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Structure of Methoxysilane at 110K

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Abstract. CH_3OSiH_3, $M_r = 62{\cdot}148$, orthorhombic, *Pnma*, $a = 7{\cdot}816\,(6)$, $b = 7{\cdot}561\,(4)$, $c = 6{\cdot}4252\,(21)$ Å, $V = 379{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}087$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}333$ mm^{-1}, $F(000) = 136$, $T = 110$ K, $R = 0{\cdot}0536$ for 454 observed reflections. Molecules lie on crystallographic mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$ and each is linked to two others in the same plane by Si$\cdots$O contacts of 2·8470 (19) Å [*cf.* 3·115 (5) Å in disiloxane], forming zigzag chains. However, these interactions do not significantly affect the molecular geometry and the heavy-atom parameters [Si–O, C–O bond lengths 1·6510 (19), 1·424 (3) Å; SiOC angle 120·13 (16)°] are not significantly different from those found in the gas phase.

Introduction. Among the principal aims of our work on the crystal structures of low-melting inorganic compounds is comparison of the gas-phase and solid-state geometries of a species and examination of the structures of related series of molecules. In this case we have determined the crystal structure of CH_3OSiH_3 whose structure in the vapour phase has been determined by electron diffraction (Glidewell, Rankin, Robiette, Sheldrick, Beagley & Freeman, 1970) and which is intermediate between dimethyl ether where the angle at O is essentially tetrahedral (Kimura & Kubo, 1959) and disiloxane where the angle is 144° (Almenningen, Bastiansen, Ewing, Hedberg & Traetteberg, 1963; Barrow, Ebsworth & Harding, 1979).

Experimental. Compound prepared in 90% yield by reaction of dried CH_3OH with the 1:1 SiH_3Br:$(CH_3)_3N$ adduct at ambient temperature, product fractionated at 195 K to remove excess CH_3OH. Colourless, cylindrical crystal, 0·4 × 0·4 × 0·5 mm, grown *in situ* on a Weissenberg camera equipped for low-temperature studies from sample sealed in Pyrex capillary tube, space group identified by photography and ultimate successful refinement, m.p. 174 K. Crystal transferred without melting or other phase change as described previously (Blake, Cradock, Ebsworth, Rankin & Welch, 1984) to CAD-4 diffractometer equipped for low-temperature data collection, 110 K, 25 reflections ($13{\cdot}9 < \theta < 15{\cdot}5°$) for refinement of orientation matrix.

For data collection, graphite-monochromated Mo $K\alpha$ X-radiation, $\theta_{\max} = 30°$, ω–2θ scans with ω-scan width $1{\cdot}6° + 0{\cdot}8° \tan\theta$, 645 reflections, 535 unique, $h\,0\rightarrow9$, $k\,0\rightarrow10$, $l\,0\rightarrow10$, in 11 X-ray hours. Three standards, no significant crystal movement or decay, no absorption correction.

For structure solution and refinement 454 amplitudes [$F \geq 6\sigma(F)$], automatic direct methods (Sheldrick, 1984), full-matrix least-squares refinement, (Sheldrick, 1976), $w^{-1} = \sigma^2(F) + 0{\cdot}00688\,F^2$, anisotropic thermal parameters for Si, O and C, isotropic for H. Silyl H refined freely, methyl H as part of rigid group, $R = 0{\cdot}0536$, $wR = 0{\cdot}0775$, $S = 0{\cdot}908$, data: variable ratio 14:1, $(\Delta/\sigma)_{\max}$ in final cycle 0·006, max. peak and min. trough in final ΔF synthesis 0·44 and $-0{\cdot}63$ e Å^{-3} respectively. Neutral-atom scattering factors were inlaid (Sheldrick, 1976), other computer programs *SHELX*84 (Sheldrick, 1984), *CALC* (Gould & Taylor, 1985), *ORTEP*II (interactive version) (Mallinson & Muir, 1985) and *PLUTO* (Motherwell, 1976).

Discussion. Table 1 lists selected molecular geometry parameters; refined fractional coordinates and anisotropic thermal parameters appear in Table 2.* Fig. 1 is a view of a single molecule while the packing of molecules in planes is illustrated in Fig. 2: the zigzag chains of molecules related by the *a* glide plane are characterized by the Si$\cdots$O distance of 2·8470 (19) Å, O$\cdots$Si–O angle of 174·35 (8)° and C–O$\cdots$Si and Si–O$\cdots$Si angles of 117·51 (14) and 122·36 (9)°

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44309 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

Si–H(1*S*)	1·39 (4)	Si–O	1·6510 (19)
Si–H(2*S*)	1·32 (3)	O–C	1·424 (3)
H(1*S*)–Si–H(2*S*)	111·9 (22)	H(2*S*)–Si–H(2*S*′)	113·2 (21)
H(1*S*)–Si–O	105·7 (16)	Si–O–C	120·13 (16)
H(2*S*)–Si–O	106·7 (15)		
H(1*S*)–Si–O–C	179·9 (17)	Si–O–C–H(1)	−179·92 (23)
H(2*S*)–Si–O–C	−60·7 (16)	Si–O–C–H(2)	59·0 (3)

Table 2. *Positional (fractional coordinates) and thermal* ($Å^2$) *parameters with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Si	0·68798 (9)	0·25	0·19006 (12)	0·0207 (5)
O	0·4981 (3)	0·25	0·0774 (4)	0·0267 (12)
C	0·4850 (4)	0·25	−0·1436 (5)	0·0243 (14)
H(1*S*)	0·656 (6)	0·25	0·404 (7)	0·025 (10)
H(2*S*)	0·766 (5)	0·105 (4)	0·130 (5)	0·032 (7)
H(1)	0·3626 (4)	0·25	−0·1858 (5)	0·013 (9)
H(2)	0·5482 (4)	0·135 (4)	−0·2074 (5)	0·043 (10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	0·0077 (5)	0·0315 (6)	0·0229 (5)	0·0	0·0010 (3)	0·0
O	0·0075 (10)	0·0498 (15)	0·0227 (10)	0·0	0·0005 (7)	0·0
C	0·0136 (12)	0·0356 (17)	0·0237 (13)	0·0	0·0020 (10)	0·0

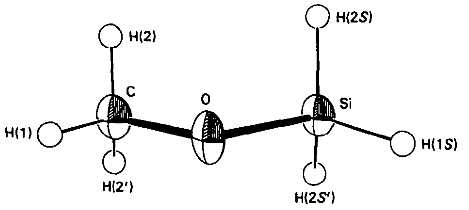

Fig. 1. *ORTEP* view of a single molecule with thermal ellipsoids at the 30% probability level except for H atoms which have a radius of 0·1 Å. Si, O, C, H(1*S*) and H(1) lie on a crystallographic mirror plane.

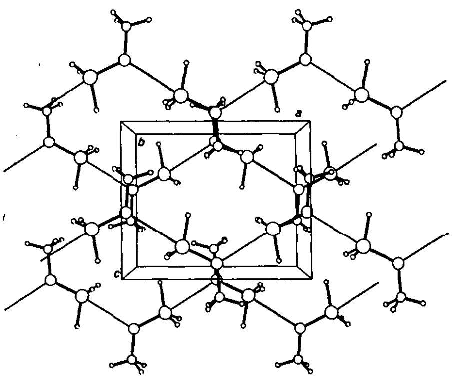

Fig. 2. A view of the structure normal to the planes of molecules at $y = \frac{1}{4}$ and $\frac{3}{4}$. The linking of molecules related by the *a* glide plane through Si···O contacts is shown.

Table 3. *Molecular parameters for* CH_3OSiH_3 *and related compounds*

Compound	Phase	*r*(Si–O) (Å)	*r*(C–O) (Å)	Angle at O (°)	Reference
CH_3OCH_3	Gas		1·416 (3)	111·5 (15)	Kimura & Kubo (1959)
$C_2H_5OC_2H_5$	Solid		1·429 (6)	111·8 (4)	André, Fourme & Zechmeister (1972)
CH_3OSiH_3	Gas	1·640 (3)	1·418 (9)	120·6 (9)	Glidewell *et al.* (1970)
CH_3OSiH_3	Solid	1·6510 (19)	1·424 (3)	120·13 (16)	This work
SiH_3OSiH_3	Solid	1·631 (5)	—	142·2 (3)	Barrow, Ebsworth & Harding (1979)

respectively. The corresponding parameters for the much longer contact in disiloxane are 3·115 (5) Å, 176·6 (4), 108·4 (2) and 109·4 (2)°, the last two being Si—O···Si angles (Barrow, Ebsworth & Harding, 1979). In methoxysilane, there is some suggestion in the angles involving the silyl H atoms (∠HSiH > ∠HSiO) of the incipient formation of an S_N2 transition state, seen in its fully developed form in the cyclic dimethylsilylamine pentamer (Blake, Ebsworth & Welch, 1984), but the differences in these angles are barely significant. However, the present compound shows no tendency to form a cyclic structure analogous to the pentamer and its chains of molecules are more reminiscent of the structure of silyl fluoride (Blake, Ebsworth, Henderson & Welch, 1985).

Otherwise, the molecular structure in the crystal is essentially identical to that in the gas phase (Table 3): however, the solid-state structure not only confirms the sp^2 hybridization of the O atom but also, through the Si···O interaction, indicates the orientation of the stereochemically active O lone pair, the other pair presumably being involved in an interaction with the vacant 3*d* oribtals on Si. The situation is therefore similar to that in disiloxane (Barrow, Ebsworth & Harding, 1979) in that the Si···O vector – and presumably the active lone pair – are coplanar with the SiOC plane, but different in that the presence of a methyl rather than a silyl group leads to a shorter intermolecular Si···O contact and a narrower angle at O as the 3*d* orbitals of only one Si are available for ($p \rightarrow d$) π bonding. As the π interaction cannot favour one conformation of the $-SiH_3$ group over any other, it is significant that these H atoms were both readily discerned in the ΔF synthesis and individually refinable thereafter while the methyl H atoms were difficult to locate and had to be refined as a rigid group. We attribute this difference to the greater van der Waals radius of the silyl group which determines the spacing between the planes of molecules: as a result the H atoms of the silyl group might be expected to be more rigidly fixed than those of the methyl group.

Knowledge of the crystal structure of methoxysilane has also assisted the interpretation and analysis of its solid-state vibrational spectra (Cradock, 1987).

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Structure of Y_2BaCuO_5

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Abstract. Diyttrium barium copper(II) pentoxide, $M_r = 458\cdot7$, orthorhombic, *Pnma*, $a = 12\cdot176\ (2)$, $b = 5\cdot655\ (2)$, $c = 7\cdot130\ (1)$ Å, $V = 491\cdot0\ (3)$ Å^3, $Z = 4$, $D_x = 6\cdot205$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 357\cdot0$ cm^{-1}, $F(000) = 812$, $T = 295\ (1)$ K. A total of 1167 unique reflections was measured with a final R of $0\cdot039$ over 907 intensities $> 2\cdot5\sigma(I)$. The lattice contains Ba^{2+}, Y^{3+}, and CuO_5^{8-} ions. Each Ba ion is closely associated with at least nine O atoms, and each Y ion is surrounded by seven O atoms. The covalently bonded anion is a distorted square pyramid, with Cu 0·22 Å above the basal plane. The Cu—O(apex) vector is tilted 9·6° from the perpendicular and is significantly longer [2·196 (7) Å] than the Cu—O(basal) distances [1·971 (6), 2·010 (6) Å]. The powder X-ray diffraction pattern for this structure has been calculated.

Introduction. The discovery that certain ternary oxides of copper exhibit the phenomenon of high-temperature superconductivity (Bednorz & Mueller, 1986; Wu, Ashburn, Torng, Hor, Meng, Gao, Huang, Wang & Chu, 1987) has resulted in intense activity to understand the physical origin of the superconductive phenomenon, and to characterize the principles of structural chemistry responsible for the electrical properties of these materials. The initial discovery of Bednorz & Mueller (1986) involved a substitution compound of La_2CuO_4 (K_2NiF_4 phase-type) in which some of the lanthanum had been substituted by an alkaline-earth ion. Further observation of increases in the superconducting transition temperature under pressure led to the eventual preparation of the 1:2:3 phase, $YBa_2Cu_3O_{7-x}$, which exhibits superconductivity above 90 K (Hor, Gao, Huang, Wang, Forster, Vassilious, Chu, Wu, Ashburn & Torng, 1987). The preparation has been generalized to include most of the lanthanides (Engler, Lee, Nazzal, Beyers, Lim, Grant, Parkin, Ramirez, Vazquez & Savoy, 1987) with the apparent requirement that the compound contain Cu; this stimulated the investigation of the ternary phase diagram of $CuO + BaO + Ln_2O_3$ (Ln = Y, lanthanide), with most of the effort concentrated on yttrium.

Most of the preparative techniques involve the sintering of oxides, carbonates, or other easily decomposed oxygen-containing precursors, and the product characterization techniques most frequently relied upon

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