

THE CRYSTAL STRUCTURE OF $t\text{-Bu}_2\text{Si}(\text{OH})\text{F}$. A CYCLIC HYDROGEN-BONDED TETRAMER

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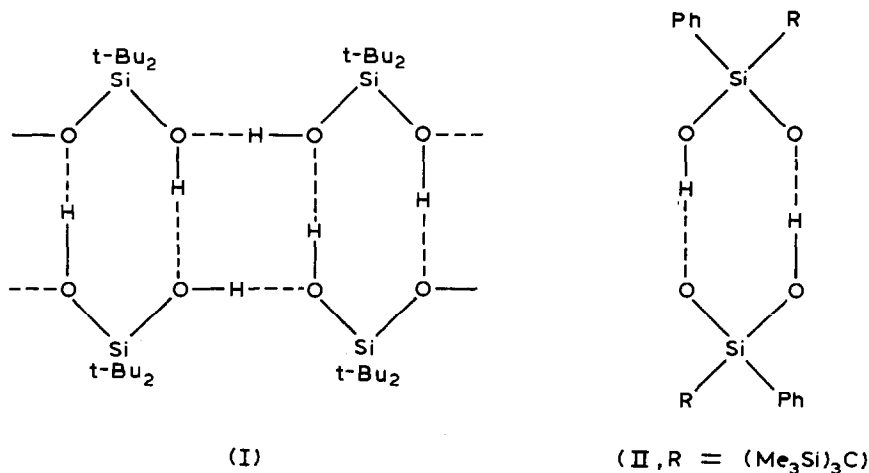
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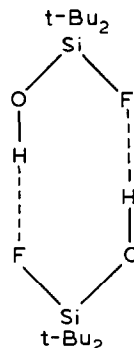
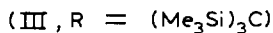
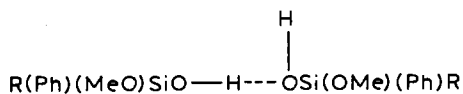
Summary

An X-ray diffraction study has shown that $t\text{-Bu}_2\text{Si}(\text{OH})\text{F}$ crystallizes as hydrogen-bonded tetramers. The fluoride ligand does not take part in the hydrogen bonding, which involves O–H...O linkages with an O–H...O angle of 160° ; the O...O...O angles are $89.7(3)^\circ$, but the four oxygen atoms are not quite coplanar (space group $I\bar{4}$). The t-Bu–Si–Bu–t angle is $120.5(6)^\circ$.

Introduction

We recently reported the crystal structure of the diol $t\text{-Bu}_2\text{Si}(\text{OH})_2$ and showed it to involve hydrogen-bonded dimers linked into a ladder structure by hydrogen bonding between the dimers, as shown in I [1]; the result was of special interest because the structure observed was closely analogous to that suggested for the





(IV)

isomeric diol $i\text{-Bu}_2\text{Si(OH)}_2$ in order to account for its ability to form a liquid crystal phase [2]. The diol $[(\text{Me}_3\text{Si})_3\text{C}]\text{Si(Ph)(OH)}_2$, however, was found to form discrete dimers, as shown in II, and the related silanol $[(\text{Me}_3\text{Si})_3\text{C}]\text{Si(Ph)(OMe)(OH)}$ was examined in the expectation that this might form analogous doubly-linked dimers, but it proved to form only the singly linked discrete dimers shown in III [3]. We decided to examine $t\text{-Bu}_2\text{Si(OH)F}$, because of the possibility that it might form discrete dimers of type IV, with fluorine ligands acting as proton acceptors in the hydrogen-bonding, but again the actual structure turned out to be quite different.

Experimental

Preparation of $t\text{-Bu}_2\text{Si(OH)F}$

This was prepared as previously described [1]. It had m.p. 44°C (lit. [4] 45°C); $\delta(\text{H})$ (CDCl_3) 1.04 (d, J 1 Hz, 18H, CH_3) and 2.31 br (s, 1H, OH); m/z 178 (10%, $[\text{M}]^+$), 121 (17, $[\text{M} - \text{Bu}]^+$), 79 (76, $[\text{M} - \text{Bu} - \text{C}_3\text{H}_6]^+$), 56 (100, $[\text{C}_4\text{H}_8]^+$). Crystals suitable for the X-ray study were obtained by recrystallization from n -pentane.

Crystal data

$\text{C}_8\text{H}_{19}\text{OFSi}$, $M = 178.3$, tetragonal, a 15.862(2), c 9.126(1) Å, U 2296.2 Å³, $Z = 8$, D_c 1.03 g cm⁻³, $F(000) = 392$. Monochromated Mo- K_α radiation, λ 0.71069 Å, μ 1.7 cm⁻¹. Space group $I\bar{4}$ from successful structure refinement.

Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size $0.4 \times 0.35 \times 0.25$ mm. Preliminary cell dimensions were found using the SEARCH and INDEX routines of CAD4, and final values were calculated from the setting angles for 25 reflections with $\theta \approx 15^\circ$. Intensities for hkl reflections with $2 < \theta < 25^\circ$ were measured by an ω - 2θ scan with a scan width of $\Delta\theta = (1.00 + 0.35 \tan \theta)^\circ$. The scan rate for each reflection was determined by a rapid pre-scan at $10^\circ \text{ min}^{-1}$ 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 to give a minimum value of $\sigma(I)/(I)$ of 0.05, subject to a maximum scan time of 60 sec. 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 equivalent reflections 542 reflections with $|F^2| > \sigma(F^2)$ were used in the

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$ for Si, C, F, O; $\times 10^3$ for H) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Si	2154(2)	74(2)	4182(4)
F	2376(4)	-889(4)	4064(11)
O(1)	1224(4)	58(4)	4896(9)
C(1)	2950(7)	525(7)	5470(17)
C(2)	2771(11)	224(15)	6967(20)
C(3)	3833(8)	305(9)	4914(31)
C(4)	2884(10)	1506(8)	5558(27)
C(5)	2102(9)	447(9)	2216(17)
C(6)	1469(15)	-139(13)	1438(17)
C(7)	2995(11)	499(12)	1482(18)
C(8)	1762(12)	1347(10)	2060(22)
H(1)	96(5)	39(5)	511(10)

structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

Attempts were made to solve the structure by direct methods using the MULTAN program [5] in the three space groups $I4$, $I4/m$ and $I\bar{4}$. A reasonable solution was found by using $I\bar{4}$. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least-squares. The only hydrogen atom which was located on a difference Fourier map was that attached to the oxygen, which was refined with an isotropic temperature factor. Refinement converged at $R = 0.075$, $R' = 0.081$, when the maximum shift/error was 0.01 and the weighting scheme was $w = 1/\sigma^2(F)$.

TABLE 2

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

Si-F	1.571(7)	Si-O(1)	1.613(7)
Si-C(1)	1.868(14)	Si-C(5)	1.89(2)
O(1)-H(1)	0.71(8)	C(1)-C(2)	1.48(2)
C(1)-C(3)	1.53(2)	C(1)-C(4)	1.56(2)
C(5)-C(6)	1.54(3)	C(5)-C(7)	1.57(2)
C(5)-C(8)	1.53(2)	O(1)---H(1)'	2.08
F-Si-O(1)	102.6(4)	F-Si-C(1)	105.3(5)
F-Si-C(5)	104.4(6)	O(1)-Si-C(1)	111.7(5)
O(1)-Si-C(5)	110.4(5)	C(1)-Si-C(5)	120.5(6)
Si-O(1)-H(1)	130(7)	Si-C(1)-C(2)	109(1)
Si-C(1)-C(3)	109(1)	Si-C(1)-C(4)	112(1)
C(2)-C(1)-C(3)	114(1)	C(2)-C(1)-C(4)	105(2)
C(3)-C(1)-C(4)	108(1)	Si-C(5)-C(6)	106(1)
Si-C(5)-C(7)	112(1)	Si-C(5)-C(8)	113(1)
C(6)-C(5)-C(7)	115(1)	C(6)-C(5)-C(8)	107(1)
C(7)-C(5)-C(8)	103(1)	H(1)-O(1)---H(1)'	101
O(1)-H(1)---O(1)''	160		

^a Hydrogen bonding. The O(1)---O(1)' distance is 2.756(9) Å and the O---O---O angles are 89.7(3)°. The symmetry elements are: ' y, \bar{x}, \bar{z} ; '' \bar{y}, x, \bar{z} .

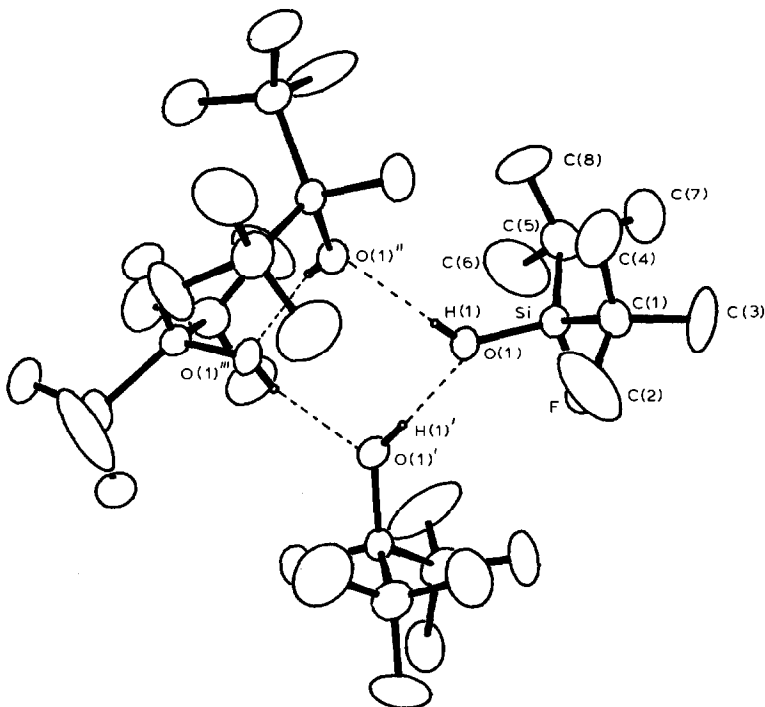


Fig. 1. An ORTEP drawing [7] showing the hydrogen-bonded tetramer of $t\text{-Bu}_2\text{Si}(\text{OH})\text{F}$ and the atom numbering. The atoms are shown as 20% thermal vibrational ellipsoids.

A final difference map had peaks of up to $0.2 \text{ e}\text{\AA}^{-3}$ near the Si atom but was elsewhere featureless.

The structure solution and refinement were carried out on a PDP 11/34 computer using the Enraf-Nonius structure determination package. Scattering factors for neutral atoms were taken from ref. 6. Final coordinates are listed in Table 1, and bond lengths and angles in Table 2. Lists of temperature factors and final structure factors are available from the authors.

Results and discussion

The compound crystallizes as hydrogen-bonded tetramers, as shown in Fig. 1. The hydroxylic protons are fully used in hydrogen bonding, but the bonding is only to oxygen, with none to fluorine. The O-H---O links are not linear (the angle at H is 160°), and although the O---O---O angles ($89.7(3)^\circ$) are not significantly different from 90° the four oxygen atoms are (as is evident from the space group) not quite coplanar; in terms of Fig. 1, the O(1), and O(1)''' atoms are 0.2 \AA above the plane of the paper and the O(1)' and O(1)'' atoms the same distance below it.

To our knowledge this is the first example of the formation of a hydrogen-bonded tetramer by a silanol.

The noteworthy features of the parameters within each $t\text{-Bu}_2\text{Si}(\text{OH})\text{F}$ molecule are; (i) the substantial opening of the $t\text{-Bu-Si-Bu-t}$ angle (to $120.5(6)^\circ$) (as a result of repulsion between the bulky $t\text{-Bu}$ groups) and corresponding closing of the

O–Si–F angle ($102.6(4)^\circ$); (ii) the significant opening of the C(2)–C(1)–C(3) and C(6)–C(5)–C(7) angles ($114(1)$ and $115(1)^\circ$, respectively).

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