The crystal structure of a 1,2-disilanediol, (t-Bu₂SiOH)₂

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Abstract

The synthesis and structure of the first 1,2-disilanediol, (t-Bu₂SiOH)₂ (2) is reported. Crystal data: 2, triclinic, $P\bar{1}$ (No. 2), a 9.486(3), b 16.680(3), c 10.681(4) Å, α 76.71(2), β 85.10(2), γ 78.59(2)°, and $Z = 2$. The unit cell of 2 contains two discrete monomers hydrogen-bonded as a chain. The long distances for Si–Si (2.453 Å) and Si–C (1.88 Å) bonds in 2 indicate a high degree of steric strain in this molecule.

Introduction

Disilenes, the silicon congener of alkenes, are now well established in the chemical literature [1]. In a few cases they can be prepared thermally by reduction of 1,2-dihalodisilanes [2]. We have explored the reductive chemistry of tetra-t-butyl-1,2-diiododisilane (1), and during the course of these studies, we have isolated a 1,2-disilanediol (2), whose novel structure is discussed here.

Experimental section

All reactions were performed under an atmosphere of nitrogen or argon. Air-sensitive materials were handled using standard Schlenk techniques. Tetra-t-butyl-1,2-diiododisilane (1) was prepared according to the literature procedure [3].

Dehalogenation of 1

Typically, a solution of 1 (0.50 g, 0.9 mmol) in THF (25 mL) was added dropwise with stirring over 15 min to a cold (−78°C), dark green, THF (15 mL) solution of lithium naphthalenide prepared from lithium (25 mg, 3.6 mmol) and naphthalene (0.23 g, 1.8 mmol). The mixture was stirred for about 2 h at this temperature and then allowed to warm up to room temperature. After stirring for 1 h at room temperature, the orange-colored solution was evaporated under vacuum. The oily residue was extracted into pentane followed by filtration under argon. Removal of

pentane left a solid residue out of which naphthalene was sublimed. Crystallization from hexane afforded colorless rods of $(t\text{-Bu}_2\text{Si})_3$ (3), identified by its melting point (180 °C) and ^1H NMR (C_6D_6) 1.40 (s) [Lit. [4] m.p. 180°C, ^1H NMR (C_6D_6) 1.40(s)]. The residual yellow-orange oil could not be purified nor conclusively identified.

Several attempts were made to dehalogenate 1 in the presence of trapping agents. The following experiment is illustrative: to a Schlenk flask containing a THF solution of 1 and two molar equivalents of $\text{LiC}_{10}\text{H}_8$ at −78°C, an excess of methanol (2mL) was added by syringe. The mixture was then allowed to warm to ambient temperature. The resulting pale yellow solution was worked up in air. No $t\text{-Bu}_2\text{Si}(\text{OCH}_3)\text{SiH-t-Bu}_2$ was detected. Only $(t\text{-Bu}_2\text{Si})_3$ (3, 20–30% yields) and an unidentifiable yellow oil were isolated.

Tetra-t-butyl-1,2-dihydroxydisilane, $(t\text{-Bu}_2\text{SiOH})_2$ (2)

A sample of 1 (1.0 g, 1.9 mmol) was treated with water. An exothermic reaction ensued, generating HI fumes. The mixture was extracted into Et_2O (4 × 25mL). The combined Et_2O extracts were dried over MgSO_4, filtered and evaporated. Recrys-

Table 1

Crystal and refinement data for $(t\text{-Bu}_2\text{SiOH})_2$

Empirical formula	$C_{16}H_{38}O_2Si_2$
Color; habit	colorless rods
Crystal size (mm)	$0.12 \times 0.25 \times 0.38$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	9.486(3)
b, Å	16.680 (3)
c, Å	10.681 (4)
α, deg	76.71(2)
β, deg	85.10(2)
γ, deg	78.59(2)
V, Å^3	1031.4(5)
Z	2
FW	318.65
D(calc), g/cm^3	1.026
Abs. coeff., mm^{-1}	0.17
Diffractometer	Nicolet $P\bar{1}$
Radiation	graphite mono. Mo-K_α (0.71073 Å)
2θ Range, deg	3.5–54.9
Scan type	$\theta - 2\theta$
Scan speed	var., 4–29
Standard reflections	4 std/50 reflections
Reflections collected	5443
Independent reflections	4683
Observed reflections $(F_o > 3\sigma(F_o))$	3270
Data/parameter	18/1
Final $R(F)$, $R(wF)$	5.08, 8.16%
Weighting scheme	$1/w = \sigma^2(F) + 0.002572F^2$
Final GOF	1.324
Δ/σ (mean)	0.002
Highest peak in final difference map, e/Å^3	0.40

tallization from hexane afforded colorless rods of **2** in 93% yield. M.p. 91–93°C; ^{1}H NMR (C$_6$D$_6$) 1.12(s); ^{29}Si NMR (C$_6$D$_6$) 20.61; ^{13}C{^{1}H} NMR (C$_6$D$_6$) 22.93, 29.04; HRMS 261.1699 (M^+ − t-Bu); Anal. calcd for C$_{16}$H$_{38}$O$_2$Si$_2$: C, 60.25; H, 11.93. Found: C, 59.83; H, 11.33.

X-ray data collection

Single crystals of **2** were grown by slow cooling of a saturated solution in hexane at −10°C. A suitably sized crystal was removed from the solution and mounted on a thin glass fiber with cyanoacrylate cement. Details of the crystal data and intensity collection are summarized in Table 1. Positional parameters are listed in Table 2, and selected bond lengths and angles in Table 3. The data were processed by using the SHELXTL PLUS software package on a Microvax II. The structure was solved by direct methods and only those reflections with $I_o > 3\sigma(I_o)$ were used in the full-matrix, least-squares refinements. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions (C–H = 0.96 Å; H–C–H = 109.5°) and allowed to ride with the carbons to which they are attached. They were also included as fixed atom contributions ($U_{iso} = 0.08$ Å^2). The hydroxyl hydrogen atoms could not be located from the final difference Fourier map and were not included. As a check on crystal stability during the course of the data collection at room temperature, the four standards were measured every 50 reflections and showed no significant trends.

Complete tables of bond distances and angles (1 page), hydrogen atom coordinates and displacement parameters (2 pages) and thermal parameters and listings of structure factors (17 pages) are available from the authors.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**

	x	y	z	U_{eq} [a]
Si(1)	3682(1)	2297(1)	3166(1)	37(1)
Si(2)	3011(1)	1311(1)	1496(1)	34(1)
O(1)	3895(2)	1097(2)	4477(2)	49(1)
O(2)	4583(2)	955(2)	714(2)	50(1)
C(1)	5541(3)	2766(3)	2689(3)	53(1)
C(2)	5609(4)	3563(3)	1297(3)	65(1)
C(3)	6666(3)	1485(4)	2796(3)	69(1)
C(4)	5992(5)	3548(4)	3565(4)	83(2)
C(5)	2272(4)	3606(3)	3772(3)	61(1)
C(6)	2678(5)	3772(5)	5070(4)	92(2)
C(7)	830(4)	3116(5)	4020(5)	102(2)
C(8)	2021(6)	4924(4)	2858(5)	116(2)
C(9)	2443(3)	−335(3)	2283(3)	47(1)
C(10)	1290(4)	−210(3)	3354(3)	70(1)
C(11)	1917(4)	−971(3)	1303(4)	67(1)
C(12)	3794(4)	−1282(3)	2858(3)	62(1)
C(13)	1778(3)	2373(3)	164(3)	47(1)
C(14)	1928(4)	1749(4)	−1008(3)	63(1)
C(15)	180(3)	2607(4)	590(3)	69(1)
C(16)	2275(5)	3701(3)	−306(4)	78(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.
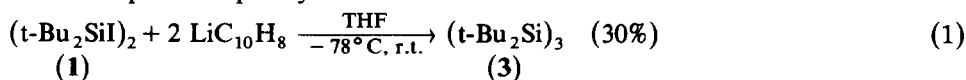
Table 3

Principal bond lengths (Å) and angles (°) for **2** (estimated standard deviations are in parentheses)

Bonds

Si(1)–Si(2)	2.543(1)	Si(1)–O(1)	1.663(2)
Si(2)–O(2)	1.665(2)	Si(1)–C(1)	1.923(3)
Si(1)–C(5)	1.921(3)	Si(2)–C(9)	1.925(3)
Si(2)–C(13)	1.922(3)		

Angles

Si(2)–Si(1)–O(1)	105.3(1)	Si(2)–Si(1)–C(1)	108.4(1)
Si(2)–Si(1)–C(5)	118.3(1)	O(1)–Si(1)–C(1)	106.6(1)
O(1)–Si(1)–C(5)	101.7(1)	C(1)–Si(1)–C(5)	115.1(2)
Si(1)–Si(2)–O(2)	102.1(1)	Si(1)–Si(2)–C(9)	109.6(1)
Si(1)–Si(2)–C(13)	119.5(1)	O(2)–Si(2)–C(9)	106.4(1)
O(2)–Si(2)–C(13)	103.7(1)	C(9)–Si(2)–C(13)	113.9(1)

Selected torsion angles

O(1)–Si(1)–Si(2)–O(2)	− 97.3(1)	O(1)–Si(1)–Si(2)–C(9)	15.2(1)
O(1)–Si(1)–Si(2)–C(13)	149.1(1)	C(1)–Si(1)–Si(2)–O(2)	16.4(1)
C(1)–Si(1)–Si(2)–C(9)	129.0(1)	C(1)–Si(1)–Si(2)–C(13)	− 97.1(1)
C(5)–Si(1)–Si(2)–O(2)	149.9(1)	C(5)–Si(1)–Si(2)–C(9)	− 97.6(1)
C(5)–Si(1)–Si(2)–C(13)	36.4(2)		

Hydrogen bonds

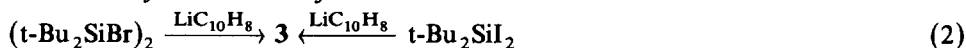|			
O(1)–O(1)′	2.896Å	O(2)–O(2)″	2.775Å
Si(1)–O(1)–O(1)′	137.5°	Si(2)–O(2)–O(2)″	127.9°

Symmetry elements indicated as: ′ = 1 − x, − y, 1 − z; ″ = 1 − x, − y, − z
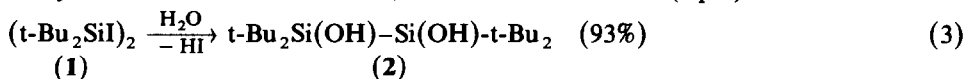
Results and discussion

When **1** was titrated with two molar equivalents of lithium naphthalenide followed by workup at room temperature, the cyclotrisilane **3** was isolated in 30% yield along with an unidentifiable yellow-orange oil (eq. 1). When the same reaction was repeated in the presence of trapping agents such as methanol and sulfur, no disilene adducts, e.g., t-Bu$_2$(CH$_3$O)Si-SiH-t-Bu$_2$ or (t-Bu$_2$Si)$_2$S, were isolated or observed spectroscopically.

$$(\text{t-Bu}_2\text{SiI})_2 + 2 \text{ LiC}_{10}\text{H}_8 \xrightarrow[-78°\text{C, r.t.}]{\text{THF}} (\text{t-Bu}_2\text{Si})_3 \quad (30\%) \qquad (1)$$
$$\mathbf{(1)} \qquad\qquad\qquad\qquad\qquad \mathbf{(3)}$$

The findings are in accord with those of Weidenbruch [4] who carried out dehalogenation experiments on tetra-t-butyldibromodisilane and di-t-butyldiiodosilane (eq. 2). The only isolated product was **3**, and no evidence was reported for the intermediacy of tetra-t-butyldisilene.

$$(\text{t-Bu}_2\text{SiBr})_2 \xrightarrow{\text{LiC}_{10}\text{H}_8} 3 \xleftarrow{\text{LiC}_{10}\text{H}_8} \text{t-Bu}_2\text{SiI}_2 \qquad (2)$$

While **1** is stable to oxygen, it is sensitive to moisture, liberating clouds of HI upon contact with moist air. Thus hydrolysis of **1** afforded **2** in nearly quantitative yield. Because **2** has an extremely weak OH absorption in the infrared, it was initially thought that **2** might be a cyclic disiladioxetane, but X-ray crystallographic study established that **2** has the 1,2-disilanediol structure (eq. 3).
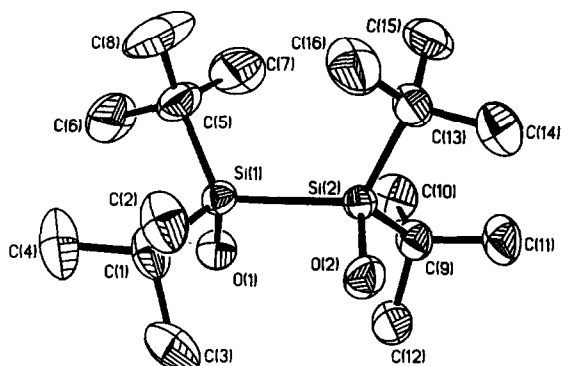
$$(\text{t-Bu}_2\text{SiI})_2 \xrightarrow[-\text{HI}]{\text{H}_2\text{O}} \text{t-Bu}_2\text{Si(OH)-Si(OH)-t-Bu}_2 \quad (93\%) \qquad (3)$$
$$\mathbf{(1)} \qquad\qquad\qquad \mathbf{(2)}$$

Fig. 1. Thermal ellipsoid plot of 2 (50% probability). Hydrogen atoms omitted for clarity.

Compound 2 is the first 1,2-disilanediol to be structurally characterized. Figure 1 shows the ORTEP drawing of 2 with the atom labeling scheme. The molecule has approximate C_2 symmetry, with the two-fold axis perpendicular to and bisecting the Si(1)–Si(2) bond. Moreover, the six substituents attached to the two silicons adopt a nearly eclipsed configuration (the C(5)–Si(1)–Si(2)–C(13) torsion angle is 36.4(2)°). This is surprising since a staggered conformation about the Si(1)–Si(2) bond would be expected to minimize steric repulsion between the bulky t-butyl groups. The two OH groups are on opposite sides of the mean plane thus disfavoring intramolecular hydrogen bonding, but there is strong evidence in favor of intermolecular hydrogen-bonding. As shown in Fig. 2, the unit cell of 2 contains two discrete monomers linked as a chain by hydrogen-bonding. This contrasts with the structure of t-Bu$_2$Si(OH)$_2$ [5] in which hydrogen-bonding results in cyclic dimers which are further linked to form chains. The distances between inversion-related hydroxyl
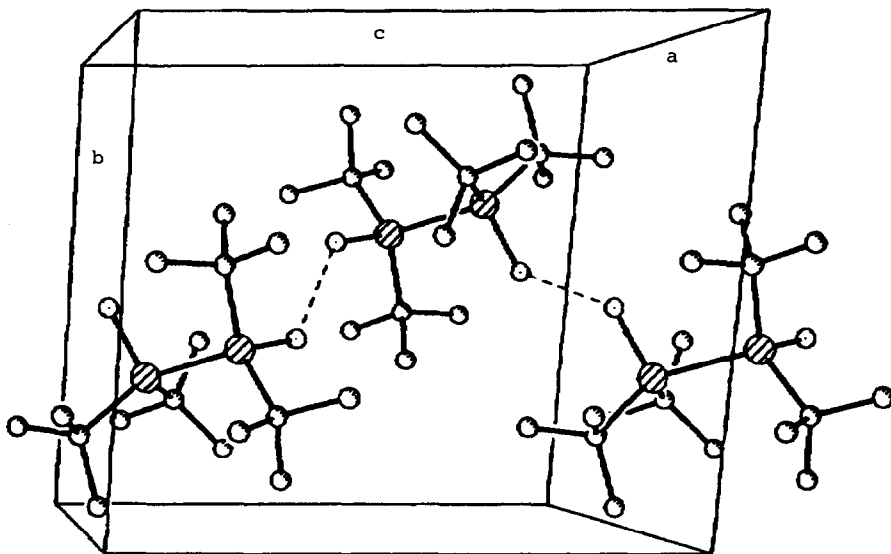

Fig. 2. View along the c axis of the crystal packing in 2; broken lines indicate hydrogen bonds.

oxygen atoms $(O(1)–O(1') = 2.896$ Å, $O(2)–O(2') = 2.775$ Å) and the Si–O–O′ angles (127.9 and 137.5°) are also commensurate with a hydrogen-bonded chain of molecules. Furthermore, the oxygen–oxygen distances in **2** are in the range of those in t-Bu$_2$Si(OH)$_2$ (2.69, 2.77 Å) [5]. The structure also shows large Si–Si (2.453(1) Å) and Si–C (1.92 Å) distances compared to the normal single bond lengths (Si–Si, 2.35 Å; Si–C, 1.88 Å) [6]. The peripheral C–C bonds are normal (1.53 Å). In spite of the steric repulsion between the bulky t-butyl groups, the t-Bu–Si–t-Bu angles in **2** (113.9(1), 115.1(2)°) are smaller than that in t-Bu$_2$Si(OH)$_2$ (118.4(9)°) [5] and surprisingly compare more favorably with the corresponding angles in the less bulky silanediols, Et$_2$Si(OH)$_2$ (111°) [7] and Ph$_2$Si(OH)$_2$ (112.9(3)°) [8]. Like other t-butyl substituted polysilanes [9], **2** can be viewed as highly strained and energy rich. It also exhibits a relatively downfield chemical shift of +20.61 ppm in the ^{29}Si{^{1}H} NMR.

Acknowledgment

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