

# Synthesis and crystal structure of disiloxane-1,3-diols and disiloxane-1,1,3,3-tetraol

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## Abstract

1,3-Dimethyl- or 1,3-divinyl-1,3-di-*t*-butoxydisiloxane-1,3-diol and 1,3-diphenyldisiloxane-1,1,3,3-tetraol were synthesized by hydrolysis of the corresponding diisocyanatodisiloxanes and tetrachlorodisiloxane. The disiloxanediols were soluble in common organic solvents and thermally very stable, therefore, they could be sublimed without decomposition. X-ray crystallography showed that the disiloxane-1,3-diols in the crystal feature a 1.21 nm diameter columnar array with intermolecular hydrogen bonding. The disiloxane-1,1,3,3-tetraol, on the other hand, revealed molecules with a *gauche*- and *anti*-conformation depending on crystallization method which formed a columnar array and a sheet-like array, respectively. It was confirmed that these silanols can be potential building blocks for ladder oligosilsesquioxanes.

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**Keywords:** Disiloxanepolyol; Crystal structure; Hydrogen bond assembly; Silsesquioxane

## 1. Introduction

Silanol compounds serve as not only an interesting model for surface hydroxyl groups of silica, but also are building blocks of two- and three-dimensional metal-siloxanes and silsesquioxanes [1,2]. Especially, siloxanepolyols can be a material for the potential synthesis of siloxanes and/or silsesquioxanes with ladder and cage structures because they are constructed of the unit structures of the siloxanepolyols such as disiloxane and cyclotetrasiloxane.

On the other hand, silanol compounds have been reported to form hydrogen-bonded assemblies with themselves [3], alcohols [4], ethers [5], water [6], or amines [7]. For example, disiloxane-1,3-diols  $[\text{R}_2\text{Si}(\text{OH})_2\text{O}]_n$  ( $\text{R} = \text{Me}$  [8], Et [9], Pr [10], Ph [11]) have a columnar array with an intermolecular hydrogen-bonded assembly. A 1.16 nm diameter tube-like array was formed by the hydrogen bond

between the all-*cis*-[*i*-PrSi(OH)O]<sub>4</sub> and *i*-Pr<sub>2</sub>Si(OH)<sub>2</sub> [12]. Because the ladder, sheet, cycle, and column type assemblies are generated by various types of hydrogen bondings, the siloxanepolyols are also an interesting material for the study of supramolecular organosilicon compounds [13].

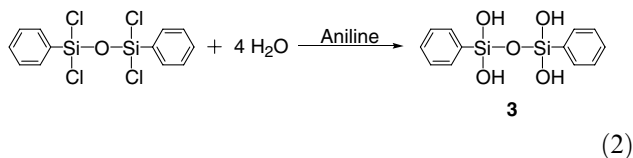
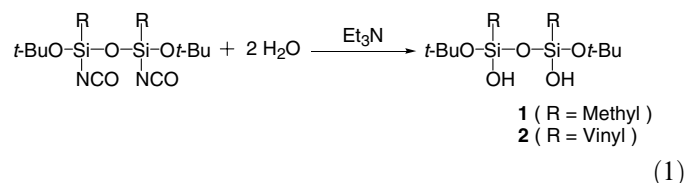
From the viewpoint of silanols and, especially siloxanepolyols, as a building block, the stability against the self-condensation reaction is a serious problem to be overcome because it decreases with an increase in the number of silanol groups as well as the decrease in the steric hindrance of the substituent [3,14]. According to this dependence, silanols  $\text{R}_{4-n}\text{Si}(\text{OH})_n$  can be obtained by the hydrolysis of  $\text{R}_{4-n}\text{SiCl}_n$ . However, disiloxanepolyols cannot be selectively obtained, for the silanols are also formed as a by-product provided that the substituents are not sterically hindered [15]. This can be solved by using the sila-functional disiloxanes as a starting material. However, very few such materials are known so that it is practically important to develop new synthetic routes of the sila-functional disiloxane and oligosiloxanes, which allows us to produce siloxanepolyols.

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Due to the difficulty on the synthesis and instability against the self-condensation of siloxanepolyols, the X-ray crystallography studies are limited to the study of the siloxanepolyols such as disiloxane-1,3-diols [R'Si(OH)<sub>2</sub>]<sub>2</sub>O (R' = Ph [16], *t*-Bu [17], (*t*-BuO)<sub>3</sub>SiO [18], 2,6-*i*-PrC<sub>6</sub>H<sub>3</sub>N(SiMe<sub>3</sub>) [19]) and cyclotetrasiloxane-1,3,5,7-tetraols [R''Si(OH)O]<sub>4</sub> (R'' = Ph [20], *i*-Pr [6]), which are the target material for the study of supramolecular organo-silicon compounds.

We have reported that sila-functional disiloxanes [RSiX<sub>2</sub>]<sub>2</sub>O (R = Me, Vi, Ph, X = NCO, Cl) are selectively synthesized by the vapor-phase hydrolysis of the trifunctional silane RSiX<sub>3</sub> [21] and also the reaction of the disiloxanes with alcohols [22] or amines [16b] moderately progresses to give partially substituted products. The results revealed that isocyanatosilanes can be an appropriate material to control the substitution reactions and/or to prepare sila-functional oligosiloxanes such as isocyanatodisiloxanes and disiloxanepolyols. We now report the results for the synthesis and X-ray crystallography study of the disiloxane-1,3-diols **1** and **2**, and also the disiloxane-1,1,3,3-tetraol **3** as shown:



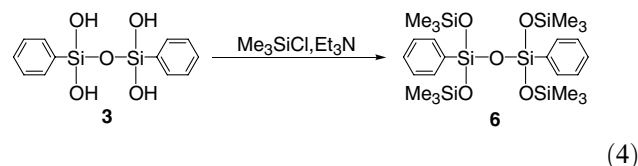
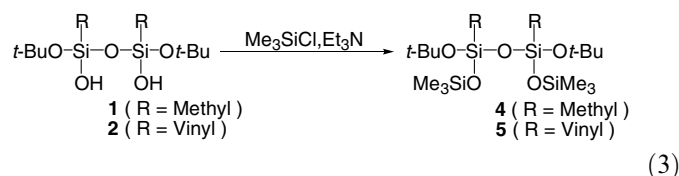
## 2. Results and discussion

### 2.1. Syntheses and properties of disiloxane-1,3-diol (**1**) (R = Me), **2** (R = Vinyl), and disiloxane-1,1,3,3-tetraol (**3**)

According to the literature [21], [MeSi(*Ot*-Bu)(NCO)]<sub>2</sub>O and [ViSi(*Ot*-Bu)(NCO)]<sub>2</sub>O were synthesized by the vapor phase hydrolysis of MeSi(NCO)<sub>3</sub> or ViSi(NCO)<sub>3</sub> followed by alcoholysis using *t*-butyl alcohol in the presence of triethylamine. The hydrolysis of [MeSi(*t*-OBu)(NCO)]<sub>2</sub>O and [ViSi(*Ot*-Bu)(NCO)]<sub>2</sub>O in the presence of triethylamine in THF followed by recrystallization of the hydrolyzate using pentane produced the corresponding disiloxane-1,3-diols **1** and **2** as white solids in the yield of 78% and 63%, respectively (Eq. (1)). The recrystallization of **1** and **2** by a solvent evaporation method using pentane produced a single crystal of a colorless plate **1** and needle **2**, respectively.

The hydrolysis of [PhSiCl<sub>2</sub>]<sub>2</sub>O, which was synthesized by the vapor phase hydrolysis of PhSiCl<sub>3</sub>, in the presence of aniline in Et<sub>2</sub>O followed by recrystallization in Et<sub>2</sub>O/hexane produced the 1,3-diphenyldisiloxane-1,1,3,3-tetraol **3** in 76% yield as a white solid (Eq. (2)).

Thermal gravimetric analyses of the disiloxanepolyols in air showed that **1** and **2** melted at 79 °C and 76 °C, and then rapidly vaporized above 145 °C and 147 °C, respectively. In addition, the weight loss due to the condensation of the silanol groups followed by water elimination was not observed during the thermal gravimetry. On the other hand, **3** showed a weight loss in the two stages from at 120–250 °C due to thermal condensation (12%), and at 500–800 °C due to the thermal decomposition of the condensed products (55%), which are almost identical to that of silanetriol PhSi(OH)<sub>3</sub>: 100–200 °C and 400–700 °C [23]. Although the thermal condensation of **3** took place at the same temperature as that of PhSi(OH)<sub>3</sub>, **3** was decomposed at a higher temperature above 100 °C compared to PhSi(OH)<sub>3</sub>.



In order to investigate the reactivity of the disiloxanepolyols, the reactions with Me<sub>3</sub>SiCl (Eqs. (3) and (4)) were carried out in the presence of triethylamine as an HCl scavenger at room temperature or under reflux in THF and monitored by gas chromatography. The reaction of **1** and **2** with Me<sub>3</sub>SiCl at room temperature gave a mixture of mono- and di-substituted products. In contrast, the reaction under reflux gave the corresponding di-substituted products, the 3,5-di-*t*-butoxy-1,1,1,7,7,7-hexamethyl-3,5-di-R substituted tetrasiloxanes **4** (R = Me) and **5** (R = Vinyl), respectively, via the mono-substituted products. They were purified by distillation as a colorless liquid in 80% yield for **4** (83–85 °C/2.0 mmHg) and 70% yield for **5** (111–112 °C/2.0 mmHg). Similarly, **3** gave 1,1,3,3-tetra-trimethylsiloxy-1,3-diphenyldisiloxane **6** when all four hydroxyl groups of **3** were silylated. Compound **6** was isolated as a colorless liquid in 80% yield using Kugel-Rohr distillation apparatus. Consequently, these results prove that the disiloxanepolyols can be used as a building block for the formation of novel siloxane compounds.

### 2.2. Crystal and molecular structure of 1,3-di-*t*-butoxy-1,3-di-R substituted disiloxane-1,3-diols **1** (R = Me) and **2** (R = Vinyl)

The molecular structure of **1** is shown in Fig. 1. The molecule **1** was crystallized in the triclinic system *P* $\bar{1}$  with two independent molecules in the asymmetric units with a meso body. The average bond lengths and angles were 1.63 Å for Si–O(Si), 1.64 Å for Si–O(H), 145.7° for

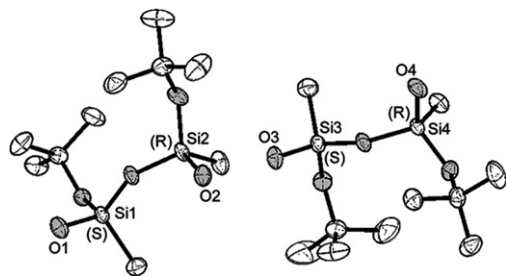


Fig. 1. Molecular structure of **1**. Thermal ellipsoids shown at 50% probability level. Hydrogen atoms are omitted for clarity.

Si–O–Si, and  $105.0^\circ$  for O–Si–O(H), respectively. These bond lengths and angles are comparable to those found in the conventional disiloxanepolyols [3]. The hydrogen-bonded network structure and packing diagram of **1** are shown in Fig. 2. Two independent molecules of **1** interact with each other by the intermolecular hydrogen bonds O(1)–O(4) and O(2)–O(3) to form the chains which are further linked by hydrogen bonds O(1)–O(3), O(2)–O(2'), and O(4)–O(4') to form the double chains as shown in Fig. 2a. All the hydroxyl groups were not used for the intramolecular bonds but intermolecular hydrogen bonds. The average O–O bond lengths in their hydrogen bonds were 2.70 Å. This value is similar to that found in the other disiloxane-1,3-diols [3]. The double chains, which are formed by a ladder type hydrogen-bonded network, form a 1.21 nm diameter (calculated by the space-filling model) columnar array; the surface layer of the column is occupied by the *t*-butyl and methyl groups. The columns in the crystal of **1** are packed in the pseudohexagonal mode (Fig. 2b). No hydrogen bonds are observed between the columns. The crystal is, therefore, formed by the hydrophobic interaction between the organic groups.

The molecular structure of **2** is shown in Fig. 3. The molecule **2** crystallizes in the triclinic system  $P\bar{1}$  with four independent molecules in the asymmetric units with the *RR* and *SS* body. The average bond lengths and angles were 1.62 Å for Si–O(Si), 1.63 Å for Si–O(H),  $151.5^\circ$  for Si–O–Si, and  $105.6^\circ$  for O–Si–O(H), respectively. These bond lengths and angles are comparable to those found

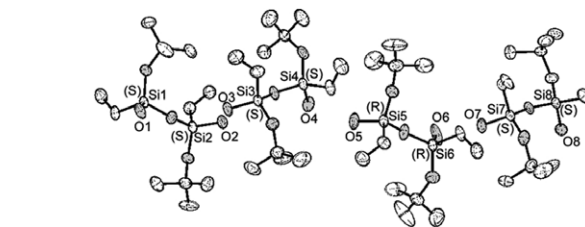
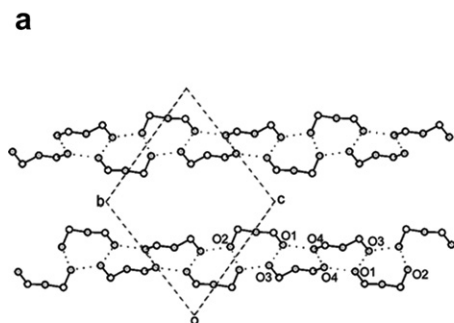


Fig. 3. Molecular structure of **2**. Thermal ellipsoids shown at 50% probability level. Hydrogen atoms are omitted for clarity.

in conventional disiloxanepolyols [3]. The hydrogen-bonded network structure and packing diagram of **2** are shown in Fig. 4. Four independent molecules of **2** interact with each other by the intermolecular hydrogen bonds O(1)–O(8), O(2)–O(3), O(4)–O(5), and O(6)–O(7) to form the chains which are further linked by hydrogen bonds O(1)–O(3), O(2)–O(2'), O(4)–O(8), O(5)–O(7), and O(6)–O(6') to form the double chains as shown in Fig. 4a. All the hydroxyl groups are used for the not intramolecular bonds, but for the intermolecular hydrogen bonds. The average O–O bond lengths in their hydrogen bonds were 2.68 Å. This value is similar to that found in other disiloxane-1,3-diols [3]. As well as **1**, the double chains, which are formed by the ladder type hydrogen-bonded network, also have a 1.21 nm diameter (calculated by the space-filling model) columnar array; the surface layer of the column is formed by the *t*-butyl and vinyl groups. The columns in the crystal of **2** are packed in a pseudohexagonal mode (Fig. 4b). There are no hydrogen bonds between the columns. This crystal was, therefore, formed by the hydrophobic interaction between the organic groups.

The formation of the columnar array by the ladder-type hydrogen-bonded network of the silanol groups have been reported for  $[R_2Si(OH)]_2O$  ( $R = \text{Me, Et, Pr, Ph}$ ) [3]. The columnar array of these disiloxane-1,3-diols are also packed in the pseudohexagonal mode. In these disiloxane-1,3-diols, it was reported that the average O–O bond lengths for the hydrogen bonds of  $[Et_2Si(OH)]_2O$  [9] and  $[Pr_2Si(OH)]_2O$  [10] are 2.73 Å and 2.70 Å, respectively, and the diameters of their columnar array are 1.06 nm

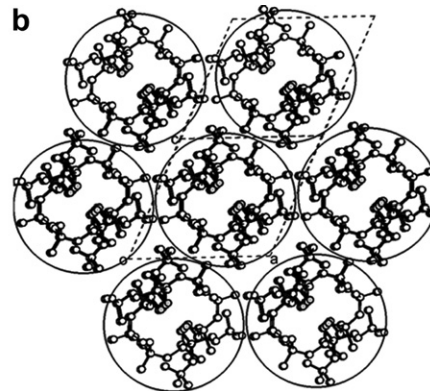


Fig. 2. Ladder like hydrogen-bonded structure with methyl and *t*-butoxy groups omitted for clarity (a) of disiloxane-1,3-diol **1** that are arranged to form pseudo-hexagonal array with hydrogen atoms omitted for clarity (b). Dashed lines represent intermolecular hydrogen bonds.

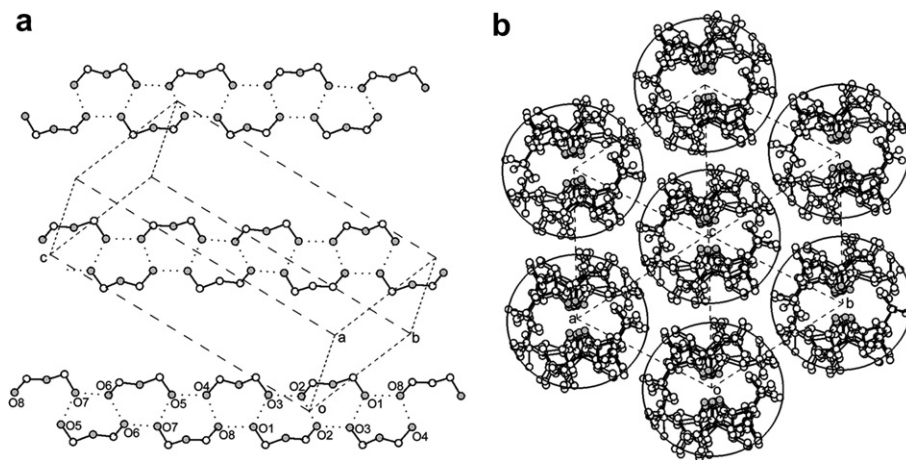


Fig. 4. Ladder like hydrogen-bonded structure with vinyl and *t*-butoxy groups omitted for clarity (a) of disiloxane-1,3-diol (**2**) that are arranged to form pseudo-hexagonal array with hydrogen atoms omitted for clarity (b). Dashed lines represent intermolecular hydrogen bonds.

and 1.26 nm, respectively. In contrast, the average O–O bond lengths for the hydrogen bonds of **1** and **2** are 2.70 Å and 2.68 Å, respectively, and both of the diameters of their columnar array are 1.21 nm. Therefore, the size of the columnar array is dependent of the substituents attached to the silicon atoms rather than the strength of the hydrogen bonds. [Et<sub>2</sub>Si(OH)<sub>2</sub>]<sub>2</sub>O and [Pr<sub>2</sub>Si(OH)<sub>2</sub>]<sub>2</sub>O have been found to be a liquid crystal due to their crystal structure. Thus far, the crystal structure of disiloxane-1,3-diol with alkyl and alkoxy groups has not been reported. The results that **1** and **2** form a columnar array as well as the above 1,1,3,3-tetraalkyldisiloxane-1,3-diol can be an interesting target for not only supramolecular organosilicon chemistry, but also liquid crystal chemistry.

### 2.3. Crystal and molecular structure of 1,3-diphenyldisiloxane-1,1,3,3-tetraol (**3**)

Single crystals of **3** were obtained by recrystallization with Et<sub>2</sub>O (a) and using the solvent evaporation method with Et<sub>2</sub>O (b). As shown in Fig. 5, X-ray crystallography of each crystal showed their conformations; the phenyl groups are arranged in a *gauche*-conformation (a) and *anti*-conformation (b). The space groups of the *gauche*- and *anti*-types were found to be monoclinic *C2/c* and mono-

clinic *P2<sub>1</sub>/n*, respectively. The Si–O–Si bond angles of the *gauche*-type and *anti*-type were 168.5° and 153.7°, respectively. The average O–O bond lengths of their hydrogen bond were 2.72 Å in the *gauche*-type and 2.68 Å in the *anti*-type. These values are similar to those found in other disiloxane-1,1,3,3-tetraols [3,17,18]. The difference between the *gauche*-type and *anti*-type is influenced by the difference in the types of their hydrogen-bonded networks. All the hydroxyl groups in both of them were used not as intramolecular, but as intermolecular hydrogen bonds. In the case of [*t*-BuSi(OH)<sub>2</sub>]<sub>2</sub>O, there are no intramolecular hydrogen bonds and the Si–O–Si linkage becomes linear (bond angle of Si–O–Si is 180°) [16]. In contrast, the molecular structures of [(*t*-BuO)<sub>3</sub>SiOSi(OH)<sub>2</sub>]<sub>2</sub>O [18] and [2,6-*i*-PrC<sub>6</sub>H<sub>3</sub>N(SiMe<sub>3</sub>)Si(OH)<sub>2</sub>]<sub>2</sub>O [19] contain intramolecular hydrogen bonds, which appear to distort the silicon–oxygen backbone linkage into a parabolic shape, and their Si–O–Si bonds are bent to 140°, respectively. The X-ray crystallography additionally shows the difference in the molecular array of the crystal between the *gauche*- and *anti*-types and also between the disiloxane-1,3-diols **1** and **2**.

The molecules of the *gauche*-type **3** are arranged in a ladder shape along the *b* axis by the intermolecular hydrogen bonds O(1)–O(2) and O(3)–O(4), and the intermolecular  $\pi$ – $\pi$  interaction between phenyl groups (Fig. 6a). The ladder chains interact due to the hydrogen bond O(1)–O(3) and O(4)–O(4') to form a columnar array (Fig. 6b) which is further linked by the hydrogen bond O(2)–O(2') in a parallel array; the surface layer of the column is occupied by the phenyl groups (Fig. 6c and d). Consequently, the crystal of the *gauche*-type is formed by the hydrogen bond between the columns and the hydrophobic interaction of the phenyl groups. As shown in Fig. 7a, the multiple intermolecular hydrogen bonds are also present in the *anti*-type **3**, resulting in the molecular assembly into a sheet-like structure in the *ac* plane in contrast to the columnar array of the *gauche*-type. In this sheet, although the surface layer is formed by the phenyl groups, there are no intermolecular  $\pi$ – $\pi$  interactions between the phenyl groups. Similarly,

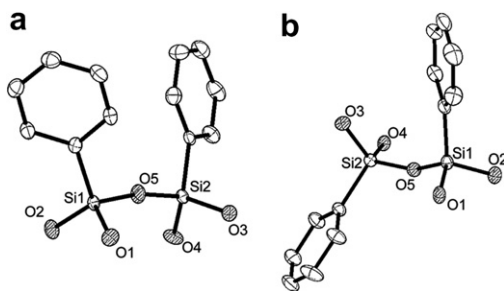


Fig. 5. Molecular structure of **3**: (a) *gauche* type, (b) *anti* type. Thermal ellipsoids are drawing at the 50% probability level. Hydrogen atoms are omitted for clarity.

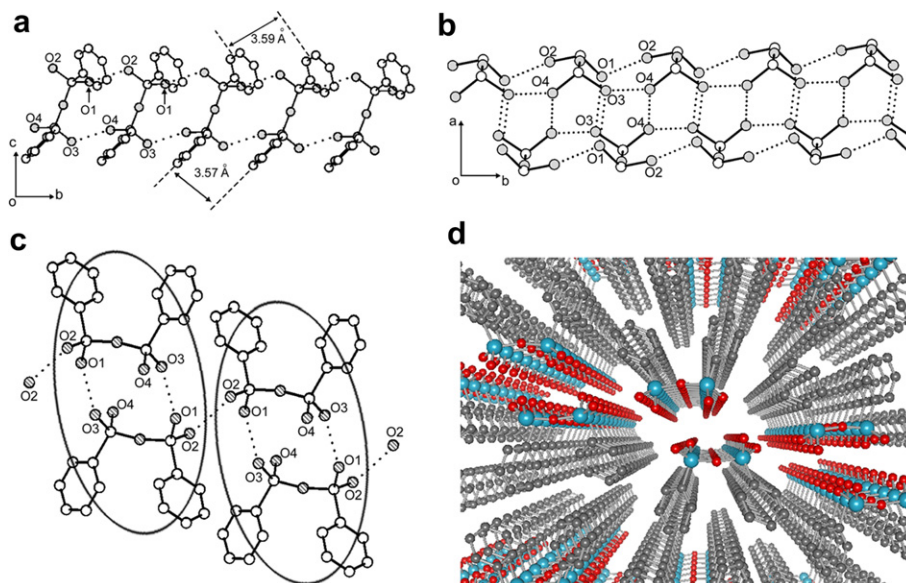


Fig. 6. Ladder like hydrogen-bonded structure (a) of *gauche* type 3 that are linked to form the columnar array (b) with phenyl groups are omitted for clarity. The columnar array in a circle linked each other by O(2)–O(2') hydrogen bond (c) and formed the three-dimensional hydrogen-bonded network (d): view down *b* axis, i.e. perpendicular to *ac* plane, Si, O, and C atoms are represented as cyan, red, and gray, respectively. Dashed lines represent intermolecular hydrogen bonds. Hydrogen atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

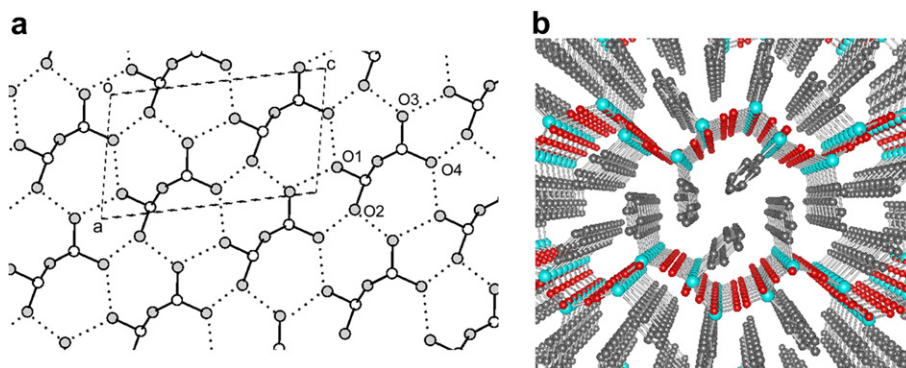


Fig. 7. The hydrogen-bonded structure of *anti* type 3 (a) with hydrogen atoms and phenyl groups are omitted for clarity that are linked to form the two-dimensional wavy sheet (b): view down *a* axis, i.e. perpendicular to *bc* plane, Si, O, and C atoms are represented as cyan, red, and gray, respectively. Dashed lines represent intermolecular hydrogen bonds. Hydrogen atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$[t\text{-BuSi}(\text{OH})_2]_2\text{O}$  with an *anti*-configuration was arranged by the hydrogen bond to form a sheet-like structure [17]. Though the surface layer consists of *t*-butyl groups, there are no interactions between the sheets. The sheets were flat planes due to the linear Si–O–Si backbone linkage. However, the sheets formed by the *anti*-type 3 have a curvature due to the bent Si–O–Si backbone linkage (Fig. 7b). In the crystal of the *anti*-type 3, stacking of the overlapped phenyl groups, but no hydrogen bonds between the sheets are observed. As a result, the type of hydrogen bond in the crystal of 3 varies with the conformation of the phenyl groups which is affected by the recrystallization method. No reports have been published that the conformation of the disiloxane-1,1,3,3-tetraols varies with the recrystallization method. This may be considered as follows: (a) in a dilute solution of diethyl ether, a hydrophobic atmosphere,

molecules are assembled very slowly in the manner that the hydrophobic groups surround the hydrophilic silanol groups inside to form a columnar array. (b) In solvent evaporation method, the fast crystallization and thereby the formation of the hydrogen bonds preferentially proceeds before the inclusion of the hydrophilics by the hydrophobics so that the molecules with an *anti*-configuration consequently form a sheet-like molecular array.

### 3. Experimental

#### 3.1. Reagents and general techniques

All chemicals were of reagent grade or higher and purified according to standard protocols. 1,1,3,3-Tetraiso-cyanato-1,3-dimethyldisiloxane, 1,1,3,3-tetraiso-cyanato-1,

3-divinylidisiloxane, and 1,1,3,3-tetrachloro-1,3-diphenyldisiloxane were prepared according to the literature [21]. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were recorded using a JEOL ECP-500 ( $^1\text{H}$  at 500.00 MHz,  $^{13}\text{C}$  at 125.00 MHz, and  $^{29}\text{Si}$  at 99.00 MHz) spectrometer. Chemical shifts were reported as  $\delta$  units (ppm) relative to  $\text{SiMe}_4$ , and the residual solvent peaks were used as the standard. The Fourier transform infrared (FTIR) spectra were measured using a JEOL FT-IR-400 IR spectrophotometer using the KBr disk method and  $\text{CCl}_4$  solution method. The mass spectra (70 eV, EI) were obtained using a Shimadzu GCMS-QP2000A equipped with a direct insertion apparatus. The mass spectra (FAB) were obtained on a JEOL JMS-700 spectrometer. The thermal gravimetric analyses were carried out with a 10 mg sample at the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  in air using a TG-DTA 2000S from a Bruker AXS. The silicon content was determined by the following procedure: the weighed sample (0.2 g) was mixed in a flask mixed with sulfuric acid (20 mL). Into this mixture, ammonium sulfate (1 g) was added and gently heated for 6 h. After cooling to room temperature, the content was poured into ice in a beaker. After filtration using ashless filter paper, the residue and filter paper were subjected to firing in a crucible, then weighed as silica,  $\text{SiO}_2$ .

### 3.2. X-ray crystallography

A single crystal was attached to the top of a glass fiber with a cold nitrogen gas stream at 90 K, and measured using a Bruker SMART APEX equipped with a CCD diffractometer ( $\lambda(\text{Mo K}\alpha) = 0.71073\text{ \AA}$ ,  $25 \pm 2\text{ }^\circ\text{C}$ ). The structure was solved by SHELXL-97 [24] and refined by a

full-matrix least squares technique. The non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are given in Table 1. Figs. 6d and 7b were created using VICS-II developed by R.A. Dilanian and F. Izumi.

### 3.3. Synthesis of 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-dimethylidisiloxane

A solution of *t*-butyl alcohol (2.96 g, 0.04 mol) and triethylamine (0.40 g, 0.004 mol) in THF (50 mL) was slowly added to a vigorously stirred and ice-cooled ( $0\text{ }^\circ\text{C}$ ) solution of 1,1,3,3-tetraisocyanato-1,3-dimethylidisiloxane (5.43 g, 0.02 mol) in THF (30 mL). The reaction mixture was refluxed for 2 h and filtered, followed by distillation to give 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-dimethylidisiloxane (4.6 g, 70%). B.p.  $92.0\text{--}92.5\text{ }^\circ\text{C}/2.0\text{ mmHg}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.26 (s, 6H), 1.34 (m, 18H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-0.40$ , 31.5, 74.8, 123.1 ppm;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-62.3$  ppm; MS (70 eV)  $m/z$  317 ( $\text{M}^+ - 15$ ); IR ( $\text{CCl}_4$ ): 2980, 2280, 1270, 1080  $\text{cm}^{-1}$ .

### 3.4. Synthesis of 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-divinylidisiloxane

A solution of *t*-butyl alcohol (1.85 g, 0.025 mol) and triethylamine (0.20 g, 0.002 mol) in THF (50 mL) was added to a vigorously stirred and ice-cooled ( $0\text{ }^\circ\text{C}$ ) solution of 1,1,3,3-tetraisocyanato-1,3-divinylidisiloxane (2.94 g, 0.01

Table 1  
Crystallographic data for 1–3

| Compound                                | 1   | 2   | 3 ( <i>gauche</i> )                               | 3 ( <i>anti</i> )                                 |
|---|---|---|---|---|
| Formula                                 | $\text{C}_{10}\text{H}_{26}\text{O}_5\text{Si}_2$ | $\text{C}_{12}\text{H}_{26}\text{O}_5\text{Si}_2$ | $\text{C}_{12}\text{H}_{14}\text{O}_5\text{Si}_2$ | $\text{C}_{12}\text{H}_{26}\text{O}_5\text{Si}_2$ |
| Mol. wt                                 | 282.49  | 306.50  | 294.41  | 294.41  |
| Temperature $^\circ\text{C}$            | $-180$  | $-180$  | $-180$  | $-180$  |
| Crystal size (mm)                       | $0.05 \times 0.14 \times 0.46$                    | $0.02 \times 0.07 \times 0.17$                    | $0.10 \times 0.40 \times 0.50$                    | $0.20 \times 0.20 \times 0.28$                    |
| Crystal system                          | Triclinic   | Triclinic   | Monoclinic  | Monoclinic  |
| Space group                             | $P\bar{1}$  | $P\bar{1}$  | $C2/c$  | $P2_1/n$  |
| $a$ ( $\text{\AA}$ )                    | 11.7896(9)  | 12.0548 (15)                                      | 30.6927(16)                                       | 6.1142(19)  |
| $b$ ( $\text{\AA}$ )                    | 12.8225(10)                                       | 13.4814 (17)                                      | 4.9784(3)   | 21.376(7)   |
| $c$ ( $\text{\AA}$ )                    | 13.1771(11)                                       | 23.070 (3)  | 19.7723(10)                                       | 10.622(3)   |
| $\alpha$ ( $^\circ$ )                   | 68.6310(10)                                       | 99.754 (2)  |   |   |
| $\beta$ ( $^\circ$ )                    | 64.8450(10)                                       | 90.093 (2)  | 111.7520(10)                                      | 101.575(5)  |
| $\gamma$ ( $^\circ$ )                   | 74.6440(10)                                       | 107.879(2)  |   |   |
| $V$ ( $\text{\AA}^3$ )                  | 1664.8(2)   | 3510.9(9)   | 2806.1(3)   | 1360.0(7)   |
| $Z$                                     | 2   | 2   | 8   | 4   |
| $D_{\text{calc}}$ ( $\text{g m}^{-3}$ ) | 1.127   | 1.160   | 1.394   | 1.438   |
| $\mu$ ( $\text{mm}^{-1}$ )              | 0.220   | 0.213   | 0.265   | 0.273   |
| $2\theta_{\text{max}}$ ( $^\circ$ )     | 55.74   | 55.76   | 56.62   | 56.46   |
| Number of reflections measured          | 7830  | 15781   | 3493  | 3053  |
| Number of observed reflections          | 6774  | 8357  | 3175  | 2507  |
| Number of parameters                    | 355   | 779   | 176   | 172   |
| $S$                                     | 1.022   | 1.023   | 1.081   | 1.033   |
| $R_1$ ( $I > 2\sigma(I)$ )              | 0.0373  | 0.0624  | 0.0421  | 0.0656  |
| $wR_2$ (all reflections)                | 0.1052  | 0.1774  | 0.1259  | 0.2022  |

mol) in THF (20 mL). The reaction mixture was refluxed for 2 h and filtered, followed by distillation to give 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-divinyldisiloxane (2.1 g, 59%). B.p. 100–102 °C/2.0 mmHg;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.30 (s, 18H), 5.89 (m, 4H), 6.10 (m, 4H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -0.40, 31.5, 75.8, 123.1, 130.4, 136.5 ppm;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -76.5 ppm; MS (70 eV)  $m/z$  341 ( $\text{M}^+ - 15$ ); IR ( $\text{CCl}_4$ ) 2980, 2280, 1076, 1020  $\text{cm}^{-1}$ .

### 3.5. Synthesis of 1,3-di-*t*-butoxy-1,3-dimethyldisiloxane-1,3-diol (**1**)

A solution of water (0.72 g, 0.04 mol) and triethylamine (4.04 g, 0.04 mol) in THF (100 mL) was added to a rapidly stirred cold (0 °C) solution of 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane (6.64 g 0.02 mol) in THF (30 mL), and the mixture was refluxed for 2 h, filtered, and evaporated to give the crude **1**. Recrystallization from pentane (50 mL) afforded the pure **1** (4.3 g, 78%). M.p. 78–79 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.18 (s, 6H), 1.33 (s, 18H), 4.40 (br, 2H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -1.95, 31.6, 73.0 ppm;  $^{29}\text{Si}$  NMR (79.3 MHz,  $\text{CDCl}_3$ )  $\delta$  -53.1 ppm; MS  $m/z$  = 267 ( $\text{M}^+ - 15$ ); IR (KBr) 3250, 2980, 1280, 1060, 1020  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{10}\text{H}_{26}\text{O}_5\text{Si}_2$ : Si, 19.9. Found: Si, 19.9%.

### 3.6. Syntheses of 1,3-di-*t*-butoxy-1,3-divinyldisiloxane-1,3-diol (**2**)

A solution of water (0.90 g, 0.05 mol) and triethylamine (5.05 g, 0.05 mol) in THF (100 mL) was added to a rapidly stirred cold (0 °C) solution of 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-divinyldisiloxane (8.90 g 0.025 mol) in THF (30 mL), and the mixture was refluxed for 2 h, filtered, and evaporated to give the crude **2**. Recrystallization from hexane (50 mL) afforded the pure **2** (4.9 g, 63%). M.p. 76–78 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (s, 18H), 3.84 (s, 2H), 5.97 (m, 4H), 6.10 (m, 2H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  31.7, 73.6, 132.7, 135.4 ppm;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -67.9 ppm; MS  $m/z$  = 294 ( $\text{M}^+ - 15$ ); IR (KBr) 3220, 2977, 1241, 1062, 964  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{12}\text{H}_{26}\text{O}_5\text{Si}_2$ : Si, 18.3. Found: Si, 18.5%.

### 3.7. Synthesis of 1,3-diphenyldisiloxane-1,1,3,3-tetrol (**3**)

A solution of 1,1,3,3-tetrachloro-1,3-diphenyldisiloxane (7.36 g, 0.02 mol) in diethyl ether (40 mL) was added to a suspension of water (1.44 g, 0.08 mol) and aniline (7.44 g, 0.08 mol) while stirring at 0 °C and kept for 1 h. The reaction mixture was filtered to remove the aniline hydrochloride. Recrystallization of the filtrate from hexane (40 mL) afforded **3** (4.5 g, 76%). M.p. 114–115 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.81 (br, 4H), 7.20–7.72 (m, 10H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  127.7, 129.7, 135.1, 136.9 ppm;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -62.1 ppm; IR (KBr) 3200, 1429, 1110, 911  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{12}\text{H}_{14}\text{O}_5\text{Si}_2$ : Si, 19.0. Found: Si, 19.1%.

### 3.8. Synthesis of 3,5-di-*t*-butoxy-1,1,1,3,5,7,7,7-octamethyltetrasiloxane (**4**)

A solution of  $\text{Me}_3\text{SiCl}$  (2.72 g, 0.025 mol) in THF (30 mL) was added to a rapidly stirred cold (0 °C) solution of **1** (2.82 g 0.01 mol) and triethylamine (2.53 g, 0.025 mol) in THF (30 mL), and the mixture was refluxed for 1 h, filtered, and evaporated to give the crude **4**, followed by distillation to give **4** (3.40 g, 80%). B.p. 83.0–85.0 °C/2.0 mmHg;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.04 (s, 6H), 0.10 (s, 18H), 1.27 (s, 18H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -1.2, 1.7, 31.7, 72.3 ppm;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.6, -64.0 ppm; MS (FAB+)  $m/z$  = 427 [ $\text{M} + \text{H}$ ] $^+$ . Exact mass: calcd for  $\text{C}_{16}\text{H}_{43}\text{O}_5\text{Si}_4$ : 427.2188, Found 427.2205; IR ( $\text{CCl}_4$ ) 2975, 1549, 1252, 1204, 1061  $\text{cm}^{-1}$ .

### 3.9. Synthesis of 3,5-di-*t*-butoxy-1,1,1,7,7,7-hexamethyl-3,5-divinyldisiloxane (**5**)

A solution of  $\text{Me}_3\text{SiCl}$  (2.72 g, 0.025 mol) in THF (30 mL) was added to a rapidly stirred cold (0 °C) solution of **2** (3.06 g 0.01 mol) and triethylamine (2.53 g, 0.025 mol) in THF (30 mL), and the mixture was refluxed for 1 h, filtered, and evaporated to give the crude **5**, followed by distillation to give **5** (3.15 g, 70%). B.p. 111–112 °C/2.0 mmHg;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.12 (s, 18H), 1.29 (s, 18H), 5.89–5.93 (m, 6) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.7, 31.7, 72.5, 133.6, 134.5 ppm;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.3, -79.1 ppm; MS (FAB+)  $m/z$  = 451 [ $\text{M} + \text{H}$ ] $^+$ . Exact mass: calcd for  $\text{C}_{18}\text{H}_{43}\text{O}_5\text{Si}_4$ : 451.2188, Found: 451.2174; IR ( $\text{CCl}_4$ ) 2976, 1549, 1404, 1365, 1251, 1202, 1066  $\text{cm}^{-1}$ .

### 3.10. Synthesis of 1,1,3,3-hexamethyl-3,5-diphenyl-3,5-bis(trimethylsiloxy)tetrasiloxane (**6**)

A solution of  $\text{Me}_3\text{SiCl}$  (5.44 g, 0.05 mol) in THF (30 mL) was added to a rapidly stirred cold (0 °C) solution of **3** (2.94 g 0.01 mol) and triethylamine (5.06 g, 0.05 mol) in THF (30 mL), and the mixture was refluxed for 1 h, filtered, and evaporated to give the crude **6**, followed by distillation to give **6** (5.1 g, 89%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.13 (s, 18 H), 7.33–7.68 (m, 5H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.7, 127–134.9 ppm;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$  9.6, -79.2 ppm; MS (FAB+)  $m/z$  = 582 [ $\text{M}$ ] $^+$ . Exact mass: calcd for  $\text{C}_{24}\text{H}_{46}\text{O}_5\text{Si}_6$ : 582.1961, Found 582.1957; IR ( $\text{CCl}_4$ ) 3074, 2959, 1429, 1252, 1132, 1059, 845  $\text{cm}^{-1}$ .

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## Appendix A. Supplementary material

CCDC 630785, 630786, 236204, and 630787 contain the supplementary crystallographic data for **1**, **2**, *gauche-3*, *anti-3*. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.01.016](https://doi.org/10.1016/j.jorganchem.2007.01.016).

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