Crystal Structures of Silyl Acetate at 150 K and Methyl Acetate at 145 K, and the Molecular Structure of Silyl Acetate in the Gas Phase

By **Michael J. Barrow,* Stephen Cradock, E. A. V. Ebsworth,** and **David W. H. Rankin,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The molecular structure of silyl acetate has been determined in the gas phase by electron diffraction and in the crystalline state by *X*-ray diffraction. The Si–O bond length is 1.685(3) Å in the gas and 1.696(4) Å in the solid. In both phases the heavy-atom skeleton is almost planar with the Si–O and C=O bonds arranged *cis* to one another giving intramolecular Si · · · O (carbonyl) distances of 2.795(14) Å (gas) and 2.832(4) Å (solid). The crystal structure is distinguished by having unusually short Si · · · O (carbonyl) intermolecular contacts of length 2.721(4) Å; these interactions exhibit the stereospecificity associated with secondary bonds. Solid methyl acetate, studied to provide a reference structure, has no short intermolecular contacts.

THE n.m.r. spectra of a number of carboxyl derivatives containing silyl, germyl, or trimethylsilyl groups suggest that there is intramolecular exchange of silyl or germyl groups between oxygen atoms that is rapid on the n.m.r. time scale at room temperature.[1] This has been taken as implying that silicon and the carbonyl oxygen are mutually *cis*, and suggesting that interaction between the two should lead to short non-bonded Si · · · O distances. We have shown [2] that the marked reduction in C=O stretching frequencies of the silyl esters from the vapour to the solid state is characteristic also of methyl esters and other carboxyl compounds, and is thus not due to any special structural features of solid silyl esters. Our recent *X*-ray studies of the structures of simple silyl and germyl compounds in the crystalline phase have shown that there are often weak but stereochemically well defined intermolecular contacts between silicon (or germanium) and oxygen or nitrogen.[3,4] We have therefore undertaken a study of the structure of silyl acetate in the vapour and crystalline phases in order to explore the extent to which inter- and intra-molecular non-bonded interactions occur in this compound, and how such interactions affect one another.

Surprisingly, there has been no report of the solid-phase structure of a simple organic ester. We have therefore included methyl acetate in our *X*-ray investigations, to provide a reference structure for the case where intra- and inter-molecular interactions are likely to be negligible.

EXPERIMENTAL

A sample of silyl acetate was prepared by the reaction of silyl bromide with tributyltin acetate,[2] and was purified by fractional condensation *in vacuo*. Methyl acetate was purchased. Purities were checked spectroscopically.

X-Ray Diffraction.—Crystal data. (*a*) *Methyl acetate.* CH_3OCOCH_3, $M = 74.08$, Monoclinic, $a = 7.70$, $b = 6.96$, $c = 7.97$ Å, $\beta = 109°$ [estimated standard deviations (e.s.d.s.) 0.3% assumed for a and b, 0.6% assumed for c and β], $U = 403.9$ Å^3, $Z = 4$, $D_c = 1.22$, Cu-K_α radiation (nickel filter), $\lambda = 1.5418$ Å, μ(Cu-K_α) = 8.3 cm^{-1}, space group $P2_1/n$ (C_{2h}^5, no. 14) by systematic absences.

Melting point 175 K: cell parameters and intensities were measured at 145 K. The final least-squares weighting scheme was $w^{-1} = 1 + 0.06(3 - F_o)^2$ for $F_o < 3$, and $w^{-1} = 1 + 0.04(F_o - 3)^2$ for $F_o \geqslant 3$. Final values of the discrepancy indices, over 382 reflections, were $R = \Sigma|\Delta|/\Sigma|F_o| = 0.049$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.068$.

(*b*) *Silyl acetate.* SiH_3OCOCH_3, $M = 90.15$, Orthorhombic, $a = 4.47$, $b = 10.11$, $c = 10.90$ Å (e.s.d.s 0.3% assumed), $U = 492.6$ Å^3, $Z = 4$, $D_c = 1.22$, Cu-K_α radiation (nickel filter), $\lambda = 1.5418$ Å, μ(Cu-K_α) = 30.9 cm^{-1}, space group $P2_12_12_1$ (D_2^4, no. 19) by systematic absences.

Melting point 208 K: cell parameters and intensities were measured at 150 K. The final least-squares weighting scheme was $w^{-1} = 1 + 0.0009(F_o - 6)^2$. Final values of the discrepancy indices were $R = 0.049$ and $R' = 0.063$ over 785 reflections.

Procedure. Samples were sealed in Lindemann glass capillaries (internal diameter 0.5 mm) mounted on goniometer heads using heat-insulating Tufnol inserts. Single crystals were grown '*in situ*' on a Nonius Weissenberg goniometer fitted with a modified Nonius low-temperature nitrogen-gas-stream equipment. Intensity films were exposed for the Weissenberg levels 0—5*kl* for methyl acetate and 0—4*kl* for silyl acetate using Cu-K_α radiation and the multiple film pack method.

During crystal growing we were only able to obtain specimens with the '*a*' axes aligned along the camera axis. Furthermore only one specimen tube of methyl acetate, out of many examined, yielded crystals suitable for single-crystal diffraction. This sample was lost afterwards through fracture of the capillary during a heating–cooling cycle. Subsequently we examined several different samples of methyl acetate using a Nonius Guinier-Simon low-temperature powder diffraction camera. In every case the powder diffraction was somewhat weak and diffuse (perhaps indicating a 'plastic-crystal' phase) and was definitely incompatible with the single-crystal structure. As a result the monoclinic angle for the methyl acetate crystal is known only from measurements of reflection positions on oscillation photographs and from the fitting of cell dimensions to the co-ordinates of reflections as determined by microdensitometer scanning of the multiple film pack intensity photographs. The e.s.d. appropriate for β (and hence c, though not c^* or U) is therefore somewhat larger than usual.

Integrated intensities were obtained from microdensitometer measurements performed by the S.R.C. Microdensitometer Service at Daresbury Laboratory, Warrington. The data were corrected for adsorption effects using the SHELX program: [5] for each crystal a sufficient number of

faces were defined in order to approximate the required shape (cylindrical) and orientation of the crystal. The intensities were further corrected for Lorentz and polarisation effects. For methyl acetate, 748 intensities were obtained from measurements of the *hkl*, *hkl*, *hkl*, and *hkl* regions of reciprocal space. After data reduction and merging of equivalents 390 unique reflections remained. Eight reflections were subsequently removed on the grounds of persistently poor agreement with F_c so that the final least-squares calculations utilised 382 reflections. Similarly for silyl acetate 946 intensities were obtained from measurements of the *hkl*, *hkl*, and *hkl* octants which after data reduction and merging yielded 786 unique reflections (full anomalous scattering data: *hkl* and *hkl*). One reflection was later removed for bad agreement so that the analysis used 785 reflections.

Structure solution and refinement. For $Z = 4$ the space groups impose no restriction on the molecular symmetries. The structure of methyl acetate was solved by direct methods and the silyl acetate structure was deduced from Patterson and Fourier syntheses. Hydrogen atoms were located from difference-Fourier syntheses and their parameters (assuming isotropic vibration) refined together with anisotropic parameters for all other atoms. The least-squares calculations minimised the quantity $\Sigma w(|F_o| - |F_c|)^2$.

The hydrogen atoms attached to C(5) in methyl acetate gave rise to a broken torus of residual electron density in the difference-Fourier synthesis. This would be consistent with (*a*) rotational vibration of the CH_3 group about the C(3)–C(5) bond, (*b*) disorder of the H atoms, or (*c*) some mixture of these possibilities. In the event the observed electron density could be modelled fairly satisfactorily by dividing the hydrogens into two groups each consisting of three partial hydrogen atoms. Group 1 contained H(51), H(53), H(55) (see Figure 1), and was assigned a population parameter, pp(1), which was refined. The population parameter for Group 2, H(52), H(54), H(56), was set equal to 1 − pp(1). A single variable was used to define the isotropic vibration parameter for all these H atoms while their positional parameters were allowed to refine subject to two ' slack constraints ': (*a*) all C–H bonds approximately equal with $\sqrt{w} \propto$ e.s.d. = 0.05 Å, (*b*) a constraint on non-bonded distances, H(31) · · · H(33) ≈ H(32) · · · H(34) ≈ H(33) · · · H(35) *etc.*, all with $\sqrt{w} \propto$ e.s.d. = 0.05 Å.

Inter-layer scale factors were refined at various stages of the refinement processes. Empirical isotropic extinction corrections were applied through a variable parameter during the least-squares calculations but in both structures the corrections were found to be negligibly small and were omitted from the final refinements. Empirical least-squares weighting schemes were included: the final schemes are listed above. Atomic scattering factors for Si (sp^3 valence) were taken from ref. 6, those for O and C from ref. 7, and those for H from ref. 8. Allowance was made for the real and imaginary components of the anomalous-dispersion effect for Si, O, and C atoms using $\Delta f'$ and $\Delta f''$ values from ref. 9.

Just prior to the final refinement of silyl acetate two comparative least-squares calculations were undertaken to discriminate between the enantiomorphs. The structure corresponding to that reported here gave $R = 0.049$ and $R' = 0.065$, while its enantiomorph gave $R = 0.054$ and $R' = 0.070$.

All calculations were performed using computers of the Edinburgh Regional Computing Centre, using programs written here and the program systems *X*-Ray '76,[10] SHELX,[5] 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 54 kV, and were converted into digital form using a Jarrell–Ash rotating table microdensitometer.[14] The sample was maintained at 250 K and the nozzle at 293 K during experiments. Three plates taken at each of two camera distances, 128 and 285 mm, were used, giving data over a range of 28—328 nm^{-1} in the scattering variable, *s*.

All calculations were carried out on ICL 2970 and 2980 computers at the Edinburgh Regional Computing Centre, using established data reduction [13] and least-squares refinement [15] programs. Weighting points, used in setting up the off-diagonal weight matrix used in the refinements, are given in Table 1, together with correlation parameters and scale factors. The electron wavelength, 5.121 ± 0.003 pm, was determined from the diffraction pattern of gaseous benzene. In all calculations the scattering factors of Schäfer *et al.*[16] were used.

TABLE 1

Weighting functions, scale factors, and correlation parameters

Camera height / mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor
			nm^{-1}				
285	2	28	36	140	162	0.408	0.886(16)
128	4	76	80	300	328	0.251	1.027(49)

In the model used for the refinement of the structures of silyl acetate it was assumed that the $OSiH_3$ and CCH_3 groups had local C_{3v} symmetry and that the co-ordination of the central carbon atom was planar. The geometry was then defined by 14 parameters, chosen to be the six bond lengths, five valence angles, and three dihedral angles. The SiH_3 and CH_3 twist angles were defined to be zero when one Si–H or C–H bond was staggered with respect to the C–O bond.

The geometrical parameters involving heavy atoms, with the exception of the O=C–O–Si dihedral angle, all refined easily, although it was necessary to fix several amplitudes of vibration at reasonable values. The best value of the dihedral angle was determined by performing a series of refinements with it fixed at values in the range 0—30°, and although the minimum *R* factor was 0.1190 at 10°, this only rose to 0.1200 at 0° and 0.1205 at 20°. It is only possible to say with confidence that the value is less than 25°, and it may be that any apparent deviation from planarity of the skeleton is caused by a large-amplitude torsional motion. The optimum value of the SiH_3 twist angle was fixed by a similar procedure.

RESULTS

Final values of atomic parameters for methyl acetate and silyl acetate in the crystalline phase are given in Tables 2 and 3 respectively. Details of the intramolecular and intermolecular geometries are given in Tables 4 and 5. The molecular geometries and atomic labelling schemes are illustrated by Figures 1 and 3. Figure 2 shows the packing of molecules in solid methyl acetate while Figure 4 illustrates the intermolecular interactions in solid silyl acetate.

TABLE 2

Atomic parameters for CH_3OCOCH_3 with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	0.331 0(7)	−0.188 7(4)	0.572 2(5)
O(2)	0.331 7(4)	0.019 3(3)	0.587 9(3)
C(3)	0.203 4(5)	0.109 7(4)	0.457 0(4)
O(4)	0.098 0(4)	0.025 6(3)	0.334 4(3)
C(5)	0.214 2(6)	0.322 6(4)	0.481 0(4)
H(11)	0.225(8)	−0.230(6)	0.586(5)
H(12)	0.354(6)	−0.222(5)	0.466(5)
H(13)	0.433(7)	−0.209(5)	0.677(6)
H(51)	0.254(10)	0.359(9)	0.594(6)
H(52)	0.121(10)	0.338(11)	0.531(11)
H(53)	0.094(6)	0.369(9)	0.422(8)
H(54)	0.176(13)	0.394(11)	0.374(7)
H(55)	0.286(9)	0.358(9)	0.408(7)
H(56)	0.326(7)	0.350(12)	0.554(9)

Occupation factor: 0.57(4) for H(51), H(53), H(55); 0.43(4) for H(52), H(54), H(56).

TABLE 3

Atomic parameters for SiH_3OCOCH_3 with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Si(1)	0.356 97(30)	0.219 16(13)	0.176 56(11)
O(2)	0.252 5(9)	0.350 0(3)	0.089 1(3)
C(3)	0.336 5(14)	0.470 5(4)	0.117 4(4)
O(4)	0.497 2(11)	0.490 5(4)	0.206 1(3)
C(5)	0.236 3(20)	0.574 6(6)	0.031 8(6)
H(11)	0.649(14)	0.219(5)	0.177(5)
H(12)	0.218(11)	0.236(4)	0.292(3)
H(13)	0.165(19)	0.115(5)	0.120(5)
H(51)	0.272(15)	0.670(5)	0.060(5)
H(52)	0.039(24)	0.567(7)	0.027(6)
H(53)	0.349(41)	0.543(11)	−0.051(10)

TABLE 4

Intramolecular geometries in the crystal

(a) Distances (Å)	CH_3OCOCH_3	SiH_3OCOCH_3	Gaseous SiH_3OCOCH_3 (see Table 6)
M(1)–O(2)	1.453(4)	1.696(4)	1.685(3)
M(1)–H(11)	0.90(5)	1.31(6)	1.521(13)
M(1)–H(12)	0.95(4)	1.41(4)	
M(1)–H(13)	0.95(5)	1.49(7)	
M(1) · · · O(4)	2.611(4)	2.832(4)	2.795(13)
O(2)–C(3)	1.337(4)	1.312(6)	1.358(4)
C(3)–O(4)	1.200(4)	1.221(7)	1.214(4)
C(3)–C(5)	1.493(4)	1.476(8)	1.487(6)
C(5)–H(51)	0.89(4) *	1.03(5)	1.127(11)
C(5)–H(52)	0.93(4) *	0.89(11)	
C(5)–H(53)	0.95(4) *	1.08(13)	
C(5)–H(54)	0.95(4) *		
C(5)–H(55)	0.95(4) *		
C(5)–H(56)	0.89(4) *		
(b) Angles (°)			
M(1)–O(2)–C(3)	114.9(3)	120.9(3)	116.5(7)
O(2)–C(3)–O(4)	122.5(3)	120.6(4)	121.7(8)
O(2)–C(3)–C(5)	111.8(3)	115.2(5)	115.9(15)
O(4)–C(3)–C(5)	125.7(3)	124.1(5)	
O(2)–M(1)–H(11)	107(3)	106(2)	
O(2)–M(1)–H(12)	109(2)	107(2)	
O(2)–M(1)–H(13)	96(2)	99(2)	
H–M(1)–H (mean)	114(4)	114(4)	
C(3)–C(5)–H (mean)	107(5)	107(5)	
H–C(5)–H (mean)	112(5)	111(7)	
C(3)–O(4) · · · M(1)	64.2(2)	67.6(3)	
O(2)–M(1) · · · O(4)	58.4(2)	50.9(1)	

TABLE 4 (*continued*)

(c) Torsion angles (°)	CH_3OCOCH_3	SiH_3OCOCH_3
M(1)–O(2)–C(3)–O(4)	−1.2(5)	1.6(7)
M(1)–O(2)–C(3)–C(5)	−179.3(3)	178.6(4)
H(11)–M(1)–O(2)–C(3)	−67(3)	−59(3)
H(12)–M(1)–O(2)–C(3)	61(3)	65(2)
H(13)–M(1)–O(2)–C(3)	179(3)	171(3)

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

CH_3OCOCH_3: C(1) −0.003(5); O(2) −0.000(3); C(3) 0.011(4); O(4) −0.004(3); C(5) −0.005(4); H(11) 0.80(5); H(12) −0.79(5); H(13) −0.03(5)

SiH_3OCOCH_3: Si(1) 0.006(1); O(2) −0.003(4); C(3) −0.017(6); O(4) 0.004(5); C(5) 0.010(8); H(11) 1.07(6); H(12) −1.23(4); H(13) −0.22(8)

* Disordered H atoms refined under geometric constraints, see text.

TABLE 5

Intermolecular geometry

(*a*) Closest intermolecular constants (Å) for CH_3OCOCH_3

(*i*) H · · · H

H(13) · · · H(52^{I}) 2.52; H(11) · · · H(51^{I}) 2.58; H(11) · · · H(53^{II}) 2.62; H(11) · · · H(52^{II}) 2.63

(*ii*) O · · H

O(4) · · · H(13^{III}) 2.65; O(4) · · · H(55^{IV}) 2.65

(*iii*) C · · · H

C(1) · · · H(51^{I}) 2.96; C(1) · · · H(52^{I}) 3.07

(*iv*) O · · · O

O(2) · · · O(2^{V}) 3.33; O(4) · · · O(4^{II}) 3.46

(*v*) O · · · C

O(4) · · · C(1^{III}) 3.36; O(4) · · · C(3^{II}) 3.40

(*vi*) C · · · C

C(1) · · · C(5^{VI}) 3.53; C(1) · · · C(5^{I}) 3.69

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

(*b*) Closest intermolecular contacts (Å) for SiH_3OCOCH_3

(*i*) H · · H

H(53) · · · H(13^{I}) 2.26; H(11) · · · H(13^{II}) 2.61; H(12) · · · H(51^{III}) 2.80; H(12) · · · H(53^{IV}) 2.83

(*ii*) H · · · O or C

H(11) · · · O(4^{V}) 2.72; H(13) · · · O(4^{V}) 2.73

(*iii*) H · · · Si

H(11) · · · Si(1^{II}) 3.16; H(51) · · · Si(1^{VI}) 3.35

(*iv*) O or C · · · O or C

O(2) · · · O(2^{I}) 3.58; O(4) · · · C(5^{IV}) 3.76

(*v*) Si · · · O or C

Si(1) · · · O(4^{V}) 2.721(4); Si(1) · · · O(2^{I}) 3.464(4); Si(1) · · · C(3^{V}) 3.64; Si(1) · · · C(5^{V}) 3.94

(*vi*) Si · · · Si

None < 4.0 Å

(*vii*) Important intermolecular angles (°)

O(2)–Si(1) · · · O(4^{V}) 173.1(2); C(3)–O(4) · · · Si(1^{VI}) 130.8(3); O(2)–Si(1) · · · O(2^{I}) 80.1(2); H(12)–Si(1) · · · O(2^{I}) 173(2); Si(1)–O(2) · · · Si(1^{VII}) 117.0(1); C(3)–O(2) · · · Si(1^{VII}) 122.0(3)

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

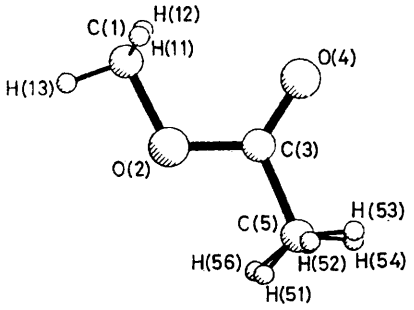

FIGURE 1 View of methyl acetate molecule in the crystal, and showing the partial hydrogen atoms about C(5); see text

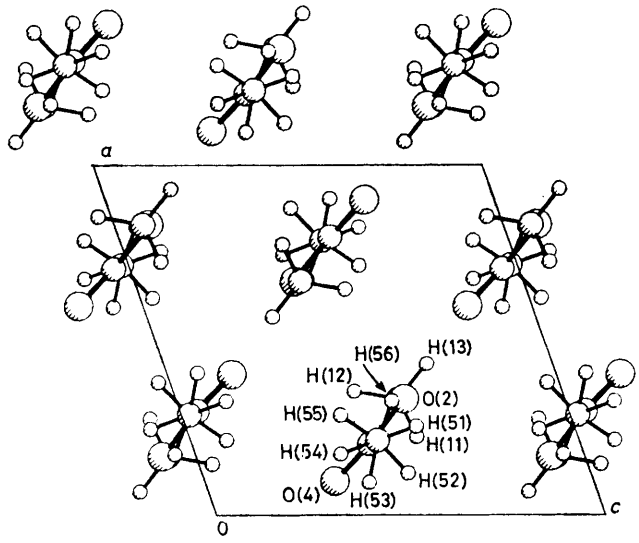

FIGURE 2 Arrangement of methyl acetate molecules in the crystal structure viewed down *b*

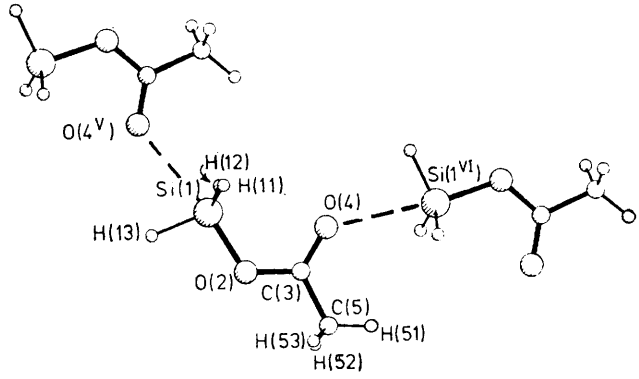

FIGURE 3 View of silyl acetate molecules in the crystal to highlight the O(4^{V}) · · · Si intermolecular contacts

Tables of observed and calculated structure factors and thermal vibration parameters are available as Supplementary Publication No. SUP 23090 (11 pp.).*

The cell parameters are subject to the usual errors associated with the Weissenberg film method and the errors are probably accentuated by the use of split-film cassettes

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

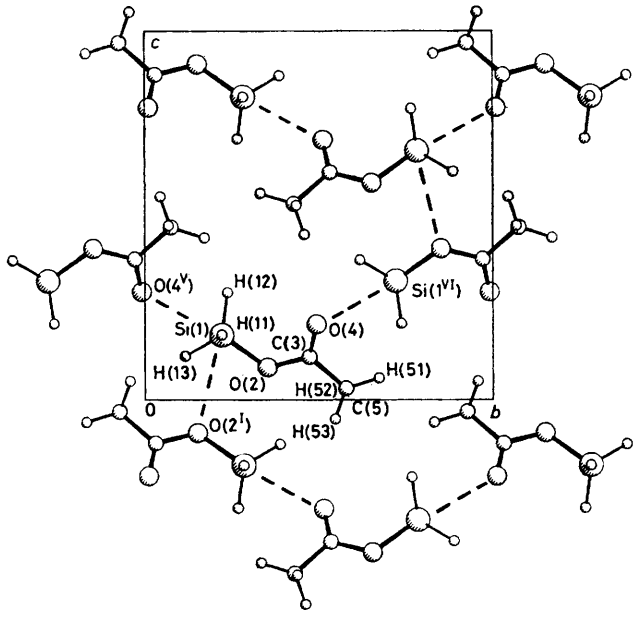

FIGURE 4 Arrangement of silyl acetate molecules in the crystal structure viewed down *a*. Both the short O(4) · · · Si(1) contacts and long Si(1) · · · O(2) contacts are indicated. The latter serve to cross-link the chains since each molecule participitates in an Si(1) · · · O(2) contact to a molecule ' above ' and in an equivalent O(2) · · · Si(1) contact to a molecule ' below '

for low-temperature work. The monoclinic angle for methyl acetate is rather poorly determined, as explained earlier. All e.s.d.s of results (whether given in the abstract, text, or Tables) exclude contributions from errors in the cell parameters. The accuracy of the atomic vibration parameters is likely to be adversely affected by the lack of direct, experimentally obtained, layer scale factors.

TABLE 6

Gas-phase molecular parameters for silyl acetate

	Distance (Å)	Amplitude (Å)
(*a*) Independent distances		
r_1 (C–C)	1.487(6)	0.045 [a]
r_2 (C–H)	1.127(11)	0.061 [a]
r_3 (C=O)	1.214(4)	0.049(6)
r_4 (C–O)	1.358(4)	0.045 [a]
r_5 (Si–O)	1.685(3)	0.059(5)
r_6 (Si–H)	1.521(13)	0.087 [a]
(*b*) Dependent distances		
d_7 (C · · · O)	2.372(15)	
d_8 (C · · · O)	2.412(13)	0.072(9)
d_9 (O · · · O)	2.247(7)	
d_{10} (Si · · · O)	2.795(13)	0.155(16)
d_{11} (Si · · · C)	2.593(9)	0.100 [a]
d_{12} (Si · · · C)	3.956(9)	0.084(9)
Two-bond H · · · C/O		0.100 [a]
Three-bond H · · C/O		0.173(54)
Four-bond H · · · C/O/Si		0.270(66)
(*c*) Angles (°)		
Angle 1 (C–C–O)	115.9(15)	
Angle 2 (O–C=O)	121.7(8)	
Angle 3 (C–O–Si)	116.5(7)	
Angle 4 (O–Si–H)	111.2 [a]	
Angle 5 (C–C–H)	110.4 [a]	
Angle 6 (dihedral O=C–O–Si)	10.0 [b]	
Angle 7 (twist SiH_3)	7.0 [b]	
Angle 8 (twist CH_3)	0.0 [a]	

[a] Fixed. [b] See text.

TABLE 7

Gaseous silyl acetate: portion of the least-squares correlation matrix showing all the off-diagonal elements greater than 50%

		Angle								
r_3	r_6	2	3	u_3	u_5	u_7	u_{10}	u_{14}	k_2	
−61	−83	58			−57		−58			r_1
				−68						r_2
	58									r_3
		−50			61		63			r_6
			−59							1 } Angle
						50	−66			2 } Angle
									56	u_5
								64		u_{10}

The final parameters for silyl acetate in the gas phase are listed in Table 6, and the least-squares correlation matrix is given in Table 7. The errors quoted in Table 6 are estimated standard deviations obtained in the least-squares analysis, increased to allow for systematic errors. Observed and final difference molecular scattering curves are shown in Figure 5, and radial distribution curves are shown in Figure 6.

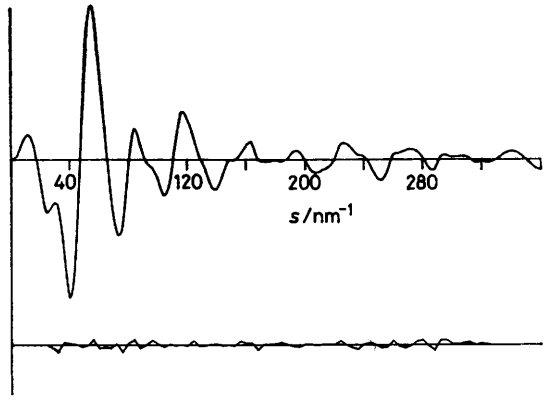

FIGURE 5 Observed and final weighted difference combined electron scattering intensities for silyl acetate

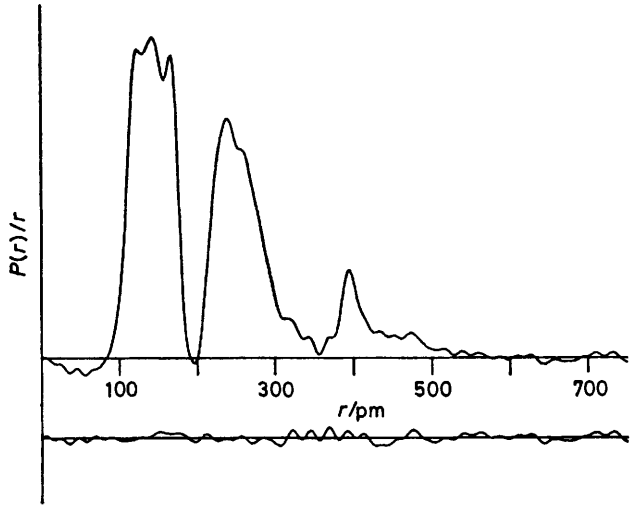

FIGURE 6 Gaseous silyl acetate: observed and final difference radial distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s \exp[-0.002\ s^2/(Z_{Si} - f_{Si})(Z_c - f_c)]$

DISCUSSION

The molecular dimensions determined for gaseous silyl acetate agree closely with the corresponding parameters obtained by electron diffraction for silyl formate.[17] Both molecules adopt the configuration in which the Si–O bond is *cis* to the C=O bond, with dihedral angles Si–O–C=O of 10 and 20° respectively. The Si–O–C angle is unchanged, 116.8(5) against 116.5(7)°, and similarily the unusually long Si–O bond, 1.695(3) Å, found in the formate, is again found in silyl acetate [1.685(3) Å]. Other long Si–O bonds occur in bis(trimethylsilyl) peroxide [1.681(3) Å] in the gas phase,[18] and in the crystalline phases of bis(benzyldimethylsilyl) peroxide [1.687(1) Å],[19] and of two silyl esters of aci-nitroalkanes [1.709(1) and 1.716(1) Å].[20] In all these examples the group bonded through oxygen to silicon is unsaturated or electronegative, so there may be a parallel with the pattern of Si–N bond lengths, where the longest bonds occur in species like $Me_3Si–N=N–SiMe_3$.[21]

In the solid state silyl acetate, like methyl acetate, has an essentially planar heavy-atom skeleton. Both solid-state species have the *cis* configuration of the M–O bond relative to the C=O bond, giving intramolecular M(1) · · · O(4) distances which are 2.611(4) Å in methyl acetate (0.6 Å less than the sum of van der Waals radii) and 2.832(4) Å in silyl acetate (0.8 Å less than the sum of van der Waals radii). In both the *X*-ray structures, the configuration of the MH_3 group is such that one M–H bond is *trans* to the O(2)–C(3) bond.

The most striking feature of the arrangement of the ester molecules in the crystalline state is that molecules of methyl acetate exist as discrete entities, with no short intermolecular contacts, whereas in solid silyl acetate the molecules form chains, with short, directionally specific, O(4) · · · Si(1) intermolecular interactions.

The intermolecular O(4^V) · · · Si(1) distance is 2.721(4) Å and the O(4^V) · · · Si(1)–O(2) angle is 173.1(2)°. This arrangement of four short and one very long bond to Si is entirely analogous to, although more striking than, the situation in crystalline disiloxane where there are intermolecular O · · · Si contacts of 3.115(5) Å. Such examples of incipient five-co-ordination environments at silicon have long been recognised for those cases where the donor atom is nitrogen (*i.e.* N · · · SiR_3–X species). These N · · · Si interactions have been analysed in terms

of intermediate points along an S_N2 reaction pathway leading to substitution and inversion of configuration at Si.[4,22] The O(4^V) · · · Si contact in crystalline silyl acetate is, to our knowledge, the shortest such interaction occurring between O and Si atoms in otherwise discrete molecules. Yet even though this contact is 0.9 Å less than the sum of van der Waals radii there must be some doubt about its role bearing in mind that the *intra*molecular O(4) · · · Si distance across the molecule is also considerably less than the sum of van der Waals radii. Nevertheless it is worth noting that the angle at the carbonyl oxygen, C(3^V)–O(4^V) · · · Si, is 130.8(3)°, a value similar to those found in structures where a carbonyl oxygen forms a strong intermolecular hydrogen bond. So in all stereochemical aspects the O(4^V) · · · Si contact fully satisfies the requirements for a directionally specific secondary bond.

A second, much longer, intermolecular contact occurs between Si(1) and O(2). This contact bisects the external Si(1)–O(2)–C(3) angle and is *trans* to one of the Si–H bonds. However, the Si · · · O distance is 3.46 Å, only slightly less than the sum of van der Waals radii for silicon and oxygen, and this interaction must be very weak compared to the O(4) · · · Si(1) interaction.

In general the gas- and solid-phase structures of silyl acetate are in very close agreement (see Table 3), but there are two parameters which change significantly. The Si–O–C angle is 120.9(3)° in the solid, but only 116.5(7)° in the gas, and the O(2)–C(3) distance is increased from 1.312(6) Å in the solid to 1.358(4) Å in the gas phase. This is unexpected. These parameters should be among those least likely to be affected by perturbations arising from the intermolecular interactions in the crystal. The differences cannot be fully explained on the basis of the differing nature and parameter correlations that are implicit when comparing electron with *X*-ray diffraction. Moreover it should be noted that the gas-phase structure for silyl acetate agrees well with that for silyl formate,[17] while the *X*-ray parameters for silyl acetate fall neatly midway between the solid-state geometries found for methyl acetate and for SiH_3OCSCH_3.[23]

There are small but probably significant differences between the intramolecular geometries of the methyl and silyl acetates in the solid phase. First, the angle at O(2) is 121° in the silyl ester, but only 115° in the methyl ester: this is in accord with the general observation that angles at oxygen increase when a carbon substituent is replaced by a silicon substituent. Secondly, there are differences in the geometry around C(3), so that in the silyl compound the C(3)=O(4) bond is 0.02 Å longer, but the C(3)–C(5) and C(3)–O(2) bonds are about 0.02 Å shorter than in the methyl compound, while the O(2)–C(3)–C(5) angle is increased by some 3°, at the expense of the other two angles, in the silyl compound. These changes are found to follow the pattern of bond length–bond angle correlations established by a statistical analysis of crystal structures containing $-CO_2^-$, $-CO_2H$, and $-CO_2Me$ fragments.[24] (Both the present crystal structures fall, at appropriate places, on the regression line in Figure 1 of ref. 24.) Interestingly, while the molecular parameters for solid methyl acetate agree well with the mean carboxyl geometry established for a $-CO_2Me$ group, the carboxyl geometry in solid silyl acetate corresponds closely with the mean geometry for a $-CO_2H$ group in a *crystal* environment. In drawing attention to the similarities between the $-CO_2H$ and $-CO_2SiH_3$ groups these observations emphasise the parallels between the O–SiH_3 · · · O interaction and the O–H · · · O hydrogen bonds which are so common a feature in crystal structures of carboxylic acids.

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