Molecular and crystal structure of 1,6-dihydroxydodecamethylhexasilane

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As found using X-ray diffraction data, the molecules of 1,6-dihydroxydodecamethylhexasilane in a crystal have the all-*trans* conformation of the six-atomic chain and the *trans* orientation of hydroxyl groups.

Dihydroxydiorganooligosilanes, $HO(R_2Si)_nOH$, are important starting compounds in the synthesis of copolymers containing oligosilane fragments in the backbone. It was reported earlier[1–7] that the hydrolysis of α,ω-dichloroperphenyloligosilanes, $Cl(Ph_2Si)_nCl$ (n = 2–7), results in the formation of corresponding α,ω-dihydroxyperphenyloligosilanes. The structure of these diols (n = 4, 7) was determined by X-ray diffraction analysis.[6,7] However, at present, in contrast to α,ω-dihydroxyperphenyloligosilanes, their permethylated analogues have not been widely known. Only 1,6-dihydroxydodecamethylhexasilane **1** was obtained in 40% yield by the hydrolysis of 1,6-dichlorododecamethylhexasilane.[8] This is related to the fact that the hydrolysis of α,ω-dichloropermethyloligosilanes containing 2–5 silicon atoms leads to the formation of corresponding diols; however, these compounds are unstable. During their synthesis or isolation, they readily condense *via* an intramolecular or intermolecular mechanism resulting in the formation of organosilicon heterocycles, namely, permethyloxycyclosilanes (Scheme 1).[8–10]

Here, we report on the synthesis of compound **1** in 58% yield† by a modified method.[8] The molecular and crystal structure of **1** was established by X-ray diffraction analysis.‡

All four independent molecules of **1** in the crystal have the all-*trans* conformation of the six-atomic silane chain (Figure 1). Some variations in torsion angles within the chains in the independent molecules may be caused by the participation of terminal hydroxyl groups in the intermolecular O–H···O bonds. Mutual orientations of hydroxyl groups may be described as *trans*; the pseudotorsion angle O(1)–Si(1)–Si(6)–O(6) varies in a wide range of 158.1–13.1°. Similar orientation of hydroxyl groups was observed in 1,7-dihydroxy-1,1,2,2,3,3,4,4,5,5,6,6,7,7-tetradecaphenylheptasilane having a seven-atomic silane chain.[7]

The bond lengths and bond angles in **1** are close to those in analogous compounds.[11] Note that the terminal Si–C bonds are somewhat shorter than those in the middle of the chains (Figure 1). This fact can be explained by the electron-withdrawing effect of the hydroxyl groups.

In the crystal of **1**, molecules are assembled into tetramers by O–H···O bonds (Figure 2). These tetramers may be divided into three types *a*, *b* and *c*. The tetramers of the type *b* are formed by the four independent molecules, while the tetramers *a* and *c* are formed by only two independent molecules, and they have an inversion centre. These tetramers form a three-dimensional framework in which eight-membered H-bonded rings are parallel to the *ab* plane (Figure 3). In turn, silane six-atomic chains of the molecules of **1** are directioned along the *a* axis.

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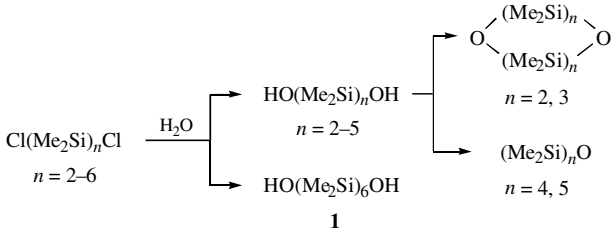

Scheme 1

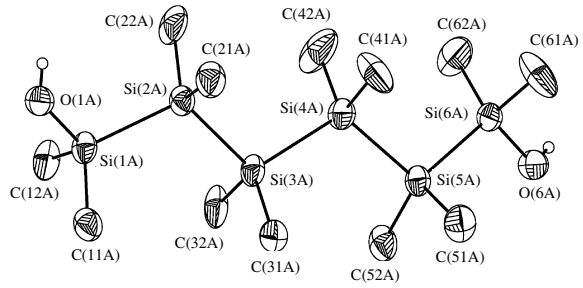

Figure 1 General view of one of the four independent molecules of **1**; the atoms are presented by thermal ellipsoids drawn at a 50% probability level. Selected averaged bonds (Å): Si(1)–O(1) 1.658, Si(6)–O(6) 1.657, Si(1)–C(11) 1.855, Si(1)–C(12) 1.863, Si(2)–C(21) 1.877, Si(2)–C(22) 1.867, Si(3)–C(31) 1.886, Si(3)–C(32) 1.883, Si(4)–C(41) 1.887, Si(4)–C(42) 1.886, Si(5)–C(51) 1.879, Si(5)–C(52) 1.871, Si(6)–C(61) 1.851, Si(6)–C(62) 1.856, Si–Si 2.346. Selected averaged angles (°): O–Si–C 107.2, O–Si–Si 110.8. Mean standard deviations are 0.004, 0.006 and 0.003 Å for the Si–O, Si–C and Si–Si bonds, respectively, and 0.2° for the angles.

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† A solution of 6.0 g (14.3 mmol) of 1,6-dichlorododecamethylhexasilane in 10 ml of Et_2O was added dropwise to a mixture of 20 ml of H_2O, 2.4 g (28.6 mmol) of $NaHCO_3$ and 5 ml of acetone in 10 ml of Et_2O with cooling (–5 °C) and stirring. After stirring for 1 h at this temperature, the reaction mixture was warmed slowly to room temperature and additionally stirred for 2 h. The organic layer was separated, washed three times with H_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* at room temperature. Compound **1** was obtained by the crystallization of the solid residue from pentane. Yield, 3.18 g (58%); mp 80 °C. ^{29}Si NMR ($CDCl_3$) δ: 16.56 (OHSi), –40.62 (HOSiSi*Si*), –46.24 (HOSi*Si*). IR (hexachlorobutadiene, ν/cm^{-1}): 3281 (O–H). UV, λ_{max}/nm: 265, 308.

‡ *Crystallographic data for* **1**: crystals of $C_{12}H_{38}O_2Si_6$ are orthorhombic, space group *Pccn*, a = 37.544(8), b = 17.995(4) and c = = 29.536(8) Å, V = 19954(8) Å^3, Z = 32 (Z' = 4), M = 382.96, d_{calc} = = 1.020 g cm^{-3}, μ(MoKα) = 0.335 mm^{-1}, F(000) = 6720. Intensities of 105200 reflections were measured with a Smart CCD 1000K diffractometer at 110 K [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 50°$], and 17260 independent reflections (R_{int} = 0.0813) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms of methyl groups were calculated and refined in the rigid body approximation with U(H) = 1.5U_{eq}(C). The hydrogen atoms of hydroxyl groups were located from the difference Fourier syntesis and fixed at the idealised O–H distance 0.90 Å with the constant value of U_{eq} equal to 0.05 Å^2. The refinement converged to wR_2 = 0.1637 and GOF = 1.056 for all independent reflections [R_1 = = 0.0705 was calculated against F for 7741 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using the SHELXTL-97 V5.10 program[12] on an IBM PC. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/122.

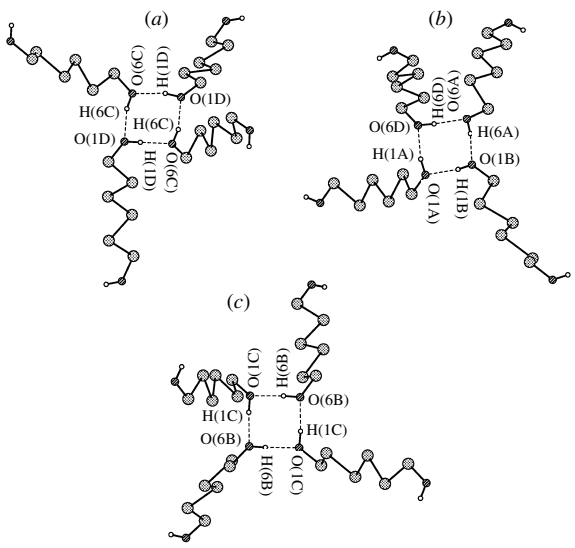

Figure 2 The formation of the O–H···H-bonded tetramers in the crystal of **1**. Tetramers *a* and *c* have an inversion centre. Methyl groups are omitted for clarity. Parameters (Å and °) of O–H···H bonds: (*a*) O(1D)–H(1D)···O(6C): H(1D)···O(6C) 1.83, O(1D)···O(6C) 2.707(5), O(1D)–H(1D)–O(6C) 165; O(6C)–H(6C)···O(1D) [$-x + 0.5$, $-y - 0.5$, z]: H(6C)···O(1D) 1.84, O(6C)···O(1D) 2.701(4), O(6C)–H(6C)–O(1D) 162; (*b*) O(1A)–H(1A)···O(6D) [x, $-y - 0.5$, $z - 0.5$]: O(1A)–H(1A) 1.87, O(1A)···O(6D) 2.751(6), O(1A)–H(1A)–O(6D) 166; O(6A)–H(6A)···O(1B) [x, $-y - 0.5$, $z + 0.5$]: H(6A)···O(1B) 1.86, (O6A)···O(1B) 2.743(5), O(6A)–H(6A)–O(1B) 170; O(1B)–H(1B)···O(1A) [$-x$, $-y$, $-z$], H(1B)···O(1A) 1.85, O(1B)···O(1A) 2.711(6), O(6A)–H(6A)–O(1B) 162; O(6D)–H(6D)···O(6A) [$-x$, $-y - 1$, $-z + 1$]: H(6D)···O(6A) 1.83, O(6D)···O(6A) 2.705(5), O(6D)–H(6D)–O(6A) 169; (*c*) O(1C)–H(1C)···O(6B) [x, $-y + 0.5$, $z - 0.5$]: H(1C)···O(6B) 1.84, O(1C)···O(6B) 2.734(6), O(1C)–H(1C)–O(6B) 173; O(6B)–H(6B)···O(1C) [$-x + 1/2$, y, $z + 1/2$]: H(6B)···O(1C) 1.84, O(6B)···O(1C) 2.726(6), O(6B)–H(6B)–O(1C) 170.

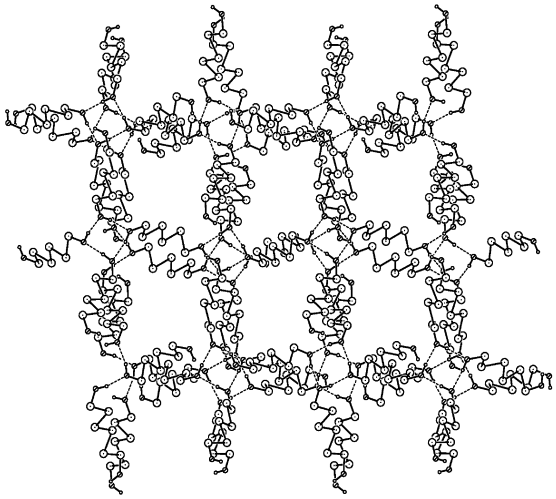

Figure 3 Three-dimensional framework formed by the O–H···O bonds in the crystal of **1**. Methyl groups are omitted for clarity.

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