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Communication

Self-organization of a rigid α,ω-bis-silanediol determined by X-ray crystal structure

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Abstract

The X-ray crystal structure of the 1,4-bis(dihydroxymethylsilyl)benzene exhibits an unusual crystal packing with a hydrogen bonded network locking the orientation of the molecules to an approximate head-to-tail arrangement. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dialkoxysilanes; Hydrolysis; Silanediols; Crystal structures; Hydrogen bonding

1. Introduction

The chemistry of compounds containing Si–OH groups has attracted considerable interest among chemists in recent decades [1–3]. In the course of our studies concerning the preparation of nanostructured hybrid organic–inorganic materials [4], we have been interested in finding an alternative route to the commonly used hydrolytic process. In this context, we have reported the synthesis of the first stable silanetriols containing two $Si(OH)_3$ groups in the same molecules [5]. These compounds are prepared by controlled hydrolysis of bis(trimethoxysilyl) precursors in a biphasic medium which allows and favors the formation of hydrophilic layer (hydrogen bonded network) in the aqueous phase, while the polycondensation reaction is strongly slowed down. They are stabilized by their molecular association in the solid state through hydrogen bonding. A double sheet structure consisting in alternating hydrophobic sheets (organic groups) and hydrophilic sheets (hydrogen bonds) has been shown [5].

2. Results and discussion

It was attractive to investigate the formation of organo bis-silanediols in order to explore their organization in the solid. Only few organo silanediols $R_1R_2Si(OH)_2$ containing one $Si(OH_2)$ group and bulky organic groups have been isolated [6–10] because of their ability to self-condense into polysiloxanes [1]. Tetrahydroxydisiloxanes containing two $Si(OH)_2$ groups in the same molecule have also been reported [11,12]. We first looked at the transformation of 1,4-bis(dimethoxymethylsilyl)benzene **1** [13] into 1,4-bis(dihydroxymethylsilyl)benzene, $(HO)_2MeSiC_6H_4SiMe(OH)_2$ (**2**). The reaction was carried out by controlled hydrolysis of **1** in a biphasic medium (ethylether–water) in the presence of acetic acid (Eq. (1)). The reaction mixture was stirred vigorously for 2h at room temperature. A white precipitate formed. It was filtered and gave **2** as a white crystalline powder in 95% yield. Compound **2** was soluble in usual organic solvents (methanol, ethanol, THF) and DMSO. The FTIR spectrum (KCl pellet) showed mainly a broad absorption band centered at ~ 3125 cm^{-1} attributable to hydrogen bonded hydroxy groups and an intense band at ~ 900 cm^{-1} assigned to Si–O(H) vibrations. No free ν OH vibration was detected. The ^{29}Si-

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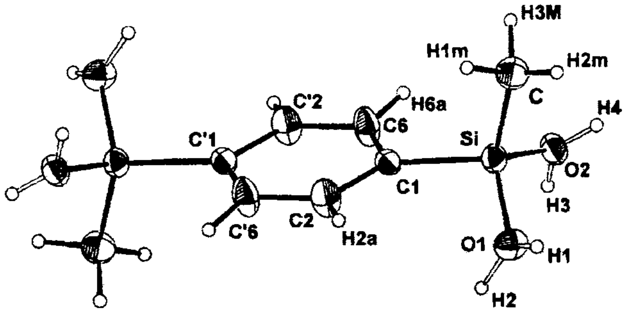
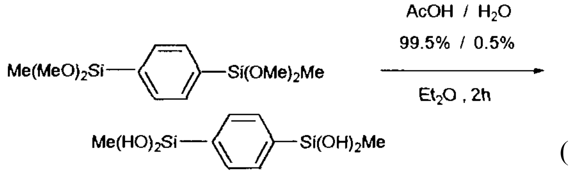


Fig. 1. ORTEP view of compound **2**. The thermal ellipsoids are at the 20% probability level. The occupancy factor for each of the disordered hydroxyle hydrogen atoms is assumed to be 0.5. Important bonds (Å) and angles (°): Si–O1, 1.633(2), Si–O2, 1.639(2), Si–C, 1.838(3), Si–Cl, 1.864(3), O1–Si–O2, 110.1(1), O1–Si–C, 109.7(1), O2–Si–C, 109.1(1), C2–C1–C6, 116.6(2).

NMR spectrum displayed a signal at −21.3 ppm in agreement with chemical shifts already reported for silanediols [9]. The thermal stability of **2** was studied by differential scanning calorimetry under nitrogen at a heating rate of 10°C min^{-1}. Compound **2** appeared to be stable up to 150°C.



(1)

The DSC curve displayed two endothermic peaks, respectively centered at 184 and 206°C. They corresponded to the polycondensation of the silanol groups as shown by IR spectroscopy: the Si–O(H) vibration band at ~900 cm^{-1} disappeared and a broad Si–O–Si absorption band centered at 1048 cm^{-1} was detected after heating at 350°C.

Single crystals of **2** have been isolated for a crystal structure analysis (Fig. 1). The molecules of compound **2** crystallize in the monoclinic space group $P2/c$ with $z = 2$, Its symmetry allows the centers of the phenyl rings to lie on inversion centers at coordinates: 1/2, 1/2, 0 and 1/2, 1/2, 1/2. Other inversion centers occur at the middle of atom pairs O1...O'1 whereas atom pairs O2...O'2 are set around two-fold axes. The general features of the molecules are bond lengths Si–O1, 1.63 3(2) and Si–02, 1.639(2) Å, typical of Si–O bond lengths (1.63(4) Å) found in silicates [14]. The Si–C_{Ar} bond, 1.864(3) Å, is in agreement with literature data for arylsilicon compounds [15]. The Si–CH_3 distance, 1.838 Å, appears shorter than in silanols [8]. The C2–C1–C6 angle value is decreased to 116.6 (2)°. The silicon atoms exhibit almost perfect tetrahedral structure.

The molecules of compound **2** form an extensively hydrogen bonded network of $Si(OH)_2$ moieties (Figs. 2 and 3). These bonds are positioned close to/and on both sides of the *b*, *c* faces of the unit cell and all hydrogen atoms are disordered with the ratio 1:1 (Figs.

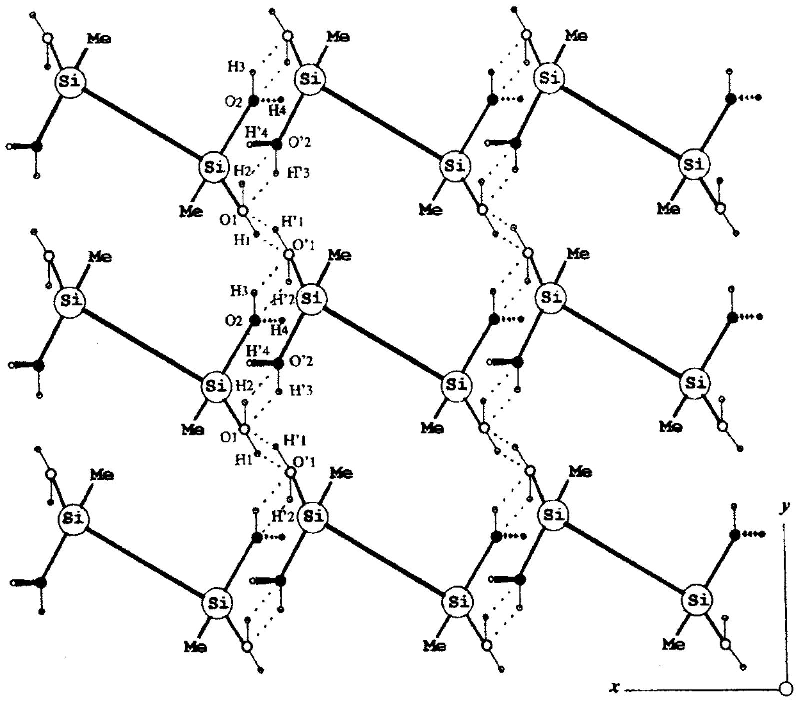


Fig. 2. Packing diagram of the molecules of compound **2** as a projection on the *ab* plane. The O–H...O bonding is fully represented. The C_6H_4 groups are depicted as thick straight lines. Chains of molecules formally result from O1...O'2 and O2...O'1 hydrogen bonding. The chains are tied together by the O1...O'1 and O2...O'2 links. All this bonding is confined to a limited part of the crystal, ca. just to and below the *bc* faces of the unit cell.

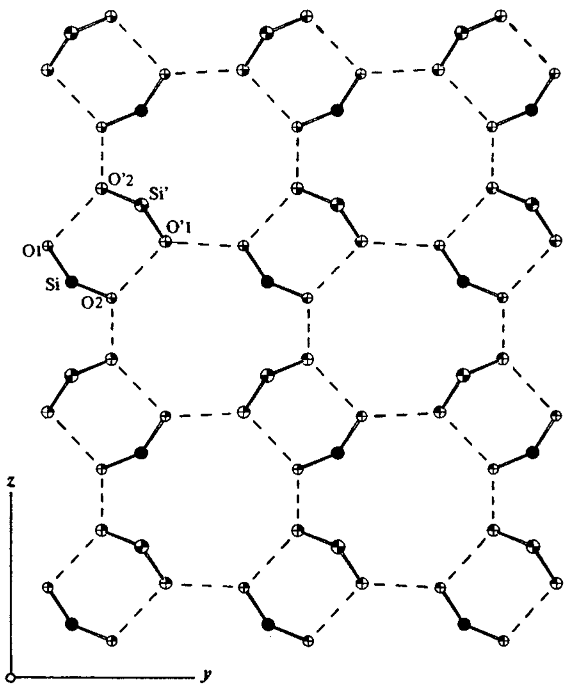


Fig. 3. Projection of the packing diagram of the hydrogen bonded network of compound **2** on the *bc* plane showing the different O...O bonding. The methyl and phenyl groups have been omitted for clarity. The atoms of the $Si(OH)_2$ moieties are located close to and under the plane. They are drawn with a smaller diameter with black dots for the Si atoms, the C_6H_4–Si units stand away from the present plane and are directed to the following plane. In the same manner, the $Si'(O'H)_2$ moieties (drawn with a larger diameter) are located close to and above the *bc* plane, with the $C_6'H_4'$–Si' units further off the plane.

1 and 4). The distances of oxygen atoms O1 and O2 to this face are 0.48 and 0.72 Å, respectively. Both ends of the molecule of **2** are tied with hydrogen bonding inside *y*, *z* planes. Overall, the crystal packing of **2** can be described as a repeated addition of silanediol areas (in *y*, *z* planes) with lipophilic Si–C_6H_4–Si moieties along the direction of the *x* axis (Fig. 2). Fig. 3 schematically depicts the hydrogen bonded network. The two O1...O′2 and O2...O′1 bonding with the distance 2.697(3) Å attach each molecule to its opposite (symmetry operation, $-x$, $1-y$, $-z$) thus producing a chain of molecules going through the *b*, *c* faces. The other bonding O1...O′1 (2.686(4) Å) with symmetry operation: $-x$, $-y$, $-z$ and O2...O′2 (2.674(4) Å), symmetry operation: $-x$, y, $1/2-z$, enables a three dimensional and fairly rigid construction. The crystal packing results also from the van der Waals contacts between the methyl and phenyl groups. For instance the closest distance, 2.30(2) Å, occurs between atom H1m (methyl group) and atom H6 from the nearest phenyl ring (translation: $y-1$). This kind of repulsive contact may play a major role for the spacing of the molecules and the overall packing rigidity.

The structure described here is completely different from the structures previously reported in the case of similar compounds. The diphenyldihydroxysilane $(C_6H_5)_2Si(OH)_2$ exhibits a hydrogen bonding structured colonar geometry [7]. The tetrahydroxysiloxane $[^tBu(OH)_2Si]_2O$ shows a structure in which layers are formed by hydrogen bonding, however the steric hindrance of the ^{t}Bu groups prevents any hydrogen bonding between the layers [11]. Finally, the very close 1,4-bis(dimethylhydroxysilyl)benzene exhibits a solid geometry in which the driving forces of the solid formation are helicoidal arrangements of hydrogen bonding linked through the other silanol group of the molecule to similar helicoidal arranged hydroxyle groups [16].

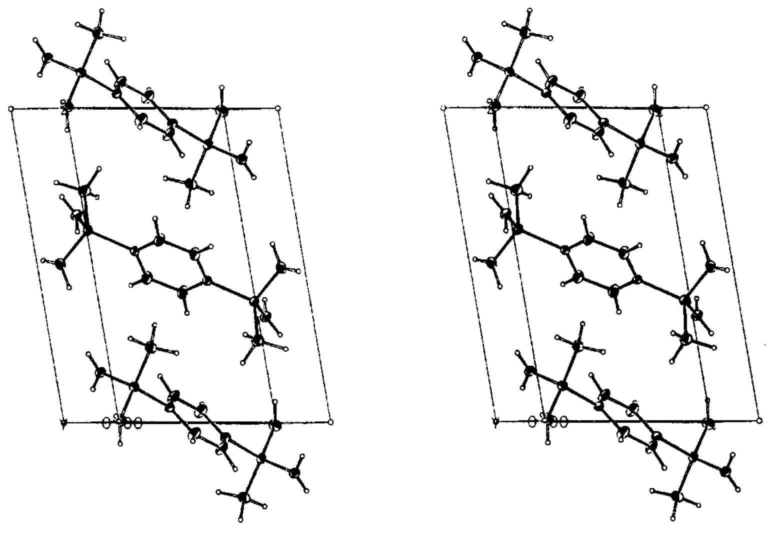


Fig. 4. Stereoscopic drawing of the unit cell viewed approximately down the *b* axis, and showing how spacing between the molecules is mainly determined by $H_{Me}/C_{Ar}/H_{Me}$ close contacts.

3. Conclusions

In conclusion, we have reported here the preparation of a stable bis(alkylsilanediol). The crystal structure shows a remarkable hydrogen bonded network leading to three-dimensional packing. Each $Si(OH)_2$ moiety is thus linked to four oxygen atoms belonging to three different molecules and is cross-linked through the aromatic ring with the second $Si(OH)_2$, thus achieving a rigid three-dimensional structure. In contrast to the observation of Ref. [5,17], compound **2** cannot be considered as having a lamellar structure. We are currently investigating this type of bis(alkylsilanediols) in order to prepare organized hybrid organic–inorganic materials.

4. Experimental

*4.1. Preparation of 1,4-bis(dihydroxymethylsilyl) benzene **2***

The synthesis of 1,4-bis(dimethoxymethylsilyl)-benzene **1** was achieved as described in literature for the corresponding ethoxy compound [13]. A mixture of **1** (1.0 g, 3.49 mmol) in 5 ml of ether and 1.6 ml of an aqueous solution of AcOH (0.5% volume) was vigorously stirred at room temperature (r.t.) for 2 h. During this period a white precipitate formed gradually and was then filtered. The resulting white powder was washed with ethylether (3 × 20 ml). The resulting solid was then dried under vacuum (2 mBar) at 20°C during 24 h and yielded to 95% of **2** (0.76 g, 3.31 mmol) as a white powder. ^{1}H-NMR (DMSO-d_6): δ 0.14 (s, 6H, CH_3), 6.32 (s, 4H, OH), 7.53 (s, 4H, C_6H_4). ^{13}C-NMR (DMSO-d_6): δ 0.3 (CH_3), 133.2 and 141.0 (aromatic carbons). ^{29}Si-NMR (DMSO-d_6): δ −21.3. Anal. Calc. for $C_8H_{14}O_4Si_2$: C, 41.71; H, 6.12; Si, 25.38. Found: C, 41.51; H, 6.19; Si, 25.30%.

5. Crystal data for 2

Nonius CAD 4 automated diffractometer, crystal of dimensions 0.50 × 0.25 × 0.08 mm^3 mounted in a glass capillary, $C_8H_{14}O_4Si_2$, $M = 230.4$, monoclinic, space group $P2/c$, $a = 8.162(2)$, $b = 6.311(1)$, $c = 11.331(4)$ Å, $\beta = 99.68(2)°$, $V = 575.4(2)$ Å^3, $D_{calc} = 1.330$, D_m 1.31(2) g cm^{-3}, $T = 295$ K, $Z = 2$, $F(000) = 244$, μMo–K$_\alpha$ = 0.296 mm^{-1}, 1767 reflections measured, 1548 unique ($R_{int} = 0.032$) which were used in all calculations. The structure was solved by direct methods using SHELXS 86 [18], and refined by least squares on F^2 with the help of SHELXL 93 [19]. The hydrogen atoms on the aromatic ring and the methyl group were positioned by calculation [19]. The disordered positions of the hydrogen hydroxyle groups were obtained from a different Fourier synthesis and their coordinates were not refined. The final $R(F)$ value was 0. 0440 for $729F_o > 4\sigma(F_o)[wR(F^2) = 0.1062]$.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 149 676. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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