

Crystal and molecular structures of 4,4'-bis(dimethylhydroxysilyl)-biphenyl and *m*-bis(dimethylhydroxysilyl)benzene

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We dedicate this paper to Professor Fausto Calderazzo to mark the occasion of his 70th birthday.

Abstract

The crystal structures of 4,4'-bis-(dimethylhydroxysilyl)biphenyl (**1**) and *m*-bis(dimethylhydroxysilyl)benzene (**2**) are reported. Crystals of (**1**) are monoclinic, $P2_1/n$, with a 9.970(2), b 7.185(1), c 24.134(2) Å, β 98.795(8)°, and Z 4. Crystals of (**2**) are monoclinic, $P2_1/n$, with a 5.960(1), b 24.205(10), c 18.635(9) Å, β 97.14(1)°, and Z 8. In compound **1**, a combination of O–H⋯O hydrogen bonds and C–H⋯ π interactions results in the formation of sheets of enantiomeric pairs of helices, and these sheets are linked by additional C–H⋯ π interactions into a continuous three-dimensional network. In compound **2** both O–H⋯O hydrogen bonds and C–H⋯ π interactions are also present but, in this case, hexagonal arrays of stacks of molecular dimers are formed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Silanol; Hydrogen bonding

1. Introduction

We have recently shown that 'extended reach' O-donor ligands comprising pairs of lactams [1], pyridones [2] or amide groups [3] connected by lengthy spacer units are very effective at generating novel polymeric array structures with a wide range of metal ions. We are now extending this work to involve spacer-linked bis-silanols as precursors for the bridging groups. Attractive candidates for this include 4,4'-bis(dimethylhydroxysilyl)biphenyl, **1**, *m*-bis(dimethylhydroxysilyl)benzene, **2**, and its *para*-analogue, **3**.

As well as the preferred metal coordination geometry, the various factors influencing the types of networks formed by metal complexes with extended-reach ligands include, inter alia, the conformational preferences of those ligands, the presence of π - π interactions, and/or hydrogen bond formation. For this reason it is desirable to examine such features in the structures of the metal-free precursor molecules as a guide in the

design of the metal-linked products that might be obtained from them.

The solid state structure of **3**, which has been used as a precursor to polysiloxanes containing aryl spacers [4,5], is already known [6]. It forms a complicated hydrogen bonded arrangement of three independent molecules, two of which hydrogen bond to form chains whilst the third serves as a linker between these chains so as to give a three-dimensional network. Although compounds **1** and **2** are both already known [4,5,7] their structures do not appear to have been reported. We report here the results of single-crystal X-ray studies on both **1** and **2**.

2. Results and discussion

2.1. Structure of 4,4'-bis(dimethylhydroxysilyl)biphenyl (**1**)

Initially, perhaps the most surprising feature of the structure adopted by compound **1** in the solid state is

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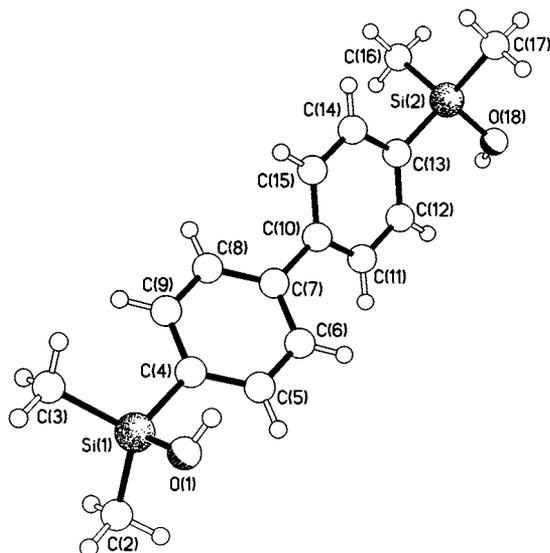


Fig. 1. The molecular structure of **1**.

the absence of any molecular symmetry (Fig. 1). The central biphenyl spacer has a twisted conformation, the two phenyl groups being rotated by ca. 39° with respect to each other about the linking C(7)–C(10) bond. Furthermore, the Si–(C₆H₄)₂–Si backbone has a slightly folded conformation, the two Si–Ph bonds subtending an angle of ca. 12° . The two Si–O bonds are rotated by appreciably different amounts out of the planes of their adjacent phenyl rings (O(1) by ca. 49° , O(18) by only ca. 6°). These conformational features, we believe, are to a large extent controlled by the extensive *intermolecular* non-covalent interactions.

The two hydroxy-groups act both as hydrogen bond donors and acceptors. Firstly, the molecules link head-to-tail (linkage *a* in Fig. 2) to form, by action of the 2_1 screw, simple, flattened helices. This geometry is stabilised by a secondary C–H \cdots π interaction [8] (*c* in Fig. 2) between one of the methyl hydrogen atoms in one molecule and one of the phenyl rings in the next-an interaction that is further facilitated by the near-orthogonal relationship (88°) between the H \cdots (ring centroid) vector, and the phenyl ring plane. These helices are cross-linked by a further pair of O–H \cdots O hydrogen bonds (*b* in Fig. 2) to form enantiomeric pairs (denoted X and Y in Fig. 2) which are then similarly linked to their neighbours to form an extended sheet. These sheets, which have a stepped pattern, are, in turn, cross-linked by additional C–H \cdots π interactions (*d* in Fig. 3) to form a continuous three-dimensional network. Here again we see a near orthogonal relationship (79°) between the vector linking the methyl hydrogen atom and the ring centroid, and the ring plane.

The precise hydrogen bonded arrangement seen in **1** does not seem to have been found in other silanol structures [9]. The structure of *trans*-2,8-dihydroxy-2,4,4,6,6,8,10,10,12,12-decamethylcyclohexasiloxane [10] does, however, comprise groups of four molecules hydrogen bonded together to give cyclic units which are then further hydrogen bonded to give sheets in a manner similar to that shown in Fig. 3.

2.2. Structure of *m*-bis(dimethylhydroxysilyl)benzene (**2**)

Compound **2** crystallises with two independent molecules in the asymmetric unit that are linked head-to-tail via O–H \cdots O hydrogen bonds to form an approximately C_i symmetric cyclic dimer pair (Fig. 4). In both independent components the two Si–O bonds adopt a pseudo-gauche relationship with respect to the phenyl ring plane, with the Si(1)–O(1) and Si(2)–O(12) bonds being rotated by ca. 40 and 39° respectively out of the C(4)–C(9) ring plane, whereas Si(1')–O(1') and Si(2')–O(12') are rotated by ca. 35 and 43° , respectively. The two phenyl rings are mutually inclined by ca. 6° .

The dimeric units are stacked one above another along the crystallographic *a* direction and are cross-linked by additional O–H \cdots O hydrogen bonds (*c* and *d* in Fig. 5). These hydrogen bonds are supplemented by weaker, but cooperative, C–H \cdots π interactions (*e*, *f*, *g* and *h* in Fig. 5). These O–H \cdots O and C–H \cdots π linked stacks are arranged to form an elegant pseudo-close-packed hexagonal array (Fig. 6), there being no linkages other than van der Waals forces between adjacent stacks, the exteriors of which are totally hydrophobic. Similar stacks or chains of hydrogen bonded pairs of silanols are also found in the structures of R₂Si(OH)₂ (R *i*-Pr [11], *t*-Bu [12,13] and *c*-C₆H₁₁ [14]) and in [(3-thienyl(HO)MeSi)₂O] [15].

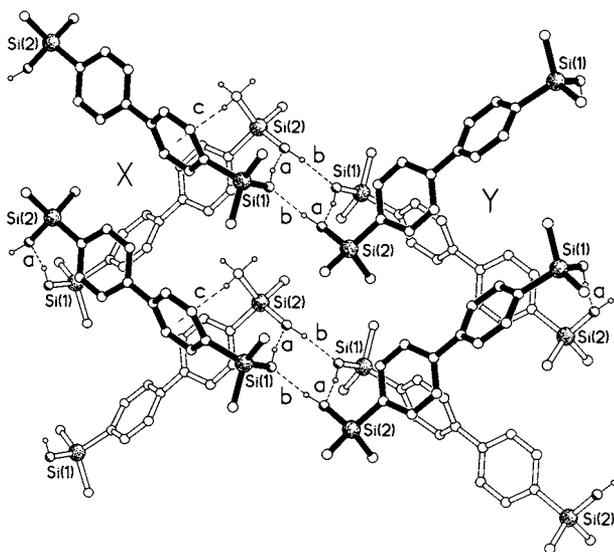


Fig. 2. Two adjacent enantiomeric (X and Y) hydrogen-bonded helices present in the structure of **1**. Hydrogen bonding geometries are: *a*, [O \cdots O] 2.75 Å, [H \cdots O] 1.88 Å, [O–H \cdots O] 162° ; *b*, [O \cdots O] 2.73 Å, [H \cdots O] 1.84 Å, [O–H \cdots O] 171° .

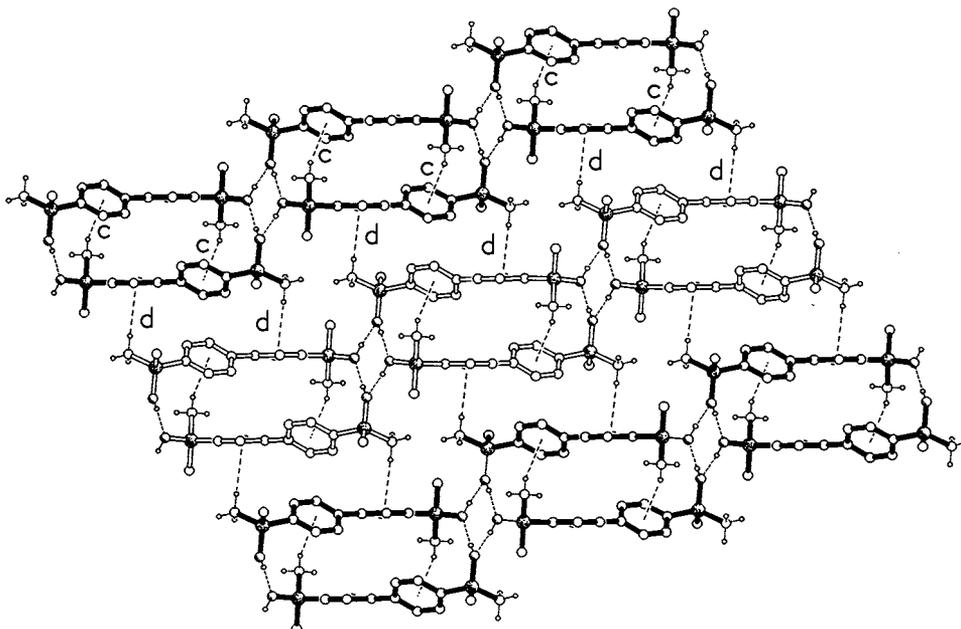


Fig. 3. The cross-linking of the hydrogen-bonded stepped sheets by C–H \cdots π interactions, d , [H \cdots π] 2.86 Å, [C–H \cdots π] 163°.

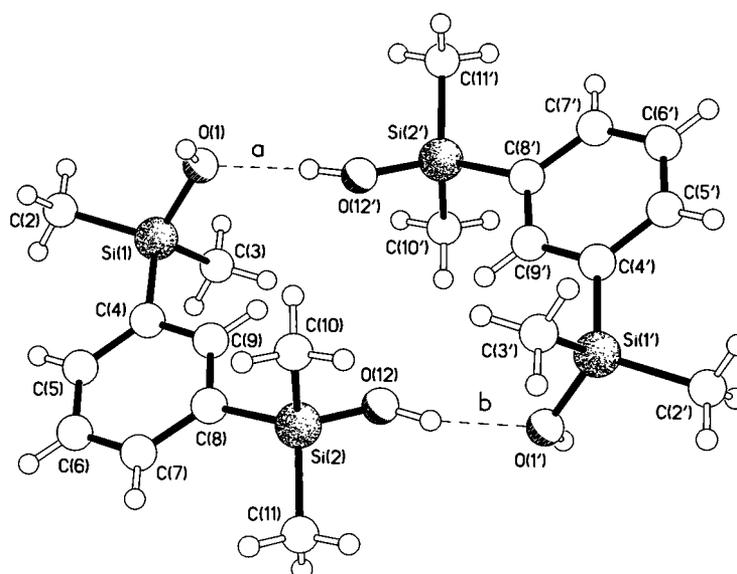


Fig. 4. One of the hydrogen-bonded dimer pairs present in the structure of **2**. Hydrogen bonding geometries are: a , [O \cdots O] 2.80 Å, [H \cdots O] 1.90 Å, [O–H \cdots O] 172°; b , [O \cdots O] 2.75 Å, [H \cdots O] 1.88 Å, [O–H \cdots O] 164°.

It is pertinent to note that the change from *para*- to *meta*-substitution of the dimethylhydroxysilyl groups in compounds **3** and **2** respectively produces, as might be expected, a dramatic change in the solid state structure. In **3** there are continuous cross-linked chains [6] analogous to those we observe in compound **1**, whereas in **2** discrete columnar stacks of dimers are formed with no further cross-linking (Fig. 6).

3. Experimental

3.1. Preparation of **1** and **2**

The biphenyl derivative (**1**) was prepared in low yield by hydrolysis of the hydride 4,4'-bis(dimethylsilyl)biphenyl according to the procedures of Merker and Scott [4] and of Beck and Chaffee [7]. The disilanol (**2**)

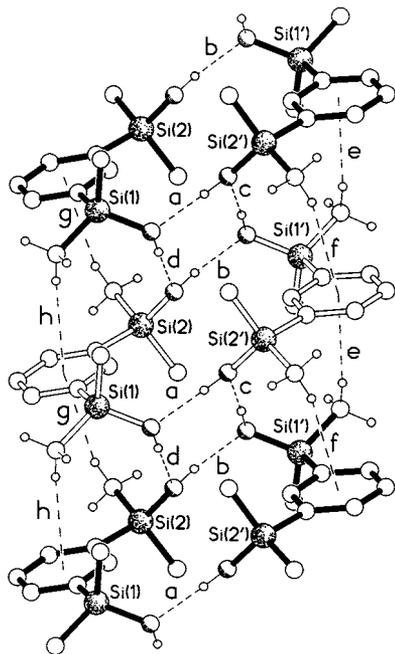


Fig. 5. Side view of part of one of the O–H...O and C–H... π linked stacks of dimer pairs present in the structure of **2**. Hydrogen bonding geometries are: *c*, [O...O] 2.75 Å, [H...O] 1.85 Å, [O–H...O] 177°; *d*, [O...O] 2.77 Å, [H...O] 1.87 Å, [O–H...O] 177°. [C–H... π] interactions: *e*, [H... π] 2.80 Å, [C–H... π] 165°; *f*, [H... π] 2.98 Å, [C–H... π] 164°; *g*, [H... π] 2.91 Å, [C–H... π] 164°; *h*, [H... π] 2.95 Å, [C–H... π] 167°.

was prepared in 63% yield in a similar manner from *m*-bis(dimethylsilyl)benzene.

Definitive identification is provided by the X-ray analyses reported here but the following, previously unreported, characterisation data were obtained.

(1) δ (H) [(CD₃)₂SO] 0.28 (s, 12H, SiMe₂), 5.95 (s, 2H, SiOH, removed on shaking with D₂O), 7.65 (s, 8H, C₆H₄); δ (¹³C) [(CD₃)₂SO] 1.20 (SiMe₂), 126.5, 134.1, 140.1, 141.3 (C₆H₄); $\nu_{\text{SiO-H}}$ (nujol mull) 3253 cm⁻¹; m.p. 174.7–175.2°C (lit. 176–180°C [7]). Mass spectrum, EI, *m/z* 302 (M⁺, 49%), 287 ([M–Me]⁺, 100%), accurate mass measurement: Found for M⁺ 302.1158, Anal. Calc. for C₁₆H₂₂O₂Si₂ 302.1177.

(2) δ (H) (CDCl₃) 0.40 (s, 12H, SiMe₂), 1.94 (s, 2H, SiOH, removed on shaking with D₂O), 7.34 (t, *J* 7.3 Hz, 1H), 7.56 (d, *J* 7.3 Hz, 2H), 7.83 (s, 1H); δ (¹³C) (CDCl₃) 0.10, (SiMe₂), 127.3, 134.3, 137.8, 138.5 (C₆H₄); $\nu_{\text{SiO-H}}$ (KBr disk) 3247 cm⁻¹; m.p. 77.9–78.1°C (lit. 79–81°C [5]). Mass spectrum, EI, *m/z* 226 (M⁺, 24%), 211 ([M–Me]⁺, 100%), accurate mass measurement: Found for M⁺ 226.0845, Anal. Calc. for C₁₀H₁₈O₂Si₂ 226.0847.

3.2. X-ray crystal structures

Data for both compounds were measured on a Siemens P4 diffractometer using graphite monochromated Cu–K α radiation (rotating anode source for compound **1**). The data were corrected for Lorentz and polarisation effects and an empirical absorption correction (based on psi scans) was carried out: the maximum and minimum transmission factors were 0.822, 0.275 for compound **1**, and 0.849, 0.390 for compound **2**. The structures were solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the C–H hydrogen atoms were idealised, assigned isotropic thermal parameters $U(\text{H}) 1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{C}_{\text{Methyl}})$] and allowed to ride on their parent carbon atoms. The positions of the hydroxy hydrogen

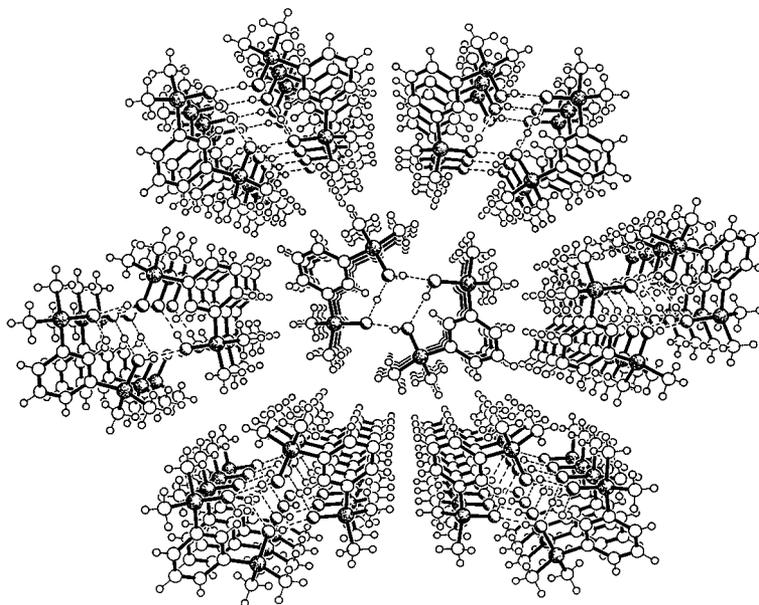


Fig. 6. The pseudo close-packed hexagonal array of stacked dimers viewed down the crystallographic *a* direction in compound **2**.

Table 1
Crystallographic data for compounds **1** and **2**

	1	2
Formula	C ₁₆ H ₂₂ O ₂ Si ₂	C ₁₀ H ₁₈ O ₂ Si ₂
Formula weight	302.52	226.42
Crystal system	Monoclinic	Monoclinic
Crystal size (mm)	0.30 × 0.24 × 0.20	0.92 × 0.44 × 0.31
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.970(2)	5.960(1)
<i>b</i> (Å)	7.185(1)	24.205(10)
<i>c</i> (Å)	24.134(2)	18.635(9)
β (°)	98.795(8)	97.14(1)
<i>V</i> (Å ³)	1708.4(4)	2668(2)
<i>Z</i>	4	8
<i>D</i> _c (g cm ⁻³)	1.176	1.128
λ (Å)	1.54178	1.54178
μ (mm ⁻¹)	1.873	2.237
θ range (°)	3.71–61.99	3.01–55.00
<i>F</i> (000)	648	976
Measured reflections	2801	3729
Unique reflections (<i>R</i> _{int})	2635 (0.0242)	3354 (0.0377)
Observed reflections [<i>F</i> > 4 σ (<i>F</i>)]	2352	2750
Data/restraints/parameters	2576/2/190	3170/4/270
Mean, maximum Δ/σ ratio	0.000, -0.003	0.000, -0.001
Largest difference peak/hole (e Å ⁻³)	0.196, -0.205	0.188, -0.282
<i>R</i> ₁	0.0401	0.0438
<i>wR</i> ₂	0.1073	0.1101

Table 2
Bond lengths (Å) and angles (°) for compound **1**

O(1)–Si(1)	1.655(2)	C(2)–Si(1)	1.847(3)
C(3)–Si(1)	1.850(3)	Si(1)–C(4)	1.873(2)
C(4)–C(5)	1.393(3)	C(4)–C(9)	1.396(3)
C(5)–C(6)	1.378(3)	C(6)–C(7)	1.397(3)
C(7)–C(8)	1.388(3)	C(7)–C(10)	1.487(3)
C(8)–C(9)	1.383(3)	C(10)–C(11)	1.389(3)
C(10)–C(15)	1.392(3)	C(11)–C(12)	1.389(3)
C(12)–C(13)	1.389(3)	C(13)–C(14)	1.396(3)
C(13)–Si(2)	1.878(2)	C(14)–C(15)	1.386(3)
Si(2)–O(18)	1.650(2)	Si(2)–C(16)	1.847(2)
Si(2)–C(17)	1.848(2)		
O(1)–Si(1)–C(2)	107.36(11)	O(1)–Si(1)–C(3)	110.56(12)
C(2)–Si(1)–C(3)	110.79(14)	O(1)–Si(1)–C(4)	106.44(9)
C(2)–Si(1)–C(4)	111.77(11)	C(3)–Si(1)–C(4)	109.80(12)
C(5)–C(4)–C(9)	116.3(2)	C(5)–C(4)–Si(1)	120.7(2)
C(9)–C(4)–Si(1)	123.0(2)	C(6)–C(5)–C(4)	122.2(2)
C(5)–C(6)–C(7)	120.7(2)	C(8)–C(7)–C(6)	118.0(2)
C(8)–C(7)–C(10)	121.2(2)	C(6)–C(7)–C(10)	120.7(2)
C(9)–C(8)–C(7)	120.6(2)	C(8)–C(9)–C(4)	122.2(2)
C(11)–C(10)–C(15)	117.4(2)	C(11)–C(10)–C(7)	121.9(2)
C(15)–C(10)–C(7)	120.6(2)	C(10)–C(11)–C(12)	121.5(2)
C(11)–C(12)–C(13)	121.6(2)	C(12)–C(13)–C(14)	116.5(2)
C(12)–C(13)–Si(2)	122.3(2)	C(14)–C(13)–Si(2)	121.1(2)
C(15)–C(14)–C(13)	122.2(2)	C(14)–C(15)–C(10)	120.8(2)
O(18)–Si(2)–C(16)	108.99(11)	O(18)–Si(2)–C(17)	108.01(10)
C(16)–Si(2)–C(17)	110.60(12)	O(18)–Si(2)–C(13)	108.48(9)
C(16)–Si(2)–C(13)	109.89(11)	C(17)–Si(2)–C(13)	110.81(10)

Table 3
Bond lengths (Å) and angles (°) for compound **2**

Si(1)–O(1)	1.652(3)	Si(1)–C(3)	1.847(4)
Si(1)–C(2)	1.852(4)	Si(1)–C(4)	1.863(3)
C(4)–C(5)	1.400(4)	C(4)–C(9)	1.403(4)
C(5)–C(6)	1.372(5)	C(6)–C(7)	1.380(5)
C(7)–C(8)	1.401(4)	C(8)–C(9)	1.392(4)
C(8)–Si(2)	1.862(3)	Si(2)–O(12)	1.644(2)
Si(2)–C(11)	1.848(4)	Si(2)–C(10)	1.851(4)
Si(1')–O(1')	1.651(2)	Si(1')–C(2')	1.843(4)
Si(1')–C(3')	1.844(4)	Si(1')–C(4')	1.864(4)
C(4')–C(5')	1.399(4)	C(4')–C(9')	1.401(4)
C(5')–C(6')	1.373(5)	C(6')–C(7')	1.374(5)
C(7')–C(8')	1.400(5)	C(8')–C(9')	1.400(5)
C(8')–Si(2')	1.866(4)	Si(2')–O(12')	1.648(3)
Si(2')–C(11')	1.842(4)	Si(2')–C(10')	1.852(4)
O(1)–Si(1)–C(3)	106.1(2)	O(1)–Si(1)–C(2)	110.8(2)
C(3)–Si(1)–C(2)	110.2(2)	O(1)–Si(1)–C(4)	108.59(13)
C(3)–Si(1)–C(4)	110.8(2)	C(2)–Si(1)–C(4)	110.2(2)
C(5)–C(4)–C(9)	116.2(3)	C(5)–C(4)–Si(1)	122.9(2)
C(9)–C(4)–Si(1)	120.9(2)	C(6)–C(5)–C(4)	121.9(3)
C(5)–C(6)–C(7)	120.2(3)	C(6)–C(7)–C(8)	121.0(3)
C(9)–C(8)–C(7)	117.1(3)	C(9)–C(8)–Si(2)	120.3(2)
C(7)–C(8)–Si(2)	122.4(2)	C(8)–C(9)–C(4)	123.6(3)
O(12)–Si(2)–C(11)	110.3(2)	O(12)–Si(2)–C(10)	109.4(2)
C(11)–Si(2)–C(10)	110.3(2)	O(12)–Si(2)–C(8)	106.03(13)
C(11)–Si(2)–C(8)	111.7(2)	C(10)–Si(2)–C(8)	109.0(2)
O(1')–Si(1')–C(2')	110.9(2)	O(1')–Si(1')–C(3')	106.4(2)
C(2')–Si(1')–C(3')	109.2(2)	O(1')–Si(1')–C(4')	108.37(13)
C(2')–Si(1')–C(4')	111.0(2)	C(3')–Si(1')–C(4')	110.9(2)
C(5')–C(4')–C(9')	116.2(3)	C(5')–C(4')–Si(1')	122.0(3)
C(9')–C(4')–Si(1')	121.7(2)	C(6')–C(5')–C(4')	121.9(4)
C(5')–C(6')–C(7')	120.1(3)	C(6')–C(7')–C(8')	121.8(4)
C(7')–C(8')–C(9')	116.2(3)	C(7')–C(8')–Si(2')	122.1(3)
C(9')–C(8')–Si(2')	121.7(2)	C(8')–C(9')–C(4')	123.9(3)
O(12')–Si(2')–C(11')	110.5(2)	O(12')–Si(2')–C(10')	108.8(2)
C(11')–Si(2')–C(10')	110.4(2)	O(12')–Si(2')–C(8')	105.94(14)
C(11')–Si(2')–C(8')	110.9(2)	C(10')–Si(2')–C(8')	110.2(2)

atoms were determined from a ΔF map and the atoms refined isotropically subject to an O–H distance constraint of 0.90 Å. The methyl groups were subjected to torsional refinement about the Si–C bonds.

Computations were carried out using the SHELXTL program system (version 5.03).

Table 1 summarises the crystal data, data collection and refinement parameters. Tables of bond lengths and angles for **1** and **2** are given in Tables 2 and 3, respectively.

4. Supplementary material

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre.

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