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THE PREPARATION AND CRYSTAL STRUCTURES OF $[(Me_3Si)_3C]PhSi(OH)_2$ AND $[(Me_3Si)_3C]PhSi(OMe)OH$ *

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Summary

The silanol Tsi(Ph)Si(H)OH (Tsi = $(Me_3Si)_3C$) was prepared by hydrolysis of Tsi(Ph)Si(H)I in aqueous dioxane, and then treated with ICl in CCl_4 to give Tsi(Ph)Si(I)OH, which in turn was hydrolysed with H_2O/Me_2SO to give the diol $Tsi(Ph)Si(OH)_2$. Treatment of Tsi(Ph)Si(I)OH with NaOMe/MeOH gave Tsi(Ph)Si(OMe)OH.

In the crystal the diol $Tsi(Ph)Si(OH)_2$ forms discrete cyclic dimers, with the component molecules held together by two unsymmetrical non-linear hydrogen bonds. The related species Tsi(Ph)Si(OMe)OH also forms dimers, but in these the component molecules are linked through a single hydrogen bond between OH groups, with no hydrogen-bonding to the OMe group.

Introduction

Interest attaches to the crystal structures of silanediols since they offer a wide range of hydrogen-bonding possibilities, and since one such diol, $i\text{-}Bu_2Si(OH)_2$, forms an unusual liquid crystal phase arising from hydrogen bonding [1,2]. Diethyl- and diallyl-silanediol both form linear chains [3], whereas diphenylsilandediol forms an intricate maximally hydrogen-bonded network in which six molecules form a cyclic hydrogen-bonded hexamer, with hexamers linked together by further hydrogen bonding [4].

Di-t-butylsilanediol, in contrast, forms cyclic dimers in which the two molecules are doubly linked by hydrogen bonds, with the dimers themselves linked together by further hydrogen bonds into a type of ladder chain, depicted in simplified form in I, all the hydroxyl hydrogens being used in the bonding [5]. This type of structure has

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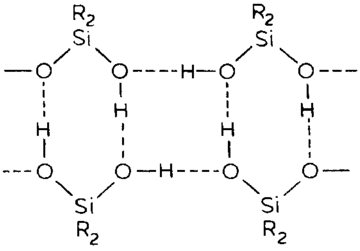
* Dedicated to Professor Oleg A. Reutov on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic chemistry and especially of his pioneering applications in that field of the concept of organic reaction mechanisms.

also been postulated for di-i-butylsilanediol to account for its ability to form a liquid crystal phase [2].

We have now determined the structure of the crowded diol Tsi(Ph)Si$(OH)_2$ (Tsi = 'trisyl' = $(Me_3Si)_3C$), (**A**) and found it to contain yet another structural form, namely discrete cyclic dimers with only half of the hydroxyl hydrogens engaged in hydrogen bonding. Since the closely related species Tsi(Ph)Si(OMe)(OH) (**B**) should be able to form similar cyclic dimers we also examined its crystal structure.

Tsi(Ph)Si$(OH)_2$ Tsi(Ph)Si(OMe)OH
(**A**) (**B**)



(I)

Experimental

Preparations of Tsi(Ph)Si$(OH)_2$ (A)

(a) A solution of TsiPhSi(H)I [6] (0.46 g, 0.99 mmol) in 6/1 v/v dioxane/water (30 cm^3) was refluxed for 1 h then cooled. Water (100 cm^3) was added, and the organic layer was washed several times with water, dried ($MgSO_4$), filtered, and evaporated. The residue was judged by ^1H NMR spectroscopy to contain ca. 7–10% of unchanged TsiPhSi(H)I, so it was refluxed with a solution of $AgClO_4$ (0.1 g) in 6/1 v/v dioxane/water (15 cm^3) for 30 min. The mixture was cooled and filtered, the filtrate was diluted with water and the organosilicon material extracted into n-pentane. The pentane extract was washed, dried ($MgSO_4$), and evaporated, to leave pure Tsi(Ph)Si(H)OH (0.33 g, 93%), m.p. 85–86°C (Found: C, 53.9; H, 9.6. $C_{16}H_{34}OSi_4$ calcd.: C, 54.2; H, 9.4%); ^1H NMR, $\delta(CCl_4)$, 0.20 (s, 27H, $SiMe_3$), 1.52 (s, 1H, SiOH), 5.08 (s, 1H, SiH) and 7.0–7.6 (m, 5H, arylH); ν(SiOH) (in CCl_4) 3680, ν(SiH) 2125 cm^{-1}; m/z 339 (100%, $[M-Me]^+$), 337 (85, $[M-OH]^+$).

(b) A solution of ICl (0.66 g, 4.06 mmol) in CCl_4 (80 cm^3) was added dropwise to a stirred solution of Tsi(Ph)Si(OH)H (1.42 g, 4.01 mmol) in CCl_4 (40 cm^3) at room temperature. The solution was then evaporated under reduced pressure to leave a solid, which was sublimed to give TsiPhSi(OH)I (1.80 g, 94%), m.p. 128–129°C (Found: C, 40.4; H, 7.0. $C_{16}H_{33}IOSi_4$ calcd.: C, 40.0; H, 6.9%), ^1H NMR (CCl_4) δ 0.34 (s, 27H, $SiMe_3$), 2.64 (s, 1H, SiOH), 7.24–7.94 (m, 5H, arylH); ν(SiOH) (in CCl_4) 3660 cm^{-1}; m/z 353 (58%, $[M-I]^+$), 337 (94, $[M-HI-Me]^+$), 275 (48), 249 (36), 187 (52), 135 (55, $[PhMe_2Si]^+$), 73 (100).

(c) A solution of Tsi(Ph)Si(OH)I (0.35 g, 0.73 mmol) in 12/1 v/v Me_2SO/H_2O (13 cm^3) was refluxed for 1 h then cooled. An excess (ca. 50 cm^3) of water was added, and the organosilicon material was extracted into n-pentane. The pentane extract was washed, dried ($MgSO_4$), filtered, and evaporated, to leave Tsi(Ph)Si$(OH)_2$ containing ca. 5% of starting material, as judged from the ^1H NMR spectrum. This mixture was stirred for 4 h at room temperature with a solution of $AgClO_4$ (0.1 g) in 6/1 v/v dioxane-water (14 cm^3), then the AgI was filtered off and the pentane extraction was repeated. Evaporation of the extract gave a solid, which was sublimed to give pure $Tsi(Ph)Si(OH)_2$, m.p. 121°C (Found: C, 51.7; H, 9.2. $C_{16}H_{34}O_2Si_4$ calcd.: C, 51.9; H, 9.2%); ^1H NMR $\delta(CCl_4)$ 0.13 (s, 27H, $SiMe_3$), 2.20 (s, 2H, OH), 6.78–7.40 (m, 5H, arylH); ν(SiOH) (in CCl_4) 3680 cm^{-1}; m/z 355 (8%, $[M - Me]^+$), 337 (53, $[M - H_2O - Me]^+$), 277 (70), 265 (40, $[M - Me_3SiOH - Me]^+$), 135 (28, $[PhMe_2Si]^+$), 73 (100%).

Crystals suitable for the diffraction study were obtained by recrystallization from n-heptane.

*Preparation of Tsi(Ph)Si(OMe)OH (**B**)*

A solution of Tsi(Ph)Si(OH)I (0.24 g) in 0.25 *M* NaOMe/MeOH (3 cm^3) was stirred for 5 min at room temperature. Water (20 cm^3) was then added and the organosilicon material was extracted into pentane. The extract was washed, dried ($MgSO_4$), filtered, and evaporated, and the residue was sublimed to give Tsi(Ph)Si(OMe)OH (0.17 g, 89%), m.p. 103–105°C (Found: C, 53.1; H, 9.2. $C_{17}H_{36}O_2Si_4$ calcd.: C, 53.1; H, 9.4%); ^1H NMR $\delta(CCl_4)$ 0.19 (s, 27 H, $SiMe_3$), 2.14 (s, 1H, OH), 3.25 (s, 3H, OMe), 7.03–7.64 (m, 5H, arylH); ν(SiOH) (CCl_4) 3690 cm^{-1}; m/z 369 (30%, $[M - Me]^+$), 353 (15, $[M - OMe]^+$, 337 (30, $[M - MeOH - Me]^+$), 291 (100, $[M - PhH - Me\}^+$), 249 (35), 175 (15), 135 (25), 73 (70).

Crystals suitable for the X-ray study were obtained by recrystallization from $MeOH-H_2O$.

Crystal structure determinations

1. $Tsi(Ph)Si(OH)_2$ (A). Crystal data: $C_{16}H_{34}O_2Si_4$, $M = 370.8$, monoclinic, a 15.973(2), b 9.276(1), c 15.841(2) Å, β 111.54(1)^0, U 2183.2 Å^3, $Z = 4$, D_c 1.128 g cm^{-3}, $F(000)$ 808. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 2.7 cm^{-1}. Space group $P2_1/c$ from systematic absences of $h0l$ for l odd and $0k0$ for k odd.

Data were measured on an Enraf–Nonius CAD4 diffractometer using a crystal of size ca. 0.35 × 0.17 × 0.10 mm. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4, and final values were calculated from the setting angles for 25 reflections with $\theta \approx 15°$. Intensities for $hk \mp l$ reflections with $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35 \tan\theta)^0$. The scan rate for each reflection was determined by a rapid pre-scan at 10^0 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 0.5 subject to a maximum scan time of 60 seconds. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarization (Lp) effects but not for absorption, and after averaging any equivalent reflections 2486 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 structure was solved by direct methods using the MULTAN program [7]. 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 $R = 0.042$, $R' = 0.043$, when the maximum shift/error was 0.44 and the weighting scheme was $w = 1/\sigma^2(F)$. 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 for neutral atoms were taken from ref. [8]. Final atom coordinates are listed in Table 1, and bond lengths and angles in Table 2. Lists of temperature factors, hydrogen atom positions, and final structure factors may be obtained from C.E. or P.B.H.

2. *Tsi(Ph)Si(OMe)OH, (B).* Crystal data: $C_{17}H_{36}O_2Si_4$. $M = 384.8$, triclinic, a 8.850(1), b 16.357(1), c 17.449(2)Å, α 71.13(2), β 74.69(2), γ 78.90(2)^0, U 2289 Å^3, $Z = 4$, D_c 1.12 g cm^{-3}, $F(000)$ 840. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 2.6 cm^{-1}. Space group $P\bar{1}$ from successful structure refinement.

A crystal of size ca. 0.50 × 0.37 × 0.47 mm was used. Procedures were as described for **A**, above with the following exceptions: (i) scan width $\Delta\theta = (1.2 + 0.35 \tan\theta)^0$; (ii) number of reflections used in final refinement, 4717; (iii) hydrogen atoms were placed at calculated positions (C–H 1.08 Å) with a common isotropic temperature factors except for the hydrogen atoms attached to oxygen, which were located on a difference Fourier map; (iv) $R = 0.050$, $R' = 0.068$.

Final atom coordinates are listed in Table 3 and bond lengths and angles in Table 4. Supplementary data may be obtained from C.E. or P.B.H.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR Tsi(Ph)Si(OH)$_2$, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	*y*	*z*		*x*	*y*	*z*
Si(1)	3117.1(6)	836.3(11)	240.1(6)	H(7)	311(2)	316(4)	−11(2)
Si(2)	2737.9(6)	−2272.0(10)	787.4(6)	H(8)	268(3)	320(4)	57(3)
Si(3)	3304.5(6)	185.8(10)	2249.6(6)	H(9)	215(3)	289(5)	−31(2)
Si(4)	1425.5(5)	181.6(9)	711.1(5)	H(10)	223(2)	−323(4)	187(2)
C(1)	2645(2)	−242(3)	1000(2)	H(11)	277(2)	−421(4)	158(2)
C(2)	4378(2)	933(5)	711(3)	H(12)	319(3)	−328(4)	225(2)
C(3)	2788(3)	75(5)	−935(2)	H(13)	432(2)	−264(4)	119(2)
C(4)	2728(3)	2748(4)	62(2)	H(14)	381(2)	−361(4)	56(2)
C(5)	2709(3)	−3427(4)	1739(3)	H(15)	384(2)	−235(4)	11(2)
C(6)	3814(2)	−2750(4)	626(2)	H(16)	175(2)	−250(3)	−74(2)
C(7)	1812(2)	−2940(4)	−249(2)	H(17)	189(2)	−397(4)	−32(2)
C(8)	2736(3)	−503(4)	3012(2)	H(18)	127(2)	−293(4)	−18(2)
C(9)	3457(4)	2169(4)	2463(2)	H(19)	219(3)	−95(4)	273(3)
C(10)	4462(3)	−629(4)	2698(3)	H(20)	309(3)	−92(5)	344(3)
C(11)	1078(2)	1814(3)	1202(2)	H(21)	255(3)	16(5)	325(3)
C(12)	943(4)	3172(4)	805(2)	H(22)	295(2)	261(3)	228(2)
C(13)	662(2)	4330(4)	1172(3)	H(23)	377(2)	264(4)	215(2)
C(14)	498(3)	4161(4)	1949(3)	H(24)	386(2)	225(4)	306(2)
C(15)	585(3)	2836(5)	2350(2)	H(25)	476(3)	−41(4)	334(2)
C(16)	873(2)	1686(4)	1981(2)	H(26)	478(3)	−36(4)	242(3)
O(1)	921(1)	477(3)	−390(1)	H(27)	439(2)	−152(4)	269(2)
O(2)	976(1)	−1200(2)	1022(1)	H(28)	100(2)	323(3)	30(2)
H(1)	474(3)	4(4)	90(2)	H(29)	58(2)	513(3)	91(2)
H(2)	451(2)	135(4)	32(2)	H(30)	28(2)	487(4)	215(2)
H(3)	458(2)	150(4)	121(2)	H(31)	48(2)	264(4)	285(2)
H(4)	216(3)	13(5)	−130(3)	H(32)	95(2)	84(3)	226(2)
H(5)	292(3)	−75(4)	−95(2)	H(33)	93(2)	−3(3)	−63(2)
H(6)	308(3)	64(5)	−118(2)	H(34)	56(2)	−117(3)	91(2)

TABLE 2

INTRAMOLECULAR DISTANCES(Å) AND ANGLES(°) FOR Tsi(Ph)Si(OH)$_2$, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bonds			
Si(1)–C(1)	1.919(3)	Si(1)–C(2)	1.875(5)
Si(1)–C(3)	1.876(4)	Si(1)–C(4)	1.866(5)
Si(2)–C(1)	1.929(3)	Si(2)–C(5)	1.864(5)
Si(2)–C(6)	1.882(4)	Si(2)–C(7)	1.866(4)
Si(3)–C(1)	1.911(3)	Si(3)–C(8)	1.869(4)
Si(3)–C(9)	1.871(4)	Si(3)–C(10)	1.878(4)
Si(4)–C(1)	1.872(3)	Si(4)–C(11)	1.877(3)
Si(4)–O(1)	1.653(3)	Si(4)–O(2)	1.631(3)
C(11)–C(12)	1.389(5)	C(11)–C(16)	1.395(4)
C(12)–C(13)	1.373(5)	C(13)–C(14)	1.359(6)
C(14)–C(15)	1.367(6)	C(15)–C(16)	1.373(5)
O(1)–H(33)	0.61(3)	O(2)–H(34)	0.63(3)
(b) Angles			
C(1)–Si(1)–C(2)	112.8(2)	C(1)–Si(1)–C(3)	113.3(2)
C(1)–Si(1)–C(4)	113.8(2)	C(2)–Si(1)–C(3)	106.3(2)
C(2)–Si(1)–C(4)	105.3(3)	C(3)–Si(1)–C(4)	104.5(3)
C(1)–Si(2)–C(5)	113.2(2)	C(1)–Si(2)–C(6)	112.7(2)
C(1)–Si(2)–C(7)	113.0(2)	C(5)–Si(2)–C(6)	105.6(3)
C(5)–Si(2)–C(7)	105.9(2)	C(6)–Si(2)–C(7)	105.7(2)
C(1)–Si(3)–C(8)	112.6(2)	C(1)–Si(3)–C(9)	112.1(2)
C(1)–Si(3)–C(10)	113.5(2)	C(8)–Si(3)–C(9)	106.3(3)
C(8)–Si(3)–C(10)	105.2(3)	C(9)–Si(3)–C(10)	106.4(2)
C(1)–Si(4)–C(11)	120.5(1)	C(1)–Si(4)–O(1)	110.7(1)
C(1)–Si(4)–O(2)	107.2(1)	C(11)–Si(4)–O(1)	101.5(1)
C(11)–Si(4)–O(2)	106.2(1)	O(1)–Si(4)–O(2)	110.5(1)
Si(1)–C(1)–Si(2)	109.0(1)	Si(1)–C(1)–Si(3)	110.4(1)
Si(1)–C(1)–Si(4)	110.5(1)	Si(2)–C(1)–Si(3)	109.6(1)
Si(2)–C(1)–Si(4)	107.5(1)	Si(3)–C(1)–Si(4)	109.8(1)
Si(4)–C(11)–C(12)	124.4(2)	Si(4)–C(11)–C(16)	120.0(3)
C(12)–C(11)–C(16)	115.5(3)	C(11)–C(12)–C(13)	122.6(4)
C(12)–C(13)–C(14)	119.7(4)	C(13)–C(14)–C(15)	120.3(4)
C(14)–C(15)–C(16)	119.6(4)	C(11)–C(16)–C(15)	122.3(4)
Si(4)–O(1)–H	114.4	Si(4)–O(2)–H	144.8
(c) Hydrogen bonding			
O(2)–H	0.63	O(2)–H---O(1)′	166°
O(1)′---H [a]	2.29		
O(2)–O(1)′	2.90		

[a] Symmetry element′ is $\bar{x}$, $\bar{y}$, $\bar{z}$.

Results and discussion

For the preparation of the diol (A) the previously reported iodide Tsi(Ph)Si(H)I [6] was treated with aqueous dioxane; interestingly the hydrolysis did not proceed to completion, and the residual starting iodide had to be removed by use of AgClO$_4$ or by repeated washing of the pentane solution of the product with aqueous alkali. (The equilibrium could also be reached from Tsi(Ph)Si(H)OH and HI in the same medium. as will be described elsewhere [9]). The Tsi(Ph)Si(H)OH was then treated

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR Tsi(Ph)Si(OMe)OH, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	*y*	*z*		*x*	*y*	*z*
Si(1)	−75.7(12)	5926.3(7)	1440.5(7)	Si(5)	−4252.8(13)	10958.3(7)	3020.8(7)
Si(2)	−2939.9(12)	6388.5(6)	2766.7(6)	Si(6)	−5361.4(12)	9589.5(6)	2480.6(6)
Si(3)	−819.2(14)	4650.4(7)	3250.2(7)	Si(7)	−5948.1(14)	11562.1(7)	1520.9(8)
Si(4)	−3079.1(13)	4960.1(7)	2038.6(7)	Si(8)	−2592.2(15)	10519.9(8)	1348.5(7)
C(1)	−1702(4)	5481(2)	2382(2)	C(2)	−4581(4)	10664(2)	2108(2)
C(3)	934(5)	6770(3)	1562(3)	C(19)	−6124(6)	11395(3)	3639(3)
C(4)	−831(5)	6473(3)	469(2)	C(20)	−2835(5)	11792(3)	2697(3)
C(5)	1546(5)	5062(3)	1203(3)	C(21)	−3405(5)	10008(3)	3793(3)
C(6)	−4477(5)	5785(3)	1464(3)	C(22)	−8087(5)	11525(3)	2045(3)
C(7)	−4323(5)	4203(3)	2923(3)	C(23)	−5557(6)	12692(3)	1410(3)
C(8)	−1961(6)	4280(3)	1330(3)	C(24)	−5816(7)	11508(3)	458(3)
C(9)	871(5)	5042(3)	3441(3)	C(25)	−1879(7)	11580(3)	674(3)
C(10)	−2262(7)	4393(3)	4274(3)	C(26)	−2654(6)	9887(3)	633(3)
C(11)	−59(6)	3570(3)	3045(3)	C(27)	−945(5)	9941(3)	1879(3)
C(12)	−2357(4)	6764(2)	3556(2)	C(28)	−6840(5)	8834(3)	1787(3)
C(13)	−1222(5)	7337(2)	3326(2)	C(29)	−6687(4)	9236(2)	3539(2)
C(14)	−881(5)	7648(3)	3906(3)	C(30)	−8287(5)	9541(3)	3701(2)
C(15)	−1672(5)	7405(3)	4723(2)	C(31)	−9260(5)	9229(3)	4474(3)
C(16)	−2800(5)	6857(3)	4959(2)	C(32)	−8676(6)	8610(3)	5090(3)
C(17)	−3142(5)	6535(2)	4387(2)	C(33)	−7103(6)	8270(3)	4941(3)
C(18)	−6064(5)	6554(3)	3372(3)	C(34)	−6151(5)	8590(3)	4182(3)
O(1)	−3061(3)	7248(1)	1973(2)	O(3)	−3894(3)	8800(2)	2490(2)
O(2)	−4685(3)	6046(2)	3226(2)	O(4)	−6304(3)	9564(2)	1791(1)

with one molar equivalent of ICl to give Tsi(Ph)Si(I)OH; * this is markedly more sterically hindered than Tsi(Ph)Si(H)I, but water in Me_2SO under reflux brought about fairly rapid conversion into the diol **A**, although again some residual starting iodide had to be removed with $AgClO_4$.

The methoxysilanol (**B**) was prepared by treatment of Tsi(Ph)Si(OH)I with MeOH containing NaOMe. The significance of the surprising ease of replacement of the iodine atom by an OMe group under these conditions has been considered previously [10].

The molecular structure of $Tsi(Ph)Si(OH)_2$ (**A**) is shown in Fig. 1, the crystal structure in Fig. 2, and some dimensions in Table 5. It is evident that in the crystals there are discrete cyclic hydrogen-bonded dimers (lying across an inversion centre), with no hydrogen bonding between the dimers, and this represents the first observation of such a structure for a silanediol. If, for simplicity, the bridging hydrogen atoms are ignored, the dimers can be regarded as six-membered rings in a chair conformation (similar to those in $t\text{-}Bu_2Si(OH)_2$ [5]), with the Tsi groups in equatorial and the Ph groups in axial positions. Details of the hydrogen bonding are given in Table 2; it will be seen that the O–H- -O linkages are not linear. Presumably

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* It is appropriate to draw attention to the fact that this compound is stable although having an iodine atom and a hydroxyl group attached to the same silicon atom. It was, in fact, purified by sublimation, and a sample remained unchanged after being melted (at 128°C) and resolidified three times while exposed to the air. Since the first report of this compound [10] the stable species $t\text{-}Bu_2Si(OH)X$ (X = Cl or Br) have been described [13].

TABLE 4

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) FOR Tsi(Ph)Si(OMe)OH, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bonds

Si(1)–C(1)	1.919(2)	Si(1)–C(3)	1.875(3)
Si(1)–C(4)	1.873(3)	Si(1)–C(5)	1.875(3)
Si(2)–C(1)	1.866(2)	Si(2)–C(12)	1.894(2)
Si(2)–O(1)	1.634(2)	Si(2)–O(2)	1.653(2)
Si(3)–C(1)	1.907(2)	Si(3)–C(9)	1.878(3)
Si(3)–C(10)	1.875(3)	Si(3)–C(11)	1.878(3)
Si(4)–C(1)	1.920(2)	Si(4)–C(6)	1.869(3)
Si(4)–C(7)	1.875(3)	Si(4)–C(8)	1.888(3)
C(12)–C(13)	1.399(3)	C(12)–C(17)	1.393(3)
C(13)–C(14)	1.388(3)	C(14)–C(15)	1.377(4)
C(15)–C(16)	1.363(4)	C(16)–C(17)	1.388(3)
C(18)–O(2)	1.352(3)	Si(5)–C(2)	1.909(2)
Si(5)–C(19)	1.875(3)	Si(5)–C(20)	1.882(3)
Si(5)–C(21)	1.877(3)	Si(6)–C(2)	1.866(2)
Si(6)–C(29)	1.884(2)	Si(6)–O(3)	1.645(2)
Si(6)–O(4)	1.649(2)	Si(7)–C(2)	1.916(2)
Si(7)–C(22)	1.876(3)	Si(7)–C(23)	1.886(3)
Si(7)–C(24)	1.857(3)	Si(8)–C(2)	1.929(2)
Si(8)–C(25)	1.871(3)	Si(8)–C(26)	1.878(3)
Si(8)–C(27)	1.869(3)	C(28)–O(4)	1.369(3)
C(29)–C(30)	1.393(3)	C(29)–C(34)	1.386(3)
C(30)–C(31)	1.390(4)	C(31)–C(32)	1.355(4)
C(32)–C(33)	1.385(4)	C(33)–C(34)	1.368(4)

(b) Angles

C(1)–Si(1)–C(3)	113.9(1)	C(1)–Si(1)–C(4)	112.9(1)
C(1)–Si(1)–C(5)	112.9(1)	C(3)–Si(1)–C(4)	104.5(1)
C(3)–Si(1)–C(5)	105.2(1)	C(4)–Si(1)–C(5)	106.6(1)
C(1)–Si(2)–C(12)	120.16(9)	C(1)–Si(2)–O(1)	108.54(9)
C(1)–Si(2)–O(2)	105.68(9)	C(12)–Si(2)–O(1)	105.95(9)
C(12)–Si(2)–O(2)	105.1(1)	O(1)–Si(2)–O(2)	111.33(9)
C(1)–Si(3)–C(9)	112.0(1)	C(1)–Si(3)–C(10)	113.4(1)
C(1)–Si(3)–C(11)	113.5(1)	C(9)–Si(3)–C(10)	105.6(1)
C(9)–Si(3)–C(11)	106.8(1)	C(10)–Si(3)–C(11)	105.0(1)
C(1)–Si(4)–C(6)	112.5(1)	C(1)–Si(4)–C(7)	113.5(1)
C(1)–Si(4)–C(8)	112.4(1)	C(6)–Si(4)–C(7)	106.3(1)
C(6)–Si(4)–C(8)	106.5(1)	C(7)–Si(4)–C(8)	105.0(1)
Si(1)–C(1)–Si(2)	110.3(1)	Si(1)–C(1)–Si(3)	110.9(1)
Si(1)–C(1)–Si(4)	108.7(1)	Si(2)–C(1)–Si(3)	109.9(1)
Si(2)–C(1)–Si(4)	106.5(1)	Si(3)–C(1)–Si(4)	110.4(1)
Si(2)–C(12)–C(13)	121.9(2)	Si(2)–C(12)–C(17)	120.9(2)
C(13)–C(12)–C(17)	117.0(2)	C(12)–C(13)–C(14)	121.1(2)
C(13)–C(14)–C(15)	120.5(3)	C(14)–C(15)–C(16)	119.4(2)
C(15)–C(16)–C(17)	120.7(2)	C(12)–C(17)–C(16)	121.3(2)
Si(2)–O(2)–C(18)	126.1(2)	C(2)–Si(5)–C(19)	112.8(1)
C(2)–Si(5)–C(20)	113.1(1)	C(2)–Si(5)–C(21)	113.5(1)
C(19)–Si(5)–C(20)	106.9(1)	C(19)–Si(5)–C(21)	104.9(1)
C(20)–Si(5)–C(21)	104.9(1)	C(2)–Si(6)–C(29)	120.6(1)
C(2)–Si(6)–O(3)	110.11(9)	C(2)–Si(6)–O(4)	107.18(9)
C(29)–Si(6)–O(3)	103.9(1)	C(29)–Si(6)–O(4)	107.82(9)
O(3)–Si(6)–O(4)	106.37(8)	C(2)–Si(7)–C(22)	113.2(1)
C(2)–Si(7)–C(23)	113.2(1)	C(2)–Si(7)–C(24)	113.1(1)
C(22)–Si(7)–C(23)	104.6(1)	C(22)–Si(7)–C(24)	105.2(2)

TABLE 4 (continued)

C(23)–Si(7)–C(24)	106.7(1)	C(2)–Si(8)–C(25)	112.8(1)
C(2)–Si(8)–C(26)	113.3(1)	C(2)–Si(8)–C(27)	113.4(1)
C(25)–Si(8)–C(26)	106.5(2)	C(25)–Si(8)–C(27)	104.2(1)
C(26)–Si(8)–C(27)	105.8(1)	Si(5)–C(2)–Si(6)	110.0(1)
Si(5)–C(2)–Si(7)	110.8(1)	Si(5)–C(2)–Si(8)	109.9(1)
Si(6)–C(2)–Si(7)	111.8(1)	Si(6)–C(2)–Si(8)	105.8(1)
Si(7)–C(2)–Si(8)	108.4(1)	Si(6)–C(29)–C(30)	122.4(2)
Si(6)–C(29)–C(34)	121.2(2)	C(30)–C(29)–C(34)	116.1(2)
C(29)–C(30)–C(31)	121.2(3)	C(30)–C(31)–C(32)	120.6(3)
C(31)–C(32)–C(33)	119.6(3)	C(32)–C(33)–C(34)	119.2(3)
C(29)–C(34)–C(33)	123.1(3)	Si(6)–O(4)–C(28)	124.1(2)
(c) Hydrogen bonding			
O(1)–H	0.73	O–H---O	158.5°
O(3)---H	2.17		
O(1)–O(3)	2.86		

the bulk of the substituents on the silicon atoms hinders hydrogen-bonding between the cyclic dimers.

In the molecular structure the bond lengths and angles within the trisyl group show the pattern which has now become familiar [11], viz. long Me$_3$Si–C and significantly shorter Me–Si bonds, with opening of the C(1)–Si–Me and closing of the Me–Si–Me angles (see Table 5).

Unexpectedly, the bond between the central carbon atom of the trisyl group and the other silicon atom, i.e. the C(1)–Si(4) bond, is markedly shorter, at 1.872(3) Å, than the other C–SiMe$_3$ bonds (mean 1.920(3)Å); (this same feature is present in **B**). The C(1)–Si(4)–Ph angle is exceptionally large at 120.5(1)° (the corresponding angle

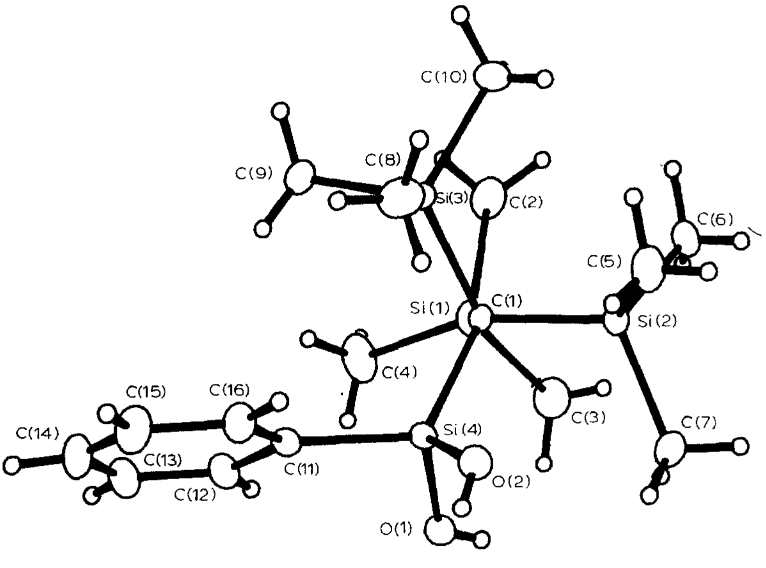


Fig. 1. ORTEP drawing showing molecular structure of Tsi(Ph)Si(OH)$_2$, with atom numbering scheme.

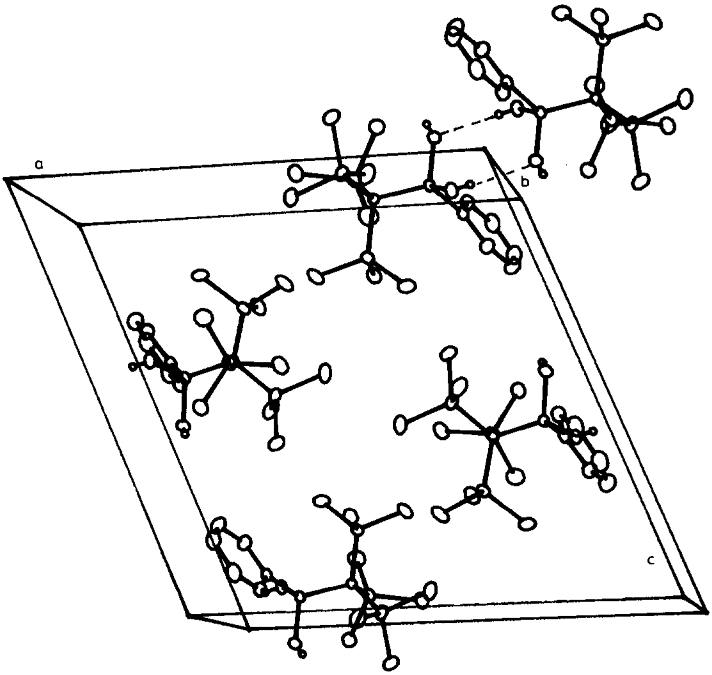


Fig. 2. Crystal structure of Tsi(Ph)Si(OH)$_2$, showing hydrogen bonding.

in TsiSiMe$_2$Ph is 116.5(4)° [11]), and the C(1)–Si(4)–O angles are correspondingly small (mean 103.9(1) Å); these angles reflect the fact that the phenyl rings lie over towards the centres of the cyclic dimers, on opposite sides, this presumably minimizing the steric strain.

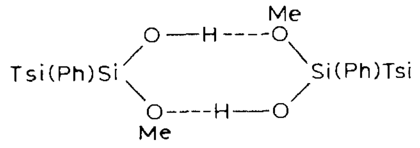
TABLE 5

SOME SELECTED BOND LENGTHS (Å) AND ANGLES (°) IN Tsi(Ph)Si(OH)$_2$ (**A**) AND Tsi(Ph)Si(OMe)OH(**B**)

	A	**B** [a]	**B′** [a]
C(central)–SiMe$_3$ [b]	1.920(3)	1.917(2)	
Si–Me [b]	1.872(4)	1.876(3)	
C(central)–SiPhO$_2$	1.872(3)	1.866(2)	
C(central)–Si–Me [b]	113.0(2)	113.1(1)	
Me–Si–Me [b]	105.7(2)	105.9(1)	
C(central)–Si–Ph	120.5(1)	120.16(9)	120.6(1)
C–C(*ipso*)–C	115.3(3)	117.0(2)	116.1(2)
C(central)–Si–O(H)---H	110.7(1)	105.95(9)	
C(central)–Si–OH---O	107.2(1)		110.11(9)
C(central)–Si–OMe		105.68(9)	107.18(9)
O–Si–O	110.5(1)	111.33(9)	106.37(8)
Si–O–Me		126.1(2)	124.1(2)

[a] **B** and **B′** denote the proton-donor molecule (containing O(1)) and proton-acceptor molecule (containing O(3)) in the hydrogen-bonded dimer. [b] Mean values; in case of **B** the averaging is over both molecules of the dimer.

There is significant distortion of the phenyl rings; e.g. the intracyclic angle at the ipso carbon, i.e. C(12)–C(11)–C(16), is only 115.3°. The origin of this type of effect has been considered previously [12].



(II)

The molecular structures of the two crystallographically independent molecules of **B** are shown in Fig. 3, the crystal structure in Fig. 4, and some selected dimensions in Table 5. Possibly for steric reasons **B** does not, as we had thought likely, form dimers of the type III corresponding to those formed by the diol **A**. Instead it forms simple dimers each held together by a single hydrogen bond, with the OMe groups and half of the hydroxyl hydrogens not involved in the bonding. Again the hydrogen bond is not linear, the O–H- - -O angle being close to that in **A**.

The two crystallographically independent molecules shown in Fig. 3 have almost identical conformations and differ only in having the OMe and OH groups interchanged and showing slightly different orientations of these groups about the Si–O bonds. If the molecules are denoted by the numbering of the central carbon atom, then the chiralities of the molecules are 1*S* and 2*R*. Since the space group is centrosymmetric, each will also be related to an enantiomeric molecule (i.e. 1*R* and 2*S*) by the crystallographic inversion centre.

The two molecules in each dimer of **B** are not chemically equivalent since one (containing C(1)) is the proton donor and the other (containing C(2)) the proton acceptor in the hydrogen bond, but there are no significant differences between the internal dimensions of the two trisyl groups, and values of such dimensions in Table 5 are averaged over both groups. As will be seen from that Table, these mean values

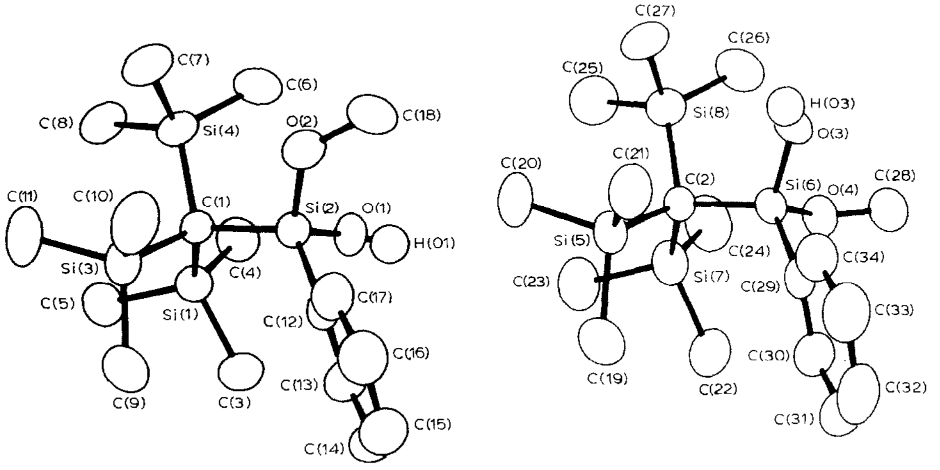


Fig. 3. ORTEP drawings showing molecular structures in Tsi(Ph)Si(OMe)(OH) (**B**) with atom numbering. The two molecules are placed in such a way as to reveal the differing orientations of the OH and OMe groups about the Si(2) and Si(6) atoms. The molecule containing C(1) is the proton donor in the dimer.

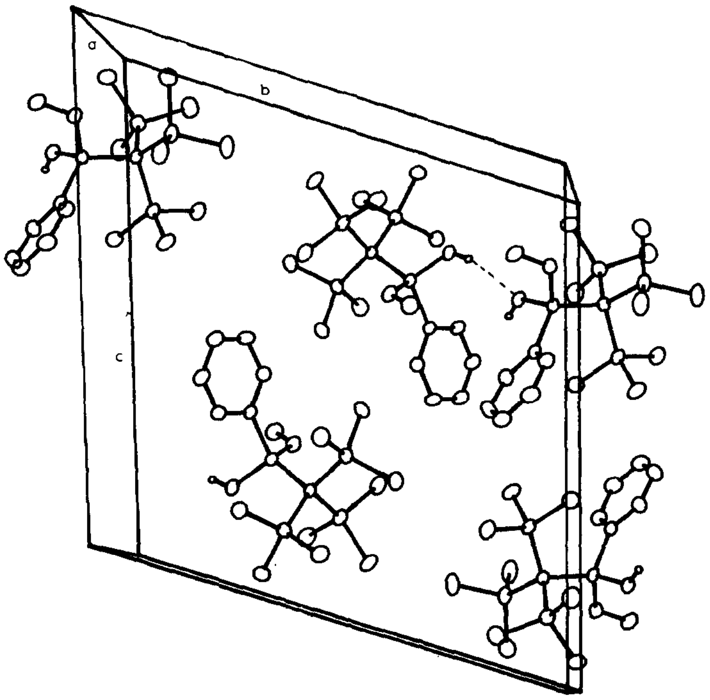


Fig. 4. Crystal structure of Tsi(Ph)Si(OMe)OH showing hydrogen bonding.

are remarkably similar to those in the diol **A**. Furthermore the (short) C(central)–$SiPhO_2$ bonds and the C(central)–Si–Ph angles are also effectively identical with those in **A**. The intracyclic angles at the *ipso* carbons, C(13)–C(12)–C(17) and C(30)–C(29)–C(34), 117.0(2) and 116.1(2)°, respectively, may possibly be significantly larger than the corresponding angle in **A** (115.3(3)°).

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