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Synthesis, structure and properties of 1,2-dihydroxy-tetramethyldisilane

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Abstract

1,2-Dihydroxy-tetramethyldisilane (**2**) has been synthesized by hydrolysis of 1,2-dichloro-tetramethyldisilane (**1**) and characterized by IR, NMR, MS and X-ray structure analysis. Compound **2** exists in crystal form in two different conformations forming a characteristic two-dimensional network by H-bonding. The title compound is water soluble and has a high condensation tendency. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Disilanediol; Crystal structure; H-bonding

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1. Introduction

While 1,2-dihydroxy-tetraphenyldisilane has been known since 1961 [1], 1,2-dihydroxy-tetra-*t*-butyldisilane as well as 1,2-dihydroxy-1,2-dimethyl-1,2-diphenyldisilane were synthesized more recently [2,3]. The tetramethyl-compound was estimated to be unstable in bulk due to its high condensation tendency [4]. A crystal structure was published only for the *t*-butyl-compound [2].

Continuing investigations on the synthesis, condensation behaviour and other properties of silanols and siloxanols [5,6], we reinvestigated the attempts to hydrolyze 1,2-dichloro-tetramethyldisilane (**1**) using methods which we found to be suitable for synthesis and isolation of condensation-sensitive silanols. Such methods were also described recently by Cella [7].

2. Results and discussion

Surprisingly, it was possible to prepare 1,2-dihydroxy-tetramethyldisilane (**2**) in a very simple manner by hydrolysis of 1,2-dichloro-tetramethyldisilane (**1**) in a homogeneous ether/acetone mixture with triethylamine as the HCl acceptor (Eq. (1)), due to the high crystallisation tendency of **2** on addition of pentane to the reaction mixture.

$$\mathrm{ClMe_2Si-\underset{\mathbf{1}}{Si}Me_2Cl+2H_2O} \xrightarrow[-\,2[\mathrm{Et_3NH}]\mathrm{Cl}]{+\,2\mathrm{Et_3N}} \mathrm{HOMe_2Si\underset{\mathbf{2}}{-}SiMe_2OH} \qquad (1)$$

Purified by recrystallisation from ether/heptane, if more compact crystals are obtained, **2** is stable at room atmosphere for some days. It can be stored in a polyethylene flask for long periods. In a glass flask slow condensation occurs due to the contact with the glass surface.

The solubility of **2** in water and the distribution constant in water/toluene have been determined. These are compared with the corresponding data of other silanols [8,9] in Table 1.

Condensation occurs on addition of a small amount of an acid ($\leq 10^{-3}$ M) to the aqueous solution under precipitation of the well known cyclosiloxane **3** [4] (Eq. (2)).

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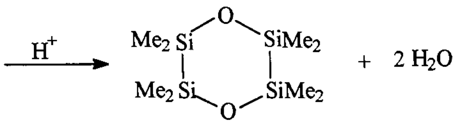
PII: S0022-328X(98)01081-X

2 $HOMe_2Si\text{-}SiMe_2OH$

2



3 (2)

The structure of **2** has been confirmed by ^{1}H-, ^{29}Si- and ^{13}C-NMR, IR and MS as well as by X-ray crystal structure analysis. In comparison to other silanols [11,12], the ν_{OH} IR band shift $\Delta\nu$ at association with diethylether has been determined as a measure of the relative OH acidity. The $\Delta\nu$ value is higher than that of Me_3SiOH but lower than those of $Me_2Si(OH)_2$ and $(HOMe_2Si)_2O$ (Table 1).

The X-ray analysis reveals that there are four half molecules per asymmetric unit. The molecules are completed by rotation around the 2-fold axes of symmetry in the orthorhombic space group *Pccn* (parallel to the *c*-axis). Molecules 1 and 3 possess the oxygen atoms at the central silicon–silicon bond in almost synclinal positions and molecules 2 and 4 in almost antiperiplanar positions (see Fig. 1).

Selected bond distances and angles are given in Table 2. Compound **2** has a standard Si–Si bond length which for the more synclinal molecules 1 and 3 is 1.8–1.4 pm shorter than for the more antiperiplanar molecules 2 and 4. The Si–Si–O angles in 2 and 4 are ca. 2° smaller than in 1 and 3. Molecules 1 and 3 as well as 2 and 4 differ slightly among one another only in the O–Si–Si–O torsion angles.

As shown in Fig. 2, a characteristic layer structure is formed by intermoleculare H-bonding in a form which does not correspond to other structural patterns investigated for silane- and siloxanediols [10]. Molecules 1 and 3 (synclinal conformation) on the same 2-fold axis are orientated toward each other. The resulting pairs of molecules 1 and 3 arranged cross wise are connected by molecules 2 and 4 (antiperiplanar conformation) in planes perpendicular to the *c*-axis.

The O–O distances of the hydrogen-bonded system (see Table 2) vary between 264.8 and 269.4 pm. A careful investigation of the difference maps of electron density did not clarify conclusions on the hydrogen positions in these bonds. But the formation of a OH-macrocycle with the sequence O1–O2A–O3A–O4A–O1–O2–O3–O4 as shown in Fig. 2 represents the most probable arrangement. In terms of a graph theoretical approach [14] the basic ring motif can be designated as $\mathbf{R}_8^8$ **(16)**. Each motif in its turn is connected via molecules 2 parallel to the *a*-axis and via molecules 4 parallel to the *b*-axis.

The large elementar cell contains 16 molecules in four layers connected in the *c* direction by van der Waals forces only.

Compared with the tetra-*t*-butyl-dihydroxydisilane reported by West [2], **2** is not sterically strained, has a standard Si–Si bond length (10 pm shorter than the *t*-butyl-compound) and also has 10–20 pm shorter intermolecular hydrogen bonds. The ^{29}Si-NMR signal (8.46 ppm) is less downfield shifted. The O–Si–Si–O dieder angle for the *t*-butyl-compound (−97.3°) is almost the mean of the corresponding dieder angles for the two different conformers of **2**. While **2** in crystal form has a more complex network formed by hydrogen bonds (Fig. 2), the *t*-butyl-compound displays a much simpler chain structure.

3. Experimental

The starting product, 1,2-dichlorotetramethyldisilane (**1**), was synthesized according to [13] from the ‘disilane fraction’ of the direct chloromethylsilane synthesis, varied only by using Bu_3N as the catalyst for the final Si–Si cleavage of the higher chlorinated disilanes by HCl.

NMR: Bruker AC 250 and (for ^{29}Si) Bruker ARX 400, TMS was taken as the internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, electron impact ionisation, 70 eV.

Table 1
Solubility s in water, distribution α in toluene/water, Si–OH IR band position ν_{OH} and Si–OH band shift $\Delta\nu_{OH}$ at association with diethylether

Compound	s (g in 100 g H_2O) at 25°C	α (c toluene/c H_2O) at 25°C	ν_{OH} (cm^{-1})	$\Delta\nu_{OH}$ (cm^{-1})
2	12.4	0.13	3682	250
Me_3SiOH	7.2	2.00[b]	3695	238
$Me_2Si(OH)_2$	245[a]	<0.01[b]	3693[c]	273[c]
$[HOMe_2Si]_2O$	11.0[a]	0.27[b]	3693	275

[a] See [8].
[b] See [9].
[c] See [11].

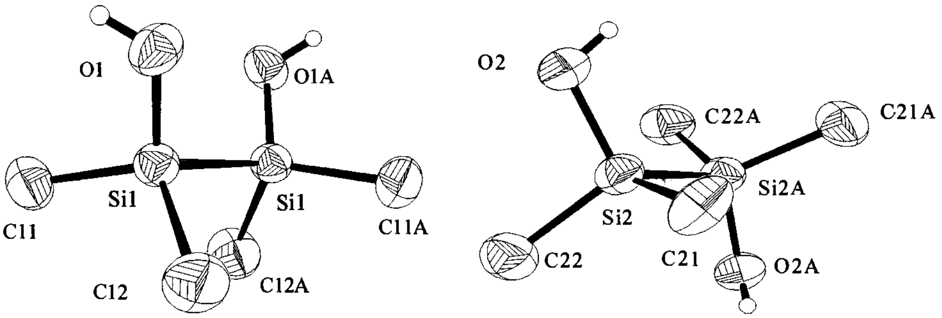


Fig. 1. Molecular structure of **2** in almost synclinal (left) and almost antiperiplanar (right) conformation, given for molecules 1 and 2 which are slightly different form 3 and 4 only in the O–Si–Si–O torsion angles. (ORTEP–plot with 50% probability of the thermal ellipsoids).

3.1. *Synthesis of 1,2-dihydroxy-tetramethyldisilanediol (2)*

While stirring, 18.7 g (0.1 M) of **1**, dissolved in ether, was gradually added to a solution of 20.4 g (0.202 M) Et_3N, 3.8 g (0.21 M) water and 35 ml acetone in 350 ml ether at 0°C. After 30 min stirring and filtration of the aminehydrochloride ca. 90% of the ether/acetone was evaporated. On addition of 80 ml pentane and continuation of solvent evaporation crystals of **2** were formed. These were separated, washed with cold pentane and recrystallized from heptane/ether. From the remaining solution a second product fraction can be isolated by removing the solvent and addition of pentane, but this fraction contains up to 50% of the condensation product **3**.

Yield 8.5 g (57%). m.p. 70–71°C. ^{1}H-NMR (benzene-d_6): δ 0.28 (s, $SiCH_3$, 12 H), 3.5 (s, OH, 2H, conc. dep.). ^{13}C-NMR (benzene-d_6). δ 1.47. ^{29}Si-NMR (benzene-d_6): δ 8.46.

MS (*m*/*z*,%): 150.0519 (15) [M^+], 149.0472 (88) [M^+–H], 135 (95) [M^+–CH_3], 133 (95) [M^+–OH],

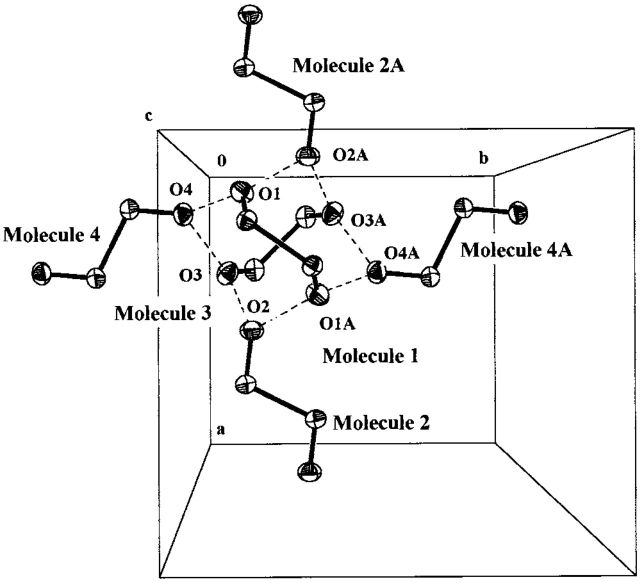


Fig. 2. Crystallographic arrangement of the two pairs of conformational isomers of **2** via hydrogen bonds. (ORTEP–plot with 50% probability of the thermal ellipsoids, methyl groups are omitted for clarity, broken lines indicate hydrogen bonds).

Table 2
Selected bond lengths (Å) and angles (°) for **2** (estimated S.D. in parentheses)

	Molecule 1	Molecule 2	Molecule 3	Molecule 4
Bond lengths (Å)				
Si–SiA	2.342(2)	2.360(2)	2.339(2)	2.353(2)
Si–O	1.659(3)	1.661(2)	1.663(3)	1.662(3)
Si–C1	1.857(4)	1.863(4)	1.856(5)	1.846(4)
Si–C2	1.866(4)	1.857(4)	1.846(5)	1.859(4)
Bond angles (°)				
SiA–Si–O	112.2(1)	109.9(1)	112.8(1)	110.6(1)
SiA–Si–C1	110.9(2)	110.3(2)	110.5(2)	113.1(2)
SiA–Si–C2	105.8(2)	112.5(2)	107.6(2)	109.4(2)
Torsion angle				
O–Si–SiA–OA	−46.1(2)	−160.5(2)	37.2(2)	165.7(2)
H-bonds				
	O1–O2	O2–O3	O3–O4	O4–O1
	2.680	2.648	2.693	2.694

Table 3
Crystal data and structure refinement for **2**

Identification code	oh2
Empirical formula	$C_4H_{14}O_2Si_2$
Formula weight	150.33
Temperature (K)	213(2)
Wavelength (pm)	71.073
Crystal system	Orthorhombic
Space group	*Pccn*
Unit cell dimensions	
a (pm)	962.10(10)
b (pm)	1021.3(2)
c (pm)	3785.9(5)
α (°)	90
β (°)	90
γ (°)	90
V (nm^3)	3.7200(10)
Z	16
$D_{calc.}$ ($Mg\ m^{-3}$)	1.074
Absorption coefficient (mm^{-1})	0.318
$F(000)$	1312
Crystal size (mm^3)	$0.78 \times 0.38 \times 0.06$
Theta range for data collection (°)	2.15–21.99
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 11$, $-45 \leq l \leq 45$
Reflections collected	4572
Independent reflections	2286 [$R_{int} = 0.0538$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2281/0/157
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1074$
R indices (all data)	$R_1 = 0.0796$, $wR_2 = 0.1233$
Largest diff. peak and hole (e Å^{-3})	0.325 and −0.278

117 (98) [M^+–CH_3–OH], 75 (100) [M^+–$SiMe_2OH$], 73 (96) [M^+–$SiMe_3$]. Anal. calc. for $C_4H_{14}O_2Si_2$ (150.32): C, 31.96; H, 9.39. Found: C, 31.80; H, 9.44%.

The distribution coefficient α(toluene/water) and the $\Delta\nu_{OH}$ value have been determined as reported in [8].

Crystal data and results of the data collection are summarized in Table 3. A crystal of compound **2** was transferred to perfluoropolyether RS-3000 (Riedel–de Haen) under cold nitrogen and fixed at 213 K. The data collection was done on a Siemens P4 four-circle diffractometer in routine ω-scan after taking a rotational photo and finding a reasonable reduced cell. The structure was solved with direct methods (Siemens SHELXTL) and refined with the full-matrix least-squares method of SHELXL-93 [15]. All non-hydrogen atoms were refined anisotropically, the hydrogen position were refined according to the riding model. The weighting scheme was calculated according to $w = 1/[s^2(F_o^2) + (0.0462P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103055. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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References

[1] H.J.S. Winkler, H. Gilman, J. Org. Chem. 26 (1961) 1265.

[2] R. West, E.K. Pham, J. Organomet. Chem. 403 (1991) 43.

[3] V.V. Semenov, E.Yu. Ladilina, Yu.A. Kurskii, S.Ya. Khorshev, N.P. Makarenko, Izv. Akad. Nauk. Ser. Khim. 10 (1996) 2550.

[4] M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima, K. Shiina, J. Org. Chem. 26 (1956) 1264.

[5] W. Sarich, A. Surkus, D. Lange, E. Popowski, H. Kelling, Z. Anorg. Allg. Chem. 581 (1990) 199.

[6] H. Spitzner, S. Wandschneider, D. Lange, H. Kelling, J. Prakt. Chem. 338 (1996) 376.

[7] J.A. Cella, J.C. Carpenter, J. Organomet. Chem. 480 (1994) 23.

[8] J.F. Hyde, J. Am. Chem. Soc. 75 (1953) 2166.

[9] W. Rutz, D. Lange, E. Popowski, H. Kelling, Z. Anorg. Allg. Chem. 536 (1986) 197.

[10] P.D. Lickiss, Adv. Inorg. Chem. 42 (1995) 147.

[11] G.I. Harris, J. Chem. Soc. B (1971) 2083.

[12] H.J. Holdt, E. Popowski, H. Kelling, Z. Anorg. Allg. Chem. 519 (1984) 233.

[13] H. Matsumoto, T. Motegi, M. Hasegawa, Y. Nagay, J. Organomet. Chem. 142 (1977) 149.

[14] J. Bernstein, R.E. Davis, L. Shimoni, N.L. Chang, Angew. Chem. 107 (1995) 1689.

[15] G.M. Sheldrick, SHLXL-93, Universität Göttingen, 1993.