Molecular structure of 1,3-dihydroxydecamethylcyclohexasilane

Alexander A. Korlyukov, Denis Yu. Larkin, Nina A. Chernyavskaya,* Mikhail Yu. Antipin and Alexey I. Chernyavskii

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: chern@ineos.ac.ru

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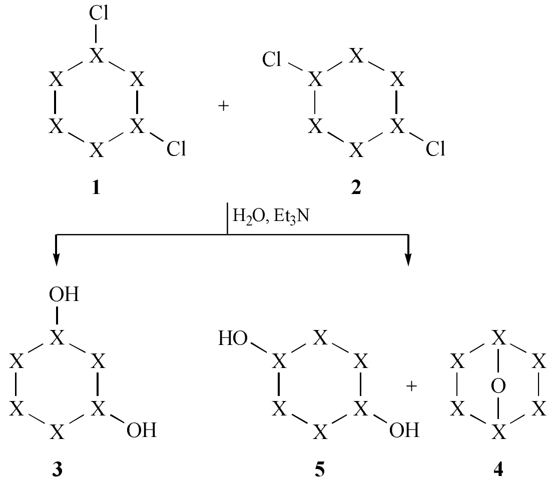
As found by X-ray diffraction analysis, oxygen atoms in the molecule of 1,3-dihydroxydecamethylcyclohexasilane occupy axial positions.

Bifunctional cyclosilanes are valuable starting compounds for the synthesis of polycyclic silanes and cyclolinear copolymers containing cyclosilane units. It was found earlier[1,2] that the interaction of dodecamethylcyclohexasilane $(Me_2Si)_6$ with $SbCl_5$ in a CCl_4 solution yields dichloro-substituted cyclohexasilanes, which are a mixture (in a ratio of ~1:1) of structural isomers, 1,3-dichlorocyclohexasilane **1** and 1,4-dichlorocyclohexasilane **2**. These isomers should be separated for their use as starting compounds for the synthesis of polymers or copolymers. Structural isomers **1** and **2** have similar physico-chemical properties; therefore, they can be separated by only chemical methods.[2–4] The simplest method is the hydrolysis of an isomeric mixture of **1** and **2** followed by the separation of reaction products **3** and **4** by vacuum distillation (Scheme 1).[4] The treatment of hydrolysis products **3** and **4** with acetyl chloride leads to dichloro-substituted cyclosilanes **1** and **2** in quantitative yields. The X-ray diffraction analysis of the hydrolysis products of compound **2** demonstrated[4] that a unit cell contains both bridged compound **4** and 1,4-dihydroxycyclosilane **5** in a ratio of 2:1. The X-ray data for compound **3** were not reported.



X = $SiMe_n$, $n = 1, 2$

Scheme 1

We reproduced the method[4] of separation of hydrolysis products by vacuum distillation, but dihydroxy derivative **3** was obtained in a low yield (< 10%), probably, due to its condensation during distillation. We obtained compound **3** in 48% yield by partial crystallization of hydrolysis products.†

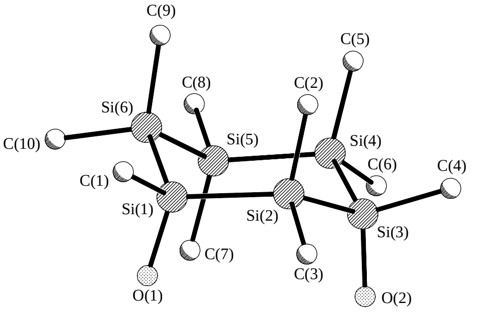


Figure 1 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si(1)–O(1) 1.671(3), Si(1)–Si(6) 2.346(3), Si(1)–Si(2) 2.350(2), Si(2)–Si(3) 2.353(3), Si(3)–O(2) 1.663(3), Si(3)–Si(4) 2.349(2), Si(4)–Si(5) 2.334(2), Si(5)–Si(6) 2.334(2), Si–C 1.872–1.897; selected bond angles (°): O(1)–Si(1)–C(1) 106.7(1), O(1)–Si(1)–Si(6) 107.6(1), C(1)–Si(1)–Si(6) 111.8(1), O(1)–Si(1)–Si(2) 111.04(7), O(2)–Si(3)–C(4) 107.0(1), O(2)–Si(3)–Si(4) 110.42(6), O(2)–Si(3)–Si(2) 109.59(6), Si(1)–Si(2)–Si(3) 115.47(3), Si(4)–Si(3)–Si(2) 111.63(3), Si(5)–Si(4)–Si(3) 112.73(3), Si(6)–Si(1)–Si(2) 111.35(3), Si(5)–Si(6)–Si(1) 108.5(1); torsion angles (°): Si(1)–Si(2)–Si(3)–Si(4) 45.33(2), Si(2)–Si(3)–Si(4)–Si(5) –46.18(4), Si(3)–Si(4)–Si(5)–Si(6) 55.35(2), Si(4)–Si(5)–Si(6)–Si(1) –59.68(4), Si(2)–Si(1)–Si(6)–Si(5) 56.42(4), Si(6)–Si(1)–Si(2)–Si(3) –51.52(4).

We determined the molecular and crystal structure of **3** by X-ray diffraction analysis.‡ The six-membered cyclosilane ring exhibits a chair conformation (Figure 1). The oxygen atoms O(1) and O(2) occupy axial positions. The positions of the oxygen atoms O(1) and O(2) may be described as *cis*; the corresponding pseudotorsion angle O(1)Si(1)Si(3)O(2) is equal to –8.0°. It is noteworthy that, in the molecule of **5**, similar oxygen atoms occupied the *trans* positions.[4] The bond lengths and bond angles are close to those in the majority of similar compounds.[5] The Si(4)–Si(5) and Si(5)–Si(6) bonds in **3** are shorter than others. The elongation of the other Si–Si bonds may be explained by an anomeric effect (n–σ^* interaction between oxygen lone pairs and vacant orbitals of the Si–Si bonds). The disordering of the

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† 12.0 g (0.034 mol) of an isomeric mixture of **1** and **2** in 100 ml of pentane, which was obtained by the interaction of 20.0 g (0.052 mol) of $(Me_2Si)_6$ with 23.6 g (0.079 mol) $SbCl_5$, was added dropwise to a mixture of 40 ml (0.45 mol) of H_2O and 15.8 g (0.157 mol) Et_3N in 100 ml of pentane. The precipitate of $Et_3N\cdot HCl$ was filtered off. The organic solvent and an excess of Et_3N and H_2O were removed *in vacuo* at room temperature. Compound **3** was obtained by partial crystallization of the residue from pentane. Yield 2.6 g (48% on a **1** basis), mp 124–126 °C. MS, m/z (%): 334 (11.9) $[M - H_2O]^+$, 319 (4.2) $[M - H_2O - Me]^+$, 293 (13.0), 259 (18.5), 245 (12.8), 217 (13.5), 189 (13.0), 175 (18.1), 147 (14.4), 117 (40.6), 73 (100) $[SiMe_3]^+$.

‡ *Crystallographic data for* **3**: $C_{10}H_{32}O_2Si_6$, $M = 352.90$, $F(000) = 1536$, monoclinic crystals, space group C_2/c, $a = 17.662(4)$ Å, $b = 10.066(2)$ Å, $c = 26.040(5)$ Å, $\beta = 107.09(3)°$, $V = 4425(2)$ Å^3, $Z = 8$, $d_{calc} = 1.059$ g cm^{-3}, μ(MoKα) = 0.372 mm^{-1}. Intensities of 5460 reflections were measured with a Siemens P3/PC diffractometer at ambient temperature [λ(MoKα) = = 0.71072 Å, $\theta/2\theta$ scan, $2\theta < 56°$], and 5285 independent reflections (R_{int} = = 0.0277) were used in a 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. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. An analysis of the Fourier electron density synthesis revealed additional maxima in the regions of shortest intermolecular O··O contacts, which were interpreted as a disorder of hydroxyl groups [H(1), H(1′) and H(2), H(2′)]. The refinement converged to wR_2 = = 0.1038 and GOF = 0.938 for all independent reflections [$R_1 = 0.0315$ was calculated against F for 4512 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL-97 V5.10[6] 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, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/97.

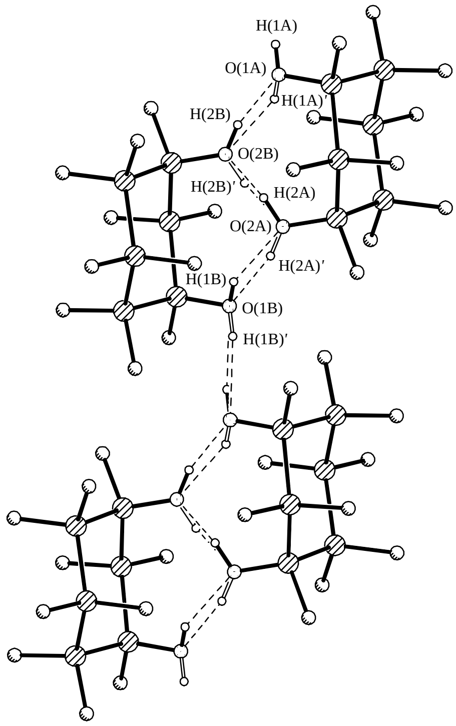

Figure 2 H-bonded chains in **3**. The second position of the hydroxyl hydrogen atom is shown by an open line. The parameters of H-bonds are: O(1A)–H(1A)′··O(2B): O(2B)··H(1A)′ 1.69 Å, O(1A)··O(2B) 2.818(2) Å, O(1A)–H(1A)–O(2B) 136°; O(2B)–H(2B)··O(1A): O(1A)··H(2B) 1.91 Å, O(1A)··O(2B) 2.818(2) Å, O(2B)–H(2B)–O(1A) 163°; O(2A)– H(2A)′··· O(2B): O(2B)··H(2A) 1.69 Å, O(2A)··O(2B) 2.701(2) Å, O(2A)–H(2A)′–O(2B) 169°; O(2B)–H(2B)′··O(2A): H(2B)′··O(2B) 1.03 Å, O(2A)··O(2B) 2.701(2) Å, O(2A)–H(2A)′–O(2B) 169°.

hydrogen atoms of hydroxyl groups may explain the elongation of both of the adjacent Si–Si bonds. In the crystal of **3**, molecules are linked by hydrogen bonds into infinite chains along the *a* axis (Figure 2).

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