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THE CRYSTAL STRUCTURE OF DI-t-BUTYLSILANEDIOL AND ITS RELEVANCE TO THE LIQUID CRYSTALLINITY OF DIISOBUTYLSILANEDIOL

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Summary

The crystal structure of t-$Bu_2Si(OH)_2$ consists of hydrogen-bonded dimers linked by further hydrogen bonding into (distorted) ladder chains, the type of structure previously postulated for solid i-$Bu_2Si(OH)_2$ to account for its ability to give a liquid crystal on heating. The six-membered rings of the dimers have a chair conformation with adjacent chairs inverted with respect to one another. The structure of the ladder chains is similar to that in t-$Bu_2Ge(OH)_2$, but the packings of the chains in the crystal are different.

Introduction

Special interest attaches to the structures of diorganosilanediols because one such species, diisobutylsilanediol, gives a thermotropic liquid crystal mesophase [1,2]. The liquid crystal is, moreover, of an unusual type; it is thought to fall into the discotic class recognised in recent years [3], and in retrospect can be seen to be the first observed member of this class [2].

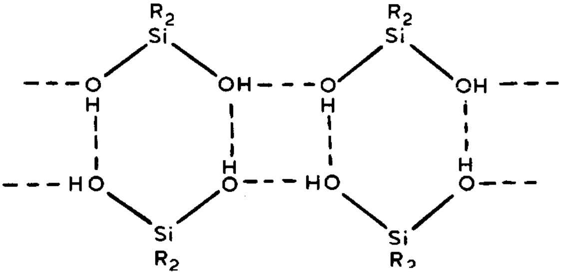

Fig. 1. Simplified version of the hydrogen bonding scheme proposed in ref. 2 for the crystalline solid of diisobutylsilanediol (R = i-Bu).

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The formation of a liquid crystal phase by i-$Bu_2Si(OH)_2$ was first tentatively interpreted in terms of a hydrogen-bonded chain of molecules, involving hydrogen bonds of the bifurcated type thought at that time to be present in diethyl- and diallyl-silanediol [4], but a recent more detailed investigation (including an X-ray diffraction study of the liquid crystal, and re-examination of earlier preliminary diffraction data [1] for the solid) suggested that the properties were best interpreted in terms of a solid-state structure in which there is a basic unit of hydrogen-bonded dimers linked together as in Fig. 1 [2]. The links between the dimeric units are assumed to be broken at the transition from the solid to the mesophase. A structure of the type proposed had not, however, been observed for any silanediol *, and attempts to determine the crystal structure of i-$Bu_2Si(OH)_2$ have so far been frustrated by the failure to grow suitable crystals [7]. Recently t-$Bu_2Ge(OH)_2$ was found to have the type of structure suggested for i-$Bu_2Si(OH)_2$ [8], and we thus thought that it might be profitable to examine the structure of t-$Bu_2Si(OH)_2$. The results are presented below.

Experimental

t-$Bu_2Si(OH)_2$

A sample of t-Bu_2SiF_2 (6 g) [9a] was refluxed with 1/1 Me_2SO/H_2O for 20 h. An excess of hot CCl_4 was added, and the organic layer washed several times with water then evaporated. The residue was fractionally distilled to give t-$Bu_2Si(F)OH$ (1.5 g, 25%), b.p. 171–173°C, m.p. 44°C (lit. 9a, 45°C) and t-$Bu_2Si(OH)_2$ (1.0 g, 16%), b.p. 210–212°C, m.p. 152°C (lit. 9b, 152°C). Crystals suitable for the diffraction study were obtained by recrystallization from 1/4 v/v pentane/CCl_4.

Crystal data. $C_8H_{20}O_2Si$, $M = 176.3$, orthorhombic, a 16.351(4), b 12.743(4), c 10.512(1) Å, U 2201.5 Å^3, $Z = 8$, D_c 1.06 g cm^{-3}, $F(000) = 784$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, μ 1.68 cm^{-1}. Space group *Ibam* from systematic absences of $0kl$ for k odd and $h0l$ for h odd and successful structure refinement.

Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size ca. $0.3 \times 0.13 \times 0.1$ mm. Preliminary cell dimensions were found using the SEARCH and INDEX routines of CAD4, and final values were calculated from the setting angles of 25 reflections with $\theta \approx 15°$. Intensities for hkl reflections with $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with scan width of $\Delta\theta = (0.8 + 0.35\tan\theta)°$. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ, at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.05 subject to a maximum scan time of 60 s. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarization effects but not for absorption, and after averaging of equivalent reflections 324 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

The systematic absences are consistent with either space group *Iba*2 or *Ibam*. The

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* The diol $[(Me_3Si)_3C]PhSi(OH)_2$ forms discrete dimers in the crystal, with no hydrogen bonding between them [5]; $Ph_2Si(OH)_2$ forms hydrogen-bonded trimers, intricately cross linked by further hydrogen bonding [6].

TABLE 1

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

Atom	x	y	z
Si	733(4)	1511(4)	0
O(1)	278(5)	995(6)	1257(8)
C(1)	568(13)	2974(13)	0
C(2)	−409(12)	3141(15)	0
C(3)	942(10)	3492(10)	1226(15)
C(4)	1828(13)	994(16)	0
C(5)	1772(14)	−236(15)	0
C(6)	2295(9)	1340(14)	1230(18)

Si atom was located by heavy atom methods and the remaining non-hydrogen atoms on successive electron-density maps. Since it was apparent that the molecule had mirror symmetry the space group was taken as *Ibam*. A difference Fourier map showed only a few possible hydrogen positions, including one for a hydroxyl hydrogen, but the latter was not confirmed by least-squares refinement and so was omitted. Refinement converged at $R = 0.10$, $R' = 0.10$ when maximum shift/error

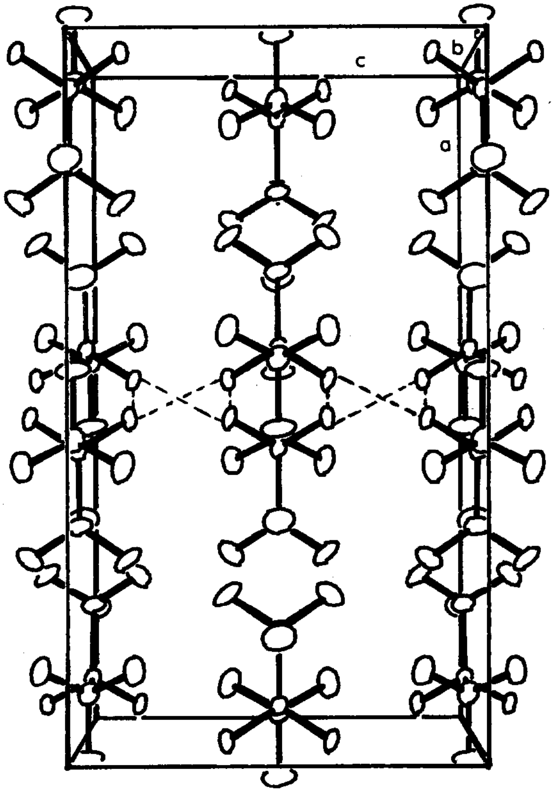

Fig. 2. View along the *b* axis of the crystal packing in t-$Bu_2Si(OH)_2$; broken lines indicate hydrogen bonds.

was < 0.01, and the weighting scheme was $w = 1/\sigma^2(F)$. A final map had a peak of up to 0.43 eÅ^{-3} near the Si 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. 10. Final atom coordinates are listed in Table 1, and lists of temperature factors and final structure factors are available from C.E.

Results and discussion

The crystal packing is shown, from different perspectives, in Fig. 2 and 3, and the essential detail of the hydrogen-bonded framework is shown in Fig. 4. It is evident that linked hydrogen-bonded dimers, of the general type postulated for i-$Bu_2Si(OH)_2$, are present in t-$Bu_2Si(OH)_2$, as they are in t-$Bu_2Ge(OH)_2$. The six-membered rings of the dimers in both t-$Bu_2Si(OH)_2$ and t-$Bu_2Ge(OH)_2$ have chair conformations, and adjacent chairs are inverted with respect to one another. Breaking of the hydrogen bonds between the dimer units, leaving the dimers intact but flexible, would give 'discs' as postulated for the liquid-crystal phase of i-$Bu_2Si(OH)_2$, and the present observations confirm that the structures proposed for the mesophase and

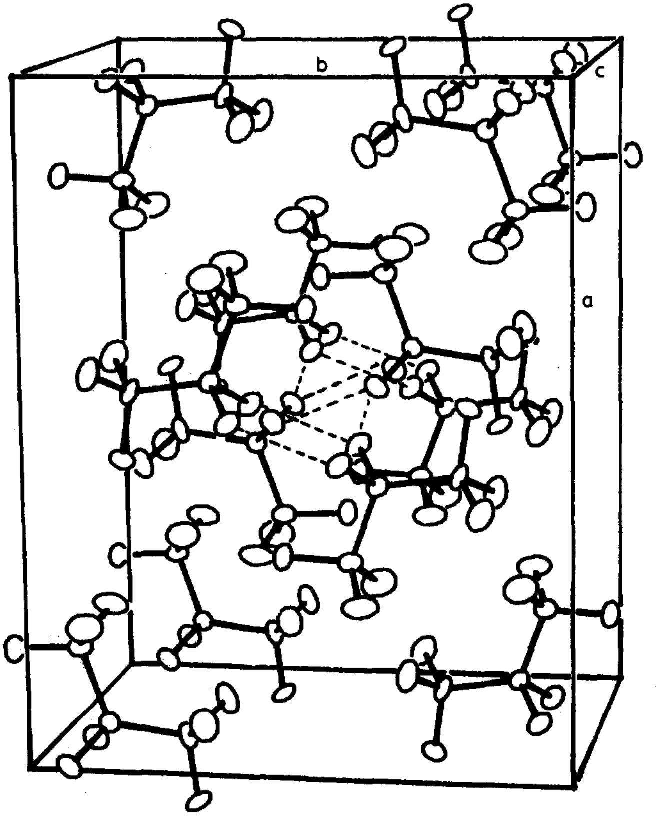

Fig. 3. View along the *c* axis of the crystal packing in t-$Bu_2Si(OH)_2$; broken lines indicate hydrogen bonds.

solid state of i-$Bu_2Si(OH)_2$ were reasonable (though not necessarily correct).

Although the essential structural features are the same in t-$Bu_2Si(OH)_2$ and t-$Bu_2Ge(OH)_2$, the packings are not identical, the space group for the latter being *C*2/*c*. In the case of t-$Bu_2Si(OH)_2$ the chains of hydrogen-bonded dimers lie along a two-fold rotation axis parallel to *c* at $x = 0$, $y = 0$. There is a mirror plane through

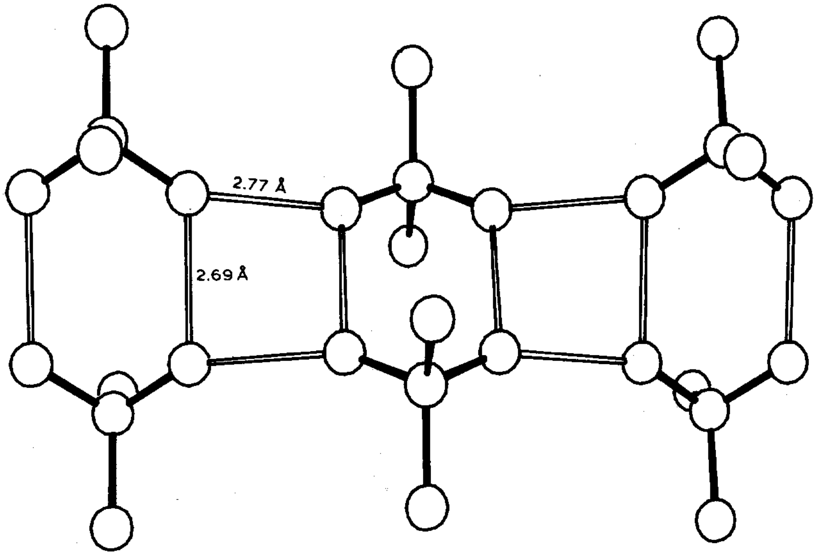

Fig. 4. Detail of the hydrogen-bonded framework in crystalline t-$Bu_2Si(OH)_2$; the Me groups are omitted for clarity.

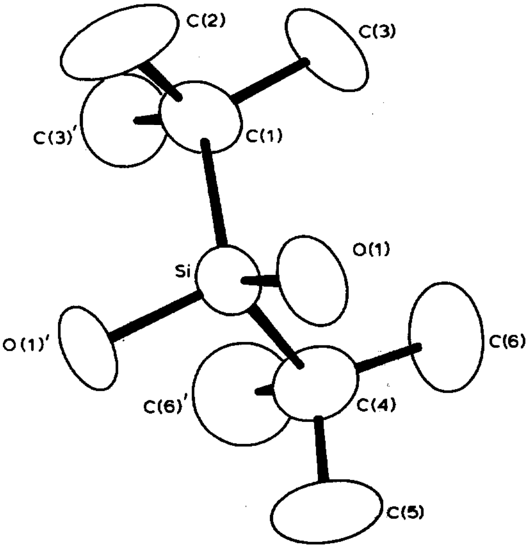

Fig. 5. An ORTEP drawing showing the molecular structure of t-$Bu_2Si(OH)_2$, with the atom numbering scheme. The atoms are shown as 50% thermal vibrational ellipsoids. Hydrogen atoms were not located.

TABLE 2

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

Bonds			
Si–O(1)	1.654(9)	Si–C(1)	1.88(2)
Si–C(4)	1.92(2)	C(1)–C(2)	1.62(3)
C(1)–C(3)	1.57(2)	C(4)–C(5)	1.57(2)
C(4)–C(6)	1.57(2)		
Angles			
O(1)–Si–O(1)′	106.0(5)	O(1)–Si–C(1)	109.2(5)
O(1)–Si–C(4)	106.7(5)	C(1)–Si–C(4)	118.4(9)
Si–C(1)–C(2)	106(1)	Si–C(1)–C(3)	111(1)
C(2)–C(1)–C(3)	109(1)	C(3)–C(1)–C(3)′	110(1)
Si–C(4)–C(5)	107(1)	Si–C(4)–C(6)	111(1)
C(5)–C(4)–C(6)	108(1)	C(6)–C(4)–C(6)′	111(2)
Selected torsion angles			
O(1)–Si–C(1)–C(2)	−58(1)		
O(1)–Si–C(1)–C(3)	61(1)		
C(4)–Si–C(1)–C(2)	180(1)		
C(4)–Si–C(1)–C(3)	−61(1)		
O(1)–Si–C(4)–C(5)	56(1)		
O(1)–Si–C(4)–C(6)	−61(1)		
C(1)–Si–C(4)–C(5)	180(1)		
C(1)–Si–C(4)–C(6)	62(1)		
Hydrogen bonds			
O(1)–O(1)″	2.69		
O(1)–O(1)‴	2.77		

Symmetry elements indicated as:
′ $x, y, \bar{z}$
″ $\bar{x}, \bar{y}, z$
‴ $\bar{x}, y, 1/2-z$

the silicon atoms of each dimer perpendicular to c, and a two-fold rotation axis parallel to b, at $x = 0$, $z = 1/4$, which relates adjacent dimers in the chain. There are four dimers in the unit cell.

In the detail of the molecular structure, shown in Fig. 5 and Table 2, the only noteworthy feature is the opening of the t-Bu–Si–Bu-t angles to 118.4(9)° as a result of steric repulsion between the bulky t-Bu groups. The corresponding angles are, as expected, smaller in $Et_2Si(OH)_2$ (111°) [4] and $Ph_2Si(OH)_2$ (112.9(3)°) [6], but, somewhat surprisingly, the t-Bu–Ge–Bu-t angle in t-$Bu_2Ge(OH)_2$ is significantly larger (122.5(3)°) [8]. (The O–Ge–O angle, viz. 103.5(2)° is correspondingly smaller than the O–Si–O angle, viz. 106.0(5)°).

Acknowledgements

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