

HYDROGEN BONDING IN ORGANOSILICON HYDROXIDES: CRYSTAL STRUCTURES OF DICYCLOHEXYLSILANEDIOL AND BIS(HYDROXYDIMETHYLSILYL)BIS(TRIMETHYLSILYL)METHANE

NABEEL H. BUTTRUS, COLIN EABORN *, PETER B. HITCHCOCK *, PAUL D. LICKISS,
and ALAN D. TAYLOR

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received January 21st, 1986)

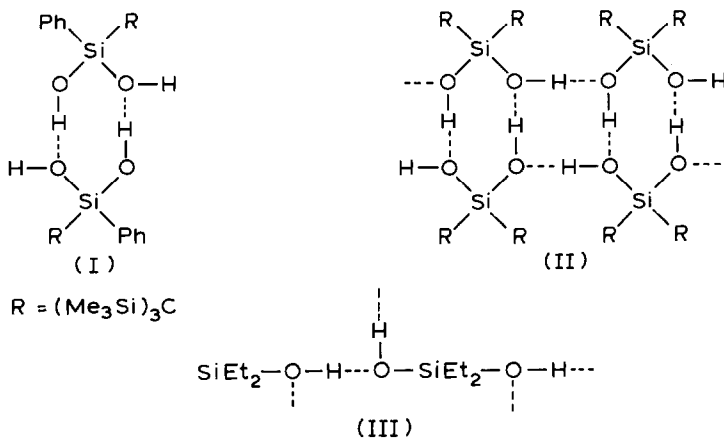
Summary

An X-ray diffraction study has shown that dicyclohexylsilanediol crystallizes as hydrogen-bonded dimers linked by further hydrogen bonding into ladder chains, the hydrogen bonding being closely similar to that in the crystal of $i\text{-Pr}_2\text{Si}(\text{OH})_2$. The diol $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$ forms infinite chains with one oxygen within a molecule linked by hydrogen bonding to the other, which in turn is hydrogen-bonded to the oxygen of another molecule.

Introduction

We have recently reported the crystal structures of some organosilanediols [1–3]. Of these the compound $(\text{Me}_3\text{Si})_3\text{CSiPh}(\text{OH})_2$ crystallizes as discrete hydrogen bonded dimers of type I [1] (with only half of the OH groups engaged in hydrogen bonding) *, whereas $t\text{-Bu}_2\text{Si}(\text{OH})_2$ [2] and $i\text{-Pr}_2\text{Si}(\text{OH})_2$ [3] form maximally hydrogen-bonded ladder chains of type II. In contrast, $\text{Et}_2\text{Si}(\text{OH})_2$ forms an infinite maximally hydrogen-bonded two-dimensional layer, which can be regarded as made up of hydrogen-bonded chains cross-linked by further hydrogen bonding to other chains, as shown in simplified form in III [5]. We have now determined the structure of the related diol dicyclohexylsilanediol, $(\text{C}_6\text{H}_{11})_2\text{Si}(\text{OH})_2$, and also that of a different type of organosilicon dihydroxide, $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$.

* The related triol $(\text{Me}_3\text{Si})_3\text{CSi}(\text{OH})_3$ crystallizes as discrete cages made up of six maximally hydrogen-bonded molecules [4].



Experimental

(C₆H₁₁)₂Si(OH)₂

A sample of this diol made some time ago [6] was recrystallized by slow evaporation of a solution in 1/1 Et₂O/hexane. A crystal of ca. 0.5 × 0.35 × 0.3 mm was used.

Crystal data

C₁₂H₂₄O₂Si, *M* 228.4, triclinic, *a* 5.191(2), *b* 10.783(1), *c* 12.529(2) Å, α 100.86(1), β 97.68(2), γ 98.74(2)°, *U* 671.2 Å³, *Z* 2, *D_c* 1.13 g cm⁻³, *F*(000) 252.

TABLE 1

FRACTIONAL ATOMIC COORDINATES (×10⁴ for Si, C, and O; ×10³ for H) FOR (C₆H₁₁)₂Si(OH)₂ (with estimated standard deviations in parentheses)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Si	4375.6(9)	761.5(5)	3411.6(4)
O(1)	7088(2)	389(1)	3987(1)
O(2)	2530(2)	961(1)	4376(1)
C(1)	5358(3)	2307(2)	2990(1)
C(2)	3034(4)	2719(2)	2344(2)
C(3)	3815(5)	4005(2)	2030(2)
C(4)	5078(4)	5045(2)	3027(2)
C(5)	7399(4)	4669(2)	3665(2)
C(6)	6656(4)	3387(2)	3982(2)
C(7)	2619(4)	-555(2)	2242(2)
C(8)	1849(5)	-1833(2)	2596(2)
C(9)	483(5)	-2914(2)	1631(3)
C(10)	2106(5)	-3089(2)	722(2)
C(11)	2817(7)	-1845(2)	342(2)
C(12)	4210(5)	-766(2)	1304(2)
H(O1)	707(5)	3(2)	429(2)
H(O2)	118(4)	87(2)	423(2)

TABLE 2

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) IN $(C_6H_{11})_2Si(OH)_2$ (with estimated standard deviation in parentheses)

Si-O(1)	1.636(1)	Si-O(2)	1.643(1)
Si-C(1)	1.861(2)	Si-C(7)	1.860(2)
O(1)-H(O1)	0.59(3)	O(2)-H(O2)	0.69(2)
C(1)-C(2)	1.531(3)	C(1)-C(6)	1.533(2)
C(2)-C(3)	1.523(3)	C(3)-C(4)	1.509(3)
C(4)-C(5)	1.506(3)	C(5)-C(6)	1.518(3)
C(7)-C(8)	1.539(3)	C(7)-C(12)	1.527(3)
C(8)-C(9)	1.520(3)	C(9)-C(10)	1.506(4)
C(10)-C(11)	1.516(4)	C(11)-C(12)	1.520(3)
O(1)-Si-O(2)	106.00(7)	O(1)-Si-C(1)	106.70(7)
O(1)-Si-C(7)	110.75(8)	O(2)-Si-C(1)	110.11(8)
O(2)-Si-C(7)	109.84(8)	C(1)-Si-C(7)	113.15(8)
Si-O(1)-H(O1)	122(3)	Si-O(2)-H(O2)	120(2)
Si-C(1)-C(2)	112.5(1)	Si-C(1)-C(6)	111.7(1)
C(2)-C(1)-C(6)	109.6(2)	C(1)-C(2)-C(3)	112.6(2)
C(2)-C(3)-C(4)	111.6(2)	C(3)-C(4)-C(5)	111.2(2)
C(4)-C(5)-C(6)	112.1(2)	C(1)-C(6)-C(5)	112.8(2)
Si-C(7)-C(8)	112.8(1)	Si-C(7)-C(12)	112.4(1)
C(8)-C(7)-C(12)	109.3(2)	C(7)-C(8)-C(9)	112.5(2)
C(8)-C(9)-C(10)	112.2(2)	C(9)-C(10)-C(11)	111.0(2)
C(10)-C(11)-C(12)	111.1(2)	C(7)-C(12)-C(11)	113.2(2)

Hydrogen bonding

- (i) H(O1)---O(2) 2.15 Å; O(1)-H(O1)---O(2)' 169.0°; at symmetry element $1-x, \bar{y}, 1-z$
(ii) H(O2)---O(1) 2.08 Å; O(2)-H(O2)---O(1)'' 170.3°; at symmetry element $-1+x, y, z$

Monochromated Mo- K_α radiation, λ 0.71069 Å, μ 1.52 cm⁻¹. Space group $P\bar{1}$ from successful structure refinement.

Data collection for $2 < \theta < 25^\circ$ was as previously described [7]; 1960 reflections with $|F^2| > \sigma(F)$ were used. The structure was solved by heavy atom methods. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least-squares. Hydrogen atoms were located on a difference map and included in the refinement with isotropic temperature factors. Refinement converged at $R = 0.04$, $R' = 0.05$, with a weighting scheme $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless.

The structure solution and refinement were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors were from ref. 8. Final atom coordinates are listed in Table 1, and bond lengths and angles in Table 2, which also gives detail of the hydrogen bonding. Lists of temperature factors, hydrogen atom coordinates, and structure factors are available from the authors.

(Me₃Si)₂C(SiMe₂OH)₂

This compound [9] was recrystallized by adding an equal volume of water to a concentrated solution in CH₂Cl₂ and setting aside overnight. A crystal of ca. 0.35 × 0.25 × 0.2 mm was used.

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$ for C, O and Si; $\times 10^3$ for H) FOR $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})$ (with estimated standard deviations in parentheses)

Atom	x	y	z
Si(1)	2693(1)	2137(1)	9597(1)
Si(2)	149(1)	2125(1)	8535(1)
Si(3)	3090(1)	1489(1)	8143(1)
Si(4)	2243(1)	4454(1)	8523(1)
O(1)	-233(3)	2026(2)	7741(1)
O(2)	1150(3)	4647(2)	7870(1)
C(1)	2061(3)	2539(3)	8716(1)
C(2)	2999(4)	226(4)	9747(2)
C(3)	4357(5)	3025(5)	9888(2)
C(4)	1427(5)	2647(5)	10162(2)
C(5)	-402(4)	399(4)	8822(2)
C(6)	-1065(4)	3414(5)	8840(2)
C(7)	2544(5)	-378(4)	8047(2)
C(8)	2919(5)	2171(5)	7294(2)
C(9)	4996(4)	1437(5)	8426(2)
C(10)	4008(5)	5011(5)	8355(2)
C(11)	1786(5)	5690(4)	9157(2)
H(O2)	101(3)	525(3)	774(1)
H(O1)	-2(2)	254(3)	759(1)

TABLE 4

INTRAMOLECULAR DISTANCES (\AA) AND ANGLES ($^\circ$) IN $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$ (with estimated standard deviations in parentheses)

Si(1)-C(1)	1.903(3)	Si(1)-C(2)	1.881(4)
Si(1)-C(3)	1.865(4)	Si(1)-C(4)	1.854(5)
Si(2)-O(1)	1.652(3)	Si(2)-C(1)	1.891(3)
Si(2)-C(5)	1.861(4)	Si(2)-C(6)	1.866(5)
Si(3)-C(1)	1.921(3)	Si(3)-C(7)	1.875(4)
Si(3)-C(8)	1.871(4)	Si(3)-C(9)	1.875(4)
Si(4)-O(2)	1.637(3)	Si(4)-C(1)	1.897(3)
Si(4)-C(10)	1.860(5)	Si(4)-C(11)	1.861(4)
O(1)-H(O1)	0.63(3)	O(2)-H(O2)	0.65(3)
C(1)-Si(1)-C(2)	112.7(2)	C(1)-Si(1)-C(3)	113.3(2)
C(1)-Si(1)-C(4)	112.9(2)	C(2)-Si(1)-C(3)	106.2(2)
C(2)-Si(1)-C(4)	104.8(2)	C(3)-Si(1)-C(4)	106.3(2)
O(1)-Si(2)-C(1)	108.6(1)	O(1)-Si(2)-C(5)	103.1(2)
O(1)-Si(2)-C(6)	107.2(2)	C(1)-Si(2)-C(5)	115.6(2)
C(1)-Si(2)-C(6)	115.6(2)	C(5)-Si(2)-C(6)	105.7(2)
C(1)-Si(3)-C(7)	114.1(2)	C(1)-Si(3)-C(8)	113.7(2)
C(1)-Si(3)-C(9)	112.3(2)	C(7)-Si(3)-C(8)	103.9(2)
C(7)-Si(3)-C(9)	105.3(2)	C(8)-Si(3)-C(9)	106.7(2)
O(2)-Si(4)-C(1)	102.6(1)	O(2)-Si(4)-C(10)	109.6(2)
O(2)-Si(4)-C(11)	109.3(2)	C(1)-Si(4)-C(10)	115.3(2)
C(1)-Si(4)-C(11)	115.8(2)	C(10)-Si(4)-C(11)	104.1(2)
Si(2)-O(1)-H(O1)	113(2)	Si(4)-O(2)-H(O2)	122(2)
Si(1)-C(1)-Si(2)	110.7(2)	Si(1)-C(1)-Si(3)	110.8(1)
Si(1)-C(1)-Si(4)	111.9(2)	Si(2)-C(1)-Si(3)	109.2(1)
Si(2)-C(1)-Si(4)	105.9(1)	Si(3)-C(1)-Si(4)	108.2(2)

Hydrogen bonding

- (i) O(1)'---H(O2) 2.07 \AA ; O(1)'---H(O2)-O(2) 169.4 $^\circ$; at symmetry element $x, 1/2 + y, 1.5 - z$
(ii) O(2)---H(O1) 2.36 \AA ; O(1)-H(O1)---O(2) 137.1 $^\circ$

Crystal data

$C_{11}H_{32}O_2Si_4$, M 308.5, monoclinic, space group $P2_1/c$, a 9.683(1), b 9.613(4), c 20.764(5) Å, β 96.28(2)°, U 1921.0 Å³, Z 4, D_c 1.07 g cm⁻³, $F(000)$ 680. Monochromated Mo- K_α radiation, λ 0.71069 Å, μ 2.95 cm⁻¹.

Data collection for $2 < \theta < 23^\circ$ was as previously described [7]; 2004 reflections with $|F^2| > \sigma(F^2)$ were used. The structure was solved by direct methods using the MULTAN program. Subsequent refinement was as described for $(C_6H_{11})_2Si(OH)_2$ above; refinement converged at $R = 0.042$, $R' = 0.050$ where the maximum shift to error was 0.16 and the weighting was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless. Final atom coordinates are listed in Table 3, and bond lengths and angles in Table 4, which also gives detail of the hydrogen bonding. Lists of thermal parameters, hydrogen atom coordinates, and structure factors are available from the authors.

Results and discussion *$(C_6H_{11})_2Si(OH)_2$*

The molecular structure of this diol, with the atom numbering, is shown in Fig. 1, and the unit cell in Fig. 2. The crystals consist of hydrogen-bonded dimers linked by further hydrogen bonding into ladder chains, detail of which is shown in Fig. 3. The

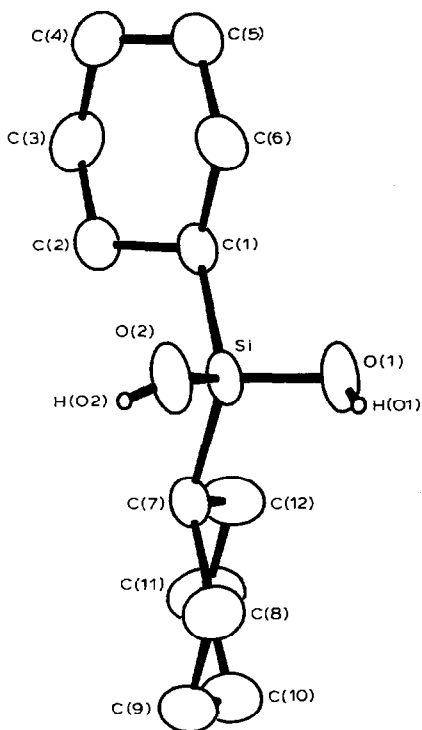


Fig. 1. An ORTEP drawing [13] of the molecular structure of $(C_6H_{11})_2Si(OH)_2$, with the atom numbering.

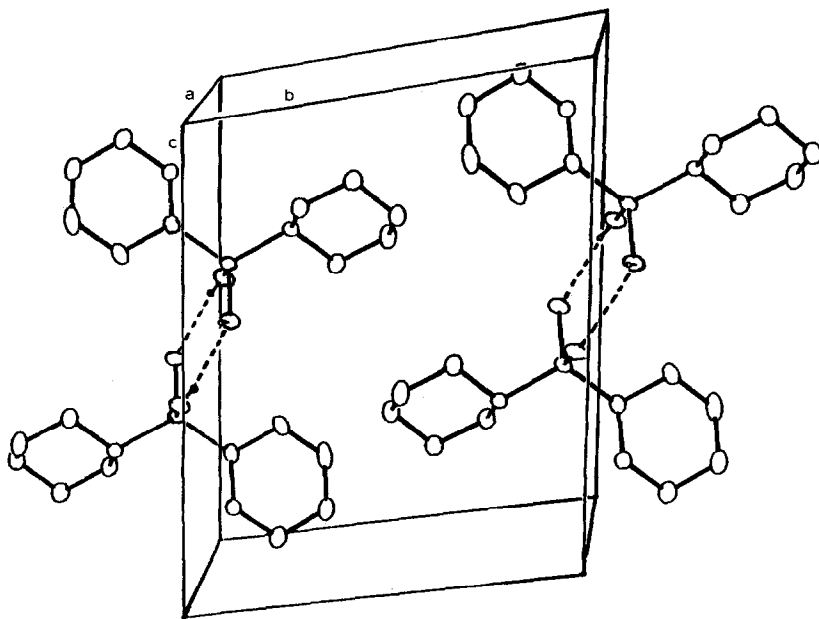


Fig. 2. Unit cell for $(C_6H_{11})_2Si(OH)_2$. Broken lines denote hydrogen bonding.

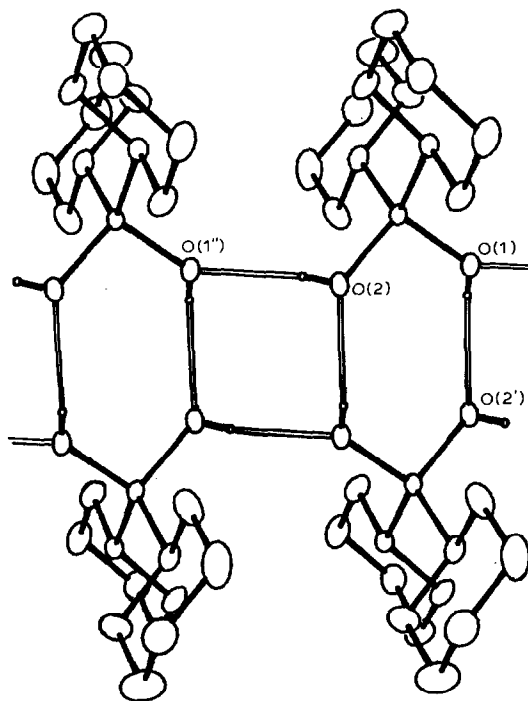


Fig. 3. Detail of the latter chain structure of $(C_6H_{11})_2Si(OH)_2$, with hydrogen bonding indicated by open lines.

ladder structure is virtually identical to that for $i\text{-Pr}_2\text{Si}(\text{OH})_2$, with a chair conformation for the Si_2O_4 rings of the dimers and with adjacent rings related by a unit translation along the axis. The location of the hydrogen atoms (which were not located for $i\text{-Pr}_2\text{Si}(\text{OH})_2$) confirms the hydrogen bonding arrangement common to the two diols. In the individual molecules the two 'ortho' carbon atoms of the cyclohexyl groups adopt positions essentially the same as those of the Me carbon atoms in the $i\text{-Pr}$ groups. The intra-chain contacts are therefore the same in both crystal structures, and the geometry of the chains and their orientations in the crystal are similar, with almost identical a axis lengths. The presence of the additional atoms in the cyclohexyl groups pushes the chains further apart, the effect being largest for the b axis, which is increased by 26% relative to that for $i\text{-Pr}_2\text{Si}(\text{OH})_2$, whereas the c axis is increased by 6%.

$(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$

The molecular structure of this compound is shown in Fig. 4 and the unit cell in Fig. 5. The crystal consists of infinite chains, as shown in Fig. 6, involving both intramolecular bonding between the two oxygen atoms in each molecule and intermolecular bonding to other molecules. The intramolecular hydrogen bond, with an O-H-O angle of 137.1° , departs markedly from linearity. We are aware of no precedent for chains of this type, involving alternating intra- and inter-molecular hydrogen bonding.

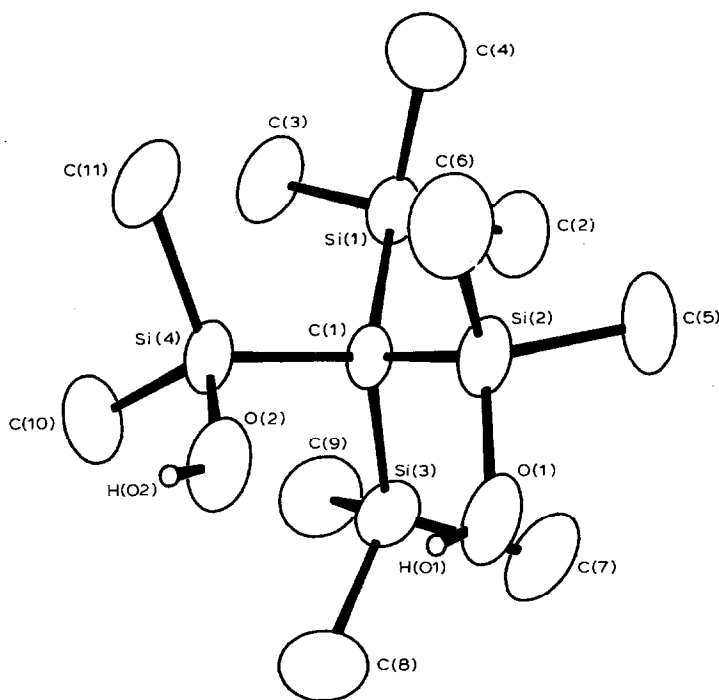


Fig. 4. An ORTEP drawing [13] of the molecular structure of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$, with atom numbering.

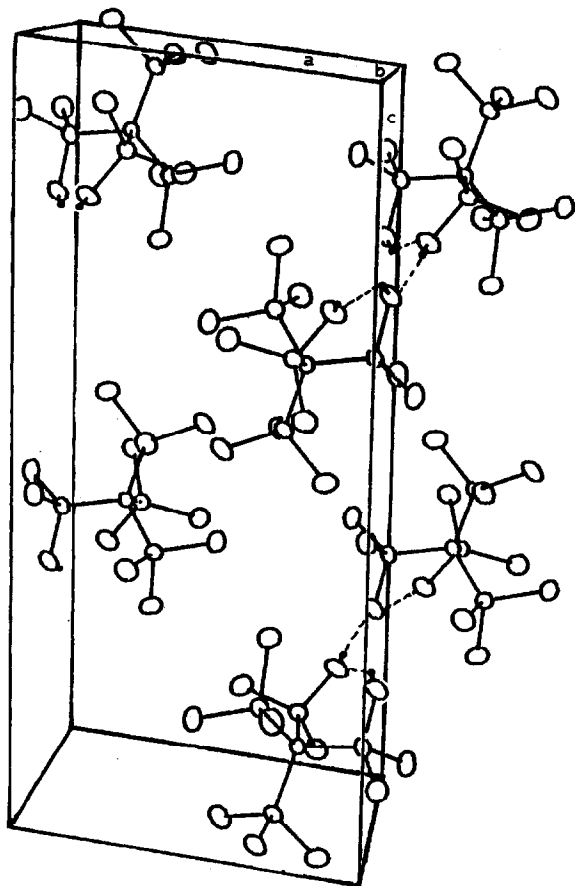


Fig. 5. Unit cell for $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$. Broken lines denote hydrogen bonding.

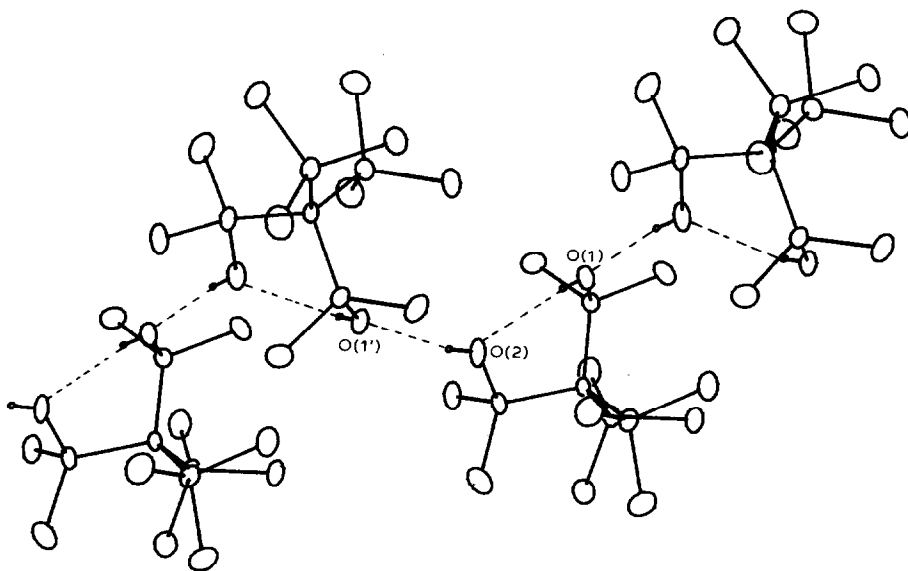


Fig. 6. The chain structure of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$. Broken lines denote hydrogen bonding.

The hydrogen bonding, possibly in particular the intramolecular bonding, seems to cause some distortion of the molecular structure. Thus the $\text{HOMe}_2\text{Si}-\text{C}-\text{SiMe}_2\text{OH}$ angle, $105.9(1)^\circ$, is markedly smaller than the $\text{Me}_3\text{Si}-\text{C}-\text{SiMe}_3$ angle, $110.8(1)^\circ$. Furthermore the $\text{C}(1)-\text{Si}(4)-\text{O}(2)$ and $\text{C}(1)-\text{Si}(2)-\text{O}(1)$ angles, $102.6(1)$ and $108.6(1)^\circ$, respectively, are markedly smaller than the $\text{C}(1)-\text{Si}(4)-\text{Me}$ and $\text{C}(1)-\text{Si}(2)-\text{Me}$ angles, which have a mean value of $115.6(2)^\circ$. Other features are similar to those observed for several related crowded molecules, such as $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Ph}$ [10], $(\text{Me}_3\text{Si})_3\text{CSiPhSi}(\text{OH})_2$ [1], $(\text{Me}_3\text{Si})_3\text{CSiPh}(\text{OMe})\text{OH}$ [1], $(\text{Me}_3\text{Si})_3(\text{Ph}_2\text{MeSi})\text{CSiMe}_2\text{ONO}_2$ [11], and $(\text{Me}_3\text{Si})_3\text{CBPh}_2$ [12], in that (i) the central $\text{C}(1)-\text{Si}$ bonds, mean $1.903(13)$ Å, are significantly longer than the peripheral $\text{Si}-\text{Me}$ bonds, mean $1.867(8)$ Å, and (ii) the $\text{C}(1)-\text{Si}-\text{Me}$ angles are opened from the tetrahedral to a mean of $114.1(13)^\circ$, and the $\text{Me}-\text{Si}-\text{Me}$ angles closed to a mean of $105.4(10)^\circ$.

Note on crystal structure of $t\text{-Bu}_2\text{Si}(\text{OH})_2$

After submission of our paper dealing with the crystal structure of $t\text{-Bu}_2\text{Si}(\text{OH})_2$ [2], a report on the same structure by Klingebiel and Sheldrick and their co-workers appeared [14]. The latter report is unclear, in that the summary refers to formation of hydrogen bonded chains *or* dimers by the three diols considered, and implies that $t\text{-Bu}_2\text{Si}(\text{OH})_2$ forms such dimers, but the discussion of this structure in the body of the paper mentions only chains. In fact, the structure contains both dimers *and* (ladder) chains. The report also, wrongly in our view, describes the chains as being along the *b* rather than the *a* axis. Also the *a* and *c*-axes were, we believe, incorrectly assigned in the unit cell; after allowance for this the data (including the atomic coordinates after an allowable transformation) are identical with ours.

Acknowledgment

We thank the S.E.R.C. for support of this work and for the award of a research studentship (to A.D.T.). N.H.B. thanks the Ministry of Higher Education of the Republic of Iraq for a scholarship.

References

- 1 Z.H. Aiube, N.H. Buttrus, C. Eaborn, P.B. Hitchcock, and J.A. Zora, *J. Organomet. Chem.*, 292 (1985) 177.
- 2 N.H. Buttrus, C. Eaborn, P.B. Hitchcock, and A.K. Saxena, *J. Organomet. Chem.*, 284 (1985) 291. (see also ref. 14 and the Note in the text above.)
- 3 N.H. Buttrus, C. Eaborn, P.B. Hitchcock, and P.D. Lickiss, *J. Organomet. Chem.*, 302 (1986) 159.
- 4 N.H. Buttrus, R.I. Damja, C. Eaborn, P.B. Hitchcock, and P.D. Lickiss, *J. Chem. Soc., Chem. Commun.*, (1985) 1385.
- 5 P.E. Tomlins, J.E. Lydon, D. Akkrig, and B. Sheldrick, *Acta Crystallogr.*, C41 (1985) 941.
- 6 C. Eaborn, *J. Chem. Soc.*, (1952) 2840.
- 7 N.H. Buttrus, C. Eaborn, P.B. Hitchcock, and A.K. Saxena, *J. Organomet. Chem.*, 287 (1985) 157.
- 8 *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.
- 9 C. Eaborn, P.D. Lickiss, and N.A. Ramadan, *J. Chem. Soc., Perkin Trans. 2*, (1984) 267
- 10 C. Eaborn, P.B. Hitchcock, and P.D. Lickiss, *J. Organomet. Chem.*, 221 (1981) 13.
- 11 C. Eaborn, P.B. Hitchcock, P.D. Lickiss, A. Pidcock, and K.D. Safa, *J. Chem. Soc., Dalton Trans.* (1984) 2015.
- 12 C. Eaborn, M.N.A. El-Kheli, P.B. Hitchcock, and J.D. Smith, *J. Organomet. Chem.*, 272 (1984) 1.
- 13 C.K. Johnson, Report ORNL-3794, (1965), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- 14 O. Graalmann, U. Klingebiel, W. Clegg, M. Haase, and G.M. Sheldrick, *Chem. Ber.*, 117 (1984) 2985.