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HYDROGEN BONDING IN ORGANOSILANEDIOLS. THE CRYSTAL STRUCTURE OF DI-i-PROPYLSILANEDIOL

NABEEL H. BUTTRUS, COLIN EABORN*, PETER B. HITCHCOCK* and PAUL D. LICKISS
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

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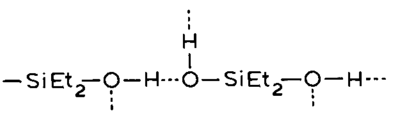
Summary

The crystal structure of i-$Pr_2Si(OH)_2$ consists of cyclic hydrogen-bonded dimers linked by further hydrogen bonding into ladder chains.

Introduction

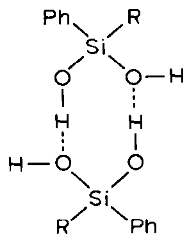
Hydrogen bonding produces a range of crystal structures for organosilanediols. Thus $Et_2Si(OH)_2$ forms an infinite maximally hydrogen-bonded two-dimensional layer, which can be regarded as made up of hydrogen-bonded chains cross-linked by further hydrogen bonding to other such chains, as shown in a simplified form in I [1] *, and $Ph_2Si(OH)_2$ forms an intricate maximally hydrogen-bonded network in which six molecules form a cyclic hydrogen-bonded hexamer, with the hexamers linked together by further hydrogen bonding [2].

The compound $[(Me_3Si)_3C]PhSi(OH)_2$, in contrast, forms discrete dimers of type II [3], whereas t-$Bu_2Si(OH)_2$ has cyclic dimers linked into a slightly distorted ladder structure, as shown in Fig. 1 [4]. It was of interest to ascertain which form was adopted by i-$Pr_2Si(OH)_2$, especially in view of the interest in the (still unknown) structure of the related species i-$Bu_2Si(OH)_2$ arising from the ability of the latter to form a liquid crystal phase [5].



$-SiEt_2-O-H\cdots O-SiEt_2-O-H\cdots$

(I)



(II, R = $(Me_3Si)_3C$)

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* Dr. Lydon informs us that in Ref. 1 the O(2)–H(O22)$\cdots$O(1) bond should have read the O(2)–H(O22)$\cdots\cdots$O(1′) bond, (at x, $y+1$, z), and thus that there is not an intramolecular hydrogen bond as implied in that paper

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Experimental

A sample of i-$Pr_2Si(OH)_2$ [6] was recrystallized from CH_2Cl_2 to give crystals suitable for the diffraction studies. A crystal of dimensions 0.5 × 0.13 × 0.18 mm was used, sealed in a thin walled capillary under argon.

Crystal data

$C_6H_{16}O_2Si$, M 148.3, triclinic, a 5.168(1), b 8.556(2), c 11.829(2) Å, α 67.69(2), β 75.52(2), γ 81.01(2)°, U 467.4 Å^3, $Z = 2$, D_c 1.05 g cm^{-3}, $F(000)$ 164. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 1.88 cm.$^{-1}$. Space group $P\bar{1}$ from successful structure refinement. Details of the data collection were similar to those described previously [4], and 1055 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement.

The structure was solved by direct methods (MULTAN). Refinement was by full matrix least-squares with all atoms anisotropic. Attempts to locate the hydrogen atoms attached to oxygen were unsuccessful. The i-Pr hydrogen atoms were placed at calculated positions (C–H 1.08 Å) and included in the refinement with an isotropic temperature factor B of 8.0 Å^2. Refinement converged at $R = 0.069$, $R' = 0.087$, when the maximum shift/error was 0.12 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map had peaks of up to 0.5 e Å^{-3} near the silicon atom but was elsewhere featureless.

The structure solution and refinement were carried out on a PDP11/34 computer using the Enraf–Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from Ref. 7.

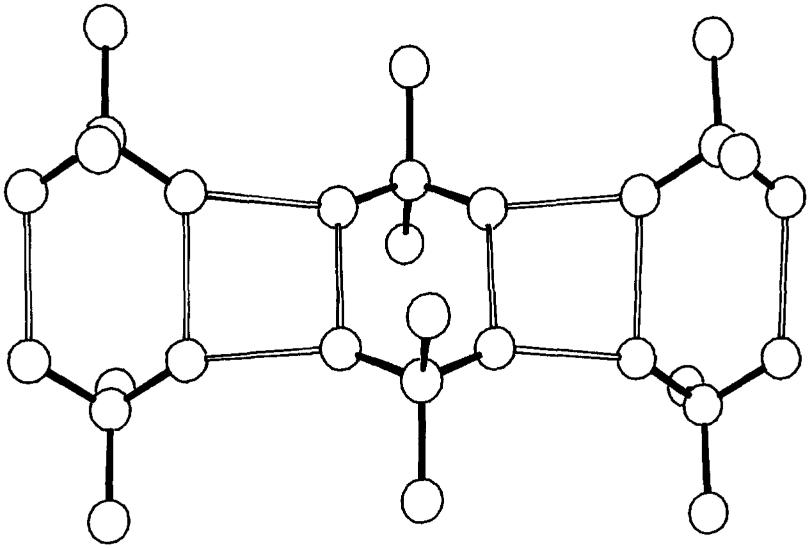

Fig. 1. Detail of the hydrogen-bonded framework in crystalline t-$Bu_2Si(OH)_2$, with the Me groups omitted for clarity.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times$ 10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Si	8984(2)	370(2)	6883(1)
O(1)	11730(5)	1033(4)	5816(3)
O(2)	6881(5)	36(4)	6151(3)
C(1)	9883(10)	−1672(7)	8105(5)
C(2)	11225(15)	−2991(8)	7570(7)
C(3)	7383(14)	−2281(10)	9144(6)
C(4)	7314(10)	2064(7)	7487(5)
C(5)	6697(14)	3665(9)	6485(7)
C(6)	8908(12)	2350(8)	8341(5)

Final atom coordinates are listed in Table 1, and lists of temperature factors and final structure factors are available from P.B.H.

Results and discussion

The crystal packing is shown in Fig. 2, and the detail of the hydrogen-bonded framework in Fig. 3. It is evident that there are again cyclic dimers linked into ladders, as in t-Bu_2SiOH_2, but the packing arrangement is simpler than for the

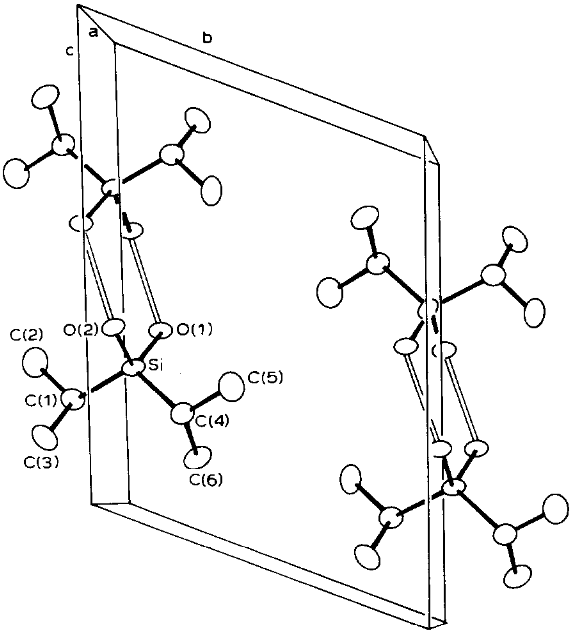

Fig. 2. Unit cell for i-$Pr_2Si(OH)_2$ viewed along the *a*-axis, with hydrogen bonds denoted by open lines. The dimers shown stack along the *a*-axis, linked by hydrogen bonds. The atom numbering scheme is also shown.

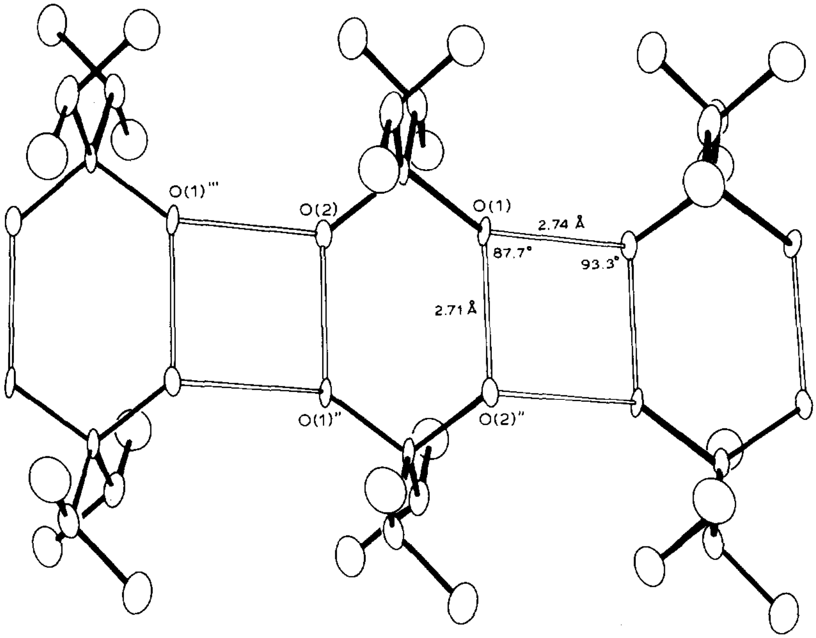

Fig. 3. Detail of the hydrogen-bonded framework in crystalline i-$Pr_2Si(OH)_2$.

latter. The two halves of the dimers are related by crystallographic inversion centres and thus the four oxygen atoms of each dimer are coplanar. The Si atoms are displaced slightly above and below this plane, with a resulting chair conformation

TABLE 2

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Si-O(1)	1.655(3)	Si-O(2)	1.663(4)
Si-C(1)	1.877(5)	Si-C(4)	1.855(6)
C(1)-C(2)	1.494(10)	C(1)-C(3)	1.543(8)
C(4)-C(5)	1.484(8)	C(4)-C(6)	1.558(10)
O(1)-Si-O(2)	106.6(2)	O(1)-Si-C(1)	108.5(2)
O(1)-Si-C(4)	110.5(2)	O(2)-Si-C(1)	109.8(2)
O(2)-Si-C(4)	106.2(2)	C(1)-Si-C(4)	114.9(3)
Si-C(1)-C(2)	112.7(4)	Si-C(1)-C(3)	109.7(4)
C(2)-C(1)-C(3)	112.9(6)	Si-C(4)-C(5)	113.0(5)
Si-C(4)-C(6)	111.8(4)	C(5)-C(4)-C(6)	112.1(6)
Hydrogen bonds and angles			
O(1)-O(2)'		2.74 Å	
O(1)-O(2)''		2.71 Å	
O(2)'-O(1)-O(2)''		87.7°	
O(1)''-O(2)-O(1)'''		93.3°	

Symmetry elements

' $1+x, y, z$

'' $1-x, -y, 1-z$

''' $-1+x, y, z$

for the six-membered ring. Successive dimers in the chain are related by a unit translation parallel to the *a* axis of the cell and are not inverted with respect to each other; thus, there is no twist between adjacent hydrogen-bounded pairs such as was observed for t-$Bu_2Si(OH)_2$. This is presumably because in i-$Pr_2Si(OH)_2$ two of the terminal Me groups in one molecule are pointing towards the positions occupied by the hydrogen atoms of the $HCMe_2$ groups in the adjacent dimer unit. In t-$Bu_2Si(OH)_2$, with its symmetrical CMe_3 groups, the steric strain would be greater, and the chain twists, with successive dimers having opposite chair conformations. In i-$Pr_2Si(OH)_2$ the four oxygen atoms forming the four-membered rings in the chain are again coplanar, with an inversion centre at the centre of the ring. There is a slight pucker in the chains, since the sets of four oxygen atoms in the four- and six-membered rings, respectively, are not parallel to each other.

There are no unusual features in the detail of the molecular structure, shown in Table 2. As expected the C–Si–C angle, 114.9(3)°, is rather smaller than that in t-$Bu_2Si(OH)_2$, viz. 118.4(9)°, and it is, in fact, very similar to that in $Et_2Si(OH)_2$, viz. $114.4(2)^0$ [1].

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