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Hydrogen bonding in organosilanediols. The crystal structure of di-*o*-tolylsilanediol

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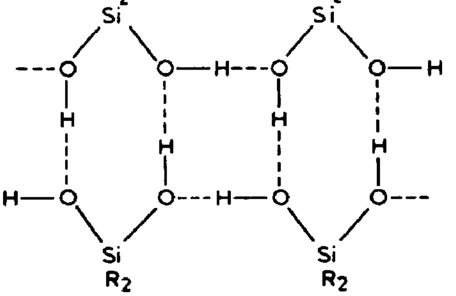
Abstract

The crystal structure of (*o*-tolyl)$_2$Si(OH)$_2$ consists of double chains, made up of a linear chain, based on hydrogen-bonding between adjacent hydroxyl groups, cross-linked to another such chain by further hydrogen bonding. The double chains show some similarity to those for R$_2$Si(OH)$_2$ (with R = i-Pr, t-Bu, or C$_6$H$_{11}$) but differ in detail of the cross-linking.

Introduction

The crystal structures of several organosilanediols have been determined and a wide variety of hydrogen bonded structures has been found. Thus (Me$_3$Si)$_3$CSiPh(OH)$_2$ containing the very bulky (Me$_3$Si)$_3$C group forms discrete hydrogen-bonded dimers [1], whereas the diols R$_2$Si(OH)$_2$ (R = i-Pr [2], t-Bu [3], or C$_6$H$_{11}$ (cyclohexyl) [4]), which contain somewhat less bulky groups, have the cyclic dimers linked by further hydrogen bonding into ladder chains, as shown diagrammatically in I, and Et$_2$Si(OH)$_2$ and Ph$_2$Si(OH)$_2$, which contain even less bulky groups, have infinite hydrogen-bonded structures, that for Et$_2$Si(OH)$_2$ having hydrogen-bonded chains cross-linked to form a layer [5], and that of Ph$_2$Si(OH)$_2$ having hydrogen-bonded hexamers linked by hydrogen bonding into an infinite three-dimensional network [6].



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In view of the variety of structures formed (with even the ladder chains having more than one form) it seemed to us of interest to find out whether the increase in the steric requirements of the aryl group on going to (o-tolyl)$_2$Si(OH)$_2$ from Ph$_2$Si(OH)$_2$ would divert the structure form that of the latter towards that of the type observed for the diols R$_2$Si(OH)$_2$ with R = i-Pr, t-Bu, or C_6H_{11}. The results of the X-ray diffraction study described below show that the structure of (o-tolyl)$_2$Si(OH)$_2$ is, indeed, fairly closely related to that of these R$_2$Si(OH)$_2$ species, but is not identical with it.

Experimental

A sample of (o-tolyl)$_2$Si(OH)$_2$ prepared some time ago [7] was recrystallised by slow evaporation of a solution in heptane/diethyl ether to give crystals suitable for

Table 1

Fractional atomic coordinates ($\times 10^4$ for Si, C, O; $\times 10^3$ for H) with estimated standard deviations in parentheses

	x	y	z
Si	3370.9(6)	1229.6(9)	1307.9(19)
O(1)	3103(1)	1670(2)	3157(5)
O(2)	3056(1)	1629(2)	−519(5)
C(1)	4174(2)	1429(3)	1395(7)
C(2)	4415(2)	1711(3)	3035(7)
C(3)	5016(3)	1770(4)	3303(8)
C(4)	5368(2)	1510(4)	1943(9)
C(5)	5151(2)	1227(4)	277(8)
C(6)	4549(2)	1177(3)	−11(7)
C(7)	4334(3)	881(4)	−1849(8)
C(8)	3246(2)	45(3)	1190(7)
C(9)	3002(2)	−311(4)	−399(8)
C(10)	2955(2)	−1196(4)	−649(9)
C(11)	3186(3)	−1732(4)	655(10)
C(12)	3423(3)	−1394(3)	2229(8)
C(13)	3456(2)	−521(3)	2534(7)
C(14)	3721(3)	−216(4)	4298(8)
H(01)	285(1)	152(2)	341(5)
H(2)	419(1)	189(2)	393(5)
H(02)	307(2)	200(3)	−82(7)
H(3)	513(2)	192(3)	450(6)
H(4)	573(2)	155(3)	200(5)
H(5)	536(2)	109(3)	−64(7)
H(7c)	462(2)	75(3)	−254(7)
H(7a)	416(2)	133(3)	−261(7)
H(7b)	401(2)	45(3)	−184(7)
H(9)	286(2)	8(3)	−133(7)
H(10)	283(2)	−139(4)	−164(8)
H(11)	310(2)	−236(4)	56(8)
H(12)	360(2)	−181(3)	309(6)
H(14b)	349(3)	25(4)	475(8)
H(14c)	379(3)	−55(5)	506(9)
H(14a)	410(3)	0(4)	406(9)

diffraction studies. A crystal of dimensions 0.10 × 0.33 × 0.13 mm, sealed in a thin-walled capillary under argon, was used for the structure determination.

Crystal data

$C_{14}H_{16}O_2Si$, M 244.4, orthorhombic, space group $Pccn$, a 22.864(4), b 15.559(1), c 7.273(1) Å, U 2587.3 Å^3, $Z = 8$, D_c 1.26 g cm^{-3}, $F(000) = 1040$. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 1.62 cm^{-1}.

Data were measured on an Enraf–Nonius CAD4 diffractometer. Intensities for 2278 unique reflections with $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with a scan width $\Delta\theta = (0.8 + 0.35 \tan \theta)°$, and a maximum scan time of 1 min. Two standard reflections were monitored every 30 min and showed no significant variation. After correction for Lorentz and polarisation effects but not for absorption, 1085 reflections with $|F|^2 > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$.

Direct methods (MULTAN) [9] were used to find the positions of C, O, and Si atoms, which were refined by full matrix least squares with anisotropic temperature factors. The hydrogen atoms were found on a difference map and were refined with isotropic temperature factors. Refinement converged at $R = 0.059$, $R' = 0.054$, with weighting scheme $w = 1/\sigma^2(F)$, and a final shift to error ratio < 0.38. A final difference map was everywhere < 0.3 e Å^{-3}.

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

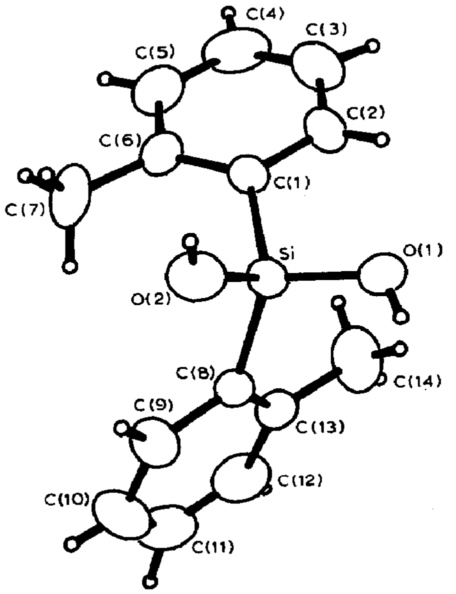

Fig. 1. An ORTEP drawing [10] of the molecular structure of (*o*-tolyl)$_2$Si(OH)$_2$, with the atom numbering.

Results and discussion

The molecular structure, together with the atom numbering scheme is shown in Fig. 1, the unit cell in Fig. 2, and the detail of the hydrogen bonding in Fig. 3. It can be seen that the structure is very different from that of $Ph_2Si(OH)_2$, but is fairly closely related to that in the diols $R_2Si(OH)_2$ with R = i-Pr, t-Bu, or C_6H_{11} in that there are hydrogen-bonded ...Si–O–H...O–Si–O–H... chains (parallel to the c axis) and two such chains are linked by hydrogen-bonds so that the oxygen atoms in one chain face those in the other. However, in the links between the chains each oxygen atom is hydrogen-bonded not to the oxygen atom facing it but to the oxygen atom next to the latter in its chain, and each O–Si–O linkage is orthogonal to the next such linkage in its chain. (Successive pairs of opposing molecules within the double chain are related by a c glide plane.) It is not obvious why this structure should be preferred to the simple ladder chains found for the diols $R_2Si(OH)_2$ with R = i-Pr, t-Bu, or C_6H_{11}.

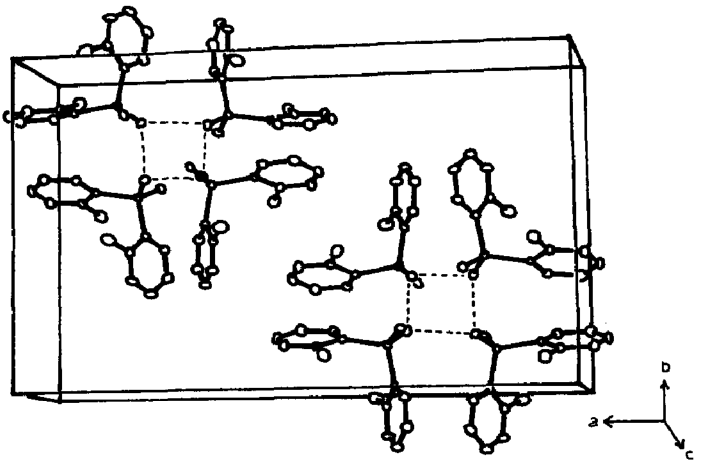

Fig. 2. Unit cell for (o-tolyl)$_2$Si(OH)$_2$. Broken lines denote hydrogen bonding.

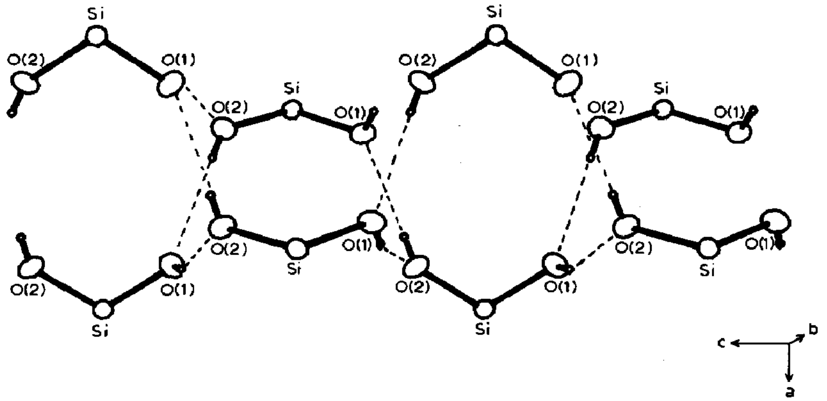

Fig. 3. Detail of the hydrogen bonding in (o-tolyl)$_2$Si(OH)$_2$ with the tolyl groups omitted for clarity. Broken lines denote hydrogen bonding.

Table 2

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Distances			
Si–O(1)	1.629(4)	Si–O(2)	1.633(4)
Si–C(1)	1.864(5)	Si–C(8)	1.867(5)
C(1)–C(2)	1.386(7)	C(1)–C(6)	1.391(7)
C(2)–C(3)	1.390(8)	C(3)–C(4)	1.338(9)
C(4)–C(5)	1.382(9)	C(5)–C(6)	1.394(7)
C(6)–C(7)	1.496(7)	C(8)–C(9)	1.397(7)
C(8)–C(13)	1.400(7)	C(9)–C(10)	1.393(9)
C(10)–C(11)	1.369(9)	C(11)–C(12)	1.371(9)
C(12)–C(13)	1.379(7)	C(13)–C(14)	1.497(8)
O(1)–H(01)	0.66(3)	O(2)–H(02)	0.62(5)
H(01)...O(2)′ [a]	2.21(3)	H(02)″...O(1) [a]	2.20(5)
O(1)...O(2)′	2.82	O(1)...O(2)″	2.82
(b) Angles			
O(1)–Si–O(2)	110.2(2)	O(1)–Si–C(1)	105.8(2)
O(1)–Si–C(8)	113.3(2)	O(2)–Si–C(1)	113.4(2)
O(2)–Si–C(8)	105.7(2)	C(1)–Si–C(8)	108.5(2)
Si–C(1)–C(2)	118.3(4)	Si–C(1)–C(6)	122.3(4)
C(2)–C(1)–C(6)	118.5(4)	C(1)–C(2)–C(3)	122.3(5)
C(2)–C(3)–C(4)	118.1(5)	C(3)–C(4)–C(5)	121.9(5)
C(4)–C(5)–C(6)	120.3(5)	C(1)–C(6)–C(5)	118.8(5)
C(1)–C(6)–C(7)	122.8(5)	C(5)–C(6)–C(7)	118.4(5)
Si–C(8)–C(9)	119.3(4)	Si–C(8)–C(13)	122.4(4)
C(9)–C(8)–C(13)	117.7(5)	C(8)–C(9)–C(10)	122.0(5)
C(9)–C(10)–C(11)	118.8(6)	C(10)–C(11)–C(12)	119.9(6)
C(11)–C(12)–C(13)	122.2(5)	C(8)–C(13)–C(12)	119.3(5)
C(8)–C(13)–C(14)	122.5(5)	C(12)–C(13)–C(14)	118.2(5)
Si–O(1)–H(01)	114(3)	Si–O(2)–H(02)	129(5)
O(1)–H(01)...O(2)′	154(4)	O(2)″–H(02)″...O(1)	179(6)

[a] Symmetry elements: ′ $\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$; ″ $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$.

There are no unusual features in the bond lengths and angles shown in Table 2, although the C_{ipso}–Si–C_{ipso} angle in (o-tolyl)$_2$Si(OH)$_2$ is somewhat smaller (108.5(2)°) than that in Ph$_2$Si(OH)$_2$ (average for three crystallographically independent molecules 112.9°). Table 3 shows the O–Si–O and the C–Si–C angles in a variety of silanediols.

Table 3

O–Si–O and C–Si–C angles in silanediols of type RR′Si(OH)$_2$

R	R′	O–Si–O angle (°)	C–Si–C angle (°)	Ref.
Et	Et	109.8	114.4	5
i-Pr	i-Pr	106.6	114.9	2
t-Bu	t-Bu	106.0	118.4	3
C_6H_{11}	C_6H_{11}	106.0	113.1	4
(Me$_3$Si)$_3$C	Ph	110.5	120.5	1
Ph	Ph	109.3	112.9	6
o-tolyl	*o*-tolyl	110.2	108.5	this work

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