Determination of the Molecular Structures of Bis(methylsilyl) Sulphide and Bis(dimethylsilyl) Sulphide in the Gas Phase by Electron Diffraction, supported by Molecular Mechanics Calculations

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The molecular structures of $S(SiH_2Me)_2$ and $S(SiHMe_2)_2$ in the gas phase have been determined by electron diffraction. In $S(SiH_2Me)_2$ the Si–S bonds are twisted by −86(2) and 31(2)° away from the positions in which they are *anti* with respect to the further S–Si bonds, and there is therefore an *gauche* CSi ··· SiC configuration when the molecule is viewed along the Si ··· Si axis. Other parameters (r_a) include r(Si–S) 214.1(1), r(Si–C) 186.9(2) pm, SSiC 112.8(7) and SiSSi 97.9(5)° Molecular mechanics calculations for $S(SiHMe_2)_2$ were used to estimate the differences between the lengths of the four Si–C bonds, the two Si–S bond lengths, and the SSiC and CSiC angles. These differences were used as constraints in the refinements of the structure using electron diffraction data, and gave the following mean values: r(Si–S) 214.6(1), r(Si–C) 186.5(1) pm, SSiC 109.1(11) and CSiC 106.6(16)°. The angle SiSSi refined to 100.8(20)°. The $SiHMe_2$ groups were twisted by 148(2) and −87(4)° about the Si–S bonds away from the position in which the Si–H bonds eclipse the further Si–S bonds.

During studies of the molecular structures of methyl-substituted disiloxanes in gaseous[1,2] and crystalline[3] phases it was noted that the conformations adopted always involved staggering of the Si–C bonds, when the molecules were viewed along the non-bonded Si ··· Si axes. However, there was no apparent preferred arrangement about the Si–O bonds. This predominance of 1,3 over 1,2 interactions was attributed to the presence of a single stereochemically active lone pair of electrons on each oxygen atom, with a consequent low six-fold barrier to rotation about the Si–O bonds. The second electron pair on each oxygen atom must occupy a 2*p* orbital. This electronic configuration is consistent with the observed structure of $O(SiH_3)_2$ in the solid phase,[3] in which one silicon atom of each molecule is involved in a close contact with the oxygen atom of an adjacent molecule. The axis of this non-bonded Si ··· O interaction is coaxial with the bond from oxygen to the silicon atom in the first molecule, and coplanar with the two O–Si bonds in the second molecule. Again, the implication is that the oxygen atom has a single stereochemically active lone pair, with the second pair of electrons occupying a 2*p* orbital.

In contrast, both lone pairs of electrons on the sulphur atom of crystalline $S(SiH_3)_2$ are involved in close interactions with silicon atoms of neighbouring molecules.[4] If both lone pairs on sulphur are stereochemically active, then both 1,2 and 1,3 interactions should be important in determining the conformations of gaseous methyl-substituted disilyl sulphides. We have therefore determined the structures of $S(SiMe_3)_2$,[5] $S(SiHMe_2)_2$, and $S(SiH_2Me)_2$ in the gas phase by electron diffraction. To improve the accuracy of the work we have used molecular mechanics (MM2) calculations in the first two cases, so that the effects of making assumptions about the local symmetry of the $SiHMe_2$ and $SiMe_3$ groups could be first assessed and then minimised. The results of our studies of $S(SiHMe_2)_2$ and $S(SiH_2Me)_2$ are reported here.

Experimental

The disilyl sulphides, $S(SiH_2Me)_2$ and $S(SiHMe_2)_2$, were prepared by the reactions of SiH_2IMe and $SiHIMe_2$ with HgS.[6] The volatile products were purified by fractional distillation and characterised by i.r. and n.m.r. spectroscopy.

Electron-diffraction scattering intensities were obtained using the Edinburgh electron diffraction apparatus,[7] with an accelerating voltage of 44.5 kV, and Kodak Electron Image plates. Three plates were exposed at each of the camera distances of 128 and 286 mm, and the sample and inlet nozzle were maintained at 295 K throughout. The intensity data were converted into digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer at the S.E.R.C. Laboratory, Daresbury.[8] The electron wavelengths and camera distances were obtained by analysis of the scattering patterns of benzene recorded immediately after those of the sample compounds. Standard data-reduction[8] and least-squares refinement[9] procedures were followed, using the scattering factors taken from ref. 10. Details of the weighting points needed to set up the off-diagonal weight matrices used in the least-squares refinements are given in Table 1 together with other experimental information.

Structural Analysis for $S(SiH_2Me)_2$.—*Molecular model.* The atomic co-ordinates of $S(SiH_2Me)_2$ were generated by a model using the parameters listed in Table 2. It was assumed that there was local C_{3v} symmetry within the $SiCH_3$ groups and local C_s symmetry within each $SSiH_2C$ fragment. The two halves of the molecule were assumed to differ only in respect of the torsion angles about the S–Si bonds. The zero positions of these angles were defined to correspond to an *anti* SiSSiC arrangement, while the origin for the methyl torsion was taken to be the staggered conformation. The SiH_2 wag angle was defined as the angle between the bisectors of the HSiH and SSiC angles, a positive angle representing movement of the hydrogen atoms towards the S atom.

Refinement of structure. The radial distribution curve for $S(SiH_2Me)_2$ [Figure 1(*a*)] is relatively uncrowded and only five major peaks are apparent. The first four are associated with the bonded distances C–H, Si–H, Si–C, and Si–S and these all refined well, along with the corresponding amplitudes of vibration. The large peak at 330 pm contains overlapping contributions from the Si ··· Si and S ··· C distances. The vibrational amplitudes for these atom pairs were therefore

Table 1. Weighting functions, correlation parameters, scale factors, and wavelengths

Compound	Camera height/mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor	Wavelength/pm
		nm^{-1}							
$S(SiH_2Me)_2$	285.9	2	20	40	122	144	0.399	0.793(9)	5.667
	128.3	4	80	100	288	336	0.295	0.698(17)	5.667
$S(SiHMe_2)_2$	285.9	2	20	40	122	144	0.407	0.730(16)	5.670
	128.3	4	60	80	260	300	0.100	0.674(19)	5.671

Table 2. Molecular parameters (distances in pm, angles in °)

		$S(SiH_2Me)_2$	$S(SiHMe_2)_2$
p_1	r(Si–S)	214.1(1)	214.6(1)[a]
p_2	r(Si–C)	186.9(2)	186.5(1)[a]
p_3	r(Si–H)	152.7(6)	154.6(18)
p_4	r(C–H)	113.5(4)	113.1(3)
p_5	SiCH	112.0[b]	112.0(5)
p_6	SSiH		110.0[b]
p_7	CSiC		106.6(16)[a]
p_8	SSiC	112.8(7)	109.1(11)[a]
p_9	SiSSi	97.9(5)	100.8(20)
p_{10}	HSiH	108.0[b]	
p_{11}	SiH_2 wag	3.0[b]	
p_{12}	Si–C torsion	0.0[b]	26.6(23)
p_{13}	S–Si torsion 1	−85.9(19)	148.4(24)
p_{14}	S–Si torsion 2	30.7(21)	−87.3(40)

[a] Mean value. [b] Fixed.

Table 3. Least-squares correlation matrices (× 100). Only elements > 50% are listed

(a) $S(SiH_2Me)_2$

p_9	u_{15}	u_{25}	k_2	
−93	−95			p_8
	95	50		p_9
			85	u_1
	55			u_{25}

(b) $S(SiHMe_2)_2$

p_7	p_9	p_{12}	p_{14}	u_9	k_2	
	64		−84	−62		p_7
−50	−97		65	89		p_8
			−75	−92		p_9
		−56				p_{13}
				72		p_{14}
					66	u_1
					71	u_3

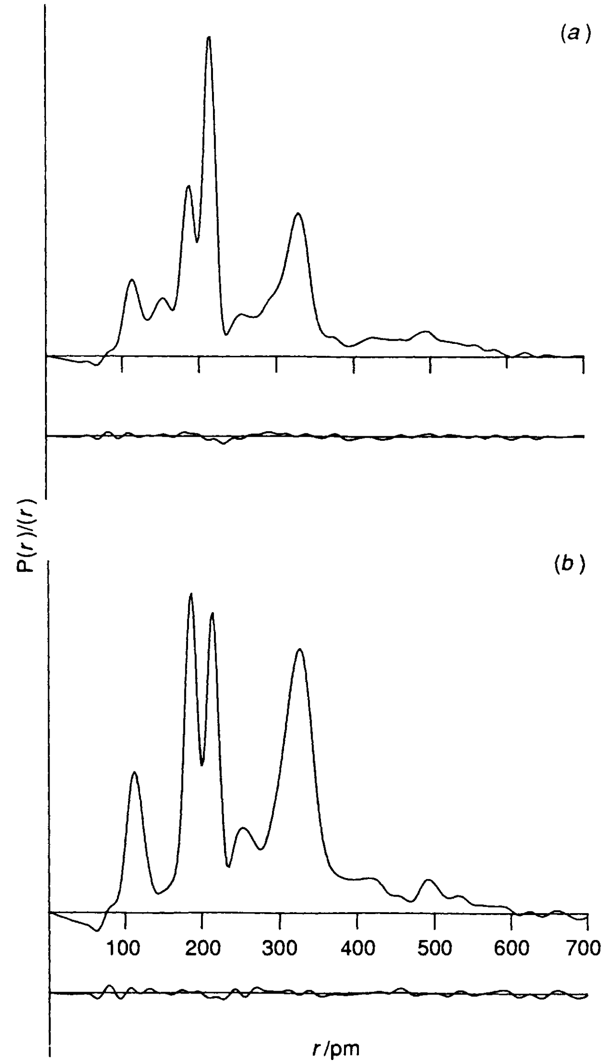

Figure 1. Observed and final weighted-difference radial distribution curves, $P(r)/r$, for (a) $S(SiH_2Me)_2$ and (b) $S(SiHMe_2)_2$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.000\,02\ s^2)/(Z_{Si} - f_{Si})(Z_S - f_S)$

constrained to be equal, but even so the SiSSi and SSiC angles were strongly correlated [Table 3(a)]. Attempts to refine the HSiH and SiCH angles were not successful, so these parameters had to be fixed. The SiCH angle was assigned a value a little greater than the tetrahedral angle, as this gave a slightly better fit to the experimental data.

The peaks beyond 350 pm contained all the conformation-dependent information, and since these peaks were small the torsion angles about the S–Si bonds required careful and thorough investigation. Both angles were varied systematically over the whole possible range, including checks of conformations with C_s and C_2 symmetry. These tests yielded two possible conformers, one *gauche-trans*, with the R factor R_G 0.075 and one *gauche-gauche* with R_G 0.085. This second conformer was rejected, because the SSiC and SiSSi angles had refined to the unreasonable values of 106.6(3) and 103.0(3)° respectively. The latter value is particularly unlikely, as the corresponding angle in $S(SiH_3)_2$ is reported to be only 97.4(7)°.[11] The conformation about the Si–C bonds was also investigated and found to be fully staggered for both CH_3 groups. The torsion angles were therefore fixed at zero.

The results of the final refinements are listed in Table 2 and the interatomic distances and amplitudes of vibration are given in Table 4. The molecular scattering intensity curves are shown in Figure 2 and a perspective view of the molecule is presented in Figure 3(a).

Table 4. Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm)[a]

		$S(SiH_2Me)_2$		$S(SiHMe_2)_2$	
		Distance	Amplitude	Distance	Amplitude
r_1	S–Si(10)	214.1(1)	4.8(1)	214.3(1)	5.1(2)
r_2	S–Si(20)			215.0(1)	
r_3	Si–C(2)			186.3(1)	4.3(2)
r_4	Si–C(6)	186.9(2)	4.6(2)	186.3(1)	
r_5	Si–C(12)			186.7(1)	
r_6	Si–C(16)			186.9(1)	
r_7	Si–H	152.7(6)	10.0(6)	154.6(18)	8.8[b]
r_8	C–H	113.5(4)	6.3(5)	113.1(3)	6.7(4)
r_9	S···C(2)			326.3(23)	12.2(9)
r_{10}	S···C(6)	334.2(12)	9.1(12)	329.3(22)	
r_{11}	S···C(12)			329.3(22)	
r_{12}	S···C(16)			323.9(23)	
r_{13}	C(2)···C(6)			300.6(30)	11.0(21)
r_{14}	C(12)···C(16)			297.7(31)	
r_{15}	Si···Si	322.9(12)	9.1(tiedto u_{10})	330.7(49)	12.2 (tied to u_{10})
r_{16}	Si(10)···C(12)	487.1(14)	16.1(15)	490.9(14)	7.8(14)
r_{17}	Si(10)···C(16)			334.5(33)	20.0[b]
r_{18}	Si(20)···C(2)			329.3(34)	15.0[b]
r_{19}	Si(20)···C(6)	423.9(30)	21.3(23)	422.4(61)	20.0[b]
r_{20}	C(2)···C(12)			512.6(26)	20.0[b]
r_{21}	C(2)···C(16)			293.9(103)	20.0[b]
r_{22}	C(6)···C(12)	553.5(38)	19.7(39)	548.8(53)	20.0[b]
r_{23}	C(6)···C(16)			357.1(84)	20.0[b]
r_{24}	Si(C)H	252.4(3)	11.8(7)	251.5(6)	10.7(6)
r_{25}	S(Si)H	297.8(5)	7.4(9)	304.1(14)	12.0[b]

[a] Other Si···H, S···H, C···H, and H···H distances were included in the refinement but are not listed here. The quoted errors are e.s.d.s, increased to allow for systematic errors. [b] Fixed.

Structural Analysis for $S[SiH(CH_3)_2]_2$.—*Initial molecular model.* For the first refinements of the structure of $S(SiHMe_2)_2$ it was assumed that the two $SSiHMe_2$ units were identical, each having C_{3v} local symmetry for the $SiCH_3$ groups, C_2 symmetry for the $SiMe_2$ groups, and C_s symmetry for the $SSiHC_2$ fragments. The structure was then defined by the four different bonded distances, the valence angles SSiC, CSiC, SiCH, SSiH, and SiSSi, and three torsion angles. The conformation of the methyl groups was defined by a torsion angle about the Si–C bonds, relative to the position in which one C–H bond of each group eclipsed an Si–S bond. The zero positions for torsions about the Si–S bonds involved the Si–H bonds eclipsing the further Si–S bonds. Positive values for these angles represented clockwise rotations, so that if the two angles were equal the molecule had overall C_2 symmetry, while if they were equal and opposite the symmetry of the molecular skeleton was C_s.

Initial structural refinements. The radial distribution curve [Figure 1(*b*)] shows clear peaks corresponding to three of the bonded distances, C–H, Si–C, and Si–S, which all refined easily. There is a weaker peak at *ca.* 150 pm attributable to the Si–H distance, which also refined, but with a large standard deviation, and the Si(C)H peak near 250 pm enabled the SiCH angle to be refined. The next large peak, centred near 330 pm, contained contributions from several pairs of atoms separated by two bonds, and thus provided information about the remaining valence angles. The SSiC, CSiC, and SiSSi angles all refined satisfactorily, so long as reasonable starting values were chosen, but it was possible to obtain a good fit to the experimental data with an unusually wide angle at sulphur, coupled with an exceptionally narrow SSiC angle. Several amplitudes of vibration associated with peaks in the radial distribution curve below 350 pm were also refined at this stage.

The region of the radial distribution curve beyond 350 pm provides information about the conformation adopted by the molecules. The two S–Si torsion angles were varied systematically over their entire ranges of possible values, and one conformation, with torsion angles of *ca.* 148 and −90°, was found to give a significantly better fit to the data than all others. The torsion angles were then allowed to refine, and the values obtained were then used in the molecular mechanics calculations. The *R* factor (R_G) at this stage was 0.099.

Molecular mechanics calculations. The program MM2[12] was used to study possible deviations of the structure of $S(SiHMe_2)_2$ from the symmetry and local symmetry assumed in the initial refinements. As this program does not include force-field parameters for silicon–sulphur systems it was necessary to estimate them. The Si–S stretching and Si–S–Si angle bending parameters were adjusted so that the MM2 calculations reproduced the experimental bond length and angle, and other parameters were assigned values by analogy with related parameters. As the sole purpose of the calculations was to study distortions within the $SiHMe_2$ groups, for which the MM2 parameters are well defined, the precise values of parameters relating to the sulphur atom are of little significance. Estimated force-field parameters are listed in Table 5. The two S–Si torsion angles were again set at series of values covering the whole range, and the rest of the structure was allowed to refine so that the total energy was minimised. Three possible conformations were identified in this way. Their torsion angles and relative energies were −60 and −60°, 150 and −60° (1.3 kJ mol^{-1} less stable), and 0 and 180° (2.6 kJ mol^{-1} less stable). The second of these was close to the structure identified by analysis of the electron diffraction data, but there was no experimental evidence for the existence of other conformers in the gas phase, although it is impossible to rule out the possibility that small amounts of other conformers could be present. The torsion angles were therefore set to the values found experimentally, and the geometry was optimised once more using the molecular mechanics program. This provided a set of bond lengths and

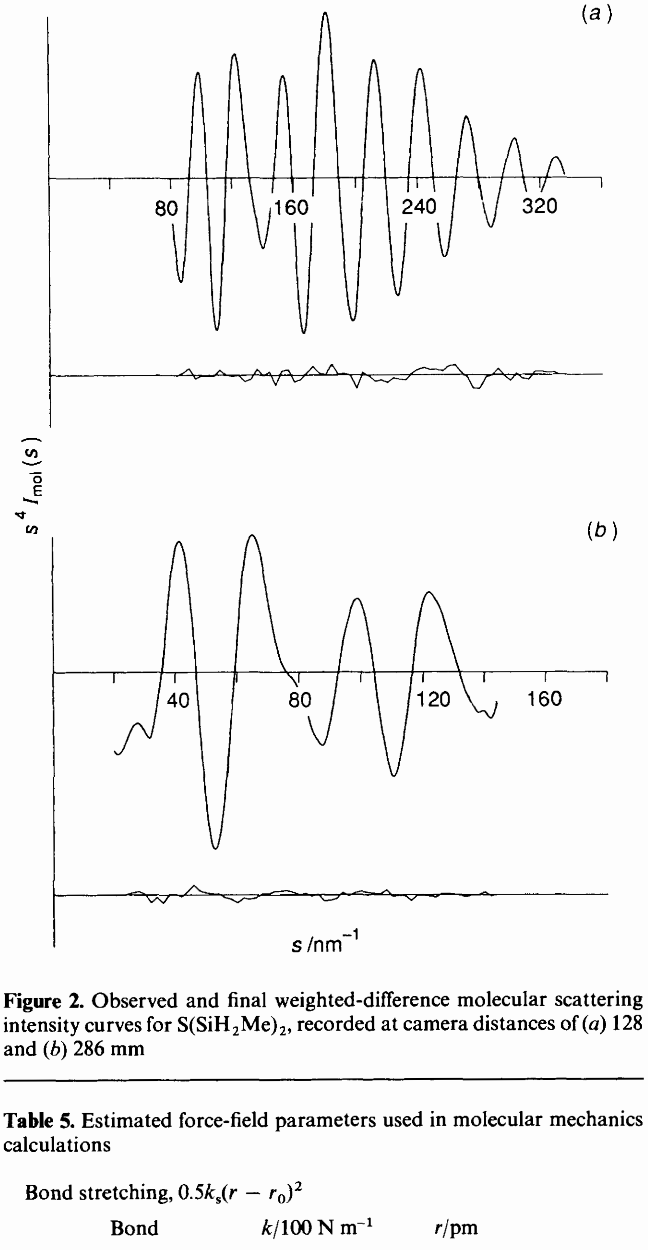

Figure 2. Observed and final weighted-difference molecular scattering intensity curves for $S(SiH_2Me)_2$, recorded at camera distances of (*a*) 128 and (*b*) 286 mm

Table 5. Estimated force-field parameters used in molecular mechanics calculations

Bond stretching, $0.5k_s(r - r_0)^2$

Bond	k/100 N m^{-1}	r/pm
Si–S	3.0	215

Angle bending, $0.5k_s(\theta - \theta_0)^2$

Angle	k/100 N rad m^{-1}	θ/°
Si–S–Si	0.42	97.4
C–Si–S	0.51	108.9
H–Si–S	0.40	108.0

Torsional parameters

Angle	v_1	v_2	v_3
H–C–Si–S	0.0	0.0	0.33
C–Si–S–Si	0.0	0.0	0.25
H–Si–S–Si	0.0	0.0	0.41

angles, which indicated that there was considerable deviation from C_s symmetry in the $SSiHC_2$ groups, and that the two groups were significantly different from one another.

Modified molecular model. The model used in analysis of the electron diffraction data was then modified to reflect the asymmetry indicated by the molecular mechanics calculations. The original parameters r(Si–S), r(Si–C), SSiC, and CSiC were replaced by mean values, which could be refined, but the individual bond lengths and angles were defined by the mean values and a set of differences, which were fixed at the values calculated by molecular mechanics. Thus the number of refining parameters was unchanged, but the assumptions of local symmetry were replaced by more realistic assumptions, based on molecular mechanics. The fixed differences were given by r[S–Si(10)] − r[S–Si(20)] = −0.72 pm, r(Si–C)(mean) = r[Si(10)–C(2)] + 2.3 = r[Si(10)–C(6)] + 2.6 = r[Si(20)–C(12)] − 1.1 = r[Si(20)–C(16)] − 3.8 pm, SSiC(mean) = SSi(10)C(2) + 0.201 = SSi(10)C(6) − 1.280 = SSi(20)C(12) −0.820 = SSi(20)C(16) + 1.889°, and C(2)Si(10)C(6) − C(12)Si(20)C(16) = 1.500°.

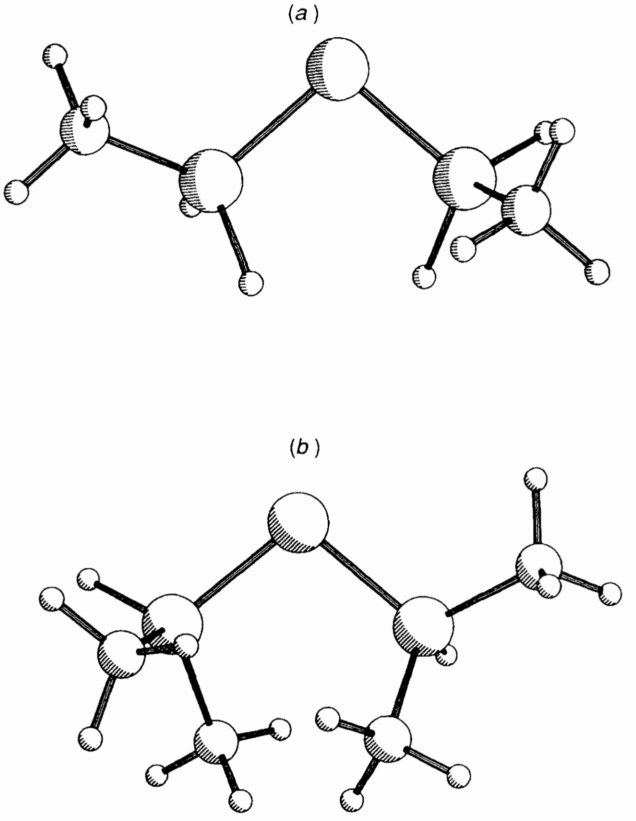

Figure 3. Perspective views of (*a*) $S(SiH_2Me)_2$ and (*b*) $S(SiHMe_2)_2$

Final refinements and results. Using the modified molecular model further refinements were performed, yielding the results given in Tables 2 and 4. The final R factor (R_G) was 0.094. The final least-squares correlation matrix is given in Table 3(*b*), and the molecular scattering intensities are shown in Figure 4. Figure 3(*b*) is a perspective view of the molecule.

Discussion

The effects of including asymmetry in the structure of $S(SiHMe_2)_2$ in this case are very small, so it may seem that the molecular mechanics calculations have added little of value. Nevertheless, they have improved the reliability of the results: if the effects of asymmetry are not investigated, how can we know that they are not significant? The most significant change in a bond length was an increase in r(Si–H) by 1.1 pm, which is much less than one estimated standard deviation (e.s.d.) while an increase in the angle SiSSi from 100.1 to 100.8(20)° was the greatest angular change. More significant

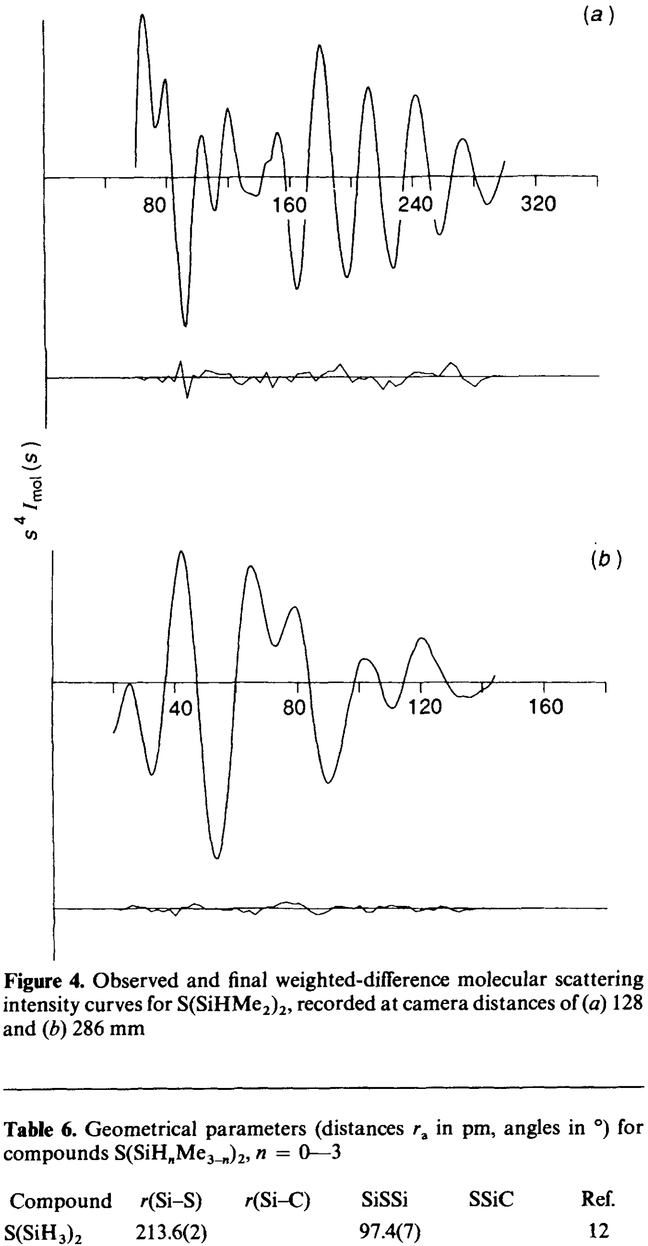

Figure 4. Observed and final weighted-difference molecular scattering intensity curves for $S(SiHMe_2)_2$, recorded at camera distances of (*a*) 128 and (*b*) 286 mm

Table 6. Geometrical parameters (distances r_a in pm, angles in °) for compounds $S(SiH_nMe_{3-n})_2$, n = 0—3

Compound	r(Si–S)	r(Si–C)	SiSSi	SSiC	Ref.
$S(SiH_3)_2$	213.6(2)		97.4(7)		12
$S(SiH_2Me)_2$	214.1(1)	186.9(2)	97.9(5)	112.8(7)	This work
$S(SiHMe_2)_2$	214.6(1)	186.5(1)	100.8(20)	109.1(11)	This work
$S(SiMe_3)_2$	215.4(1)	187.1(1)*	105.8(7)	109.2(3)*	5

* Mean value.

effects were observed in a similar combined electron diffraction–molecular mechanics study of $S(SiMe_3)_2$.[5]

The most important parameters for the series of disilyl sulphides, $S(SiH_nMe_{3-n})_2$ (n = 0—3) are listed in Table 6. This shows that there is a systematic lengthening of the Si–S bonds as the number of methyl substituents increases. The angle at the central sulphur atom changes little on the first methyl substitution, by 3° on the second, and by a further 5° in the third. This indicates very clearly how the 1,3 interactions become very significant once substitution is complete, and the methyl groups can no longer avoid one another simply by twisting about the Si–S bonds.

The views along the Si $\cdots$ Si axes (Figure 5) show that the molecules adopt conformations which involve compromises between perfect staggering along the Si–S bonds (which would minimise 1,2 interactions) and perfect staggering along the Si $\cdots$ Si axes (minimising 1,3 interactions). Thus the 1,2 interactions appear to be more important than in the corresponding disiloxanes,[1,2] and this is consistent with the hypothesis that the sulphur atoms in these compounds have two stereochemically active lone pairs of electrons.

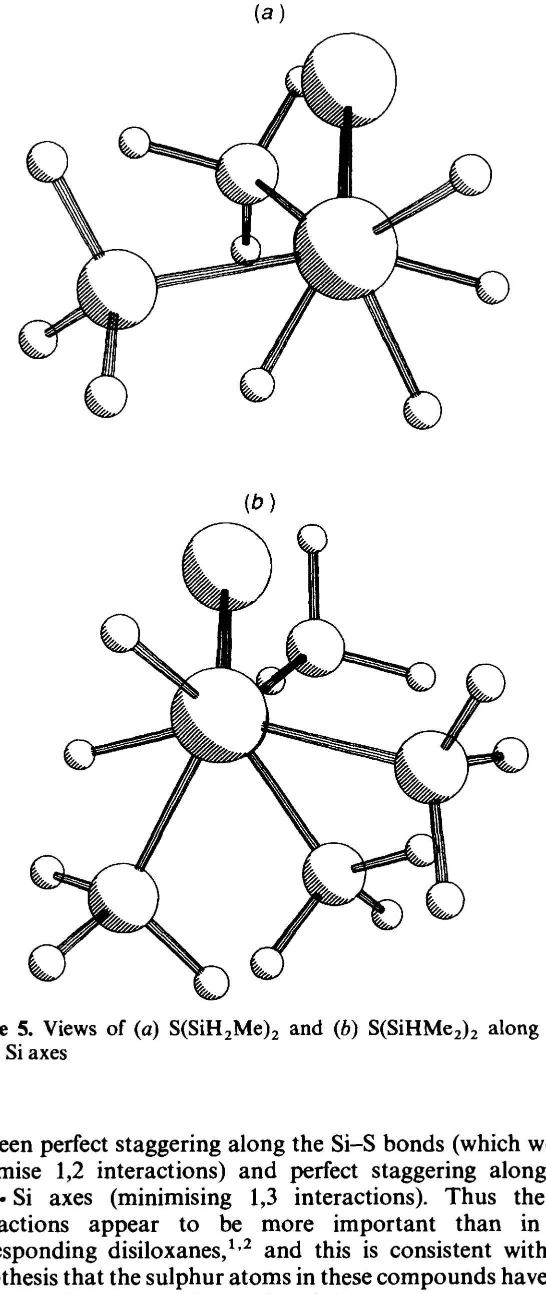

Figure 5. Views of (*a*) $S(SiH_2Me)_2$ and (*b*) $S(SiHMe_2)_2$ along their Si $\cdots$ Si axes

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References

1 D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1983, 265.
2 B. Csàkvàri, Zs. Wagner, P. Gömöry, and F. C. Mijlhoff, *J. Organomet. Chem.*, 1976, **107**, 287.
3 M. J. Barrow, E. A. V. Ebsworth, and M. M. Harding, *Acta Crystallogr., Sect. B*, 1979, **35**, 2093.
4 M. J. Barrow and E. A. V. Ebsworth, *J. Chem. Soc., Dalton Trans.*, 1982, 211.
5 D. G. Anderson, G. A. Forsyth, and D. W. H. Rankin, *J. Mol. Struct.*, in the press.

6 J. E. Drake, B. M. Glavincecski, R. T. Hemmings, and H. E. Henderson, *Inorg. Synth.*, 1979, **19**, 274.

7 C. M. Huntley, G. S. Laurenson, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.

8 S. Cradock, J. Koprowski, and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **77**, 113.

9 A. S. F. Boyd, G. S. Laurenson, and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **71**, 217.

10 L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.

11 A. Almenningen, K. Hedberg, and R. Seip, *Acta Chem. Scand.*, 1963, **17**, 2264.

12 N. Allinger and Y. H. Yuh, Q.C.P.E. program no. 423, Quantum Chemistry Program Exchange, Indiana University Chemistry Department, Indiana.

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