The Molecular Structure of Silyl Monothioacetate in the Crystal at 130 K and in the Gas Phase

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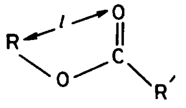
The structure of SiH_3OCSCH_3 has been determined in the solid by *X*-ray diffraction and in the gas by electron diffraction. At 130 K crystals are monoclinic, space group $P2_1/n$, with a = 5.40, b = 8.77, c = 11.47 Å, β = 96.0° (estimated standard deviations 0.3% assumed), and Z = 4. The final R value was 0.032 over 739 reflexions. The silyl group is bonded through oxygen: Si–O 1.699(5) Å (crystal) and 1.717(6) Å (gas). The Si–O and C=S bonds are eclipsed so that the intramolecular Si · · · S separations, 3.185(9) Å in the crystal and 3.143(9) Å in the gas, are appreciably less than the van der Waals distance. The heavy-atom skeleton deviates slightly, but significantly, from planarity in the crystal, where ϕ(Si–O–C=S) = −6.0(4)°. In the gas this torsion angle is *ca.* 10°. Interactions between neighbouring molecules in the crystal are consistent with weak secondary bonding between S and Si. The intermolecular C=S · · · Si–O systems have geometry: S · · · Si 3.382(10)Å, C=S · · · Si 100.8(4)°, and S · · · Si–O 166.3(3)°.

CRYSTALLINE carboxylic acids adopt a planar *cis* configuration for the acidic hydrogen with respect to the carbonyl oxygen (1a).



(1a; R = H)
(1b; R = CH_3)
(1c; R = SiH_3)

The same planar *cis* conformation is found in organic esters both in the solid, as in crystalline methyl acetate,[1] and in the gas, as in methyl formate [2] (1b). This conformation leads to intramolecular non-bonded distances, *l*, which are rather less than the sum of van der Waals radii. In crystalline methyl acetate the C · · · O separation is 2.61 Å; in gaseous methyl formate the separation is 2.68 Å, but the sum of the van der Waals radii for C and O atoms is 3.2 Å. Silyl esters also adopt the planar *cis* conformation, (1c), and the discrepancy between the Si · · · O(carbonyl) distance and the sum of the van der Waals radii becomes even more pronounced. Recent electron-diffraction analyses of gaseous silyl formate [3] and gaseous silyl acetate [1] indicate some distortion of the Si–O–C=O torsion angle away from zero but only by *ca.* 15°. The resulting Si · · · O distances are 2.87 Å in the formate and 2.80 Å in the acetate, distances to be contrasted with a sum of van der Waals radii for Si and O atoms of 3.6 Å. In *crystalline* silyl acetate the heavy-atom skeleton is nearly planar but here the intramolecular Si · · · O(carbonyl) distance of 2.83 Å is overshadowed by an even shorter *inter*molecular O′ · · · Si contact of 2.72 Å. The intermolecular O′ · · · Si interaction is between the carbonyl oxygen atom of one molecule and the silicon atom of another and this O–Si · · · O′ system is almost linear.

We have now completed structural studies of silyl monothioacetate, in both gas and crystalline phases. As compared with silyl acetate, the monothioester presents additional structural possibilities. The substitution of one oxygen by sulphur introduces variations in atomic size and donor–acceptor character, the silyl group could be bonded through oxygen or through sulphur, and in the crystal there may be O · · · Si or S · · · Si interactions (we have recently shown that S · · · Si interactions occur in crystalline disilyl sulphide [4]).

EXPERIMENTAL

Samples of silyl monothioacetate were prepared by condensing silyl bromide into tributyltin monothioacetate.[5] Purification was by fractional distillation ***in vacuo*** and purities were checked by i.r., n.m.r., and molecular-weight determinations.

X-*Ray Diffraction.—Crystal Data.* C_2H_6OSSi, M = 106.2, Monoclinic, a = 5.40, b = 8.77, c = 11.47 Å, β = 96.0° [estimated standard deviations (e.s.d.s) 0.3% assumed], U = 540.2 Å^3, Z = 4, D_c = 1.31 g cm^{-3}, Cu-K_α radiation (nickel filter), λ = 1.541 8 Å, μ(Cu-K_α) = 62.5 cm^{-1}, space group $P2_1/n$ (C^5_{2h}, no. 14) by systematic absences.

The compound melts at 210 K; cell parameters and intensities were measured at 130 K. The final least-squares weighting scheme was $w^{-1} = 1 + 0.0005\ F_o^2$. The final value of the isotropic extinction parameter was g = 1.07(8) × 10^{-5} where $F_c' = F_c(1 - gF_c^2/\sin\theta)$. The final values of the discrepancy indices over 739 reflexions were $R = \Sigma|\Delta|/\Sigma|F_o| = 0.032$ and $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} =$ 0.038. A final difference-Fourier synthesis showed no peaks or troughs outside the range ±0.2 e Å^{-3}.

Procedure. Pure samples of the compound, which at room temperature is an air- and moisture-sensitive liquid, were sealed into thin-walled Pyrex capillaries (external diameter *ca.* 0.5 mm). The capillaries were mounted on goniometer heads using heat-insulating Tufnol inserts. Single crystals suitable for *X*-ray investigation were grown *in situ* on a Nonius Weissenberg goniometer. The goniometer was fitted with Nonius low-temperature nitrogen-gas-stream equipment with some locally devised modifications. Cell parameters and intensity data at 130 K were obtained from oscillation and Weissenberg photographs of two crystals, one aligned along [100], the other aligned along [1$\bar{1}$0]. Intensity films were exposed for the Weissenberg levels hkl for h = 0—4 and $n + k,k,l$ for n = 0—2 using

Cu-K_α radiation and the equi-inclination multiple-film-pack method.

Integrated intensities were derived from microdensitometer measurements performed by the S.E.R.C. Microdensitometer Service at Daresbury Laboratory, Warrington.

The data from each crystal were corrected for absorption (numerical integration) and for Lorentz and polarisation effects after which the data levels were scaled together using common reflexions. In all, 1 831 intensities were measured in the hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$, $\bar{h}\bar{k}l$, and $\bar{h}kl$ regions of reciprocal space. After merging, there remained 739 unique observed reflections (merging R factor = 0.035).

TABLE 1

Weighting functions, correlation parameters, and scale factors for electron diffraction

Camera height/ mm	Δs	$s_{\min.}$	sw_1	sw_2	$s_{\max.}$	Correlation parameter	Scale factor
			nm^{-1}				
286.34	2.0	20	35	125	144	0.2939	0.651 (16)
128.40	4.0	52	70	220	280	0.0045	0.521 (21)

Structure solution and refinement. The space group imposes no restriction on molecular symmetry for $Z = 4$. The structure was solved by Patterson and Fourier methods and refined by weighted least-squares calculations to minimise the quantity $\Sigma w(|F_o| - |F_c|)^2$. All hydrogen atoms were located from a difference-Fourier synthesis and their positional and isotropic vibrational parameters were refined. Non-hydrogen atoms were refined with anisotropic vibrational parameters. During the later stages of refinement an empirical isotropic extinction correction was applied by means of a variable parameter in the least-squares calculations; an empirical least-squares weighting scheme was also introduced. Atomic scattering factors for H atoms were from ref. 6 and for other atoms from ref. 7. Allowance was made for the real and imaginary parts of the anomalous dispersion effect using $\Delta f'$ and $\Delta f''$ values from ref. 8. Calculations were performed using computers of the Edinburgh Regional Computing Centre and using programs written here and the program systems X-RAY 76,[9] SHELX,[10] and PLUTO.[11]

Electron Diffraction.—Scattering intensities were recorded photographically on Kodak Electron Image plates using the Cornell–Edinburgh diffraction apparatus [12,13] operating at 43 kV and with the sample and nozzle maintained at room temperature. Three plates were exposed at each of two nozzle-to-plate distances (128 and 286 mm), so providing data over the range 20—280 nm^{-1} in the scattering variable s. Separate diffraction experiments for benzene were used to calibrate the camera distances and electron wavelength [$\lambda = 0.057\,41(3)$ Å]. The photographic plates were traced by the S.E.R.C. Microdensitometer Service, using a Joyce-Loebl Microdensitometer 6.[14]

Calculations were performed using computers of the Edinburgh Regional Computing Centre and using established data-reduction [13,14] and least-squares [15] programs. Scattering factors were from ref. 16. Table 1 lists scale factors, correlation parameters, and the weighting points used to construct the weight matrix for least-squares refinements.

In the structural model used for refinements it was assumed that the central carbon atom is planar and that the $OSiH_3$ and CCH_3 groups have local C_{3v} symmetry. The molecular geometry is then defined by six bond lengths, five valence angles, and three torsion angles (see Table 2). The SiH_3 and CH_3 torsion angles were defined as zero when one Si–H (or C–H) bond was staggered with respect to the C=S bond.

The refinement required care since there are several sets of overlapping peaks in the radial distribution curve (see Figure 1). The Si–H distance was fixed to permit refinement of the C–C distance. The three torsion angles were optimised by considering variations of the R factor as the angles were fixed at different values. Bonded distance amplitudes refined to sensible values although u(Si–H) was fixed and u(Si–O) and u(C–O) were constrained, in appropriate ratios, to u(C–S) and u(C–C) respectively. However this model still had a rather high R factor, $R_G = 0.16$. A dramatic improvement was possible when an allowance was included for contamination of the gaseous samples by disilyl sulphide which we know to be formed in a disproportionation reaction. The model was expanded to include (fixed) distances and amplitudes for Si–S, Si · · · Si, Si–H, Si · · · H, and S · · · H with values taken from ref. 17. The proportion of $S(SiH_3)_2$ present was varied and a minimum R_G value was obtained for 3.2% impurity (mole : mole basis) for the plates at the short camera distance and 11.5% impurity for the plates at the long distance. The final R factors were $R_G = 0.102$ and $R_D = 0.078$.

TABLE 2

Gas-phase molecular parameters

(*a*) Independent parameters

	Distance (Å) or angle (°)	Amplitude (Å)
r_1(C–H)	1.048(10)	0.061(15)
r_2(C–C)	1.484(14)	0.059(25)
r_3(C=S)	1.615(8)	0.032(24)
r_4(C–O)	1.345(7)	0.055 [a]
r_5(Si–O)	1.717(6)	0.034 [b]
r_6(Si–H)	1.480 (fixed)	0.088 (fixed)
Angle 1 (C–C–O)	111.4(8)	
Angle 2 (O–C=S)	127(2)	
Angle 3 (Si–O–C)	118(2)	
Angle 4 (H–Si–O)	110 (fixed)	
Angle 5 (H–C–C)	110 (fixed)	
Torsion 1 (Si–O–C–S)	10 [c]	
Torsion 2 (H–Si–O–C)	35 [c]	
Torsion 3 (H–C–C–S)	70 [c]	

(*b*) Dependent distances (Å) and amplitudes (Å)

d_7(C · · · S)	2.075(15)	0.103(7)
d_8(C · · · O)	2.339(10)	0.060(18)
d_9(C · · · H)	2.088(18)	0.099(45)
d_{10}(C · · · Si)	2.632(22)	0.103 [d]
d_{11}(S · · · O)	2.652(20)	0.103 [d]
d_{12}(Si · · · C)	3.948(15)	0.092(15)
d_{13}(Si · · · S)	3.143(9)	0.138(9)

[a] Proportional to u_2, see text. [b] Proportional to u_3, see text. [c] Torsion angles optimised by R-factor minimisation, see text. [d] Tied to u_7(C · · · S).

RESULTS

Final values of atomic parameters for crystalline SiH_3OCSCH_3 are given in Table 3 and details of the intramolecular

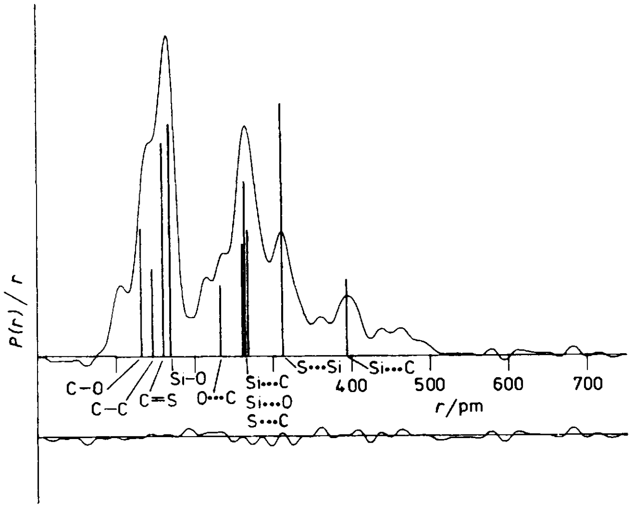


FIGURE 1 Gaseous silyl thioacetate: observed and final difference radial distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s.\exp[-0.000\,015\ s^2/(Z_{Si} - f_{Si})(Z_O - f_O)]$

and intermolecular geometry in Tables 4 and 5. Figure 2 indicates the molecular geometry and atomic labelling scheme. Figure 3 shows the arrangement of molecules in the unit cell. Tables of observed and calculated structure factors and thermal vibration parameters are available as Supplementary Publication No. SUP 23254 (14 pp.).*

TABLE 3

Atomic parameters (with e.s.d.s in parentheses) for the crystal

Atom	*X/a*	*Y/b*	*Z/c*
Si(1)	0.251 66(17)	0.182 17(9)	0.070 02(7)
O(2)	0.475 6(4)	0.091 11(24)	0.159 18(18)
C(3)	0.498 6(6)	0.096 36(33)	0.274 69(24)
S(4)	0.327 99(16)	0.205 62(9)	0.348 55(6)
C(5)	0.698 4(7)	−0.006 58(40)	0.326 82(32)
H(11)	0.027(7)	0.134(4)	0.095(3)
H(12)	0.273(6)	0.332(3)	0.087(3)
H(13)	0.314(7)	0.140(5)	−0.034(3)
H(51)	0.704(7)	−0.022(4)	0.413(4)
H(52)	0.843(9)	0.027(5)	0.311(3)
H(53)	0.670(8)	−0.112(5)	0.288(3)

The cell parameters are subject to the usual errors associated with the Weissenberg film method; these errors are probably accentuated by the use of split-film cassettes for low-temperature work. Estimated standard deviations (e.s.d.s) given in Tables 3—5 do not include contributions from errors in the cell parameters but the e.s.d.s in the abstract and in Table 7 do include such contributions.

The final parameters for silyl thioacetate in the gas phase are listed in Table 2, and details of the least-squares correlation matrix are given in Table 6. The errors in Table 2 are e.s.d.s obtained from the least-squares analysis increased to allow for systematic errors. Observed and final difference molecular scattering curves are shown in Figure 4.

DISCUSSION

Gaseous silyl monothioacetate is difficult to study by electron diffraction (e.d.). The overlap of distances in the radial distribution function leads to high correlations between structural and vibrational parameters. The presence of small quantities of $S(SiH_3)_2$ in the gaseous samples adds a further complication. The e.d. results cannot therefore be of high precision. Nevertheless, they provide interesting parallels to and contrasts with the solid-phase results.

TABLE 4

Intramolecular geometry in the crystal

(*a*) Distances (Å) with e.s.d.s in parentheses

Si(1)–O(2)	1.699(2)	C(3)–C(5)	1.484(4)
Si(1)–H(11)	1.35(4)	C(5)–H(51)	0.99(4)
Si(1)–H(12)	1.33(3)	C(5)–H(52)	0.87(5)
Si(1)–H(13)	1.33(4)	C(5)–H(53)	1.03(4)
O(2)–C(3)	1.319(3)	Si(1) · · · S(4)	3.185(1)
C(3)–S(4)	1.627(3)		

(*b*) Angles (°)

O(2)–Si(1)–H(11)	108.9(14)	S(4)–C(3)–C(5)	125.2(2)
O(2)–Si(1)–H(12)	109.4(13)	C(3)–C(5)–H(51)	115.4(22)
O(2)–Si(1)–H(13)	100.3(17)	C(3)–C(5)–H(52)	109.9(27)
Si(1)–O(2)–C(3)	125.1(2)	C(3)–C(5)–H(53)	107.4(23)
O(2)–C(3)–S(4)	123.0(2)	O(2)–Si(1) · · · S(4)	54.4(1)
O(2)–C(3)–C(5)	111.8(3)	C(3)–S(4) · · · Si(1)	57.4(1)

(*c*) Torsion angles (°)

Si(1)–O(2)–C(3)–S(4)	−6.0(4)
Si(1)–O(2)–C(3)–C(5)	174.8(3)
H(11)–Si(1)–O(2)–C(3)	−58.9(15)
H(12)–Si(1)–O(2)–C(3)	61.7(14)
H(13)–Si(1)–O(2)–C(3)	179.9(17)

(*d*) Distances (Å) of atoms from the least-squares best plane defined by Si(1), O(2), C(3), S(4), and C(5)

Si(1)	0.032(1)
O(2)	−0.049(2)
C(3)	−0.005(3)
S(4)	−0.006(1)
C(5)	0.027(4)
H(11)	1.19(3)
H(12)	−1.00(3)
H(13)	−0.06(4)
H(51)	0.23(4)
H(52)	−0.73(4)
H(53)	0.76(4)

The crystallographic study, like our previous *X*-ray studies of low-melting-point compounds of Si and Ge, was also faced with adverse factors. Low melting points, difficulties in crystallisation, ready decomposition, radiation damage, high *X*-ray absorption, and fluorescence all create problems. The nature of the low-temperature Weissenberg apparatus imposes some extra constraints particularly on the options available for measuring cell parameters and evaluating experimental layer scale factors. However this present analysis was one of the few where it proved possible to measure cell parameters and intensities from two different single crystals in different orientations and it is worth noting that there was very close agreement between the two sets of measurements.

Gas-phase and crystal structures confirm that the silyl group is bonded through oxygen, although the possibility of a very small amount of a sulphur-bonded species being present in the gas phase cannot be excluded. The Si–O bond lengths are 1.717(6) Å in the gas phase and 1.699(5) Å in the crystal and are equal within experi-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 5

Intermolecular geometry in the crystal *

(*a*) Shortest intermolecular contacts (Å)	
(*i*) Shortest H ··· H	
H(12) ··· H(51$^{\text{I}}$)	2.60
H(12) ··· H(52$^{\text{II}}$)	2.85
H(11) ··· H(53$^{\text{III}}$)	2.86
H(12) ··· H(51$^{\text{III}}$)	2.88
(*ii*) Shortest C ··· H	
C(5) ··· H(12$^{\text{IV}}$)	3.16
C(3) ··· H(53$^{\text{II}}$)	3.25
(*iii*) Shortest O ··· H	
O(2) ··· H(13$^{\text{V}}$)	2.79
O(2) ··· H(11$^{\text{VI}}$)	3.16
(*iv*) Shortest S ··· H	
S(4) ··· H(52$^{\text{VII}}$)	3.05
S(4) ··· H(13$^{\text{VIII}}$)	3.13
(*v*) Shortest Si ··· H	
Si(1) ··· H(53$^{\text{III}}$)	3.45
Si(1) ··· H(51$^{\text{I}}$)	3.48
(*vi*) Shortest contacts between non-hydrogen atoms	
Si(1) ··· S(4$^{\text{I}}$)	3.382(1)
O(2) ··· S(4$^{\text{IV}}$)	3.754(2)
S(4) ··· C(5$^{\text{VII}}$)	3.861(4)
Si(1) ··· C(5$^{\text{III}}$)	3.919(4)
(*b*) Important intermolecular angles (°)	
O(2)–Si(1) ··· S(4$^{\text{I}}$)	166.3(1)
C(3)–S(4) ··· Si(1$^{\text{VIII}}$)	100.8(1)

* Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: I $x - \frac{1}{2}, \frac{1}{2} - y, -\frac{1}{2} + z$; II $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; III $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; IV $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; V $1 - x, -y, -z$; VI $1 + x, y, z$; VII $x - 1, y, z$; VIII $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

mental error. These distances, although rather long for Si–O bonds, are close to values reported for other silyl esters.[1,3,18] The Si and S atoms are in the planar *cis* conformation in both phases. The apparent torsion angle of 10° found in the gas phase may be a shrinkage effect. The intramolecular Si ··· S contacts are 3.14 Å, gas, and 3.19 Å, solid. The sum of van der Waals radii for Si and S atoms is 3.9 Å so the intramolecular Si(1) ··· S(4) separation here is some 0.8 Å less than the van der Waals distance, the same as in silyl acetate.

In view of the fairly large uncertainties in some molecular parameters in the gas phase, a detailed comparison between molecular geometries in gas and solid is not appropriate but attention should be drawn to the two parameters which show greatest divergence. First the O(2)–C(3) bond length is 1.345(7) Å in the gas but only 1.319(5) Å in the crystal, and secondly the angle Si(1)–O(2)–C(3) is much narrower [118(2)°] in the gas than in the crystal [125.1(4)°]. Similar changes to the O(2)–C(3) bond length and Si(1)–O(2)–C(3) bond angle were reported in the comparison between gaseous and crystalline silyl acetate.[1]

Details of molecular geometries collected together in Table 7 point to a number of structural differences between crystalline methyl acetate, crystalline silyl

TABLE 6

Electron-diffraction analysis: portion of the least-squares correlation matrix showing all the off-diagonal elements greater than 50%

	Angles						
r_5	1	2	3	u_2	u_3	u_7	
	−57	67	−64	86		54	r_1
−83					91		r_3
	−50				−85		r_5
		−59	59	53	52		1 Angles
			−96	−52			2 Angles
						56	u_2

TABLE 7

Comparison of crystal structures of methyl acetate, silyl acetate, and silyl monothioacetate (distances in Å, angles in degrees) [a]

	CH_3-$OCOCH_3$ [b]	SiH_3-$OCOCH_3$ [b]	SiH_3-$OCSCH_3$ [c]
M(1)–O(2)	1.453(6)	1.696(6)	1.699(5)
O(2)–C(3)	1.337(6)	1.312(7)	1.319(5)
C(3)–Y(4)	1.200(5)	1.221(8)	1.627(6)
C(3)–C(5)	1.493(6)	1.476(8)	1.484(6)
M(1) ··· Y(4)	2.611(9)	2.832(9)	3.185(9)
M(1)–O(2)–C(3)	114.9(5)	120.9(5)	125.1(4)
O(2)–C(3)–Y(4)	122.5(5)	120.6(6)	123.0(4)
ϕ[M(1)–O(2)–C(3)–Y(4)]	−1.2(5)	1.6(7)	−6.0(4)
ϕ[H(13)–M(1)–O(2)–C(3)]	179(3)	171(3)	180(2)
Y(4′) ··· M(1)		2.721(9)	3.382(10)
Y(4′) ··· M(1)–O(2)		173.1(4)	166.3(3)
C(3′)–Y(4′) ··· M(1)		130.8(5)	100.8(4)

[a] E.s.d.s given here include contributions from errors in cell parameters; M = C or Si. [b] Ref. 1, Y = O. [c] This work, Y = S.

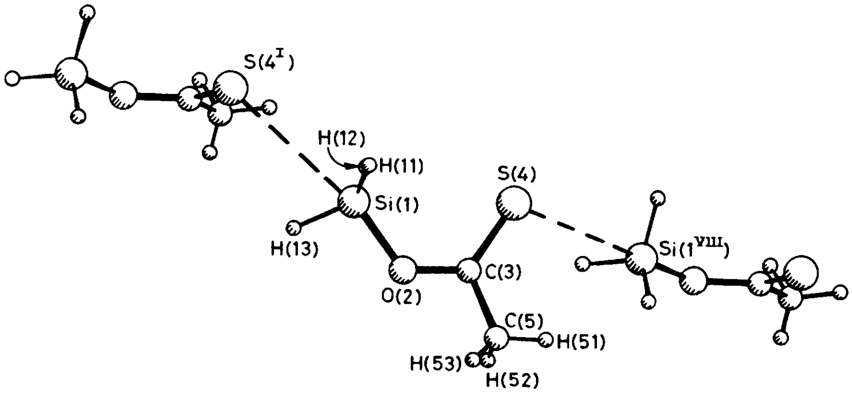

FIGURE 2 Crystalline silyl thioacetate: view of reference molecule and two neighbouring molecules showing labelling scheme and intermolecular Si ··· S contacts

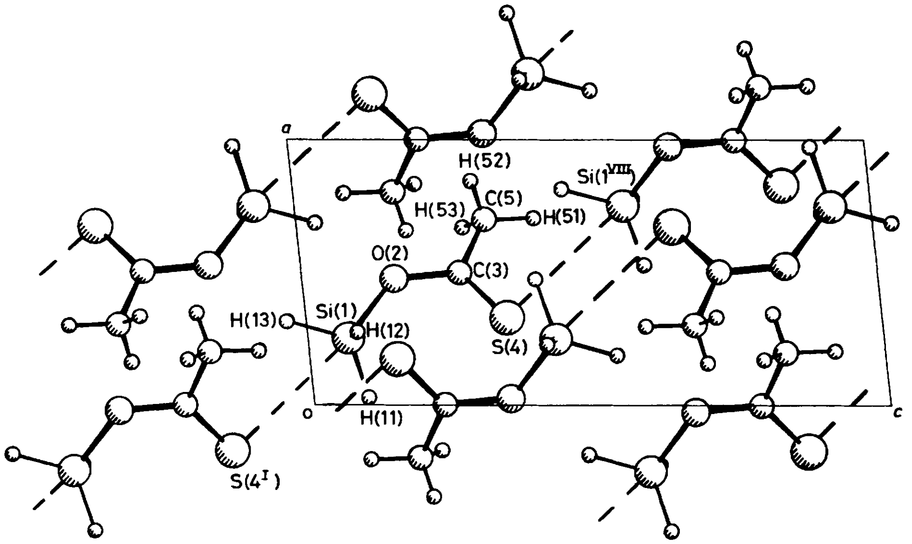

FIGURE 3 View of silyl thioacetate molecules in the crystal structure viewed down *b*. The Si · · · S′ interactions are between molecules related by the *n* glide. Roman numeral superscripts are defined in Table 5

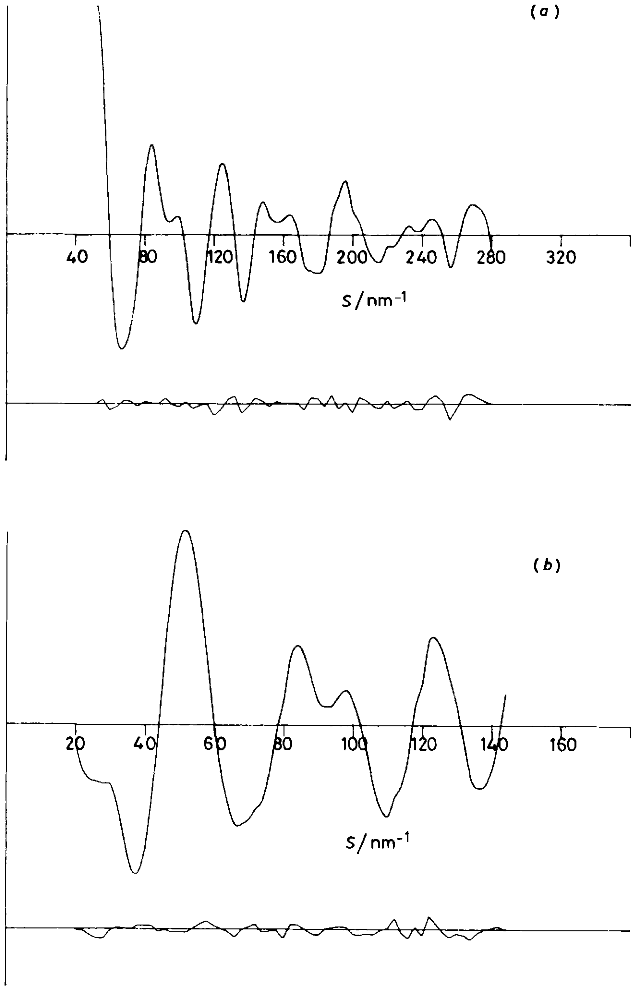

FIGURE 4 Gaseous silyl thioacetate: observed and final weighted difference molecular scattering intensities at camera distances of 128 (*a*) and 286 mm (*b*)

acetate, and crystalline silyl thioacetate. Going from methyl to silyl acetate results in a contraction of the O(2)–C(3) bond length from 1.34 to 1.31 Å while the angle at O(2) opens from 115 to 121°. [There are further, smaller, changes to bond lengths and angles at C(3).] Substitution of the C=O group in silyl acetate by C=S, in the thioacetate, leaves the O(2)–C(3) bond length essentially unchanged, now 1.32 Å, but the angle at O(2) widens still further to 125°. There are concomitant deviations from molecular planarity. In methyl acetate the five heavy atoms are accurately coplanar, in silyl acetate the deviations from planarity are just about significant, but the thioacetate is non-planar: ϕ(Si–O–C=S) = $-6.0(4)^\circ$ and ϕ(Si–O–C–C) = $174.8(3)^\circ$. These changes are obviously in accord with an increasing size effect for the M(1) and Y(4) (Y = S or O) substituents although the nature of the intramolecular interaction between M(1) and Y(4) is unclear. In all three crystal structures the H_3M group is so orientated that H(13) is planar *trans* with respect to Y(4). In addition, although the hydrogen atoms are not very accurately located, the H–M(1)–O(2) bond angles do imply that again in all three structures the C_3 axis of the H_3M group is not collinear with the M(1)–O(2) bond but is shifted slightly to point more towards the Y(4) substituent. These features were first reported, and well established, through two crystal-structure analyses of dimethyl(t-butyl)silyl esters of *aci*-nitroalkanes, when the intramolecular Si · · · O contacts were also much less than the van der Waals distance and were interpreted in terms of incipient intramolecular bond formation between O and Si.[18]

The dominating feature of the crystal structure of silyl thioacetate, as of silyl acetate, is the exceptionally short *inter*molecular contact between Si and S(4′), or O(4′) in silyl acetate. Not unexpectedly there are no comparable interactions in crystalline methyl acetate nor in the two dimethyl(t-butyl)silyl esters of *aci*-nitroalkanes. In both silyl acetate and thioacetate the intermolecular Si · · · Y(4′) distances are much shorter than the sum of the van der Waals radii and the stereochemistries at silicon are appropriate for S_N2-type interactions (see Table 7). However, the intermolecular geometries do vary in two respects. First, in crystalline silyl acetate the angle C(3)=O(4) · · · Si′ is 131° but in the thioester the angle C(3)=S(4) · · · Si′ is only 101°. Secondly, whereas in crystalline silyl acetate the *inter*molecular O(4′) · · · Si distance (2.72 Å) is less than the *intra*-molecular Si · · · O(4) distance (2.83 Å) in the thioacetate the situation is reversed with S(4′) · · · Si 3.38 Å being greater than Si · · · S(4) 3.19 Å. The first comparison is especially significant. That the C(3)=O(4) · · · Si′ angle in the acetate should be so close to typical angles in, for instance, C=O · · · H hydrogen bonds, and that the C(3)=S(4) · · · Si′ angle in the thioacetate is typical of two-coordinated sulphur argues strongly that the intermolecular interactions are highly directional in character notwithstanding that the O′ · · · Si and S′ · · · Si distances imply that the interactions are very weak.

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