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The Molecular Structure of Gaseous Disilylmethane

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The structure of gaseous disilylmethane has been studied by electron diffraction. Results of various kinds of least-squares refinements are compared. The equilibrium conformation seems to have C_{2v} symmetry with rather large oscillations around the Si–C bonds. The SiCSi angle is considerably larger than the tetrahedral angle, *i.e.* 114.4(0.2)°. The bond distances (r_{a_1} values [1]) were r(Si–C) = 1.873(0.002) Å, r(Si–H) = 1.512(0.006) Å, and r(C–H) = 1.11(0.02) Å.

The molecular structures of some silyl compounds have previously been determined by electron diffraction by Almenningen *et al.*[2–4] The present investigation was undertaken because the Si–C stretching frequencies for disilylmethane indicated an interestingly large SiCSi bond angle, i.e. $\geq 116°$.[5]

EXPERIMENT AND THEORY

The sample of $(SiH_3)_2CH_2$ was kindly supplied by Dr. D. C. McKean, University of Aberdeen. The electron diffraction photographs were obtained in the usual way with the Oslo apparatus.[6,7] The nozzle temperature was about 15°C and the electron wavelength 0.064825 Å. Pictures were recorded at two nozzle-to-plate distances, *i.e.* 48.217 cm and 20.216 cm, giving intensity data in the s ranges 1.50–20 Å^{-1} and 7.0–44 Å^{-1}, respectively. The intensity data were read off at intervals $\Delta s = 0.125$ Å^{-1} and 0.25 Å^{-1}. Five plates from the first set and three plates from the latter set were used. The data were corrected in the usual way,[7] and the modified molecular intensities were calculated using the modification function [7]

$$s/(|f_{Si}'| \cdot |f_C'|)$$

Average intensities were calculated for each plate set (see Fig. 1). The data from the two nozzle-to-plate distances were scaled and combined into one composite intensity curve, which was used in the initial stage of the investigation.[7] The final least-squares calculations were carried out using the observed intensity data from the two plate sets simultaneously, but without combining the data to one curve. Since the quality of the data was not satisfactory for all s values, the curves used in the final stage covered the s ranges 2.0–18.5 Å^{-1} and 9.0–30.0 Å^{-1}.

The theoretical molecular intensities were calculated according to eqn. 10 of Ref. 7. The scattering amplitudes were calculated by the partial wave method [7,8] using Hartree-Fock potentials.[9]

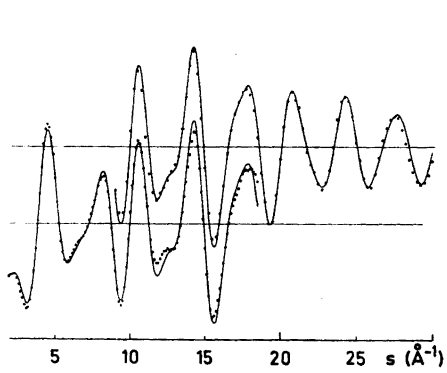

Fig. 1. Experimental (dotted) and theoretical intensity curves. The data corresponding to the two nozzle-to-plate distances are shown separately. The theoretical values have been calculated with the parameters given in the two last columns of Table 1.

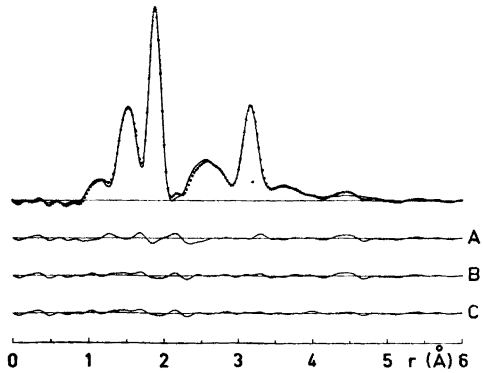

Fig. 2. The two upper curves show the experimental (dotted) and theoretical radial distribution functions. The theoretical curve was calculated with the parameters given in the two last columns of Table 1. An artificial damping constant [7] of 0.002 Å² was applied. Curve A shows the differences between the experimental and theoretical values. The differences between the experimental data and theoretical values calculated with the parameters in the two first columns of Table 1 are shown by Curve B. Curve C illustrates in the same way the agreement for a model with $\beta = \pm 15°$.

STRUCTURE ANALYSIS AND REFINEMENT

The experimental radial distribution (RD) function [7] calculated by Fourier transformation of the composite intensity curve is shown in Fig. 2. The Si – C distance corresponds to the dominant peak about 1.87 Å. The Si – H distances give the peak near 1.50 Å, and the C – H distances give the small inner peak. The complex between 2.3 and 2.9 Å contains contributions from the C···H distances as well as from the distances between Si and the H atoms in the methylene group. The non-bonded Si···Si distance corresponds to the peak near 3.15 Å. Fairly reliable values for most of the parameters were easily obtained from this curve.

The parameters were refined by various least-squares calculations. C_{2v} symmetry with four hydrogen atoms towards the twofold axis was assumed in most of the refinements. Further, we assumed no tilt of the silyl groups, and the mean amplitudes of vibration (u) for some nonbonded distances were assumed to be equal. The first column in Table 1 gives the results obtained using the composite intensity in the refinement. The values given in Table 2 are results from various calculations using the data from the two plate sets simultaneously, but not combined to one single curve.

The least-squares procedure leads to the normal equations ($\mathbf{B}\ \mathbf{X} = \mathbf{Y}$). The calculations are usually carried out with a diagonal weight matrix. How-

Table 1. Results obtained for the structural parameters in $(SiH_3)_2\ CH_2$. Mean amplitudes of vibration are denoted by u. The first set of results (*a*) corresponds to least-squares refinement on the composite experimental intensity curve obtained by combining the data from the two nozzle-to-plate distances. We regard the values in the second set as our final results. Standard deviations are given in parentheses.

	a		Final results	
	r_a (Å)	u (Å)	r_a (Å)	u (Å)
Si—C	1.875	0.0404	1.873 (0.002)	0.040 (0.003)
C—H	1.135	0.078[a]	1.11 (0.02)	0.078[a]
Si—H	1.516	0.088	1.512 (0.006)	0.085 (0.005)
Si···Si	3.152	0.082	3.149 (0.003)	0.080 (0.003)
Si···H_{met}	2.47	0.17	2.455 (0.013)	0.13 (0.012)
C···H	2.74		2.749 (0.017)	
Si···H	4.42	0.20	4.426 (0.012)	0.21 (0.03)
Si···H	3.49		3.498 (0.020)	
	angles (degrees)		angles (degrees)	
∠SiCSi	114.4		114.4 (0.2)	
∠HSiH	107.2		108.1 (1.1)	
∠HCH	110.0[a]		110.0[a]	

[a] Assumed values.

ever, the optimum weight matrix (which is the inverse of the moment matrix for the observations) contains non-zero off-diagonal elements if the data are correlated as the intensity data obtained by electron diffraction.[10] A diagonal weight may still be used to obtain estimates of the parameter. The corresponding standard deviations may also be calculated, but not simply from the diagonal elements of $\mathbf{B}^{-1}$ as is usually done. Table 2 gives some results obtained with two weight matrices, one diagonal and the other of the type discussed in Ref. 10. The latter matrix (**P**) has $P_{kl}=0$ if $|k-l|>2$, otherwise $P_{kl}=\sqrt{w_k w_l}\ p_j$, where $j=1+|k-l|$.* In all cases $p_1=1$, while the values applied for p_2 and p_3 are given in Table 2.

Table 2 shows that the inclusion of off-diagonal elements different from zero in the weight matrix gives only small changes in the parameters with u_4 as the only exception. However, the values given in parentheses in the table show more important differences. Accepting the matrix **P** described above as a reasonable approximation to the optimum weight matrix, the numbers in parentheses in the two last columns represent actual standard deviations, a term which should not be used for the corresponding values in the two first columns, since these results were obtained directly from the diagonal elements of $\mathbf{B}^{-1}$. The ratio between corresponding values ranges from 1.0 to 2.5, except for u_4 where the shift in the parameter is large. The ratio is larger for the bond distances than for the angles.

* w_k and w_i were close to 1 in these calculations, though the weights for the data near the ends of the curves were slightly reduced.

Table 2. Results of least-squares calculations using the data from the two nozzle-to-plate distances simultaneously without combining them to one intensity curve.

Diagonal weight matrices were assumed in I, the weight matrices used to obtain the results in II are described in the text and in Ref. 10. ($p_2 = -0.64$, $p_3 = 0.146$ for the long nozzle-to-plate distance, $p_2 = -0.60$, $p_3 = 0.125$ the short distance).

The values given in parentheses in II are standard deviations, the meaning of the corresponding values in I is discussed in the text.

One common scale factor (in the columns *a*) or two scale factors (in *b*) were applied as discussed in the text.

	I		II	
	a	b	a	b
r_a(Si−C)	1.8738 (0.0007)	1.8738 (0.0007)	1.8723 (0.0011)	1.8724 (0.0011)
r_a(C−H)	1.125 (0.0075)	1.125 (0.0075)	1.099 (0.0171)	1.101 (0.0174)
r_a(Si−H)	1.515 (0.0020)	1.515 (0.0021)	1.510 (0.0043)	1.509 (0.0043)
∠SiCSi	114.61 (0.12)	114.61 (0.12)	114.47 (0.19)	114.45 (0.18)
∠HCH	102.5 (4.9)	102.2 (5.2)	99.3 (6.1)	100.2 (6.0)
∠CSiH	108.59 (1.03)	108.29 (1.08)	107.99 (1.10)	108.05 (1.06)
u(Si−C)	0.0422 (0.0011)	0.0425 (0.0018)	0.0399 (0.0023)	0.0379 (0.0027)
u(Si−H)	0.0903 (0.0020)	0.0905 (0.0021)	0.0830 (0.0043)	0.0816 (0.0044)
u(Si···Si)	0.0802 (0.0016)	0.0804 (0.0018)	0.0807 (0.0024)	0.0793 (0.0025)
u_4[a]	0.161 (0.0136)	0.166 (0.0146)	0.095 (0.0089)	0.093 (0.0088)
u_5[a]	0.202 (0.0169)	0.201 (0.0168)	0.222 (0.0413)	0.221 (0.0413)
Scale	19.73 (0.24)		18.98 (0.57)	
Scale 1		19.77 (0.28)		19.39 (0.62)
Scale 2		19.86 (0.48)		18.17 (0.72)

[a] The mean amplitudes of vibration for Si···H_{met} and C···H were assumed equal (u_4), and the mean amplitudes for the longer Si···H distances were also refined together (u_5).

Table 2 also illustrates the difference in the results between two procedures for finding the scale between experimental and theoretical intensities. The experimental curves were first scaled by comparison of the values in the overlap region. The results obtained by refining one common scale factor were only slightly different from those obtained by refinements of separate scale factors.

The results given in the two last columns of Table 1 were used to calculate the theoretical intensity and RD curves shown in Figs. 1 and 2. These values may be regarded as our final results, since they are based on a number of refinements including those discussed above.

The theoretical RD curve (Fig. 2) deviates somewhat from the experimental values in the range 1.5 − 2.5 Å. This is clearly illustrated by curve A, which shows the differences between experimental and theoretical values. Much of this disagreement vanishes if the theoretical RD curve is calculated with the parameters in the two first columns of Table 1 (see Fig. 2, curve B), a fact that may be understood considering that these parameters as well as the experimental RD curve are based on the composite intensity curve. As Table 1 shows, the differences between the results in the two sets are small except for one u value (u(Si···H_{met}) = u(C···H)).

The refinements described above were all based on the assumption of C_{2v} symmetry. Models with the SiH_3 groups rotated an angle $\pm\beta$ around the Si–C bonds preserving the twofold symmetry axis, were also considered. Refinements of the most important parameters were carried out for fixed values of β, *i.e.* 5, 10, 15, and 20 degrees.* The minimum for [7]

$$S = \sum_k W_k (I_k^{obs} - \text{Scale} \times I_k^{theor})^2$$

was found for $\beta \approx 15°$, the ratio between S for $\beta = 0°$ and S for $\beta = 15°$ being 1.125. The square root of this number may be used in Hamilton's R factor test [11] for the significance of this result. It is thus found that the model with $\beta = 0$ may be rejected at the 1 % level. However, it seems very likely that the equilibrium structure corresponds to $\beta = 0$, while the value obtained for β indicates fairly large oscillations around the Si–C bonds. The differences between the experimental RD curve and the theoretical curve corresponding to $\beta = 15°$ are shown in Fig. 2 (curve C). Comparison of curves B and C reveals a slight improvement in the outer part of the difference curve when β is changed from 0 to 15°.

DISCUSSION

The SiCSi angle in disilylmethane is considerably larger than the tetrahedral angle, and also larger than the CCC angle found in propane.[12] However, our result is somewhat smaller than predicted from the Si–C stretching frequencies.[5] Considering the large SiCSi angle it would have been interesting to have an accurate value for the HCH angle as well. However, by refining this parameter an unreasonably small value with a large standard deviation is obtained (Table 2).

A comparison of some SiXSi angles to the corresponding CXC angles is given below.

	∠SiXSi (degrees)	Ref.		∠CXC (degrees)	Ref.
$(SiH_3)_2O$	144	2	$(CH_3)_2O$	111.5	14,15
$(SiH_3)_2S$	97.4	3	$(CH_3)_2S$	98.9	16
$(SiH_3)_2Se$	96.6	4	$(CH_3)_2Se$	96.1	17
$(SiH_3)_3N$	120.0	13	$(CH_3)_3N$	110.6°	18
$(SiH_3)_2CH_2$	114.4	this work	$(CH_3)_2CH_2$	112.4	12

A large difference in the SiXSi and CXC angles is only observed when X has lone-pair electrons and belongs to the first row of the periodic table. The difference of about 2° in disilylmethane and propane may be due to repulsions arising from the short Si···Si distance of about 3.15 Å, which is shorter than in disilylsulphide (3.21 Å) an disilylselenide (3.40 Å).

The Si–C bond seems to be slightly longer than in methylsilane where Kilb and Pierce found 1.867 Å.[19] The difference may not be real considering

* The composite intensity curve and a diagonal weight matrix were applied in these calculations.

that the distances have been determined by different methods without recalculating the results to directly comparable values. The Si – H distance found in disilylmethane seems slightly longer than usually found in silyl groups.

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