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The structure of 1,1,3,3,5,5-hexaphenyl-1,3-5-trisiloxane-1,5-diol

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Abstract

1,1,3,3,5,5-Hexaphenyl-1,3,5-trisiloxane-1,5-diol has an approximately planar, eight-membered Si_3O_4H ring structure, in which cyclization is achieved through an O–H ··· O hydrogen bond. In addition, adjacent molecules dimerize through an eight-membered H_4O_4 ring to yield a stepped tricyclic array.

1. Introduction

Low molecular weight compounds containing Si-OH bonds, *i.e.* siloxane diols and triols, have been, and continue to be, the focus of much research interest [1]. Such compounds can act as models for macromolecular Si–O species, for example organosilane triols, $RSi(OH)_3$, have been used to replicate the surface of silica, and as synthetic precursors for metallosiloxanes which mimic surface adsorbed metal-centred fragments [2]. Hydrolysis of R_2SiCl_2 leads to the formation of industrially important siloxane chains, α-,ω-(HO)-$R_2SiO(R_2SiO)_nSiR_2(OH)$, and linear, low molecular weight siloxanols represent early stages in the growth of such species. Not surprisingly, the structural chemistry of these compounds is concentrated at the begining of the series, with the majority of reports devoted to the initial hydrolysis product, $R_2Si(OH)_2$. For a variety of R [Et, ^{i}Pr, ^{t}Bu, c-C_5Me_5, c-C_6H_{11}, $(Me_3Si)_3C$, Ph, allyl], the geometric parameters within the repeat unit are remarkably consistent, with d(Si–O) and the O–Si–O angle covered by the ranges 1.637–1.659 Å and 106–110°C, respectively. The main structural differences arise through the wide variety of hydrogen bonding networks that are adopted, with 3-D and layer structures evident for compounds with small R, whilst self-association into chains or discrete oligomers is favoured by diols with bulky substituents on silicon [1,3]. The structures of a smaller range of linear 1,3-siloxane diols, $(HO)R_2SiOSiR_2(OH)$ have also been reviewed [1,4], and again the main structural differences lie in the patterns of solid-state hydrogen-bonding and hence intermolecular associations. Double-stranded chains dominate (R = Me, ^{n}Pr, ^{i}Pr, Ph), although a sheet structure is preferred by Me(3-C_4H_3S)(OH)SiOSi(OH)(3-C_4H_3S)Me.

Only one structure has been reported previously for a trisiloxane-1,5-diol, $(HO)^tBu_2SiOSiMe_2OSi^tBu_2(OH)$ (**1**), prepared in step-wise fashion from $^tBu_2Si(OH)(OLi)$ and Me_2SiCl_2 [5]. We have now succeeded in isolating the homoleptic organotrisiloxane-1,5-diol, $(HO)Ph_2SiOPh_2SiOSiPh_2(OH)$ (**2**), from the controlled hydrolysis of Ph_2SiCl_2, and report the structure of this compound.

2. Experimental details

The sample of $HO(SiPh_2O)_3H$ (**2**) was prepared by a modification of that described by Harris [6].

Dichlorodiphenysilane (37.9 g, 0.15 mol) was added dropwise during a 45-min period to a stirred mixture of ammonium carbonate (20.1 g, 0.21 mol), diethyl ether (150 cm^3) and water (2.7 g, 0.15 mol). The mixture was heated under reflux for 12 h, cooled and then stirred with 100 cm^3 of water and the ethereal phase sepa-

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rated, dried over sodium sulphate and evaporated. Extraction of the residue five times with cold benzene (40 cm^3) separated insoluble $Ph_2Si(OH)_2$ (8.0 g) from oligomeric siloxanols and cyclic siloxanes, which were recovered on evaporation of the combined extracts. Washing the residue successively with a 1:5 and a 1:1 benzene/petrol mixture (120 cm^3) yielded crude tetraphenyldisiloxane-1,3-diol, which was recrystallized from 5:1 benzene/petrol (yield, 8.3 g). Fractional crystallization of the combined extracts yielded $HO(SiPh_2O)_3H$, which was recrystallized from benzene/petrol (1:1) to give the pure product.

2.1. *Tetraphenyldisiloxane-1,3-diol*

^1H NMR: 4.10 (2H, brs, OH); 7.20–7.56 (20H, m, C_6H_5). ^{29}Si NMR: −36.0 (all NMR spectra are as $CDCl_3$ solutions, ppm ref. TMS). Mass spectral data (EI 70eV, *m/z*): 414 (M^+), 337 (M − Ph), 319 (M − $PhOH_2$).

2.2. *Hexaphenyltrisiloxane-1,5-diol*

^1H NMR: 4.26 (2H, s, OH); 7.15–7.68 (30H, m, C_6H_5). ^{29}Si NMR: −36.5, −44.0. Mass spectral data: 594 (*cyclo*-$Ph_6Si_3O_3$), 517 (M^+ − Ph − H_2O), 439 (M^+ − Ph − H_2O − PhH).

TABLE 1. Fractional atomic coordinates and equivalent isotropic thermal parameters * (Å^2) for **2**

Atom	x	y	z	U_{eq}
Si1	0.5097(3)	0.3525(2)	0.2458(2)	0.044(1) *
Si2	0.5105(3)	0.1275(2)	0.2151(2)	0.041(1) *
Si3	0.3758(3)	0.2768(2)	−0.0020(2)	0.046(2) *
O1	0.5322(7)	0.2304(4)	0.2387(4)	0.059(4) *
O2	0.4479(7)	0.1780(4)	0.1022(4)	0.052(4) *
O3	0.3785(7)	0.4034(4)	−0.0095(4)	0.055(4) *
O4	0.4679(7)	0.4541(5)	0.1342(4)	0.059(4) *
C4	0.1846(14)	0.4034(11)	0.4908(9)	0.107(10) *
C5	0.2102(16)	0.4959(11)	0.4096(11)	0.124(12) *
C6	0.3010(13)	0.4822(9)	0.3332(8)	0.090(9) *
C8	0.7031(16)	0.3690(10)	0.3652(8)	0.104(10) *
C9	0.8362(20)	0.3725(13)	0.3842(12)	0.121(13) *
C10	0.9432(20)	0.3601(12)	0.3189(15)	0.124(15) *
C11	0.9244(16)	0.3490(12)	0.2336(13)	0.107(13) *
C12	0.7941(12)	0.3453(8)	0.2171(8)	0.072(8) *
C14	0.7981(12)	0.0250(9)	0.2652(8)	0.082(8) *
C15	0.9225(14)	−0.0599(11)	0.2767(10)	0.104(11) *
C16	0.9330(12)	−0.1473(9)	0.2489(8)	0.073(9) *
C17	0.8194(13)	−0.1526(9)	0.2095(8)	0.079(8) *
C21	0.1444(11)	0.0625(10)	0.3701(8)	0.070(8) *
C22	0.1936(15)	−0.0283(10)	0.4563(8)	0.083(9) *
C23	0.3307(14)	−0.0734(10)	0.4707(8)	0.077(9) *
C27	0.6802(15)	0.1533(11)	−0.1791(11)	0.103(11) *
C28	0.6301(14)	0.2149(12)	−0.2755(11)	0.103(11) *
C29	0.5059(15)	0.2950(11)	−0.2892(8)	0.098(10) *
C32	0.1511(14)	0.1764(10)	0.0310(8)	0.089(9) *
C33	0.0201(17)	0.1736(15)	0.0240(11)	0.123(13) *
C34	−0.0866(17)	0.2729(19)	−0.0194(13)	0.159(17) *
C35	−0.0420(19)	0.3686(14)	−0.0566(12)	0.137(15) *
C36	0.0892(14)	0.3735(11)	−0.0481(10)	0.107(11) *
C1	0.3737(10)	0.3722(7)	0.3387(6)	0.055(2)
C2	0.3381(10)	0.2821(8)	0.4192(7)	0.064(3)
C3	0.2474(12)	0.2969(9)	0.4948(8)	0.073(3)
C7	0.6800(10)	0.3580(7)	0.2795(6)	0.051(2)
C13	0.6811(9)	0.0215(6)	0.2261(6)	0.041(2)
C18	0.6957(12)	−0.0692(8)	0.1994(7)	0.069(3)
C19	0.3814(9)	0.0626(6)	0.3082(5)	0.041(2)
C20	0.2412(11)	0.1064(8)	0.2959(7)	0.069(3)
C24	0.4304(12)	−0.0301(8)	0.3981(7)	0.071(3)
C25	0.4830(1)	0.2494(7)	−0.1095(6)	0.048(2)
C26	0.6066(12)	0.1692(9)	−0.0979(8)	0.073(3)
C30	0.4262(11)	0.3150(8)	−0.2083(7)	0.063(3)
C31	0.1902(10)	0.2762(8)	−0.0058(6)	0.051(2)
H4	0.409(7)	0.449(6)	0.084(4)	0.05

2.3. Crystal data for 2

$C_{36}H_{32}O_4Si_3$, $M_r = 612.8$ triclinic, space group $P\bar{1}$, $a = 9.934(3)$, $b = 13.299(3)$, $c = 14.459(4)$ Å, $\alpha = 65.92(2)$, $\beta = 82.95(3)$, $\gamma = 73.16(3)°$, $U = 1669.2$ Å^3, $Z = 2$, $D_x = 1.23$ g cm^{-3}, MoKα, $\lambda = 0.71069$ Å, μ(MoKα) = 1.40 cm^{-1}, $F(000) = 644$.

A cube-shaped crystal of approximation dimensions $0.25 \times 0.25 \times 0.35$ mm^3 was selected and used for data collection. Data were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2 < \theta < 22°$ using ω–2θ scans, covering the ranges h $-10 \rightarrow 0$, k $-13 \rightarrow 13$, l $-14 \rightarrow 14$. Cell dimensions were based on 12 accurately centred reflections with $14 < \theta < 17°$. A total of 4382 reflections were collected of which 2186 were unique and observed with $I \geq 3\sigma(I)$. A standard reflection measured after every 50 reflections showed no systematic crystal decay throughout data collection. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by conventional Patterson methods and refined using full matrix least squares based on F, using the SHELX suite of programs [7,8]. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography* [9]. In the final least squares cycles, the silicon and oxygen atoms along with those carbons which exhibited high isotropic thermal parameters in the penultimate least squares refinement (C4–6, 8–12, 21–23, 27–29 and 32–36) were treated anisotropically. All other atoms were treated isotropically. The hydrogen atom, H4, was located and refined at a fixed distance of 1.03 Å from O4, with its isotropic thermal parameter fixed at 0.05 Å^2. The remaining hydrogens were included at calculated positions (C–H 1.08 Å) with a common, fixed thermal parameter ($U = 0.05$ Å^2). Final residuals after 10 cycles of least squares were $R = R_w = 0.0657$ for unit weights. Max. final shift/e.s.d. was 0.012. The max. and min. residual densities were 0.14 and -0.12 e Å^{-3} respectively.

Final fractional atomic coordinates and isotropic thermal parameters are given in Table 1 with selected bond lengths and angles in Table 2. Tables of anisotropic temperature factors, a full listing of bond lengths and angles and hydrogen atom positions are available as supplementary data. The asymmetric unit is shown in Fig. 1, along with the labelling scheme used.

3. Discussion

Hydrolysis of Ph_2SiCl_2 in diethyl ether yields $Ph_2Si(OH)_2$ as the major product, which can be separated from higher oligomers by extraction of the mixture, after solvent evaporation, with benzene, in which it has very low solubility. After distillation of the benzene *in vacuo*, sequential extraction of the residue with 1:5 then 1:1 benzene/petrol separates $(HO)Ph_2SiOSiPh_2(OH)$ from the more soluble cyclics and higher oligomers. Crystals of the title 1,5-diol (**2**) were obtained by fractional crystallization from the combined extracts.

The structure of **2** (Fig. 1) shows that it contains a novel eight-membered HSi_3O_4 heterocycle, with the two ends of the nominally acyclic array linked through a hydrogen bond O(4)–H(4) · · · O(3). This hydrogen bond is by no means symmetrical [O(4)–H(4) 1.03; O(3)–H(4) 1.78 Å], though the intramolecular O · · · O

TABLE 2. Selected bond lengths (Å) and angles (°) for **2**

Si1–O1	1.618(6)	Si1–O4	1.631(6)
Si1–C1	1.827(9)	Si1–C7	1.847(9)
Si2–O1	1.614(6)	Si2–O2	1.618(6)
Si2–C13	1.839(9)	Si2–C19	1.863(8)
Si3–O2	1.617(6)	Si3–O3	1.651(5)
Si3–C25	1.875(9)	Si3–C31	1.854(10)
O4–Si1–O1	109.1(3)	C1–Si1–O1	111.0(4)
C1–Si–O4	110.5(4)	C7–Si1–O1	107.9(4)
C7–Si1–O4	106.9(4)	C7–Si1–C1	111.2(4)
O2–Si2–O1	109.3(3)	C13–Si2–O1	108.8(4)
C13–Si2–O2	110.6(3)	C19–Si2–O1	108.4(3)
C19–Si2–O2	108.9(4)	C19–Si2–C13	110.8(4)
O3–Si3–O2	110.4(3)	C25–Si3–O2	107.5(4)
C25–Si3–O3	108.3(3)	C31–Si3–O2	109.8(4)
C31–Si3–O3	108.5(4)	C31–Si–C25	112.4(4)
Si2–O1–Si1	163.1(5)	Si3–O2–Si2	155.7(4)

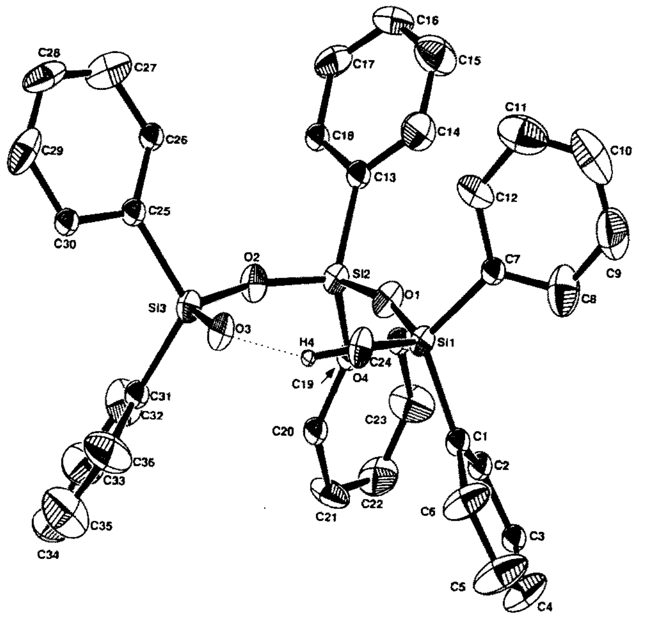

Fig. 1. The asymmetric unit of 2 showing the atomic labelling used in the tables. Thermal ellipsoids are at the 30% probability level.

separation (2.74 Å) is typical of analogous intermolecular hydrogen bonds [1,4]. The angle at the hydrogen (155.9°) causes it to sit above the Si(1)Si(3)O(3)O(4) plane (Fig. 3(a)). For comparison, the O–H ··· O angle which forms part of a five-membered CSi_2O_2 ring in $(HO)Me_2SiC(SiMe_3)_2SiMe_2(OH)$ is 137.1° [10]. The non-terminal Si–O bond lengths in **2** are remarkably uniform, the spread over the four values being less than the standard deviation in the measurement (mean 1.617(6) Å). The Si–O–Si angles are 155.7(4) and 163.1(5)°, and thus accommodate the ring strain, while the angles at silicon vary only marginally from their ideal tetrahedral value (109.1–110.4°). Two points of comparison are worth noting. Firstly, the analogous Si–O distances and Si–O–Si angles in the related, unsymmetrical $(HO)^tBu_2SiOSiMe_2OSi^tBu_2(OH)$ (**1**) are similar to those in **2** (mean values 1.612 Å, 161.6°, respectively) [5]. Secondly, in both 1,5-diols, these short Si–O bonds are associated with rather wide Si–O–Si angles, following a trend we have noted previously [11]. For comparison, we note that in $(HO)Me_2SiOSiMe_2(OH)$ the more acute angle at oxygen (141.4°) is accompanied by longer Si–O bonds (1.627 Å) [4]. The terminal Si–O(H) bonds in **2** are noticably longer than the internal Si–O lengths [1.631(6), 1.651(5) Å] and fall towards the top of the range observed in a series of $R_2Si(OH)_2$ compounds (1.63–1.66 Å) [1]. A similar comparative lengthening of the Si–O(H) bonds is evident in **1** (mean 1.630 Å) [5].

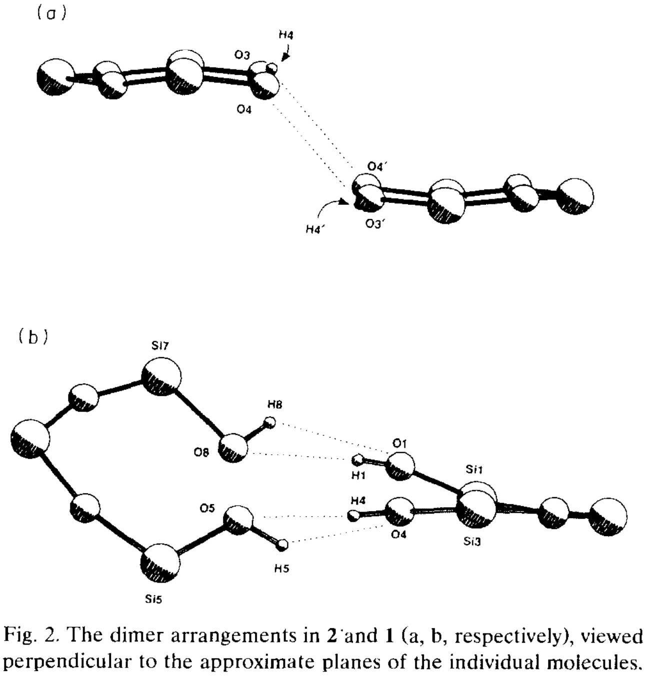

Fig. 2. The dimer arrangements in **2** and **1** (a, b, respectively), viewed perpendicular to the approximate planes of the individual molecules. Organic fragments on silicon have been omitted for clarity. The structure of **1** has been redrawn using the coordinates given in ref. 5.

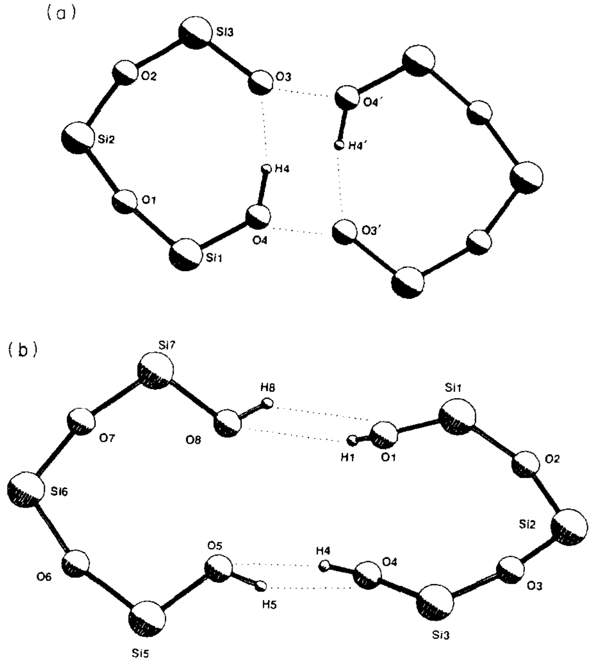

Fig. 3. The dimer arrangements in **2** and **1** (a, b, respectively), viewed orthogonal to the approximate planes of the individual molecules. Organic fragments on silicon have been omitted for clarity. The structure of **1** has been redrawn using the coordinates given in ref. 5.

The lattice structure of **2** is also different from that of **1**, even though the dimeric nature of both species is their most striking feature (Fig. 2(a,b)). At the heart of the dimer of **2** is a square of four oxygen atoms, in which the intermolecular O(4) ··· O(3′) separation (2.72 Å) is similar to the intramolecular O(4) ··· O(3) distance (2.74 Å) noted earlier. The O_4 square in **1** is less regular, but the distances involved are not dissimilar (2.578–2.824 Å). In this latter case, however, none of the available hydrogen atoms on the four terminal hydroxyl groups appears to be hydrogen bonded internally to generate the HSi_3O_4 ring of **2**, and the deviation from planarity of the molecule is notably greater (Fig. 2(a,b)). Furthermore, the "open-jaws" orientation of both molecules in **1** (Fig. 2(b), 3(b)) implies than the intermolecular hydrogen bonding is somewhat weaker than the O ··· O separation suggests.

Although we have been unable to locate with confidence the position of the hydrogen atom of the second hydroxyl group in the title compound, the short intermolecular O ··· O separation suggests that dimer formation is real, even if the orientation of the bridging hydrogen is potentially less than ideal *cf*. **1**, above. The overall structure therefore can be described as dimeric, in which two eight-membered HSi_3O_4 rings are linked through an eight-membered O_4H_4 heterocycle, the latter being not uncommon in silanol chemistry [1,4]. The overall structure can be regarded as being a two step section of a "staircase", there being no further contacts between these dimer units to produce a more extended array (Fig. 3(a)). The parallel stacking of relatively planar **2** is in contrast to **1**, where the two rings are twisted with respect to each other (Fig. 2(b)).

Interestingly, the 1,4-silane diol $(HO)(Ph_2Si)_4(OH)$ adopts a cyclic seven-membered Si_4O_2H ring structure, in which the termini of the silane are also linked through an O–H ··· O hydrogen bond [2.804(4) Å]. The ring however, unlike **2**, does not approximate planarity, instead preferring a "chair" conformation. Furthermore, molecules dimerize through a pair of hydrogen bonds with an O ··· O separation of 2.745(4) Å, although as with **2**, difficulty was experienced in locating the position of the intermolecularly bonded hydrogen. However, from the relative disposition of the two halves of the silane dimer about its inversion centre, the unit holding the two molecules together is a four-membered O_2H_2 ring, as occurs in part in **1**, not an O_4H_4 heterocycle as found in **2** [12].

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