

The Molecular Structure of Disiloxane, $(\text{SiH}_3)_2\text{O}$ *

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The structure of gaseous disiloxane (disilyl ether) has been studied by electron diffraction. The Si—O—Si angle is extraordinarily large, in agreement with conclusions from infrared and Raman spectroscopy, and with results of an earlier electron-diffraction investigation. The structural results derived from a least squares analysis based on intensity curves are as follows. $r_{\text{Si-H}} = 1.486 \pm 0.010$ Å, $r_{\text{Si-O}} = 1.634 \pm 0.002$ Å, $r_{\text{Si...Si}} = 3.107 \pm 0.009$ Å, $r_{\text{O...H}} = 2.556 \pm 0.021$ Å., $\angle \text{Si-O-Si} = 144.1^\circ \pm 0.8_6^\circ$, $\angle \text{H-Si-O} = 109.9^\circ \pm 1.2_6^\circ$, $\angle \text{H-Si-H} = 109.1^\circ \pm 1.2_9^\circ$. $l_{\text{Si-H}} = 0.076_3 \pm 0.008_7$ Å, $l_{\text{Si-O}} = 0.038_8 \pm 0.002_0$ Å, $l_{\text{Si...Si}} = 0.093_2 \pm 0.008_2$ Å, and $l_{\text{O...H}} = 0.080_1 \pm 0.018_1$ Å. The standard errors contain estimates of systematic errors. The large Si—O—Si bond angle and the short Si—O bond distance are most likely due to conjugation of unshared electron pairs on the oxygen atom with *d* orbitals from the silicon atom.

The angles formed by bonds to oxygen atoms ordinarily have values in the range 105° — 125° corresponding to what is expected from hybrid orbitals composed largely of *s* and *p* atomic orbitals. When the two ligands are silicon atoms, however, as in the silicates, an average value of 140° is observed¹ and examples of 150° — 160° are not uncommon. The bond lengths, too, are suggestive of an unusual bonding situation, being in general shorter than the covalent radius sum for oxygen and silicon. An obvious and plausible explanation of these large angles and shortened distances may be made in terms of conjugation of unshared electron pairs on the oxygen atoms with *d* orbitals from the silicon atoms. A similar suggestion has been advanced in explanation of the coplanar heavy-atom structure and shortened Si—N distances in trisilyl amine,² where support for the idea is given by the non-basic character of the compound.

The structure of disiloxane (disilyl ether), the simplest molecule having an Si—O—Si grouping, is thus of special interest. The infrared and Raman

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spectrum has been extensively studied³⁻⁵ and the results indicate a large oxygen angle, as in the silicates. (The early report⁶ of a linear Si—O—Si configuration seems to have been based on spurious data⁷). This conclusion is supported by a preliminary electron-diffraction study⁸ in which the angle was found to be 141° . The current work was undertaken to determine accurately the values for distances, bond angles, and amplitudes of vibration.

EXPERIMENTAL AND DATA REDUCTION

Samples of disiloxane were obtained from Dr. D. W. Robinson of Johns Hopkins University, U.S.A. and Dr. D. C. McKean of the University of Aberdeen, Scotland. The electron-diffraction intensity data were obtained with the Oslo electron diffraction camera.⁹ Diffraction diagrams were taken using nozzle-to-plate distances of approximately 49, 18, and 12 cm, at nozzle temperature of about 20°C . The usual corrections and background subtraction were carried out in order to obtain the molecular intensity curve.¹⁰ The atomic form factors were those of Ibers¹¹ ($s \geq 9$) and Viervoll and Øgrim¹² ($s > 9$). The final background was based upon information from the theoretical background and upon corrections deduced from a trial structure very close to the final structure. As is usually found in this laboratory the background corrections that had to be made on the preliminary background were rather small. The resulting experimental intensity curve is shown in Fig. 1.

STRUCTURE ANALYSIS, REFINEMENT, AND FINAL RESULTS

Several radial distribution curves were calculated¹³ from the observed intensity curve using different damping factors; one of these is shown in Fig. 2. All interatomic distances except the long Si...H (which are apparently "smeared out" in the range $3.5\text{--}4.2 \text{ \AA}$) were located accurately from these curves, and the usual analysis of the peaks in terms of Gaussians led to the results in the first column of Table 1.

The diffraction results leave no doubt about the nonlinearity [of the Si—O—Si skeleton. The nearly symmetric, not unusually broad character of

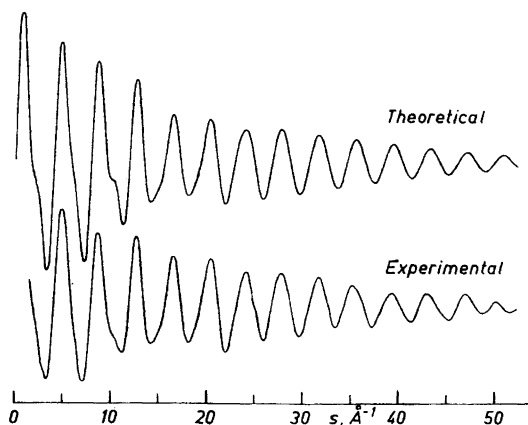


Fig. 1. Intensity curves. The theoretical curve was calculated from the least squares parameter values in Table 1.

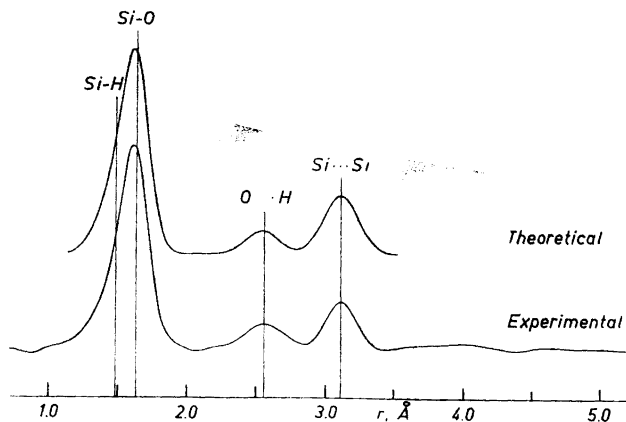


Fig. 2. Radial distribution curves. The experimental curve was calculated from the experimental intensity curve multiplied with $\exp(-0.0035 s^2)$. The theoretical curve was calculated from the least squares parameter values of Table 1 with each l value increased by $(2 \times 0.0035)^{1/2}$.

the Si...Si peak at about 3.10 Å rules out the linear equilibrium configuration which would require a peak centered near, but because of the "shrinkage effect" not exactly at, $2 \times r_{\text{Si-O}} = 3.27$ Å. This conclusion was verified by investigating the shape and position of the Si...Si peak to be expected in consequence of a very large bending amplitude for a linear Si—O—Si configuration. Assuming approximately harmonic behavior for the angular displacement it was found that even a rough fit to the observed Si...Si peak was quite impossible. Further, although it was not investigated, we are certain that no

Table 1. Parameter values with standard errors. Distances (r) and root-mean-square amplitudes of vibration (l) in Å; angles in degrees. k is an amplitude scale factor of no structural interest.

	Trial structure	Least squares refinement (a)	Final results (b)
k	—	$4.669_1 \pm 0.079_2$	4.669 ± 0.112
$r_{\text{Si-H}}$	1.4800	$1.486_5 \pm 0.006_8$	1.486 ± 0.010
$r_{\text{Si-O}}$	1.6334	$1.633_6 \pm 0.000_8$	1.634 ± 0.002
$r_{\text{Si...Si}}$	3.1075	$3.107_3 \pm 0.005_4$	3.107 ± 0.009
$r_{\text{O...H}}$	2.5436	$2.556_2 \pm 0.014_2$	2.556 ± 0.021
$l_{\text{Si-H}}$	0.090	$0.088_4 \pm 0.004_3$	$0.076_3 \pm 0.008_2$
$l_{\text{Si-O}}$	0.041	$0.041_4 \pm 0.000_8$	$0.038_9 \pm 0.002_0$
$l_{\text{Si...Si}}$	0.080	$0.093_2 \pm 0.004_5$	$0.093_2 \pm 0.008_2$
$l_{\text{O...H}}$	0.122	$0.083_4 \pm 0.011_6$	$0.080_1 \pm 0.018_1$
$\angle \text{Si-O-Si}$	144.1	$144.1 \pm 0.6_1$	$144.1 \pm 0.8_6$
$\angle \text{O-Si-H}$	109.5	$109.9 \pm 0.8_9$	$109.9 \pm 1.2_6$
$\angle \text{H-Si-H}$	109.5	$109.1 \pm 0.9_1$	$109.1 \pm 1.2_9$

(a) The 4th decimal is of no significance. The standard errors contain no estimates of systematic effects.

(b) The standard errors contain estimates of systematic effects.

remotely possible anharmonicity in this vibration would lead to an acceptable fit.

The trial structure was refined by least squares based on intensity curves, using the method previously described.¹⁴ H...H and non-bond Si...H terms were omitted and for other terms constant coefficients $A_n = nZ_iZ_jr_{ij}^{-1}$ were used. The refinement conditions included the data range $1.50 \leq s \leq 52.50$, data interval $\Delta s = 1/4$, and a weight function of unity. The results of the fourth cycle of refinement are given in the second column of Table 1, and the error matrix **M** is shown in Table 2.

The final results shown in the third column of Table 1 were obtained in the way described for disilyl sulfide.¹⁵ The corrections to the mean amplitude values, necessary because of the phase shift effect, were based on $B_{\text{Si-O}} = 1.0 \times 10^{-4} \text{ \AA}^2$, $B_{\text{Si-O}} = 1.0 \times 10^{-3} \text{ \AA}^2$, and $B_{\text{O-H}} = 2.7 \times 10^{-4} \text{ \AA}^2$.

DISCUSSION

The structure of disiloxane strongly resembles the structure of Si—O—Si groupings in the silicates as outlined in the introduction, and it would appear that the bonding picture must therefore also be similar. This picture may be plausibly interpreted in terms of conjugation of electrons from the oxygen atom to silicon atoms by use of *d* orbitals from the latter. The extent to which these oxygen electrons are involved may be roughly estimated from the observed bond shortenings and Pauling's semi-empirical relation involving "single-bond: triple-bond" resonance.¹⁶ We take as a fair estimate of the normal Si—O single-bond length the value $1.77 = 1.17 + 0.74 - 0.08[3.5 - 1.8]$ (this is the Schomaker-Stevenson¹⁷ radius sum with a slightly smaller electronegativity correction constant¹⁶). If the Si—O double-bond distance is now assumed to be $0.24 - 0.18 \text{ \AA}$ shorter, the observed Si—O distance corresponds to 30–60 % double-bond character. We conclude that the two lone electron pairs are each about 50 % involved in π bonding to the silicon atoms. It is interesting that the corresponding calculation for trisilylamine² led to the same estimate for that molecule. Since the *s*–*p* promotion energy for the valence shell of oxygen and nitrogen are about equal the agreement is not unexpected, despite the fact that in disiloxane two electron pairs are divided between two bonds and in trisilylamine one among three.

It is more difficult to draw quantitative conclusions about the π bonding from the values of the bond angles, but qualitative agreement with expectation is evident. If no conjugation existed one might look for an oxygen angle of about 110° ; if the oxygen electrons were completely conjugated the value should be 180° . The estimated 50 % conjugation and the observed 144° angle are clearly compatible.

Because of the presumed partial double-bond character of the Si—O bonds, the $-\text{SiH}_3$ groups would be expected to face a large rotational barrier and thus have preferred orientations. Unfortunately, the diffraction data do not settle this question. The radial distribution curve does provide clear indication of the long Si...H distances in the range $3.5 - 4.0 \text{ \AA}$ and the most obvious inter-

pretation of the distribution leads to C_{2v} molecular symmetry with one hydrogen on each $-\text{SiH}_3$ group nearest the 2-fold axis. However, we do not feel the data warrant this as a firm conclusion.

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