å for the orthorhombic and monoclinic modifications respectively), and the positions of two parallel layers with respect to each other.

During the measurement of lattice constants of the monoclinic modification at different temperatures, we discovered a phase change at *ca* 180 K. The monoclinic changes into the orthorhombic modification. A

differential thermal analysis showed the temperature where the phase transition takes place to be 182 K. The phase transition is exothermic and irreversible. Fig. 5 is a plot of the unit-cell volume of the monoclinic modification and half the unit-cell volume of the orthorhombic modification against temperature. The unit-cell volume of the monoclinic modification is 1.3% greater than half the unit-cell volume of the orthorhombic modification. This difference is due to the difference in distance between two parallel planes (0.9%) and to the small differences in atomic positions in the planes (0.4%).

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The Crystal and Molecular Structures of Disiloxane (at 108 K) and Hexamethyldisiloxane (at 148 K)

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Abstract

At 108 K crystals of disiloxane, $\text{SiH}_3\text{OSiH}_3$, are orthorhombic, space group $P2_12_12_1$, with $a = 4.66$, $b = 7.79$, $c = 12.97$ Å (e.s.d.'s 0.3% assumed) and $Z = 4$.

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Crystals of hexamethyldisiloxane (at 148 K) are monoclinic, space group $P2_1/c$, with $a = 12.53$, $b = 8.34$, $c = 12.16$ Å, $\beta = 120.9^\circ$ (e.s.d.'s 0.3% assumed) and $Z = 4$. Crystals were grown *in situ* on a Weissenberg goniometer fitted with low-temperature

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equipment and microdensitometer intensities were obtained from films exposed using Cu $K\alpha$ radiation. The structures were refined to $R = 4.2\%$ over 403 reflexions for disiloxane, and $R = 3.5\%$ over 1256 reflexions for hexamethyldisiloxane. Crystalline disiloxane has distorted $mm2$ molecular symmetry with Si—O = 1.631 (6) Å and Si—O—Si = 142.2 (3)°. Crystalline hexamethyldisiloxane has distorted m molecular symmetry with Si—O = 1.626 (5) Å and Si—O—Si = 148.8 (2)°. Molecules of disiloxane form infinite chains as a result of weak, but highly directional, intermolecular Si...O interactions (3.115 Å). Hexamethyldisiloxane exists as discrete molecules with no short intermolecular contacts.

Introduction

In water, dimethyl ether, F₂O and Cl₂O, the angle at oxygen is close to or less than the tetrahedral value. In silicates and disiloxanes, the angle at oxygen is very much wider. Moreover, it increases from the apparent value of 144.1° in disiloxane itself (as measured by electron diffraction in the gas phase) to 180° in crystalline hexaphenyldisiloxane. Values for Si—O—Si and Si—O distances in a number of disiloxanes and related compounds are given in Table 7.

Most of the features in the vibrational spectra of disiloxane can be interpreted in terms of a model with a linear heavy-atom skeleton (Lord, Robinson & Schumb, 1956). This apparently conflicts with the structure as determined by electron diffraction (Almenningen, Bastiansen, Ewing, Hedberg & Traetteberg, 1963); the two can be reconciled if the molecule is regarded as 'quasi-linear': bent but with a skeletal bending vibration that is low in frequency and large in amplitude. Under these conditions the language of the conventional point-group analysis becomes inappropriate; permutation group theory must be used instead. The appropriate permutation group is isomorphous with D_{3h} , leading to selection rules that are effectively the same as for a molecule with a linear heavy-atom skeleton. A detailed analysis of the weak Raman feature corresponding to the overtone of the skeletal bending mode has led Durig, Flanagan & Kalasinsky (1977) to propose a potential surface with a hump at a linear configuration of height 112 cm⁻¹, and a minimum corresponding to a Si—O—Si angle of 149°.

The concept of quasi-linearity is by now well established, but little is known about the structures of quasilinear molecules in the solid state. The vibrational spectra of disiloxane and hexachlorodisiloxane change on crystallization, implying that there might be associated changes in structure. Disiloxane is a clearly recognized example of quasi-linearity, while it is suggested that features in the Raman spectra of hexamethyldisiloxane imply that this molecule too should be

regarded as quasi-linear. We here present the crystal structures of disiloxane and of hexamethyldisiloxane.

Experimental

Crystallographic data

(a) Disiloxane. H₆OSi₂, $M_r = 78.2$. Orthorhombic, $a = 4.66$, $b = 7.79$, $c = 12.97$ Å (e.s.d.'s 0.3% assumed). $U = 470.8$ Å³, $Z = 4$, $D_c = 1.10$ Mg m⁻³. Cu $K\alpha$ radiation (Ni filter), $\lambda = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 5.43$ mm⁻¹. Space group $P2_12_12_1$ (D_{2h}^4 , No. 19) by systematic absences. Melting point 128 K, cell parameters and intensities measured at 108 K. Final least-squares weighting scheme: $w^{-1} = 1 + |F_o|$. Final value of isotropic extinction parameter: $G = 2.99$ (23) $\times 10^{-4}$, where

$$|F'_c| = |F_c| \left[1 + \frac{G|F_c|^2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta) \sin 2\theta} \right]^{-1/4}$$

Final $R = 4.2\%$ over 403 reflexions. A final $|F_o| - |F_c|$ Fourier synthesis showed peaks (0.2 e Å⁻³) and troughs (-0.4 e Å⁻³) close to Si atoms but no other significant features.

(b) Hexamethyldisiloxane. C₆H₁₈OSi₂, $M_r = 162.4$. Monoclinic, $a = 12.53$, $b = 8.34$, $c = 12.16$ Å, $\beta = 120.9^\circ$ (e.s.d.'s 0.3% assumed). $U = 1090.4$ Å³, $Z = 4$, $D_c = 0.99$ Mg m⁻³. Cu $K\alpha$ radiation (Ni filter), $\lambda = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 2.53$ mm⁻¹. Space group $P2_1/c$ (C_{2h}^2 , No. 14) by systematic absences. Melting point 208 K, cell parameters and intensities measured at 148 K. Final least-squares weighting scheme: $w^{-1} = 2 + |F_o|$. Final value of isotropic extinction parameter (as defined above): $G = 0.88$ (5) $\times 10^{-4}$. Final $R = 3.5\%$ over 1256 reflexions. A final $|F_o| - |F_c|$ Fourier synthesis showed two peaks (0.3 e Å⁻³), one close to each Si atom, but no other significant features.

Procedure

Pure samples of disiloxane and hexamethyldisiloxane were sealed into glass capillaries, which were mounted on Tufnol inserts and attached to standard goniometer heads. Hexamethyldisiloxane, a liquid at room temperature, was sealed in Lindemann capillaries (0.5 mm internal diameter). Disiloxane, which is a gas at room temperature (b.p. 258 K), could not be contained in Lindemann capillaries and the material was sealed in thin-walled Pyrex capillaries; the specimen used for intensity-data measurements had an external-wall diameter of 0.64 mm.

Single crystals suitable for X-ray investigation were grown *in situ* on a Nonius Weissenberg goniometer. The goniometer was fitted with Nonius nitrogen-gas-stream low-temperature equipment with some locally devised modifications. Intensity films were exposed

using $\text{Cu K}\alpha$ radiation and the multiple-film-pack equi-inclination Weissenberg method. Integrated intensities were derived from microdensitometer measurements carried out by the SRC Microdensitometer Service at Daresbury Laboratory, Warrington WA4 4AD, England. Intensities were corrected for Lorentz and polarization effects and for absorption.

Our crystallization technique yields roughly cylindrical crystals in which a unit-cell axis is not usually coincident with the cylinder axis. When aligned for Weissenberg photography the capillary (and hence the crystal cylinder) may be severely inclined with respect to the rotation axis of the camera. Absorption corrections were calculated using the *SHELX* system of programs (Sheldrick, 1976). For each crystal a sufficient number of faces were defined in order to approximate to the required shape and orientation of the crystal cylinder.

The structure analysis for disiloxane is based on 403 unique reflexions from the Weissenberg levels 0–4*kl*. All data were obtained from one crystal but only the $+h,+k,+l$ reflexions were considered. Experimental difficulties during intensity photography led us to believe that reflexions in other octants were of reduced precision. The analysis of hexamethyldisiloxane is based on 1256 unique intensities obtained by merging equivalent reflexions measured in the *hkl*, $\bar{h}kl$, $h\bar{k}l$, and $h\bar{h}l$ regions of reciprocal space. The data were obtained from two different crystals: the Weissenberg levels *hk*0–6 were from crystal (1), the levels *hk*7–10 were from crystal (2). A third crystal, orientated along the unique axis, gave poor-quality photographs of the *h0l* zone. These photographs were used for cell-parameter calculations but not for intensity measurements.

Structure solutions were by Fourier methods and structure parameters were refined by least-squares calculations to minimize the quantity $\sum w(|F_o| - |F_c|)^2$. Inter-layer scale factors were assigned initially on the basis of exposure times. Only a single overall scale factor was varied during structure refinement. Improved individual layer scale factors were periodically evaluated by a least-squares method involving scaling the data level-by-level to the structure model. The positional and isotropic vibration parameters for

hydrogen atoms were included in the refinement process, all hydrogens having been unambiguously located from difference Fourier syntheses. Anisotropic vibration parameters were included for all non-hydrogen atoms. Empirical least-squares weighting schemes were introduced during the later stages of refinement. Empirical isotropic extinction corrections were applied by means of a variable parameter in the least-squares calculations (see crystal data above).

Atomic scattering factors for Si, O and C atoms were taken from Cromer & Mann (1968), scattering factors for H atoms were from Stewart, Davidson & Simpson (1965). Allowance was made for the real and imaginary parts of the anomalous-dispersion effect for Si atoms (Cromer & Liberman, 1970).

The imaginary part of the anomalous-dispersion effect for Si is small and the alternative (enantiomorphic) disiloxane structures are poorly distinguished. The atomic parameter set listed in Table 1 yields the lower *R* factor (by 0.1%) with respect to the F_o data set: $+h,+k,+l$ only, as described previously.

Calculations were performed using computers of the Edinburgh Regional Computing Centre and programs written here, and the program systems XRAY (1972), *SHELX* (Sheldrick, 1976), and *PLUTO* (Motherwell, 1976).

Results

(a) *Disiloxane*. Final values of atomic parameters are given in Table 1. Details of the intramolecular and

Table 2. *Intramolecular geometry for SiH₃OSiH₃*

(a) Interatomic distances (Å)

Si(1)–O	1.632 (5)	Si(2)–O	1.630 (5)
Si(1)–H(1)	1.24 (8)	Si(2)–H(4)	1.26 (15)
Si(1)–H(2)	1.48 (9)	Si(2)–H(5)	1.28 (10)
Si(1)–H(3)	1.22 (7)	Si(2)–H(6)	1.36 (12)
Si(1)···Si(2)	3.086 (2)		

(b) Interbond angles (°)

O–Si(1)–H(1)	110 (3)	O–Si(2)–H(4)	101 (5)
O–Si(1)–H(2)	107 (3)	O–Si(2)–H(5)	96 (5)
O–Si(1)–H(3)	107 (3)	O–Si(2)–H(6)	108 (5)
<H–Si(1)–H>	110 (9)	<H–Si(2)–H>	116 (9)
Si(1)–O–Si(2)	142.2 (3)		

(c) Least-squares planes, with distances (Å) of atoms from the planes

Plane (1): Si(1); Si(2); O.			
Plane (2): Si(1), –0.046 (2); Si(2), 0.042 (2); H(1), 0.04 (9); H(6), –0.04 (14).			
Plane (3): Si(1), –0.034 (2); Si(2), 0.035 (2); H(2), 0.02 (12); H(5), –0.02 (13).			
Plane (4): Si(1), –0.103 (2); Si(2), 0.100 (2); H(3), 0.08 (6); H(4), –0.08 (11).			

Angles between planes (°)

(1) and (2)	162 (5)	(2) and (3)	129 (8)
(1) and (3)	33 (6)	(2) and (4)	108 (7)
(1) and (4)	91 (7)	(3) and (4)	124 (8)

Table 1. *Atomic parameters for SiH₃OSiH₃ (with estimated standard deviations in parentheses)*

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.2207 (4)	0.49035 (20)	0.04784 (11)
Si(2)	0.4599 (4)	0.26786 (21)	0.22499 (11)
O	0.3689 (12)	0.4351 (6)	0.1569 (3)
H(1)	0.095 (22)	0.366 (9)	0.009 (5)
H(2)	0.071 (27)	0.654 (10)	0.066 (6)
H(3)	0.407 (18)	0.488 (8)	–0.018 (4)
H(4)	0.727 (31)	0.264 (14)	0.210 (8)
H(5)	0.441 (31)	0.342 (13)	0.313 (7)
H(6)	0.295 (33)	0.134 (14)	0.194 (8)

intermolecular geometry are given in Tables 2 and 3.* Fig. 1 shows the arrangement of molecules in the unit cell and indicates the atom labelling.

(b) *Hexamethyldisiloxane*. Final values of atomic parameters are given in Table 4 and details of the molecular geometry are given in Table 5.* Table 6 lists

* Lists of structure factors and atomic thermal parameters for both molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34478 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Intermolecular geometry for* $\text{SiH}_3\text{OSiH}_3$

(a) Shortest contact distances (Å) of each type

H...H				
H(6)...	H(5 ^I)	2.59 (16);	H(6)...H(4 ^{II})	2.84 (21)
H...O				
H(6)...	O ^I	2.93 (12);	H(4)...O ^I	3.12 (11)
Si...Si				
Si(1)...	Si(2 ^{IV})	3.946 (2);	Si(2)...Si(2 ^{IV})	3.966 (2)
Si...O				
Si(2)...	O ^I	3.115 (5);	Si(1)...O ^{II}	4.236 (6)
Si...H				
Si(2)...	H(6 ^{IV})	3.24 (11);	Si(2)...H(1 ^V)	3.28 (7)
O...O No contact under 4.5 Å				

(b) Important intermolecular angles (°)

O—Si(2)...	O ^I	176.6 (4)	H(4)—Si(2)...	O ^I	79 (5)
Si(1)—O...	Si(2 ^{IV})	108.4 (2)	H(5)—Si(2)...	O ^I	87 (5)
Si(2)—O...	Si(2 ^{IV})	109.4 (2)	H(6)—Si(2)...	O ^I	69 (5)

(c) Distances (Å) of atoms from the best least-squares plane defined by Si(1), Si(2), O, Si(2^{IV})

Si(1), 0.001 (2);	Si(2), 0.001 (2);	O, -0.003 (6);
Si(2 ^{IV}), 0.000 (2);	O ^{IV} , -0.028 (6);	Si(1 ^{IV}), -0.042 (2);
O ^I , 0.067 (6).		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z :

- | | |
|---|--|
| (I) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ | (IV) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$ |
| (II) $x - 1, y, z$ | (V) $\frac{1}{2} + x, \frac{1}{2} - y, -z$ |
| (III) $x - \frac{1}{2}, \frac{1}{2} - y, -z$ | |

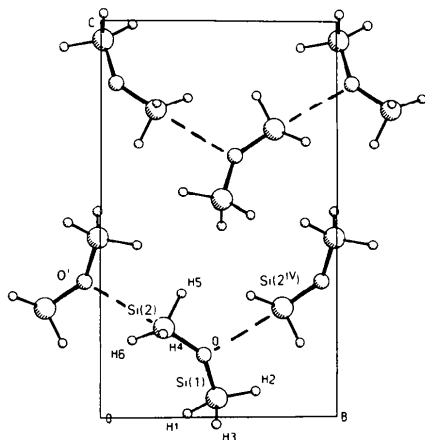


Fig. 1. Unit cell of $\text{SiH}_3\text{OSiH}_3$ viewed down the a axis. (Roman numerals as superscripts refer to the equivalent positions defined in Table 3.)

the shortest intermolecular contacts. Fig. 2 shows the atomic labelling scheme and Fig. 3 the molecular packing.

(c) *Limitations of method*. The cell parameters are subject to the usual errors associated with the Weissenberg film method; these errors are probably accentuated by the use of split film cassettes. The reliability of the atomic vibration parameters is adversely affected by the lack of direct, experimental data for the inter-layer scale factors.

(d) *Estimated standard derivations*. The e.s.d.'s listed in Tables 1 to 6 do not include contributions from errors in the cell parameters, but the data in the *Abstract* and in Table 7 do include contributions from estimated cell-parameter errors.

Table 4. *Atomic parameters for* $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ (with estimated standard deviations in parentheses)

	x	y	z
Si(1)	0.15029 (6)	-0.10040 (7)	0.23787 (7)
Si(2)	0.30441 (6)	0.19779 (8)	0.24226 (7)
O	0.19605 (17)	0.08004 (21)	0.23169 (23)
C(1)	0.2751 (3)	-0.2067 (4)	0.3793 (3)
C(2)	0.1133 (3)	-0.2103 (4)	0.0902 (3)
C(3)	0.0104 (3)	-0.0813 (3)	0.2522 (3)
C(4)	0.4291 (3)	0.0787 (4)	0.2411 (4)
C(5)	0.3690 (3)	0.3131 (4)	0.3932 (4)
C(6)	0.2328 (3)	0.3361 (4)	0.1044 (3)
H(11)	0.249 (4)	-0.306 (5)	0.388 (5)
H(12)	0.346 (3)	-0.235 (4)	0.364 (4)
H(13)	0.301 (4)	-0.154 (6)	0.458 (5)
H(21)	0.087 (4)	-0.327 (5)	0.098 (4)
H(22)	0.181 (4)	-0.213 (5)	0.078 (5)
H(23)	0.051 (5)	-0.155 (6)	0.013 (6)
H(31)	-0.023 (3)	-0.192 (4)	0.255 (4)
H(32)	-0.053 (3)	-0.033 (5)	0.173 (4)
H(33)	0.036 (3)	-0.023 (5)	0.333 (4)
H(41)	0.398 (4)	0.003 (5)	0.172 (4)
H(42)	0.467 (3)	0.001 (5)	0.318 (4)
H(43)	0.494 (3)	0.146 (5)	0.240 (4)
H(51)	0.397 (4)	0.237 (5)	0.458 (5)
H(52)	0.427 (4)	0.378 (5)	0.391 (5)
H(53)	0.298 (4)	0.372 (6)	0.399 (5)
H(61)	0.197 (3)	0.294 (5)	0.030 (4)
H(62)	0.298 (4)	0.406 (5)	0.105 (5)
H(63)	0.164 (3)	0.382 (4)	0.104 (4)

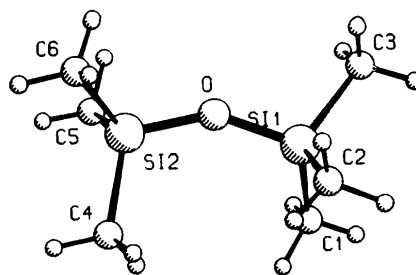


Fig. 2. Molecule of $\text{Me}_3\text{SiOSiMe}_3$, projected on to the plane defined by Si(1), Si(2), O.

Table 5. *Intramolecular geometry for*
(CH₃)₃SiOSi(CH₃)₃

(a) Interatomic distances (Å)			
Si(1)—O	1.626 (2)	Si(2)—O	1.626 (2)
Si(1)—C(1)	1.851 (3)	Si(2)—C(4)	1.857 (4)
Si(1)—C(2)	1.850 (4)	Si(2)—C(5)	1.850 (4)
Si(1)—C(3)	1.855 (4)	Si(2)—C(6)	1.844 (4)
⟨C(1)—H⟩	0.96 (6)	⟨C(4)—H⟩	1.00 (5)
⟨C(2)—H⟩	0.99 (6)	⟨C(5)—H⟩	0.97 (6)
⟨C(3)—H⟩	0.99 (5)	⟨C(6)—H⟩	0.93 (6)
Si(1)⋯Si(2)	3.132 (1)		
(b) Interbond angles (°)			
O—Si(1)—C(1)	109.67 (12)	O—Si(2)—C(4)	110.36 (13)
O—Si(1)—C(2)	109.41 (16)	O—Si(2)—C(5)	108.34 (18)
O—Si(1)—C(3)	107.31 (13)	O—Si(2)—C(6)	107.99 (13)
C(1)—Si(1)—C(2)	109.58 (16)	C(4)—Si(2)—C(5)	110.14 (15)
C(1)—Si(1)—C(3)	110.00 (18)	C(4)—Si(2)—C(6)	110.26 (20)
C(2)—Si(1)—C(3)	110.84 (16)	C(5)—Si(2)—C(6)	109.71 (16)
⟨Si(1)—C(1)—H⟩	112 (3)	⟨Si(2)—C(4)—H⟩	112 (3)
⟨Si(1)—C(2)—H⟩	111 (4)	⟨Si(2)—C(5)—H⟩	107 (4)
⟨Si(1)—C(3)—H⟩	108 (3)	⟨Si(2)—C(6)—H⟩	111 (4)
⟨H—C(1)—H⟩	107 (6)	⟨H—C(4)—H⟩	107 (5)
⟨H—C(2)—H⟩	108 (6)	⟨H—C(5)—H⟩	112 (6)
⟨H—C(3)—H⟩	111 (6)	⟨H—C(6)—H⟩	108 (8)
Si(1)—O—Si(2)	148.78 (15)		
(c) Least-squares planes, with distances (Å) of atoms from the planes			
Plane (1): Si(1); Si(2); O.			
Plane (2): Si(1), -0.049 (1); Si(2), -0.087 (1); C(1), 0.064 (4); C(6), 0.072 (4).			
Plane (3): Si(1), 0.049 (1); Si(2), 0.060 (1); C(2), -0.053 (4); C(5), -0.056 (4).			
Plane (4): Si(1), -0.053 (1); Si(2), -0.024 (1); C(3), 0.041 (3); C(4), 0.035 (4).			
Angles between planes (°)			
(1) and (2)	134.2 (4)	(2) and (3)	119.5 (4)
(1) and (3)	106.3 (4)	(2) and (4)	120.5 (4)
(1) and (4)	13.8 (3)	(3) and (4)	120.0 (4)
(d) Torsion angles (°)			
C(1)—Si(1)—O—Si(2)	45.1 (3)		
C(2)—Si(1)—O—Si(2)	-75.1 (3)		
C(3)—Si(1)—O—Si(2)	164.5 (3)		
C(4)—Si(2)—O—Si(1)	12.7 (4)		
C(5)—Si(2)—O—Si(1)	-107.9 (3)		
C(6)—Si(2)—O—Si(1)	133.3 (3)		
C(1)—Si(1)⋯Si(2)—C(4)	54.3 (2)		
C(1)—Si(1)⋯Si(2)—C(5)	-59.9 (2)		
C(1)—Si(1)⋯Si(2)—C(6)	170.6 (2)		
C(2)—Si(1)⋯Si(2)—C(4)	-58.6 (2)		
C(2)—Si(1)⋯Si(2)—C(5)	-172.8 (2)		
C(2)—Si(1)⋯Si(2)—C(6)	57.7 (2)		
C(3)—Si(1)⋯Si(2)—C(4)	174.5 (2)		
C(3)—Si(1)⋯Si(2)—C(5)	60.2 (2)		
C(3)—Si(1)⋯Si(2)—C(6)	-69.3 (2)		

Discussion

(a) The Si—O—Si skeletons

The Si—O distances in solid disiloxane, average 1.631 (5) Å, and in solid hexamethyldisiloxane, average 1.626 (2) Å, are not significantly different,

though the angle at oxygen is smaller in disiloxane, 142.2 (3)°, than in hexamethyldisiloxane, 148.8 (1)°.

Despite differences between the forces acting on the atoms of a free molecule and those in a crystal lattice, the Si—O distances and Si—O—Si angles in crystalline disiloxane and in crystalline hexamethyldisiloxane are very similar to the values determined by electron diffraction for these molecules in the gas phase (see Table 7). This is remarkable in view of the ease with which the Si—O—Si angle can be deformed and also in view of the possible effects of large-amplitude bending vibrations on the apparent dimensions of the molecules when measured by electron diffraction. The packing in the crystal appears to adapt itself to the geometry of the free molecule rather than *vice versa*.

(b) Molecular conformations

Crystalline disiloxane has distorted *C_{2v}* (*mm2*) molecular symmetry while crystalline hexamethyldisiloxane has distorted *C_s* (*m*) molecular symmetry. In

Table 6. *Intermolecular geometry for*
(CH₃)₃SiOSi(CH₃)₃

(a) Shortest intermolecular H⋯H contacts (Å)			
H(21)⋯H(63 ^I)	2.60 (6)	H(62)⋯H(42 ^{III})	2.71 (6)
H(33)⋯H(21 ^{II})	2.66 (7)	H(11)⋯H(53 ^I)	2.74 (6)
(b) Shortest intermolecular contacts between non-hydrogen atoms (Å)			
Shortest C⋯C:			
C(2)⋯C(6 ^V)	3.868 (4);	C(5)⋯C(6 ^{IV})	3.946 (7)
Shortest O⋯C:			
O⋯C(3 ^{II})	3.902 (4);	O⋯C(2 ^V)	3.993 (3)
Shortest Si⋯C:			
Si(2)⋯C(3 ^{II})	4.385 (4);	Si(1)⋯C(2 ^V)	4.473 (3)

There are no O⋯O, Si⋯O, or Si⋯Si intermolecular contacts less than 4.5 Å.

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x, y, z*:

- | | |
|---|--|
| (I) $x, y - 1, z$ | (IV) $x, \frac{1}{2} - y, \frac{1}{2} + z$ |
| (II) $-x, \frac{1}{2} + y, \frac{1}{2} - z$ | (V) $-x, -y, -z$ |
| (III) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ | |

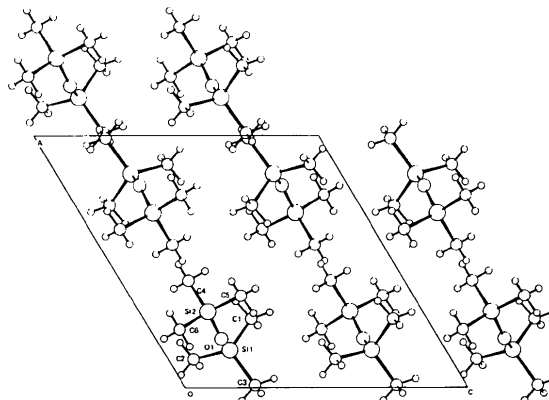
Fig. 3 Unit cell of Me₃SiOSiMe₃ viewed down the *b* axis.

Table 7. Molecular parameters for derivatives of disiloxane

Compound	Method	Si—O (Å)	Si—O—Si (°)	Reference
SiH ₃ OSiH ₃	ED	1.634 (2)	144.1 (9)	(a)
SiH ₃ OSiH ₃	X-ray	1.631 (6)	142.2 (3)	This work
(CH ₃) ₃ SiOSi(CH ₃) ₃	ED	1.631 (3)	148 (3)	(b)
(CH ₃) ₃ SiOSi(CH ₃) ₃	X-ray	1.626 (5)	148.8 (2)	This work
F ₃ SiOSiF ₃	ED	1.58 (3)	156 (2)	(c)
Cl ₃ SiOSiCl ₃	ED	1.593 (10)	146 (4)	(d)
Ph ₃ SiOSiPh ₃	X-ray	1.616 (1)	180*	(e)

References: (a) Almenningen *et al.* (1963); (b) Csakvari, Wagner, Gömöröy & Mijlhoff (1976); (c) Airey *et al.* (1970); (d) Airey, Glidewell, Robiette & Sheldrick (1971); (e) Glidewell & Liles (1978).

* Crystallographic C₁ symmetry.

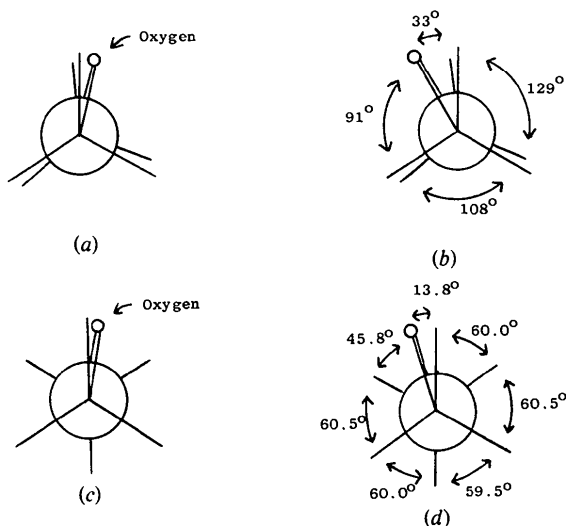


Fig. 4. (a) Fully eclipsed C_{2v} model viewed along the Si...Si vector. (b) Representation of SiH₃OSiH₃ to show the oxygen conformation. The torsion angles H—Si...Si—H are idealized to 0° [see Table 2(c)]. (c) Staggered C₃ model viewed along the Si...Si vector. (d) Representation of Me₃SiOSiMe₃ to show the oxygen conformation. The torsion angles C—Si...Si—C are idealized to 180° [see Table 5(c)].

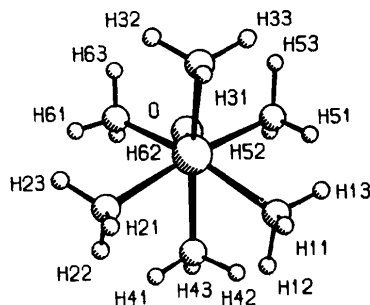


Fig. 5. Molecule of Me₃SiOSiMe₃ viewed along the Si...Si vector.

both species the oxygen atom lies out of the plane of (approximate) mirror symmetry. The distortion takes the form of a cylindrical rotation of oxygen about the Si...Si vector. In disiloxane the oxygen is rotated by some 33° from the symmetric position while in hexamethyldisiloxane the rotation is about 14°. The situations are illustrated in Fig. 4(b) and (d).

The different molecular conformations might be the result of intramolecular H...H interactions. In disiloxane the shortest H...H interaction across the molecule is H(1)...H(6) at 3.14 Å; but in hexamethyldisiloxane the shortest interactions of this type are H(12)...H(42), 2.70 Å, and H(22)...H(41), 2.96 Å, and adoption of an eclipsed (disiloxane type) conformation would further increase the number of short H...H contacts. One further observation also suggests that methyl...methyl interactions might be important in hexamethyldisiloxane: the O—Si—C angles show a gradation in value that correlates with a qualitative estimate of the probable methyl...methyl interactions across the length of the molecule. Thus the angles assume values such that O—Si(2)—C(4) > O—Si(1)—C(1) ≈ O—Si(1)—C(2) > O—Si(2)—C(5) ≈ O—Si(2)—C(6) > O—Si(1)—C(3). If methyl...methyl interactions are important then, from a simple qualitative point of view, the relative magnitudes of these angles can be predicted purely by inspection of Figs. 2 and 5.

(c) Intermolecular geometry

Disiloxane molecules are linked together in the crystal by rather long Si(2)...O intermolecular contacts (see Figs. 1 and 6). The interaction appears to cause very specific molecular alignment though the Si(2)...O distance, 3.115 Å, implies that it is weak. The O...Si(2)—O grouping is effectively linear, while the O...Si(2) vector almost exactly bisects the Si(1)—O—Si(2) angle. Furthermore, the oxygen atom is coplanar with its two close and one distant Si atom neighbours. It should be noted that Si(1) is not involved in any intermolecular interaction.

Although five-coordinated silicon has been structurally characterized (*e.g.* Rudman, Hamilton, Novick & Goldfarb, 1967; Párkányi, Nagy & Simon, 1975, and references therein), it is somewhat surprising to find a donor-acceptor interaction of this type here since the

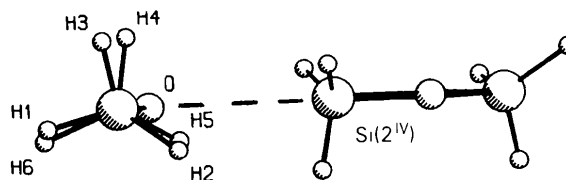


Fig. 6. Molecule of SiH₃OSiH₃ viewed along the Si...Si vector and showing the O...Si(2^{IV}) interaction.

silyl group is not a good acceptor and the oxygen atom in disiloxane is a poor donor towards such acceptors as trimethylboron. If we equate the $O \cdots Si(2)$ interaction with the incipient S_N2 reaction situation, as has been suggested for other crystalline state intermolecular interactions (Bürgi, 1975), then we expect distortions to the intramolecular geometry at Si(2), but not at Si(1). Specifically, the Si(2)—O bond is expected to lengthen and the O—Si(2)—H angles to narrow. We do not observe these distortions: the Si(2)—O and Si(1)—O bonds are of equal length, and although $\angle O-Si(2)-H$, 102° (average), is less than $\angle O-Si(1)-H$, 108° (average), the difference is within experimental error. The situation here is in contrast to that for crystalline silyl isocyanate (Barrow, Cradock, Ebsworth & Harding, 1977) where a lengthening of the Si—N bond compared with the gas-phase ED value apparently correlates well with the presence of a weak axial $N \cdots Si$ interaction in the solid state. We assume that in crystalline disiloxane the $O \cdots Si(2)$ interaction is strong enough to effect an alignment of the molecules but too weak to affect the intramolecular geometry by any significant extent.

In crystalline hexamethyldisiloxane the molecules exist as discrete entities and there are no specific intermolecular contacts involving Si or O atoms. This is in keeping with the general observation that methylation at silicon sharply reduces the σ -acceptor character of the silicon atom. Here also the six methyl groups appear to shield the Si—O—Si core from neighbouring molecules.

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The Crystal and Molecular Structure of 2,4-Di-*tert*-butyl-6-methyl-*N*-thiosulphinylaniline

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Abstract

The crystal and molecular structure of 2,4-di-*tert*-butyl-6-methyl-*N*-thiosulphinylaniline has been determined by X-ray diffraction. Crystals are monoclinic, the space group is $P2_1/a$ with cell dimensions: $a = 19.050$ (6), $b = 9.614$ (2), $c = 10.084$ (3) Å, $\beta = 118.25$ (3) $^\circ$, and $Z = 4$. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The final R value was 0.057. The molecule has a —N=S=S group. The S=S and N=S double-bond distances are 1.898 (2) and 1.548 (3) Å, respectively, and C—N=S and N=S=S bond angles are 126.4 (3) and 119.7 (1) $^\circ$, respec-

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