

The Molecular Structure of Gaseous Disilyl Selenide, (SiH₃)₂Se

A. ALMENNINGEN, L. FERNHOLT and H. M. SEIP

Department of Chemistry, University of Oslo, Oslo 3, Norway

The structure of gaseous disilyl selenide has been determined by electron diffraction. The bond angle at the apex atom is 96.6° with an estimated standard deviation of 0.7°. Very nearly the same angle has been found previously in disilyl sulfide, (SiH₃)₂S,¹ while the angle in disiloxane, (SiH₃)₂O, is much larger (144°).² The bond lengths (in terms of $r_g(1)$) were found to be: $r(\text{Si}-\text{Se}) = 2.273_8$ (0.0035) Å and $r(\text{Si}-\text{H}) = 1.516_3$ (0.0050) Å. The values in parentheses are standard deviations.

The agreement between the experimental and theoretical intensities is not best for a model with the expected C_{2v} symmetry, though this model cannot be excluded. A slightly better agreement is obtained by rotating the silyl groups about half the angle necessary to bring the molecule from one C_{2v} conformation to the other.

The molecular structures of disiloxane² and disilyl sulfide¹ have been determined previously. The SiOSi angle in disiloxane was found to be 144°. The Si—O bond was also found to be 0.13 Å shorter than estimated from the Schomaker-Stevenson rule.³ It was concluded that the Si—O bonds have partially double bond character. The SiSSi angle in disilyl sulfide was found to be 97.4° and the S—Si bond length suggested by the Schomaker-Stevenson rule was in good agreement with the observed value. These bonds seem therefore to be normal single bonds. Dimethyl selenide has, according to a recent microwave investigation,¹² C_{2v} symmetry as shown in Fig. 1.

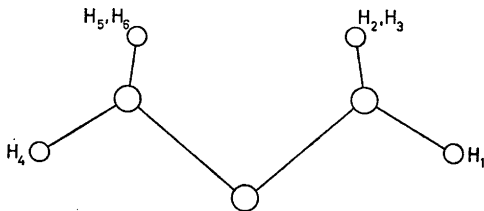


Fig. 1. Projection of a molecule (XH₃)₂Y with C_{2v} symmetry.

EXPERIMENTAL |

The sample of $(\text{SiH}_3)_2\text{Se}$ was obtained from Drs. D. C. McKean and E. A. V. Ebsworth of the University of Aberdeen. The electron diffraction photographs were taken in the usual way at the Oslo apparatus.⁴ The nozzle temperature was about 20°C and the electron wave length was 0.06451 Å. Two nozzle to plate distances were applied (47.92 cm and 19.22 cm) giving intensity data in the s ranges 1.50–20.0 Å⁻¹ and 7.0–45.0 Å⁻¹. Four plates were used for each nozzle to plate distance. The data were corrected and treated in the usual way.⁵ The intensities from the four plates were averaged and the intensity curves covering different s ranges were connected.

STRUCTURE ANALYSIS

A modified molecular intensity ($I^{k,l}$) may be obtained from the molecular intensity functions by multiplication with the function⁶ $s/|f_k||f_l|$. $f_k(s) = |f_k(s)|\exp[i\eta_k(s)]$ is the scattering amplitude for atom k . Then

$$I^{(k,l)}(s) = \text{const} \sum_{i \neq j}^N \sum_{i \neq j}^N g_{ij|kl}(s) \exp(-\frac{1}{2}u_{ij}^2s^2) \sin(r_{ij}s)/r_{ij} \quad (1)$$

N is the number of atoms in the molecule, r_{ij} is close to the equilibrium distance between the atoms i and j , and u_{ij} the corresponding root mean square amplitude of vibration.

$$g_{ij|kl}(s) = \frac{|f_i||f_j|}{|f_i||f_k|} \cos(\eta_i - \eta_j) \quad (2)$$

In this case we have chosen the modification function $s/|f_{\text{Si}}|^2$. We have then the following g functions:

$$\begin{aligned} g_{\text{SeSi/SiSi}}(s) &= \frac{|f_{\text{Se}}|}{|f_{\text{Si}}|} \cos(\eta_{\text{Se}} - \eta_{\text{Si}}) \\ g_{\text{SiSi/SiSi}}(s) &= 1.0 \\ g_{\text{SeH/SiSi}}(s) &= \frac{|f_{\text{Se}}| \cdot |f_{\text{H}}|}{|f_{\text{Si}}|^2} \cos(\eta_{\text{Si}} - \eta_{\text{H}}) \\ g_{\text{SiH/SiSi}}(s) &= \frac{|f_{\text{H}}|}{|f_{\text{Si}}|} \cos(\eta_{\text{Si}} - \eta_{\text{H}}) \\ g_{\text{HH/SiSi}}(s) &= \frac{|f_{\text{H}}|^2}{|f_{\text{Si}}|^2} \end{aligned}$$

The scattering amplitudes were calculated using the partial wave method. The applied computer program has been written by J. Peacher.⁷ Hartree-Fock potentials were applied for all the atoms.

The structure parameters (distances and u values) have been determined by least-squares refinements on the intensity data in the s range 1.5–40 Å⁻¹. The theoretical intensity was calculated according to eqn. (1). This implies that every pair of atoms have been considered as an harmonic oscillator. We assumed that the silyl groups were not tilted, *i.e.* that all the Se...H distances

are equal. The starting parameters were obtained from an experimental radial distribution (RD) curve calculated according to

$$\sigma(r)/r = \int_0^{s_{\max}} I(\text{Si}, \text{Si}) \exp(-ks^2) \sin(rs) \, ds \quad (3)$$

k is an artificial damping constant.

The experimental intensity curve is shown in Fig. 2 (curve A). The dotted inner part corresponds to theoretical values. The experimental RD curve calculated by Fourier inversion of the curve A in Fig. 2. ($k = 0.003 \text{ \AA}^2$) is shown in Fig. 3 (curve A). The outer part of the curve is shown enlarged in Fig. 4 (curve A). The inner peaks near 1.52 \AA and 2.27 \AA correspond to the Si-H and Si-Se bond distances. The main contributions to the complex

Fig. 2. Final experimental (A) and theoretical (B) intensity curves. Curve B was calculated using the parameters given in Table 1 for the first four distances (Si-Se, Si-H, Si...Si, Se...H). The non-bonded Si...H distances were as given in Table 2. Curve C shows the difference between the curves A and B.

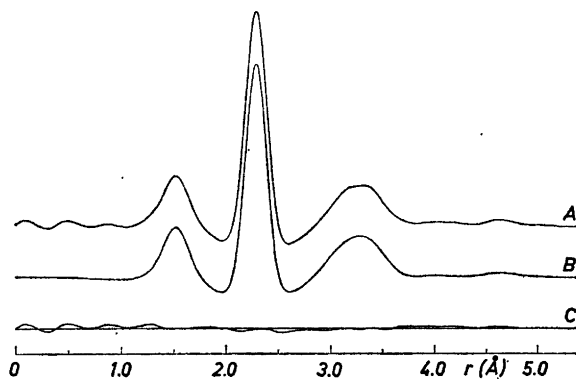
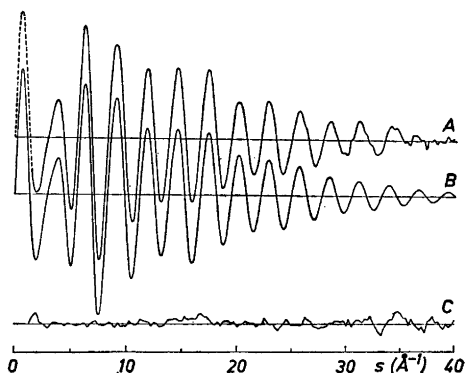


Fig. 3. Final experimental (A) and theoretical (B) radial distribution curves ($k = 0.003 \text{ \AA}^2$) calculated by Fourier transformation of the intensity curves in Fig. 2. Curve C shows the difference between the curves A and B.

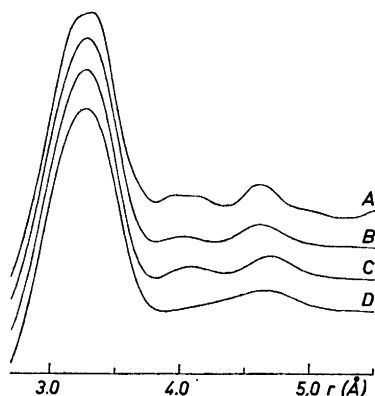


Fig. 4. The outer parts of the experimental (A) and various theoretical radial distribution curves. Curve B corresponds to curve B in Fig. 3. C was calculated using the parameter values in Table 1. D corresponds to freely rotating silyl groups.

centered near 3.25 Å originate from the Se...H distances (a peak near 3.10 Å) and the Si—Si distance (a peak near 3.39 Å). In the C_{2v} conformation with two hydrogens from each silyl group nearest to the twofold axis (see Fig. 1), there will be two different non-bonded Si...H distances; one at approximately 3.61 Å (occurring four times) and one near 4.77 Å (occurring twice). The conformation may now be changed by rotating both the silyl groups an angle φ around the Se—Si bond.* For $0^\circ < \varphi < 60^\circ$ there will be three different non-bonded Si...H distances (each occurs twice). The molecule has again C_{2v} symmetry for $\varphi = 60^\circ$. The two different non-bonded Si...H distances should then be approximately 3.12 Å (occurring twice) and 4.42 Å (occurring four times). The RD curve in Fig. 3 (A) has indications of a very low, broad peak in the region 3.85—4.20 Å (corresponding to the intermediate non-bonded (Si...H) distance) and a more distinct peak in the region 4.5—4.8 Å (corresponding to the long (Si...H)). These two peaks indicate that φ is between 0° and 60° . The third non-bonded Si...H distance gives a small contribution to the complex centered at 3.25 Å.

In the least-squares refinement the weight function was of the form

$$\begin{aligned} W &= \exp[-W_1(s-s_1)^2] & \text{for } s < s_1 \\ W &= 1.0 & \text{for } s_1 \leq s \leq s_2 \\ W &= \exp[-W_2(s-s_2)^2] & \text{for } s > s_2 \end{aligned}$$

In the refinement to be described below we used $W_1 = 0.1$, $W_2 = 0.005$, $s_1 = 5 \text{ \AA}^{-1}$, $s_2 = 25 \text{ \AA}^{-1}$. Five distances were first refined as independent parameters, *i.e.* the bond distances, Si...Si, Se...H, and the longest of the non-bonded Si...H distances. The two other non-bonded Si...H distances were treated as dependent parameters. We tried to refine the u values for all the distances except those between two hydrogens. However, the estimates of the u values for the non-bonded Si...H distances are very uncertain. The H...H

* It is impossible by means of the electron diffraction data to distinguish between a model with a twofold symmetry axis and a model with a symmetry plane, since only H...H distances are different in these models.

distances were calculated from the trial structure (assuming C_2 symmetry) and included in the calculation of the theoretical intensity, but not in the refinement. The H...H distances were adjusted after some cycles of least-squares refinement. The results are given in Table 1. The distances are given in terms of $r_s(1)$.⁸ The structure parameters found in $(\text{SiH}_3)_2\text{S}$ are also given in Table 1. The values in parentheses are standard deviations in 10^{-4} Å. The first standard deviations in a column is the value obtained by the least-squares refinement.

Table 1. Structure parameters in $(\text{SiH}_3)_2\text{Se}$ and $(\text{SiH}_3)_2\text{S}$.

	X = Se (SiH_3) ₂ Se		X = S (SiH_3) ₂ S	
	<i>r</i>	<i>u</i>	<i>r</i>	<i>u</i>
Si—X	2.273 ₈ (6) (35)	0.052 ₁ (8) (25)	2.136 ₀ (5) (20)	0.045 ₈ (7) (19)
Si—H	1.516 ₃ (40) (50)	0.071 ₁ (41) (45)	1.494 ₁ (51) (80)	0.105 ₅ (40) (66)
Si...Si	3.395 ₅ (140)	0.144 ₀ (153)	3.209 ₉ (126)	0.119 ₉ (77)
X...H	3.107 ₃ (121)	0.139 ₂ (185)	2.974 ₄ (451)	0.233 ₀ (397)
S...H	4.682	0.127 (641)		
Si...H	4.026	0.162 (700)		
Si...H	3.266	0.135 (539)		
H...H ^a	2.866			
∠SiXSi	96.6 ₂ (0.52)		97.4 (0.51)	
∠XSiH	108.4 ₆ (0.67)		108.7 (2.55)	
φ	29.6° (5.1°)			

^a The shortest H...H distance between the silyl groups assuming C_2 symmetry.

The general experience has shown that these standard deviations are too small at least for the best determined parameters.⁹⁻¹¹ The standard deviations in the wave length amounts to about 0.15 %, and this uncertainty must be taken into account for the distances. The uncertainty in the blackness correction and scattering amplitudes necessitates an increase in the standard deviations for the *u* values. We have therefore given a second set of standard deviations for the distances and *u* values for the bonds. These values include systematic errors. The standard deviations for the other distances and *u* values are much greater, and the experience shows that these values give a more reliable estimate of the error. (The final standard deviations were not estimated in the same way in this investigation as in the investigation of $(\text{SiH}_3)_2\text{S}$).

The theoretical RD curve calculated with the parameters in Table 1 deviates slightly from the experimental curve for $r > 3.5$ Å (see Fig. 4, curves A and C). This part of the curve depends heavily on the value used for φ. In Table 1 we have given φ \simeq 30°. The corresponding standard deviation is of

course large (5.1°). To test the reliability of this conclusion the three non-bonded Si...H distances were refined independently keeping all the other parameters constant. The distances obtained and the corresponding values for φ are given in Table 2.

Table 2. Values obtained by refining the non-bonded Si...H distances as independent parameters keeping the bond distances and the Si...Si and Se...H distances fixed.

$r(\text{Si}\cdots\text{H})$	φ
4.606 Å	40.4°
3.960 »	24.8°
3.285 »	27.5°

The outer part of the RD curve calculated with these $r(\text{Si}\cdots\text{H})$ distances is shown in Fig. 4 (curve B). These results are in rather satisfactory agreement with the φ value given previously, though the standard deviation given in Table 1 may be too small. The shrinkage effect has been neglected in this discussion, though the effect may be up to some hundredth of an Ångström for the non-bonded Si...H distances. The effect is probably largest for the longest Si...H distance and a smaller φ angle would be obtained by including the shrinkage effect for this distance.

If the SiH_3 groups are assumed to rotate freely, curve D in Fig. 4 is obtained. This curve was calculated by superposition of RD curves calculated for $\varphi = 5^\circ, 15^\circ, 25^\circ, 35^\circ, 45^\circ, 55^\circ$. A peak with maximum near 4.7 Å is obtained, but the argument is obviously not as good as for curve B.

The final experimental (A) and theoretical (B) intensity curves are compared in Fig. 2. The theoretical curve was calculated using eqn. (1) and the r and u values given in Table 1 for the Si—Se, Si—H, Si...Si, and Se...H distances. The Si...H distances were taken from Table 2. Curve C shows the difference between the curves A and B. The experimental (A) and theoretical (B) RD curves calculated from the intensity curves in Fig. 2 are compared in Fig. 3. Curve C shows the difference between the curves A and B.

DISCUSSION

The angles given in Table 1 are seen to be the same in $(\text{SiH}_3)_2\text{S}$ and $(\text{SiH}_3)_2\text{Se}$ within the standard deviations. The Schomaker-Stevenson rule³ in the form

$$r(\text{Se}-\text{Si}) = R_{\text{se}} + R_{\text{si}} - C(x_{\text{se}} - x_{\text{si}})$$

(where R is the covalent atomic radii, x the electronegativity, and C may be taken as 0.06–0.08 Å) suggests a pure single bond between Se and Si. The same conclusion was drawn for the S—Si bond in $(\text{SiH}_3)_2\text{S}$, while the O—Si bond in $(\text{SiH}_3)_2\text{O}$ seems to have appreciably double bond character. The Si—H

distance is found to be greater in $(\text{SiH}_3)_2\text{Se}$ than in $(\text{SiH}_3)_2\text{S}$. The standard deviation for the difference is 0.0065 Å by using the standard deviations obtained by the least-squares refinement and 0.0094 Å by using the final standard deviations given in Table 1. The difference is less than three times the latter value given above. The Si—H distance in $(\text{SiH}_3)_2\text{O}$ was 1.486 (0.010) Å which is slightly shorter, but not significantly different from the value in $(\text{SiH}_3)_2\text{S}$. The value for $u(\text{Se}\cdots\text{H})$ seems reasonable. This supports our assumption that all the Se \cdots H distances are nearly equal. The corresponding parameter in $(\text{SiH}_3)_2\text{S}$ (*i.e.* $u(\text{S}\cdots\text{H})$) was more difficult to determine. The obtained value is rather large with a very large standard deviation.

A C_{2v} conformation with two hydrogens from each silyl group near the twofold axis ($\varphi = 0^\circ$) was suggested for $(\text{SiH}_3)_2\text{S}$ though the evidence was rather weak.

The agreement between the experimental and theoretical intensity and RD curves is not best for the expected C_{2v} symmetry nor for a model with free rotation of the silyl groups. However, we want to emphasise that the difference between the RD curves for a model with $\varphi = 30^\circ$ and a model with $\varphi = 0^\circ$ is too small to draw any certain conclusions concerning the positions of the silyl groups, particularly since the shrinkage effects for the Si \cdots H distances are not known.

As mentioned, dimethyl selenide¹² has C_{2v} symmetry, and the barrier hindering internal rotation was found to be 1500 ± 20 cal/mole. C_{2v} symmetry and a somewhat smaller barrier were expected for $\text{Se}(\text{SiH}_3)_2$. If the structure indicated by this electron diffraction investigation is correct, a possible reason for the difference in the conformation of the two compounds ($\text{Se}(\text{CH}_3)_2$ and $\text{Se}(\text{SiH}_3)_2$) seemed to be the greater attractive forces between the non-bonded atoms in the silyl compound. However, a calculation based on the formula for the van der Waals' energy (E_v) given in Ref. 13 gave a very small difference in E_v for $\varphi = 0^\circ$ and $\varphi = 30^\circ$. E_v depends of course on the applied van der Waals' radii (r^*). Some values for E_v (in kcal/mole) are given below:

	$r_{\text{H}}^* = 1.20 \text{ \AA}$ $r_{\text{Si}}^* = 2.00 \text{ \AA}$	$r_{\text{H}}^* = 1.20 \text{ \AA}$ $r_{\text{Si}}^* = 1.90 \text{ \AA}$
$E_v (\varphi = 0^\circ)$	-0.522	-0.459
$E_v (\varphi = 30^\circ)$	-0.508	-0.465

Even if these values are very uncertain, the results seem to eliminate the van der Waals' forces as a possible explanation for any significant deviation from C_{2v} symmetry.

REFERENCES

1. Almenningen, A., Hedberg, K. and Seip, R. *Acta Chem. Scand.* **17** (1963) 2264.
2. Almenningen, A., Bastiansen, O., Ewing, V., Hedberg, K. and Trætteberg, M. *Acta Chem. Scand.* **17** (1963) 2455.
3. Schomaker, V. and Stevenson, D. P. *J. Am. Chem. Soc.* **63** (1941) 37.
4. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* **9** (1955) 232.
5. Bastiansen, O. and Skancke, P. N. *Advan. Chem. Phys.* **3** (1960) 323.
6. Seip, H. M. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 25.
7. Peacher, J. *Ph.D. Thesis, Department of Physics, Indiana University, Bloomington, Indiana* 1965.
8. Bartell, L. S. *J. Chem. Phys.* **23** (1955) 1219.
9. Almenningen, A., Bastiansen, O., Seip, R. and Seip, H. M. *Acta Chem. Scand.* **18** (1964) 2115.
10. Seip, H. M. *Acta Chem. Scand.* **19** (1965) 1955.
11. Seip, H. M. and Stølevik, R. *Acta Chem. Scand.* **20** (1966) 1535.
12. Beecher, J. F. *J. Mol. Spectry* **21** (1966) 414.
13. Eliel, E. L., Allinger, N. L., Angyal, S. J. and Morrison, G. A. *Conformational Analysis*, Interscience 1965.

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