trans-1,3-Dihydroxy-1,3-dimethyl-1,3-disilacyclobutane

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Hydrolysis of 1,3-dimethyl-1,3-dichloro-1,3-disilacyclohexane has made it possible to isolate for the first time 1,3-dimethyl-1,3-dihydroxy-1,3-disilacyclobutane, with subsequent establishment of its crystalline structure by X-ray diffraction.

In recent years, various reviews[1,2] have summarised the use of organosilanes with different reactive groups in the preparation of monomeric organosilanes and in the possible formation of intra- and intermolecular hydrogen bonds in crystals of monomeric organosilicon compounds: silanols with one to four Si–OH groups, silandiols,[3–6] and linear[7–11] and cyclic[12–14] dihydroxyorganosiloxanes. Dihydroxyorganocyclosiloxanes form cyclolinear[12] and lamellar[14] associates through intermolecular hydrogen bonding. The stereoisomerism of 2,8-dihydroxydecamethylcyclohexasiloxane determines the formation of either dimeric molecules for its *cis*-isomer (at the expense of both intra- and intermolecular hydrogen bonds) or lamellar associates for its *trans*-isomer.[14] Crystals of *cis*-2,6-dihydroxy-2,6-dimethyl-4,4,8,8-tetraphenyltetrasiloxane are assembled into cyclolinear chains as a result of intermolecular hydrogen bonding.[12] Investigation of the properties of cyclolinear polyorganosiloxanes by X-ray diffraction and atomic microscopy techniques has revealed that the molecular structure of polymers with cyclohexasiloxane chains has a layered packing over a broad temperature range, whereas the cyclolinear polymers with cyclotetrasiloxane chains are characterised by a different type of molecular structure in their chains.[15] These findings show that the molecular structure of the polymeric chain is apparently capable of inheriting the conformation and molecular structure of the initial dihydroxyorganocyclosiloxanes, assembled with the aid of intermolecular hydrogen bonds into associates of different types. The relevant literature does not contain any information on the crystalline structures of dihydroxydisilacycloalkane associates.

In order to see whether the inheritance of the conformation of dihydroxycyclocarbosilanes does take place in the cyclolinear polyorganocarbosiloxanes, we synthesised 1,3-dihydroxy-1,3-dimethyl-1,3-disilacyclobutane (compound **1**) by neutral hydrolysis of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, prepared as in ref. 16 The structure of compound **1** was confirmed by IR, ^1H and ^{29}Si NMR spectroscopy and elemental analysis.[†]

The distinctive features of the crystalline and molecular structures of 1,3-dihydroxy-1,3-dimethyl-1,3-disilacyclobutane were investigated by X-ray diffraction in order to establish the type of hydrogen bonds created in the formation of associates, to clarify the structural peculiarities of the strained disilacycloalkanes and to compare such data with the molecular structure of a cyclolinear carbosiloxane polymer formed from compound **1**.

The results of X-ray diffraction studies have demonstrated that compound **1** crystallises in the form of two independent molecules in different crystallographic centres (Figure 1). The basic geometric characteristics of the molecules are much alike and have the values expected for this class of compounds.[17,18]

The molecules of compound **1** include an inversion centre lying in the middle of the long Si–Si axis. The four-membered rings are planar. The silicon atoms are characterised by a slightly distorted tetrahedral coordination with the endocyclic angle decreasing to 91.7(2)°; this magnitude is similar to the angle in 1,3-diphenyl-1,3-dimethyl-1,3-disilacyclobutane (92.9°).

Analysis of the crystal structure of compound **1** shows that the two independent molecules perform different functions in the formation of hydrogen-bonded associates. Thus, the hydrogen bonds formed by the H(1) and H(2) atoms of molecule **A** [O(1)–O(2) 2.787(4) Å, H(1)–O(1) 1.94 Å, O(1)–H(1)–O(2) 166.7°] connect molecules into a chain of zig zag type (~**A**··**B**~) nearly parallel to the direction [$\bar{1}\bar{1}0$] in the crystal. At the same time, the hydrogen atoms of molecule **B** [H(2) and H(2A)] take part in the formation of hydrogen-bonded helixes (~**B**··**A**′~) [O(2)–O(1′) ($3/2 - x$, $-1/2 + y$, $3/2 - z$) 2.784(4) Å, H(1)–O(1) 1.94 Å, O(1)–H(1)–O(2) 162.5°] which are oriented approximately normally to the above-mentioned chain. This results in the formation of a tube 2.46 Å in diameter. The schemes illustrating the formation of such tubes are presented in Figure 2.

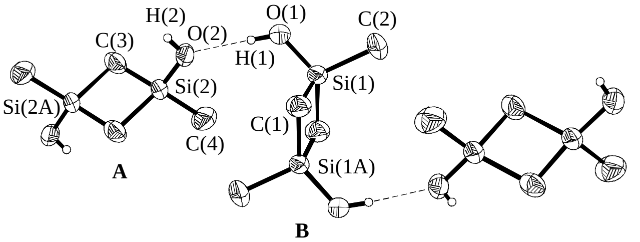

Figure 1 General view of compound **1** illustrating the formation of ~**A**··**B**~ chains. Mean bond lengths (Å) for molecule **A** in **1**: Si(1)–O(1) 1.648(3), Si(1)–C(1) 1.875(4), Si(1)–C(2) 1.860(4); bond angles (°): O(1)–Si(1)–C(2) 106.2(2), C(2)–Si(1)–C(1) 115.4(3), O(1)–Si(1)–C(1) 114.6, C(1)–Si(1)–C(1A) 91.2(2), Si(1)–C(1)–Si(1A) 88.2(2).

[†] *Procedure for preparing compound* **1**. A solution of 1,3-dimethyl-1,3-dichloro-1,3-disilacyclobutane (2.1 g, 0.011 mol) in 22 ml of diethyl ether was slowly (over 60 min) added to a mixture of aniline (2.21 g, 0.0238 mol), water (0.41 g, 0.0227 mol) and 50 ml of diethyl ether, maintained at 0–2 °C with continuous stirring. Cooling was then stopped, the reaction mixture was stirred for another hour and the precipitate formed was filtered off. The ether solution was washed three times with water, dried over Na_2SO_4 and solvent was distilled off *in vacuo*. After recrystallisation (×3) from hexane–benzene–ether (1:1:2), crystals were isolated in a 18.9% yield.

Characteristics of compound **1**: [colourless crystals (from hexane)] mp 81–82 °C. ^1H NMR (400 MHz, 25 °C, [$^2H_6$]acetone + CCl_4) δ: 0.21, 0.27 (CH_3), 0.28, 0.34 (CH_2), 4.78, 4.85 (OH); ^{29}Si NMR δ: 2.22, 5.04. IR (KBr, ν/cm^{-1}, solvent [$^2H_6$]acetone + CCl_4, $C = 0.005$ mol dm^{-3}) 827, 861 (Si–C), 1047 (SiO), 1252, 1245 (Si–C), 3200–3400 (OH), 3670 (free OH).

Crystallographic data for compound **1** at 25 °C: monoclinic crystals ($C_4H_{12}O_4Si_2$), space group $P2_1/n$, $a = 9.640(2)$ Å, $b = 7.352(2)$ Å, $c = 11.297(2)$ Å, $\beta = 99.62(3)$°, $V = 789.3(3)$ Å^3, $Z = 4$ (two independent molecules in the crystal symmetry centres), $d_{calc} = 1.248$ g cm^{-3}, μ(MoKα) = 3.74 cm^{-1}, $F(000) = 320$, $M = 148.32$. Intensities of 1761 reflections were measured with a P3/PC Siemens four-circle diffractometer (MoKα-radiation, $\theta/2\theta$-scan, $2\theta_{max} \leq 52°$); of these, 1600 independent reflections were used for computations and refinements. The structure was solved by direct methods and refined using the least-squares technique in the anisotropic–isotropic (H atoms) approximation on F^2 to $wR_2 = 0.1845$ and GOF = 1.033 for all independent reflections [$R_1 = 0.0690$ on F for all 1293 observed independent reflections with $I > 2\sigma(I)$]. All computations were performed with an IBM PC/AT using the program SHELXTL PLUS 5.0. Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details see ‘Notice to Authors’, *Mendeleev Commun.*, 1998, Issue 1. Any request to CCDC should include all literature citation and the reference number 1135/25.

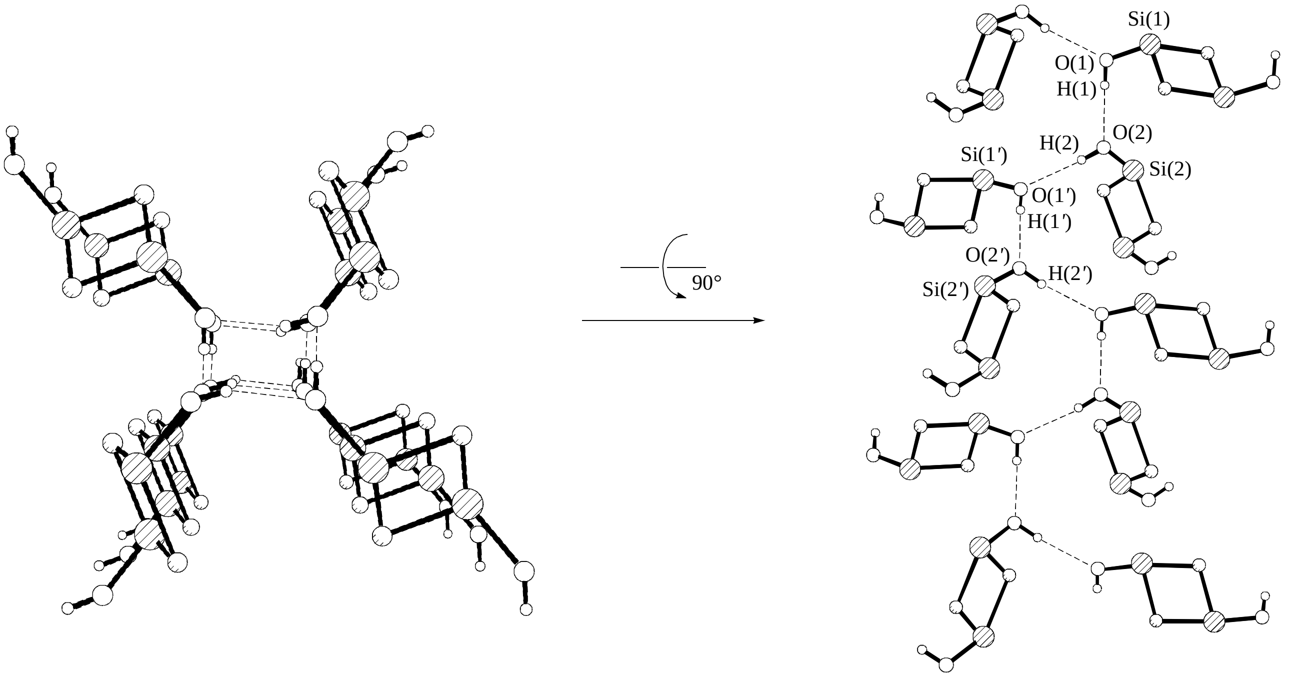

Figure 2 A packing scheme illustrating the formation of ~**A**··**B**~····**A″**··**B″**~ chains and tubes in the crystal structure of compound **1**. The methyl groups are omitted for clarity.

This work was supported by the Russian Foundation for Basic Research (grant nos. 97-03-3378 and 96-03-32645).

References

1 P. D. Lickiss, *Adv. Inorg. Chem.*, 1995, **42**, 147.
2 P. D. Lickiss, *Tailor-Made Silicon–Oxygen Compounds from Molecules to Materials*, ed. R. Corriu, Vieweg, Wiesbaden, 1996, ch. 4, p. 47.
3 N. H. Buttrus, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1986, **302**, 159.
4 N. H. Buttrus, C. Eaborn, P. B. Hitchcock and A. K. Saxena, *J. Organomet. Chem.*, 1985, **248**, 291.
5 L. Parkanyi and G. Bocelli, *Cryst. Struct. Commun.*, 1978, **7**, 335.
6 J. D. Bunning, J. E. Lydon, C. Eaborn, P. H. Jackson, J. W. Goodby and G. W. Gray, *J. Chem. Soc., Faraday Trans.*, 1982, 713.
7 A. P. Polishchuk, T. V. Timofeeva, M. Yu. Antipin, N. N. Makarova, N. A. Golovina, Yu. T. Struchkov and O. D. Lavrentovich, *Metalloorg. Khim.*, 1991, **4**, 147 [*Organomet. Chem.* (*Engl. Transl.*), 1991, **4**, 77].
8 A. P. Polishchuk, M. Yu. Antipin, T. V. Timofeeva, N. N. Makarova, N. A. Golovina and Yu. T. Struchkov, *Kristallografiya*, 1991, **36**, 92 (*Crystallography USSR*, 1991, **36**, 50).
9 A. P. Polishchuk, N. N. Makarova, M. Yu. Antipin, T. V. Timofeeva, M. A. Kravers and Yu. T. Struchkov, *Kristallografiya*, 1990, **35**, 446 (*Crystallography USSR*, 1990, **35**, 258).
10 A. P. Polishchuk, T. V. Timofeeva, N. N. Makarova, M. Yu. Antipin and Yu. T. Struchkov, *Liq. Cryst.*, 1991, **9**, 433.
11 W. Glegg, *Acta Crystallogr., Sect. C*, 1983, **39**, 901.
12 V. E. Shklover, I. L. Dubchak, Yu. T. Struchkov, V. P. Mileshkevich, G. A. Nikolaev and Yu. V. Zygankov, *Zh. Strukt. Khim.*, 1981, **22** (2), 99 [*J. Struct. Chem.* (*Engl. Transl.*), 1981, **22**, 225].
13 I. L. Dubchak, V. E. Shklover, Yu. T. Struchkov, E. S. Hynku and A. A. Zhdanov, *Zh. Strukt. Khim.*, 1981, **22** (5), 156 [*J. Struct. Chem.* (*Engl. Transl.*), 1981, **22**, 770].
14 N. G. Furmanova, V. I. Andrianov and N. N. Makarova, *Zh. Strukt. Khim.*, 1987, **28** (2), 113 [*J. Struct. Chem.* (*Engl. Transl.*), 1987, **28**, 557].
15 Yu. K. Godovsky, N. N. Makarova and E. V. Matukhina, *Polymer Preprints*, 1998, **39**, 485.
16 W. A. Krier, *J. Am. Chem. Soc.*, 1964, **86**, 1601.
17 F. H. Allen, O. Kennard, D. G. Watso, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
18 K. Haykawa, H. Tachikawa, T. Suzuki, N. Choi and M. Murakami, *Tetrahedron Lett.*, 1995, **36**, 3181.

Received: Moscow, 19th January 1998
Cambridge, 12th March 1998; Com. 8/00704G