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# The Molecular Structure of Gaseous Disilyl Sulfide, $(SiH_3)_2S$ *

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The structure of gaseous disilyl sulfide has been studied by electron diffraction. The molecule, in contrast to its analogue disiloxane ($(SiH_3)_2O$) has a normal bond angle at the apex atom. The parameter values obtained by a least squares refinement based on intensity data assuming harmonic molecular vibrations are $r_{SiS} = 2.136 \pm 0.002$ Å, $r_{SiH} = 1.494 \pm 0.008$ Å, $r_{Si...Si} = 3.210 \pm 0.019$ Å, $r_{S...H} = 2.974 \pm 0.065$ Å, $\angle SiSSi = 97.4 \pm 0.7°$, $\angle SSiH = 108.7 \pm 3.6°$, $\angle HSiH = 110.2 \pm 3.5°$, $l_{Si-S} = 0.045_6 \pm 0.001_9$ Å, $l_{Si-H} = 0.095_6 \pm 0.006_6$ Å, $l_{Si...Si} = 0.119_9 \pm 0.013_3$ Å, $l_{S...H} = 0.226_5 \pm 0.060_7$ Å. The standard errors include estimates of systematic effects. There is weak evidence that the molecule has symmetry $C_{2v}$ with two H atoms from each $-SiH_3$ group nearest the 2-fold axis as in dimethyl ether, but with greater rotational motion about the heavy-atom bonds.

The unusual structures of trisilylamine [1] and disiloxane [2] have been interpreted in terms of a type of bonding by which normally unshared electron pairs from the central atoms are conjugated to silicon atoms by use of *d* orbitals. Thus, the coplanar heavy-atom structure of trisilylamine and the extraordinary 144° oxygen bond angle in disiloxane are consistent with Si—N and Si—O bond distances, respectively, 0.06 Å and 0.13 Å shorter than the Schomaker-Stevenson radius sums corrected for electronegativity.[3] The question naturally arises as to whether this interesting bonding phenomenon is to be found in other, similar silicon compounds, and to help answer it we have undertaken an electron-diffraction investigation of gaseous disilyl sulfide, the sulfur analogue of disiloxane.

## EXPERIMENTAL AND DATA REDUCTION

The sample of disilyl sulfide was obtained from Drs. E. A. V. Ebsworth and D. C. McKean of the University of Aberdeen. It was distilled once under vacuum before use. No evidence of contamination was found in the diffraction data. Diffraction photographs

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were made in the usual way, using a rotating sector with angular opening proportional to $s^3$, in the Norwegian apparatus [4] at a nozzle temperature of about 20°C. The electron wave length was 0.06449 Å, and the two camera distances were 47.918 and 19.218 cm.

Four plates at each distance were selected for analysis, which was carried out essentially as described previously.[5] The experimental intensity curve (Fig. 1) contains the factor $Z_{Si}Z_S(Z - f)_{Si}^{-1}(Z - f)_S^{-1}$; it may be regarded, therefore, as represented by the equation

$$I = \sum_n A_n \cos \Delta\eta_n V_n \sin r_n s \tag{1}$$

where the coefficients $A_n$ differ slightly from constancy for all terms except Si—S. The dotted inner portion of the curve was obtained from theoretical intensity curves calculated according to eqn. (1): rough distance values for these were given by a radial distribution curve calculated from $I^{obs}$ without the inner portion. For sulfur and silicon the X-ray form factors of Tomiie and Stam [6] were used in the region $0 < s \leqq 19$, and of Viervoll and Ögrim [7] in the range $19 < s \leqslant 30$; extrapolated values were used for $s > 30$.

## PRELIMINARY STRUCTURE ANALYSIS

Experimental radial distribution curves were calculated according to the equation

$$P(r)/r = \sum_s I^{obs} \exp(-Bs^2) \sin rs$$

including the dotted inner portion of $I^{obs}$, using interval $\Delta s = 0.25$ and different values of the constant $B$ in the damping factor introduced to minimize series termination errors. One of these curves is shown in Fig. 2. The peaks at approximately 1.49Å and 2.14 Å are obviously due to Si—H and Si—S distances, and the asymmetric peak with maximum at about 3.20Å arises largely from the Si...Si and S...H interactions. Evidence of the long Si...H distances, which would permit determination of the orientation of the $-SiH_3$ groups, is almost non-existent, suggesting considerable freedom of rotation about the Si—S bond.

*Table 1.* Parametervalues (with standard errors) for $(SiH_3)_2S$. 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 |
|---|---|---|---|
| $k$ | — | $2.986_7 \pm 0.042_4$ | $2.987 \pm 0.060$ |
| $r_{Si-S}$ | $2.13_6$ | $2.136_0 \pm 0.000_5$ | $2.136 \pm 0.002$ |
| $r_{Si-H}$ | $1.49_5$ | $1.494_1 \pm 0.005_1$ | $1.494 \pm 0.008$ |
| $r_{Si...Si}$ | $3.18_3$ | $3.209_9 \pm 0.012_6$ | $3.210 \pm 0.019$ |
| $r_{S...H}$ | $2.98_1$ | $2.974_4 \pm 0.045_1$ | $2.974 \pm 0.065$ |
| $l_{Si-S}$ | $0.046_9$ | $0.045_8 \pm 0.000_7$ | $0.045_6 \pm 0.001_9$ |
| $l_{Si-H}$ | $0.099_0$ | $0.105_5 \pm 0.004_0$ | $0.095_6 \pm 0.006_6$ |
| $l_{Si...Si}$ | $0.124_0$ | $0.119_9 \pm 0.007_7$ | $0.119_9 \pm 0.013_3$ |
| $l_{S...H}$ | $0.149_0$ | $0.233_0 \pm 0.039_7$ | $0.226_5 \pm 0.060_7$ |
| ∠SiSSi | 96.3 | $97.4 \pm 0.5_1$ | $97.4 \pm 0.7_2$ |
| ∠SSiH | 109.1 | $108.7 \pm 2.5_5$ | $108.7 \pm 3.6_1$ |
| ∠HSiH | 109.8 | $110.2 \pm 2.4_7$ | $110.2 \pm 3.4_9$ |

*a*) standard errors contain no estimate of systematic effects.

If the longer Si...H distances are ignored, *i.e.*, they are assumed to be "washed out" by rotational motion, an analysis of the peaks of the radial distribution curve in terms of Gaussian peaks taken to represent the vibrational distribution of each remaining distance may be carried out. When this was done, the parameter values shown in the first column of Table 1 were obtained.

## STRUCTURE REFINEMENT

The essential features of the structure as revealed by the preliminary analysis are clear. However, it seemed worthwhile to carry out a least squares refinement by which error information could be obtained. The method, which is based upon intensity curves, has been described elsewhere.[8–10] The calculations were carried out at Oregon State University using three different sets of refinement conditions differing from each other in range of data and in weighting of the data. The model derived in the preliminary analysis was taken as the trial structure. H...H and Si...H terms were omitted, and for other terms constant coefficients $A_n = n_{ij} Z_i Z_j r_{ij}^{-1}$ were used. The results for each refinement were essentially the same. Those for the conditions $5.00 \leq s \leq 43.50$, $\Delta s = 0.25$, and unit weight for all observation are given in the second column of Table 1; the standard errors do *not* include estimates of systematic effects. The corresponding theoretical intensity and radial distribution curves are shown in Figs. 1 and 2.

The error matrix **M** shown in Table 2 has diagonal elements equal to the square of the standard errors assuming no correlation among the observations and ignoring systematic effects. Similarly, the off-diagonal elements are equal to the average product of the errors of the corresponding two parameters.

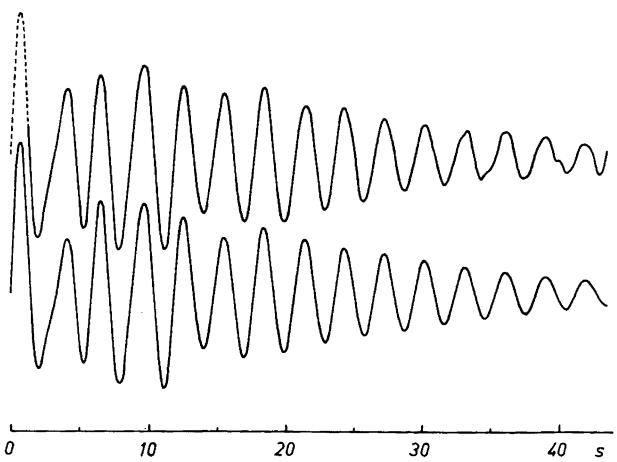


*Fig. 1.* Intensity curves. The dotted inner portion of the experimental curve was obtained from theoretical curves. The theoretical curve was calculated from the least squares parameter values in Table 1.

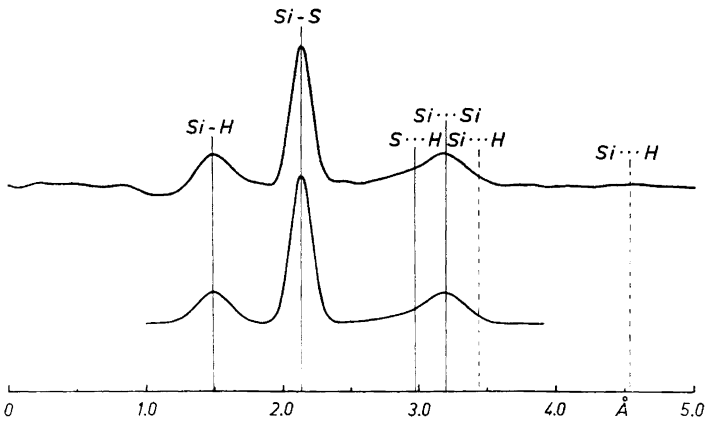


*Fig. 2.* Radial distribution curves. The experimental curve was calculated from the experimental intensity curve multiplied with $\exp(-0.0020s^2)$. The theoretical curve was calculated from the least squares parameter values of Table 1 with each $l$ value increased by $(2 \times 0.0020)^{\frac{1}{2}}$.

The bond angle parameters found in the error matrix were not adjusted in the least squares analysis, of course, but were calculated from the equation [9]

$$\mathbf{M} = S^2\mathbf{C}\mathbf{B}^{-1}\mathbf{C}'$$

## FINAL RESULTS

The best values of the distance parameters are just those found in the second column of Table 1. Except for $l_{\mathrm{Si...Si}}$, however, the mean amplitudes have values which include the effect of phase shift.[11] Corrected values may be gotten [5] from the equation

$$l_{ij}^2 = l_{\mathrm{obs}}^2 - 2B_{ij} \tag{4}$$

where $B_{ij}$ is estimated from the approximation

$$\cos(\eta_i - \eta_j) = \exp(-Bs^2) \tag{5}$$

using Ibers and Hoerni's table of values.[12] We find

$$B_{\mathrm{Si-S}} = 0.7 \times 10^{-5}\ \text{Å}^2,\ B_{\mathrm{Si-H}} = 1.0 \times 10^{-3}\ \text{Å}^2,$$
$$\text{and } B_{\mathrm{S...H}} = 1.5 \times 10^{-3}\ \text{Å}^2.$$

The standard errors found in the second column of Table 1 are unrealistic because they include no estimates of systematic errors. Plausible estimates of these may be made [5] and include (1) a doubling of each element of the error matrix to take account of correlation among the data, (2) an increase of $0.0005r_{ij}$ of each error associated with the distance $r_{ij}$ to take account of errors in measured values of wave length and camera distances, (3) an increase of $0.02\ l_{ij}$ of each mean amplitude to take account of errors in the photographic blackness correction and in the X-ray form factors.

*Table 2.* Error matrix (times $10^6$). $r$ and $l$ in Å, angles in degrees, $k$ is dimensionless. To include an estimate of correlation among the data all elements should be doubled.

| $k$ | $r_{Si-S}$ | $r_{Si-H}$ | $r_{Si...Si}$ | $r_{S...H}$ | ∠SiSSi | ∠SSiH | ∠HSiH | $l_{Si-S}$ | $l_{Si-H}$ | $l_{Si...Si}$ | $l_{S...H}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 800 | 0.597 | 24.8 | 93.2 | −578 | 3 750 | −33 700 | 32 700 | 20.5 | 44.8 | 35.9 | 473 |
| | 0.318 | −0.0637 | −0.124 | −1.77 | −24.5 | −113 | 110 | 0.0025 | 0.0317 | −0.0710 | −0.225 |
| | | 25.5 | 0.170 | 11.7 | 11.1 | −388 | 377 | 0.281 | −0.622 | 1.42 | 5.06 |
| | | | 160 | 84.6 | 6 490 | 4 770 | −4 630 | −1.00 | −3.59 | −21.8 | −0.369 |
| | | | | 2 040 | 3 550 | 115 000 | −111 000 | −6.48 | −20.4 | 121 | −246 |
| | | | | | 265 000 | 201 000 | −195 000 | −40.9 | −148 | −833 | −15 000 |
| | | | | | | $6.48 \times 10^6$ | $-6.29 \times 10^6$ | −377 | −1 130 | 6 760 | 14 100 |
| | | | | | | | $6.11 \times 10^6$ | 366 | 1 090 | −6 560 | 13 700 |
| | | | | | | | | 0.469 | 0.508 | 0.393 | 5.10 |
| | | | | | | | | | 16.3 | 1.02 | 17.7 |
| | | | | | | | | | | 59.4 | 98.1 |
| | | | | | | | | | | | 1 570 |

These considerations lead to our final results, shown in Table 1. Experience [9,13] suggests the mean amplitude values merit somewhat less confidence than the distance values. This is particularly true for $l_{Si...Si}$ and $l_{S...H}$ in disilyl sulfide, because the longer Si...H distances, which were ignored in the analysis are probably distributed over a region which includes the Si...Si and S...H peak. The error matrix provides fair estimates of correlation among the parameters, as given by the correlation coefficients

$$\varrho_{ij} = M_{ij}/\sigma_i\sigma_j \tag{6}$$

except possibly for elements involving $l_{Si...Si}$ and $l_{S...H}$. It and the third column of Table 1 constitute the fullest statement of our results.

## DISCUSSION

The general rule that multiple bonds are seldom formed between atomic pairs unless at least one is from the first row of the periodic table seems to apply also to disilyl sulfide. Thus, the single-bond radius sum for Si and S corrected for electronegativity [14] has a value in the range 2.15—2.17 Å, depending upon the value assigned to $c$ in the empirical equation $r_{Si-S} = 1.17 + 1.04 - c\,[2.5 - 1.8]$, in good agreement with the observed value of 2.136 Å for the Si—S distance. The sulfur bond angle, too, is in the normal range for two singly-bonded ligands, and one must, therefore, regard the over-all bonding picture as normal in disilyl sulfide in contrast to that in disiloxane and in trisilylamine.

An interesting question concerns the relative orientation of the silyl groups and the rotational potential barrier. Dimethyl ether was found by electron diffraction [15] and microwave spectroscopy [16] to have symmetry $C_{2v}$ with two hydrogen atoms from each methyl group nearest the 2-fold axis, and were both the structure and rotational barrier in disilyl sulfide similar, our data should surely have revealed the fact. As stated earlier, evidence of the longer Si...H distances is almost non-existent in the radial distribution curves, a fact we ascribe to their being "washed out" by a greater rotational freedom about the Si—S bonds. However, some indication of their presence does exist in the form of a very broad, low, positive bulge covering the region 4.3 — 4.8 Å and centered at 4.6 Å, the position corresponding to that the longest Si...H distance would have if the equilibrium configuration of the molecule were the same as found for dimethyl ether. The shorter of the long Si...H distances for this configuration would lie in a region obscured by the broad Si...Si and S...H peak.

Although the direct evidence cited above is meager, experience suggests it may very well be significant; we count it a strong possibility, therefore, that disilyl sulfide has an equilibrium configuration, including hydrogen atoms, similar to dimethyl ether, but with greater freedom of rotation around the heavy-atom bonds. Such a situation conforms qualitatively to what might be expected from the action of repulsive interaction between the electrons of the Si—S and Si—H bonds, and between H atoms on different silyl groups. Each of these effects lead to prediction of the suggested equilibrium configuration, and since the H atoms on different methyl groups in dimethyl ether are

considerably closer than would be the H atoms on different silyl groups in disilyl sulfide (2.3 Å *vs.* 3.0 Å), it is plausible that the rotational motion in the latter would be larger.

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