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## AN ELECTRON DIFFRACTION STUDY OF THE MOLECULAR STRUCTURE OF HEXAMETHYLDISILOXANE

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### Summary

An electron diffraction determination of the molecular geometry of hexamethyldisiloxane has removed much of the uncertainty concerning this structure. The length of the Si—O bond and the Si—O—Si bond angle were determined to be  $1.631 \pm 0.003$  Å and  $148 \pm 3^\circ$ , respectively. The experimental data are consistent with a staggered conformation ( $C_{2v}$  symmetry) while a model with twist angles around the Si—O bonds of about  $30^\circ$  cannot be excluded. The molecule is probably performing large amplitude intramolecular motion.

### Introduction

It has been noted repeatedly (see e.g. refs. 1 and 2) that when the two ligands of the oxygen atom are silicon, the oxygen bond angle is markedly greater than it is in molecules in which the ligands are carbon atoms.

Accurate electron diffraction determinations of the molecular geometry of disiloxane,  $H_3SiOSiH_3$ , as well as of other compounds have been available for some time (see Table 2). On the other hand, the results of early electron diffrac-

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tion studies [3,4] by the visual technique have represented the only direct geometrical information for vapour phase hexamethyldisiloxane,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ . The relatively large uncertainties (e.g.  $\angle\text{Si}-\text{O}-\text{Si}$   $130 \pm 10^\circ$  [3],  $137 \pm 7^\circ$  [4]) restricted the value of these, but they are much cited (e.g. [5]). Also, although many of the studies by the visual technique have withstood a comparison with up-to-date methods concerning geometrical parameters, it is the case that erroneous results are more probable for molecules that perform large amplitude motion. We considered that the reinvestigation of the hexamethyldisiloxane molecular structure by an up-to-date technique of electron diffraction was overdue.

## Experimental

A commercial sample of hexamethyldisiloxane (b.p.  $100.4^\circ\text{C}/760\text{ mmHg}$ ) was used after purification by fractional distillation. No appreciable amount of impurity could be detected by gas chromatography.

The Balzers KD-G2 apparatus of the Leiden laboratory was used to take the electron diffraction patterns during a visit by one of us (I. H.). The sample container and the nozzle were kept at temperatures of  $50^\circ\text{C}$  and  $65^\circ\text{C}$ , respectively. Three times three plates were chosen for analysis for the 50, 25 and 11 cm camera distances. For the other experimental conditions see e.g. [6].

The usual Leiden procedure [7] was used to obtain the total experimental intensities in the ranges  $3.50 \leq s \leq 14.50 \text{ \AA}^{-1}$ ,  $4.75 \leq s \leq 28.75 \text{ \AA}^{-1}$ , and  $15.75 \leq s \leq 33.00 \text{ \AA}^{-1}$  with a data interval  $\Delta s = 0.25 \text{ \AA}^{-1}$ .

The usual Budapest procedure (see e.g. [8]) was used for obtaining and eventually improving the experimental backgrounds, and all the further analysis was performed in Budapest. The reduced experimental molecular intensities \* corresponded to the expression  $sM^E(s) = s[I(s)-B(s)]/B(s)$ . Here  $I(s)$  is the total experimental intensity and  $B(s)$  is the experimental background. The composite molecular intensity distribution is shown in Fig. 1.

## Structure analysis

### Model

In most, though not all, models it was assumed that the molecule possesses two symmetry planes, one perpendicular to the SiOSi plane and bisecting the Si-O-Si angle and the other coinciding with the SiOSi plane ( $C_{2v}$  symmetry). In some models this symmetry was reduced by twisting the  $\text{OSi}(\text{CH}_3)_3$  fragments around the Si-O bonds, either with equal angles in the same direction if looking from the oxygen atom ( $C_2$  symmetry) or with two different angles, one of them being zero. The threefold axis of the  $\text{Si}(\text{CH}_3)_3$  fragment was usually considered to coincide with the Si-O bond. In all models the threefold axis of the  $\text{CH}_3$  group coincided with the Si-C bond, and the conformation of the  $\text{OSi}(\text{C}_2)\text{CH}_3$  fragment was such that the C-H bonds staggered the silicon bonds. Fig. 2 shows a model in which the Si-C bonds of the  $\text{OSiC}_3$  fragment stagger the other Si-O bond ( $C_{2v}$  symmetry).

\* The numerical data are listed in ref. 19.

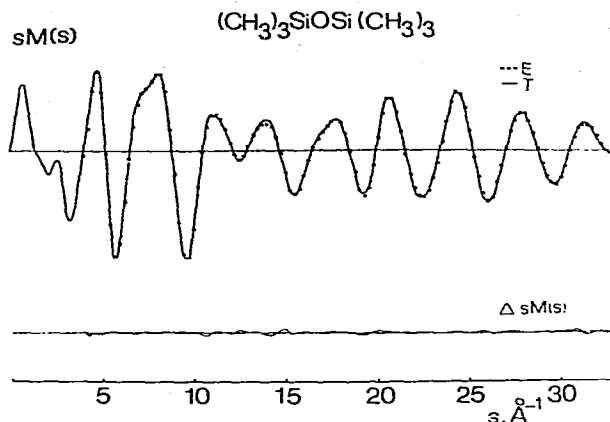


Fig. 1. Experimental (E, dots) and theoretical (T, full line) molecular intensities and difference curve ( $\Delta sM(s)$ ) for hexamethyldisiloxane. T and  $\Delta$  refer to model II of Table 1.

The following independent parameters were chosen to describe the geometry:

$$\begin{array}{lll}
 r(\text{C-H}) & \angle \text{H-C-H} & \phi_1 \\
 r(\text{Si-O}) & \angle \text{Si-O-Si} & \phi_2 \\
 r(\text{Si-C}) & \angle \text{C-Si-C} & 
 \end{array}
 \left. \vphantom{\begin{array}{l} \phi_1 \\ \phi_2 \end{array}} \right\} \begin{array}{l} \text{angles of twist} \\ \text{around the Si-O bonds} \end{array}$$

#### Experimental distributions

The molecular intensity distributions calculated for models with a series of different  $\angle \text{Si-O-Si}$  values indicated some sensitivity to this parameter in the region of  $s = 5$  to  $10 \text{ \AA}^{-1}$ . These early comparisons with the experimental data seemed to favour a larger angle than that derived from the visual studies\*.

Somewhat more information could be derived from the experimental radial distribution (Fig. 3). The features at 1.10, 1.63, 1.86, and 2.48  $\text{\AA}$  could be assigned to the C-H, Si-O, and Si-C bonds, and the Si...H nonbond distances (through one bond angle), respectively. These values could then be used in the trial structures. The data on  $r(\text{C-H})$ ,  $r(\text{Si-C})$ , and  $r(\text{Si...H})$  gave  $110.6^\circ$  for the H-Si-C angle\*\* and by virtue of symmetry  $108.3^\circ$  for  $\angle \text{H-C-H}$ .

#### Refinements and results

The least squares method was applied to the molecular intensities in a similar manner as for instance in refs. 8 and 10. The sources of the scattering functions were the same as in ref. 6.

Without describing all the refinement schemes and partial results, we mention below a few features of the refinements.

Because of strong correlation between the bond angles Si-O-Si and C-Si-C, very often one of the two angles was kept constant while the other refined. Values in a wide range have been tested and the various schemes included the mean vibrational amplitudes for many of the more important distances as independent

\* It is interesting to note, however, that Yokoi [3] found the experimental radial distribution to indicate either  $120^\circ$  or  $150^\circ$  for the angle Si-O-Si.

\*\* The bond angle H-Si-C was found to be  $110.5^\circ$  in  $(\text{CH}_3)_3\text{SiOCH}_3$ , see [9].

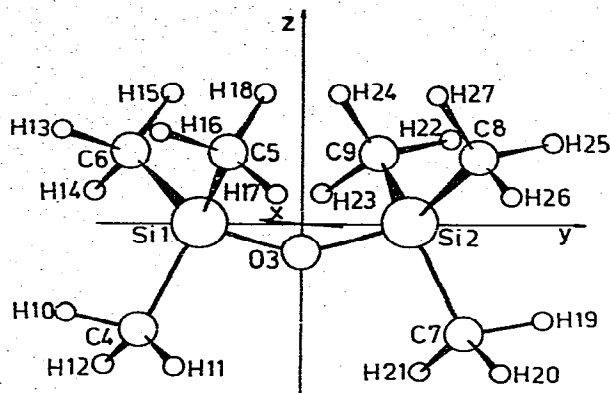


Fig. 2. The model for hexamethyldisiloxane with numbering of the atoms.

parameters. The best combinations of values for  $\angle \text{Si-O-Si}$  and  $\angle \text{C-Si-C}$  appeared to be around  $150^\circ$  and  $110^\circ$ , respectively. In these calculations it was assumed that the Si-C bonds of the  $\text{OSi}(\text{CH}_3)_3$  fragment stagger the other Si-O bond ( $C_{2v}$  symmetry,  $\phi_1 = \phi_2 = 0$ ).

As seen on the radial distributions of Fig. 3, very good agreement was achieved, and the results are presented in column I of Table 1. A closer inspection of the radial distributions reveals some slight discrepancies, however, most notably in the region where the *anti* type  $\text{Si} \cdots \text{C}$  interactions appear ( $\sim 4.4 \text{ \AA}$ ), viz., the *anti* Si  $\cdots$  C distances of the model seem to contribute at larger  $r$  values than the experimental curve would suggest.

To eliminate this discrepancy, one possible approach is to introduce twist angles  $\phi$  different from zero. Since such a model contained a very large number of dependent distances, some of the  $\text{C} \cdots \text{H}$  interactions were ignored. A model with  $\phi_1 = \phi_2 = 30^\circ$  gave better agreement than employing other twist angles including  $\phi_1 = \phi_2 = 0^\circ$  as calculated with the same conditions [ $R(\phi_1 = \phi_2 = 30^\circ) = 0.074$  vs.  $R(\phi_1 = \phi_2 = 0^\circ) = 0.086$ , see footnote *g* to Table 1]. While the twist angles,

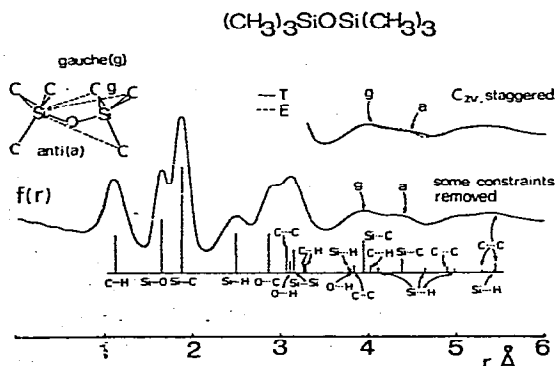


Fig. 3. Experimental (E, dotted line) and theoretical (T, full line) radial distributions for hexamethyldisiloxane. The lower and upper curves refer to Models I and II, respectively, of Table 1. The vertical bars represent contribution from interatomic distances to the radial distribution.

TABLE 1

THE RESULTS OF THE LEAST-SQUARES REFINEMENTS FOR HEXAMETHYLDISILOXANE

 $r$  and  $l$  values in Å, angles in degrees.

	$C_{2v}$ symmetry (I)	Partially removed geometrical constraints (II)	
		Parameters	Total errors <sup>a</sup>
<i>Independent parameters</i>			
$r_a(\text{Si—O})$	1.629	1.631	0.003
$l(\text{Si—O})$	0.039	0.039	0.001
$r_a(\text{Si—C})$	1.866	1.865	0.004
$l(\text{Si—C})$	0.056	0.055	0.001
$r_a(\text{C—H})$	1.104	1.102	0.003
$l(\text{C—H})$	0.081	0.078	0.002
$\angle\text{Si—O—Si}$	151.7	148.0	3.0 <sup>b</sup>
$\angle\text{C—Si—C}$	110.0	109.8	0.2
$\angle\text{H—C—H}$	108.3 (not varied)	108.3 (not varied)	
$r_a(\text{Si} \cdots \text{C})$ <i>anti</i>		4.37 <sup>c</sup>	0.02
$l(\text{Si} \cdots \text{C})$ <i>anti</i>	0.177	0.127 <sup>d</sup>	0.010
$r_a(\text{Si} \cdots \text{C})$ <i>gauche</i>		3.94 <sup>c</sup>	0.03
$l(\text{Si} \cdots \text{C})$ <i>gauche</i>	0.29	0.24 <sup>e</sup>	0.03
$r_a(\text{C4} \cdots \text{C8})$		5.44 <sup>c</sup>	0.06
$l(\text{C4} \cdots \text{C8})$		0.26	0.06
$l(\text{Si} \cdots \text{Si})$	0.080	0.078	0.004
$l(\text{O} \cdots \text{C})$	0.088	0.089	0.003
$l(\text{C4} \cdots \text{C5})$	0.107	0.130	0.012
$l(\text{C5} \cdots \text{C8})$	0.24	0.32 <sup>e</sup>	0.03
$l(\text{Si} \cdots \text{H10})$	0.122	0.121	0.004
$l(\text{Si} \cdots \text{H20})$	0.227	0.357 <sup>d</sup>	0.012
$l(\text{Si} \cdots \text{H24})$	0.30	0.39 <sup>e</sup>	0.03
<i>Dependent angles</i>			
$\angle\text{O—Si—C}$		109.1	0.2
$\angle\text{Si—C—H}$	110.6	110.6 <sup>f</sup>	
<i>Generalized</i>			
$R$ factor <sup>g</sup>	0.071	0.056	

<sup>a</sup> For distances:  $\sigma_r = [2 \sigma_{\text{LS}}^2 + (0.002 r)^2]^{1/2}$ ; for angles:  $\sigma_L = \sqrt{2} \sigma_{\text{LS}}$ ; for  $l$  values:  $\sigma_l = [2 \sigma_{\text{LS}}^2 + (0.02 l)^2]^{1/2}$ ;  $\sigma_{\text{LS}}$  is the standard deviation in the least-squares refinement. <sup>b</sup> The value calculated by the formula given in the footnote a would be 0.7°, see text. <sup>c</sup> If calculated from the bond lengths and bond angles, the values of 4.48, 3.93, and 5.43 Å, respectively, would correspond to the geometrical model. <sup>d, e</sup> The respective  $l$  values were coupled in the refinement. <sup>f</sup> Determined from the C—H, Si—C, and Si...H distances. <sup>g</sup>  $R = \{ \sum [sM^E(s) - sM^T(s)]^2 / \sum [sM^E(s)]^2 \}^{1/2}$ , where  $sM^T(s)$  is the theoretical molecular intensity.

though tested between 0° and 60°, have not been varied in these calculations, the bond angle Si—O—Si was allowed to vary. The value of 148.8° was obtained for the model with  $\phi_1 = \phi_2 = 30^\circ$ .

Another approach for improving the agreement between the experimental and theoretical data was to have as many as possible important rotation-dependent nonbond distances to refine independently. In this case the conditions of refinement were the same as for the  $C_{2v}$  symmetry model. The results of such a refinement with both *anti* and *gauche* Si...C distances and also the C4...C8 distances added to the independent geometrical parameters are presented in col-

umn II of Table 1. Here again the bond angle Si—O—Si refined to a smaller value than in the model with more geometrical constraint.

## Discussion

We believe that the present study removed much of the uncertainty about the molecular structure of hexamethyldisiloxane. The geometrical parameters determined show no unexpected features, as shown by the comparisons with those of analogous molecules in Table 2. The value determined for  $\angle$ Si—O—Si is also in good agreement with results from other physical techniques (for a compilation see e.g. [5]).

The present results also indicate that the hexamethyldisiloxane molecules perform large amplitude motion including the twisting motion around the Si—O bonds. In such a case the bond angles determined directly from the electron diffraction data without corrections for the intramolecular motion have no well-defined physical meaning [11] and should be used with caution.

In addition, the determination of the bond angle Si—O—Si in hexamethyldisiloxane requires some comment. The relaxation of the molecular geometry from the strictly symmetrical arrangement either by introducing non-zero twist angles or by letting some nonbond distances vary, not only improved the agreement between the experimental and theoretical distributions\*, but also led to a decrease in the value of  $\angle$ Si—O—Si. It does not seem to be possible on the basis of the electron diffraction data alone to decide between a  $C_{2v}$  symmetry model with large amplitude twisting motion and a  $C_2$  symmetry model with considerable twist angles\*\*. It is important, however, that the determination of the bond angle Si—O—Si should not be influenced by the choice of the model.

Of the two approaches used, the one with nonzero twist angles is less complete because of ignoring some C...H interactions. Although we prefer the bond angle that was determined by independently refining some nonbond distances,

TABLE 2

THE VALUES OF  $r_a(\text{Si—O})$  AND  $\angle$ Si—O—Si IN SOME DISILOXANE AND CYCLOSILOXANE MOLECULES

Compound	$r_a(\text{Si—O})$ (Å)	$\angle$ Si—O—Si (degrees)	Ref.
(H <sub>3</sub> Si) <sub>2</sub> O	1.634 ± 0.002	141.1 ± 0.9	1
[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> O	1.631 ± 0.003	148 ± 3	present work
(Cl <sub>3</sub> Si) <sub>2</sub> O	1.592 ± 0.010	146 ± 4	14
(F <sub>3</sub> Si) <sub>2</sub> O	1.580 ± 0.025	156 ± 2	13
[H <sub>2</sub> SiO] <sub>4</sub>	1.628 ± 0.004	148.6 ± 1.2	18
[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>3</sub>	1.635 ± 0.002	131.6 ± 0.4	17
[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>4</sub>	1.622 ± 0.003	144.8 ± 1.2	17
[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>5</sub>	1.620 ± 0.002	146.5 ± 1.2	17
[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>6</sub>	1.622 ± 0.002	149.6 ± 1.4	17

\* Introducing a tilt of the threefold axis of the Si(CH<sub>3</sub>)<sub>3</sub> fragment from the Si—O bond could also be considered; however this would substantially decrease the *gauche* Si...C distance before the correct *anti* distance was reached. A possible solution may be a combination of twist and tilt.

\*\* A detailed discussion of a similar case for C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl has been given recently [12].

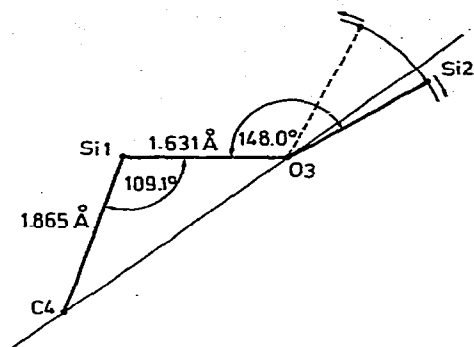


Fig. 4. The  $\text{Si2} \cdots \text{C4}$  distance would take its largest value if atoms  $\text{C4}$ ,  $\text{O3}$  and  $\text{Si2}$  were collinear, i.e. for an angle  $\text{Si-O-Si}$  of  $142^\circ$ . A decrease of the distance (as arrows indicate) involves either a decrease or an increase of the angle, depending on the magnitude of the latter.

partly because of the previously mentioned uncertainty, we propose to establish a larger error, viz.  $3^\circ$ , for  $\angle \text{Si-O-Si}$  than would follow from the usual estimation.

It has been repeatedly stated [13,14] that the angles determined by electron diffraction are probably too small if no allowance is made for shrinkage. On the other hand, twist and tilt angles have been involved to better approximate experimental data on perfluorodisiloxane [14] and perchlorodisiloxane [15]. Vilkov and Khaikin [2] pointed out that the observed structures of  $\text{F}_3\text{SiOSiF}_3$  and  $\text{Cl}_3\text{SiOSiCl}_3$  may appear with near  $C_2$  symmetry as a consequence of the low-frequency twisting vibrations of a  $C_{2v}$  symmetry equilibrium structure.

As for the effect of ignoring the influence of intramolecular vibrations in determining the geometrical parameters the following observation from the present study may be of interest. The experimental shortening of the *anti*  $\text{Si} \cdots \text{C}$  distance as a consequence of twisting motion tends to increase (and not decrease!) the  $\text{Si-O-Si}$  bond angle if a strictly staggered ( $C_{2v}$ ) model is employed. As is illustrated by the simple drawing of Fig. 4, the shortening of the *anti*  $\text{Si} \cdots \text{C}$  distance in the planar skeleton  $\text{C4-Si1-O3-Si2}$  corresponds to an increase of the bond angle  $\text{Si-O-Si}$  if it is larger than, roughly,  $142^\circ$  and to a decrease if it were smaller than  $142^\circ$ , for the geometrical arrangement given in Fig. 4. Thus it is not always obvious and cannot be stated in general how a shrinkage effect would influence the determination of a geometrical parameter like  $\angle \text{Si-O-Si}$  in such a system.

Returning to the question of possible stereochemical implications of the value of  $\angle \text{Si-O-Si}$  determined in  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , it is noteworthy that it is somewhat larger than in  $\text{H}_3\text{SiOSiH}_3$  which may be an indication of the influence of steric interactions. There is a much larger difference between the angles  $\text{Ge-O-Ge}$  in  $\text{H}_3\text{GeOGeH}_3$  ( $126.5 \pm 0.4^\circ$ ) [15] and  $(\text{CH}_3)_3\text{GeOGe}(\text{CH}_3)_3$  ( $141.0 \pm 0.5^\circ$ ) [16]. Comparing the hexamethyldisiloxane structure with those of cyclic methylsiloxanes determined by Oberhammer, Zeil and Fogarasi [17], it is seen that as the ring strain is lessened the endocyclic bond angle  $\text{Si-O-Si}$  gets closer to that observed in  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ .

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