

## Facile syntheses, structural characterizations, and isomerization of disiloxane-1,3-diols

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### Abstract

In the hydrolysis reaction of dichlorosilanes having an intramolecular coordinating atom, disiloxane-1,3-diols,  $[(\text{OH})\{o\text{-(CH}_3)_2\text{NCH}_2\text{-C}_6\text{H}_4\}\text{RSi}]_2\text{O}$  ( $\text{R} = \text{CH}_2=\text{CH}$  (**1**),  $\text{C}_6\text{H}_5$  (**2**),  $o\text{-(CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4$  (**3**),  $\text{Me}$  (**4**)), were obtained in high yields. The results of the crystal structure analyses of *meso*-**2**, *rac*-**2a**, *rac*-**2b** and **3** are reported. They showed strong intramolecular hydrogen bondings between the hydroxy group and the nitrogen atom. We have also found that the diastereomeric isomerization of *meso*-**2** to *rac*-**2** in  $\text{CDCl}_3$  solvent containing moisture occurred to result in the 55:45 equilibrium mixtures of the isomers and vice versa.  
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*Keywords:* Silanol; Disilanol; Intramolecular hydrogen bonding; Diastereomer

### 1. Introduction

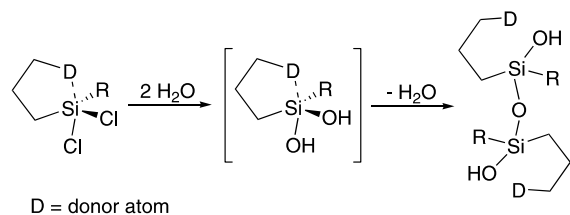
Disiloxane-1,3-diols are known as primary sources for the support of metal complexes within metal-siloxanes, and for the preparation of polysiloxanes and heterosiloxanes [1]. A variety of disiloxane-1,3-diols of general formula  $(\text{OHR}_2\text{Si})_2\text{O}$  ( $\text{R} = \text{Me}$  [2],  $\text{Et}$  [3],  $\text{Pr}$  [4],  $\text{Bu}$  [4,5] or  $\text{Ph}$  [6]) have been synthesized and structurally investigated. The simplest disiloxane-1,3-diol,  $(\text{OHMe}_2\text{Si})_2\text{O}$ , is one of the basic units from which polydimethylsiloxanes are built.

The syntheses of disiloxane-1,3-diols are not easy because of their tendency to undergo further condensation to polysiloxanes or the tendency not to be condensed from silanediols because of the size or the electronic effect of substituents at silicon atom [1b]. Many trials and errors are needed to obtain disiloxane-1,3-diols without silanediols and without further condensed silanols. Various reaction conditions such as reaction temperature, reaction time, hydrolysis reagent,

solvent, and substituent should be considered. For example,  $\text{O}(\text{Ph}_2\text{SiOH})_2$  was synthesized using pH controlled hydrolysis of  $\text{Ph}_2\text{SiCl}_2$  [7]. The reaction of dichlorodiphenylsilane (1.0 mol) with water (108 mol) and ammonium carbonate (1.4 mol) for 2.5 h gave diphenylsilanediol, while the mixture of dichlorodiphenylsilane (1.5 mol), water (1.5 mol), and ammonium carbonate (2.1 mol) in diethylether was heated at reflux for 12 h to yield tetraphenyldisiloxane-1,3-diol and hexaphenyltrisiloxane-1,5-diol. Recently, we synthesized the diastereomeric disiloxane-1,3-diols, 1,3-dihydroxy-1,3-bis[2-(dimethylaminomethyl)phenyl]-1,3-divinyldisiloxanes, **1**, in high yield from the hydrolysis reaction of [2-(dimethylaminomethyl)phenyl]vinylchlorosilane having an intramolecular coordinating arm [8]. In an extension of this work, we have investigated a new synthetic method of disiloxane-1,3-diols devoid of usual tedious processes. An introduction of intramolecular donor atom provides a convenient way to synthesize disiloxane-1,3-diols. In the hydrolysis reaction of dichlorosilanes having intramolecular coordinating atoms, silanediols might be formed first as an intermediate, which could be partially condensed to give disiloxane-1,3-diols because of the enhancement of the reactivity of

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Scheme 1.

the hydroxy group opposite to donor atoms caused by the intramolecular electron donation from donor atoms to silicon (Scheme 1) [9].

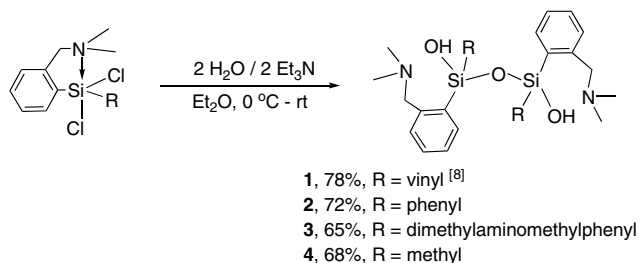
Herein, we report on the syntheses, detailed structural characterizations, and the water-induced diastereomeric isomerization of  $[(\text{OH})o\text{-(CH}_3)_2\text{NCH}_2\text{-C}_6\text{H}_4\text{RSi}]_2\text{O}$  ( $\text{R} = \text{C}_6\text{H}_5$  (**2**),  $o\text{-(CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4$  (**3**), Me (**4**)).

## 2. Results and discussion

### 2.1. Syntheses of **2**, **3** and **4**

An introduction of (dimethylaminomethyl)phenyl group into the silicon center was achieved by the reaction of *ortho*-lithiated (dimethylaminomethyl)phenyl with  $\text{Cl}_3\text{RSi}$ . The reaction of [2-(dimethylaminomethyl)phenyl]phenyldichlorosilane [10] with 2 equiv of water in the presence of triethylamine, as an acid acceptor, at room temperature for 1 h afforded diastereomeric isomers, 1,3-dihydroxy-1,3-bis[2-(dimethylaminomethyl)phenyl]-1,3-diphenyldisiloxane, **2**, as crystalline in 72% isolated yield. *Meso-2* was recrystallized from diethylether at room temperature. Interestingly, *rac-2a* was recrystallized from the mixture of *n*-hexane and methylenechloride at room temperature, and *rac-2b*, which is the conformational isomer of *rac-2a*, was recrystallized from diethylether at  $-30^\circ\text{C}$  (Scheme 2).

In the  $^1\text{H}$  NMR spectra of **2**, the broad proton absorption of the hydroxy group resonated at 10.37 ppm similar to those (9.98 and 9.90 ppm) of diastereomeric isomers, **1**. This data indicates that **2** has a very strong intramolecular hydrogen bonding in solution. In contrast, the  $^1\text{H}$  NMR resonance of OH for silanols having intermolecular hydrogen bonding appeared at 2.66 ppm

Scheme 2. Syntheses of **1-4**.

$[\text{O}(\text{Si}(\text{ferrocenyl})_2\text{OH})_2]$  [11], 5.67 ppm  $[\text{Cp}^*\text{Si}(\text{OH})_3]$  [12], and 4.30–5.30 ppm (aminosilanetriols) [13].

The reaction of bis[2-(dimethylaminomethyl)phenyl]dichlorosilane [10,14] with 2 equiv of water in the presence of triethylamine at room temperature for 1 h gave 1,3-dihydroxy-1,1,3,3-tetrakis[2-(dimethylaminomethyl)phenyl]disiloxane, **3**, to be recrystallized from *n*-hexane. The  $^1\text{H}$  NMR resonance of hydroxy group for **3** was observed at 9.98 ppm. The similar reaction was carried out in the absence of an acid acceptor by Auner et al. [15] to give disiloxane-1,3-diol's salt, **3**·2HCl recrystallized from *n*-pentane. Belzner [16] also synthe-

Table 1  
 $^1\text{H}$  NMR of OH ( $\text{CDCl}_3$ , ppm, rt)

	<i>meso-1</i>	<i>rac-1</i>	<i>meso-2</i>	<i>rac-2</i>	<b>3</b>	<b>4</b>
OH	9.90	9.98	10.37	10.37	9.98	9.53

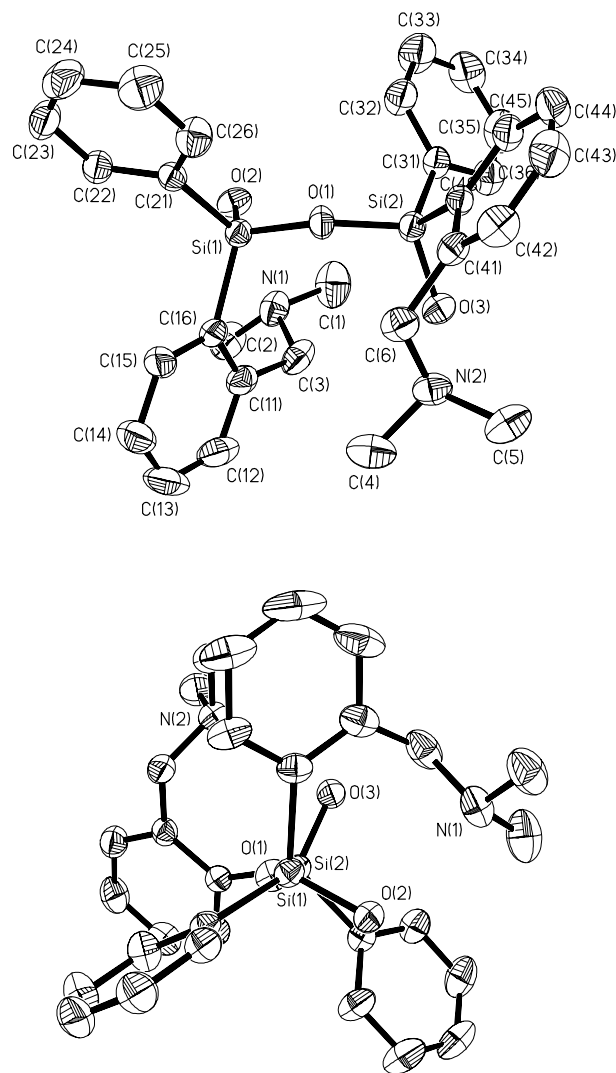


Fig. 1. ORTEP drawing of *meso-2*, showing with 30% thermal ellipsoids. H atoms are omitted for clarity.

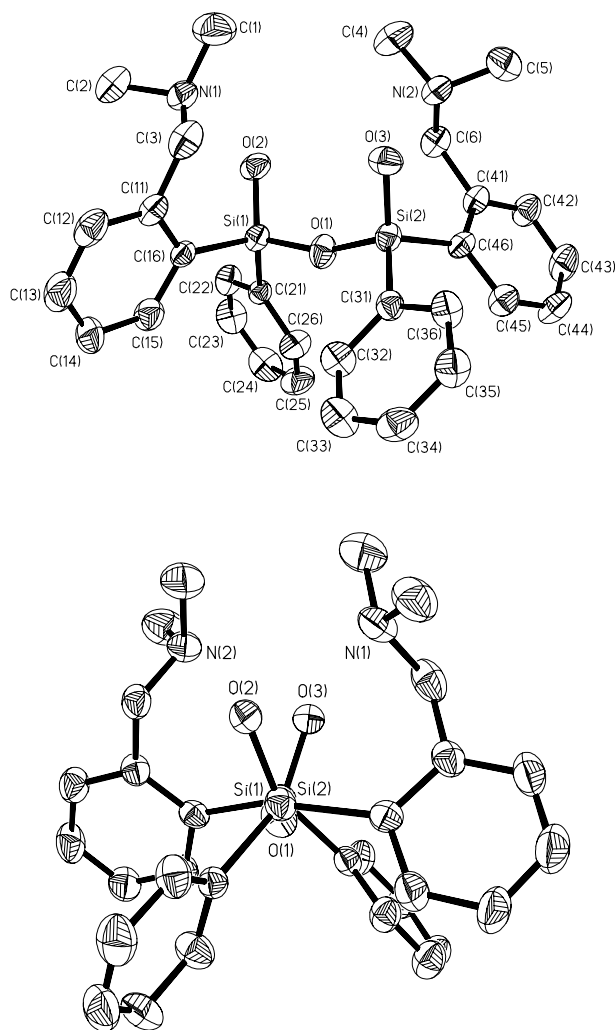


Fig. 2. ORTEP drawing of *rac*-**2a**, showing with 30% thermal ellipsoids. H atoms are omitted for clarity.

sized compound **3** using a different method of the hydrolysis of hexakis[(2-dimethylaminomethyl)phenyl]cyclotrisilane. In manners similar to the synthesis of **2** and **3**, diastereomeric 1,3-dihydroxy-1,3-bis[2-(dimethylaminomethyl)phenyl]-1,3-dimethyl-disiloxanes, **4** were obtained as colorless oil. We were unable to separate isomers (60:40) because of isomerization between them in liquid state. The  $^1\text{H}$  NMR resonance of hydroxy group for **4** was observed at 9.53 ppm. The OH resonances of **2**, **3**, and **4** were not dependent on the concentration of solution in  $\text{CDCl}_3$  (Table 1).

## 2.2. X-ray structures of **2** and **3**

X-ray crystallographic analyses of **2** and **3** reveal their structures, as shown in Figs. 1–4. The Si–O–Si angles ( $152^\circ$ – $159^\circ$ ) of **2** are similar to those of simple disiloxane-1,3-diols,  $\text{O}(\text{SiR}_2\text{OH})_2$  (R = Me [17], Et [18],  $i\text{Pr}$  [19], Phenyl [20]), whose Si–O–Si angles are in the range of  $141^\circ$ – $163^\circ$  (Tables 2 and 3). But the Si–O–Si angle of

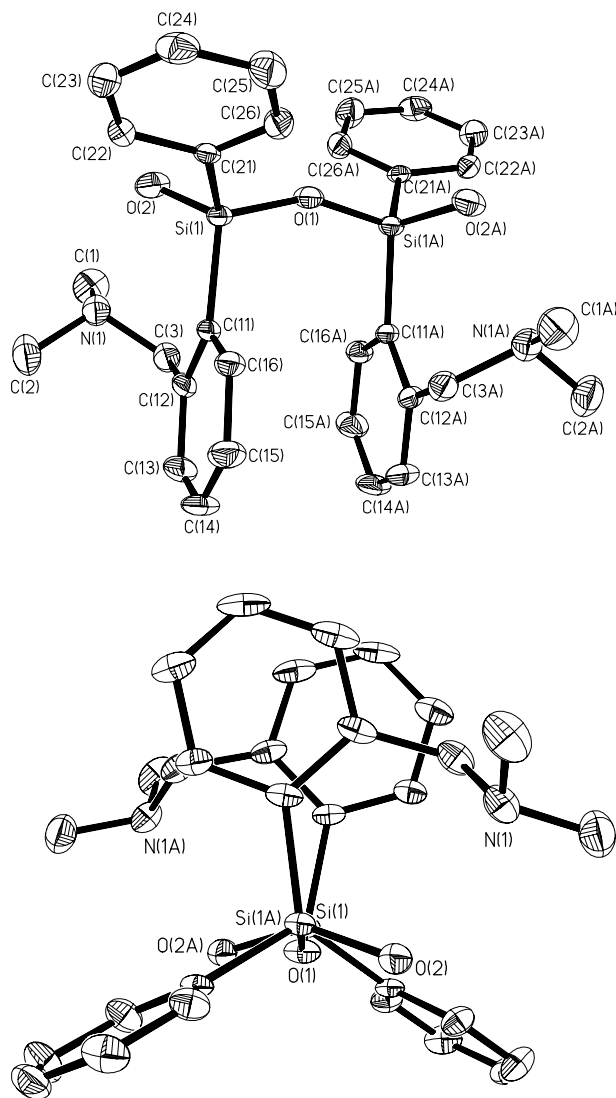


Fig. 3. ORTEP drawing of *rac*-**2b**, showing with 30% thermal ellipsoids. H atoms are omitted for clarity.

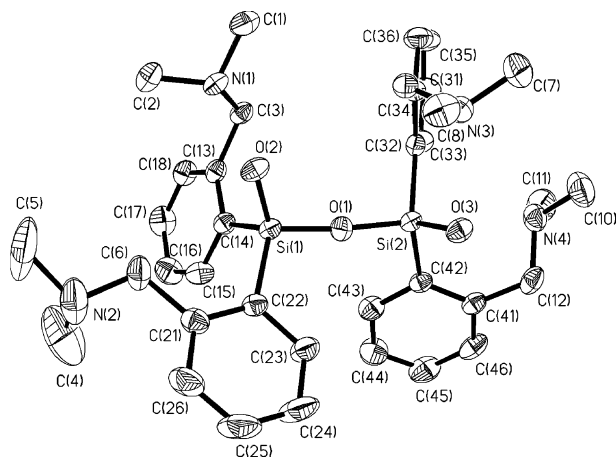


Fig. 4. ORTEP drawing of **3**, showing with 30% thermal ellipsoids. H atoms are omitted for clarity.

Table 2  
Crystal data and structure refinement for *meso-2*, *rac-2a* and *rac-2b*

	<i>meso-2</i>	<i>rac-2a</i>	<i>rac-2b</i>
Empirical formula		C <sub>30</sub> H <sub>36</sub> N <sub>2</sub> O <sub>3</sub> Si <sub>2</sub>	
Formula weight		528.79	
Temperature (K)		233(2)	
Wavelength (Å)		0.71073	
Crystal system	triclinic	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Iba</i> 2
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	9.5536(19)	9.2917(8)	19.212(9)
<i>b</i> (Å)	9.931(2)	11.1847(9)	8.985(4)
<i>c</i> (Å)	15.931(3)	14.6458(12)	16.867(8)
$\alpha$ (°)	86.994(4)	81.124(2)	90
$\beta$ (°)	86.635(4)	84.490(2)	90
$\gamma$ (°)	76.943(4)	85.139(2)	90
Volume (Å <sup>3</sup> )	1468.8(5)	1493.1(2)	2912(2)
<i>Z</i>	2	2	4
Calculated density (Mg/m <sup>3</sup> )	1.196	1.176	1.206
Absolute coefficient (mm <sup>-1</sup> )	0.153	0.151	0.154
<i>F</i> (000)	564	564	1128
Crystal size (mm <sup>3</sup> )	0.52 × 0.24 × 0.18	0.58 × 0.07 × 0.05	0.62 × 0.52 × 0.38
$\theta$ range for data collection (°)	1.28–25.54	1.41–20.00	2.12–25.52
Index ranges	–11 ≤ <i>h</i> ≤ 11, –10 ≤ <i>k</i> ≤ 12, –19 ≤ <i>l</i> ≤ 17	–8 ≤ <i>h</i> ≤ 8, –10 ≤ <i>k</i> ≤ 9, –14 ≤ <i>l</i> ≤ 12	–22 ≤ <i>h</i> ≤ 23, –10 ≤ <i>k</i> ≤ 10, –10 ≤ <i>l</i> ≤ 20
Number of reflections collected	7878	5102	7330
Number of independent reflections ( <i>R</i> <sub>int</sub> )	5418 (0.0281)	2753 (0.0678)	2051 (0.0614)
Completeness to $\theta_{\max}$ (%)	98.7	99.0	100.0
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>		
Number of data/restraints/parameters	5418/1/342	2753/0/478	2051/1/172
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.859	1.021	1.032
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0478, <i>wR</i> <sub>2</sub> = 0.1001	<i>R</i> <sub>1</sub> = 0.0581, <i>wR</i> <sub>2</sub> = 0.1282	<i>R</i> <sub>1</sub> = 0.0484, <i>wR</i> <sub>2</sub> = 0.1216
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1250, <i>wR</i> <sub>2</sub> = 0.1319	<i>R</i> <sub>1</sub> = 0.0937, <i>wR</i> <sub>2</sub> = 0.1505	<i>R</i> <sub>1</sub> = 0.0528, <i>wR</i> <sub>2</sub> = 0.1247

**3** is larger (174.4(2)°). The selected bond distances and angles are listed in Table 4. Noteworthy in the structures of **2** and **3** is the strong intramolecular hydrogen bonding between the hydroxy group and nitrogen atom, in contrast to the intermolecular hydrogen bonding of known disiloxane-1,3-diols [17–21]. In *meso-2*, the O(2)–H(1)–N(1) angle is 172(3)°; the N(1)–H distance is 1.817(18) Å and the N(1)–O(2) distance 2.692(3) Å, which is within the normal distance for hydrogen bonding (2.62–2.93 Å) [22]. Similarly, the N–O distances

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

	<b>3</b>
Empirical formula	C <sub>36</sub> H <sub>50</sub> N <sub>4</sub> O <sub>3</sub> Si <sub>2</sub>
Formula weight	642.98
Temperature (K)	298(2)
Wavelength (Å)	0.71069
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	9.3020(10)
<i>b</i> (Å)	13.878(2)
<i>c</i> (Å)	15.505(2)
$\alpha$ (°)	106.40(2)
$\beta$ (°)	100.200(10)
$\gamma$ (°)	93.020
Volume (Å <sup>3</sup> )	1878.6(4)
<i>Z</i>	2
Calculated density (Mg/m <sup>3</sup> )	1.137
Absolute coefficient (mm <sup>-1</sup> )	0.132
<i>F</i> (000)	692
Crystal size (mm <sup>3</sup> )	0.73 × 0.58 × 0.41
$\theta$ range for data collection (°)	1.54–27.50
Index ranges	–12 ≤ <i>h</i> ≤ 10, –18 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 20
Number of reflections collected	8546
Number of independent reflections ( <i>R</i> <sub>int</sub> )	8546 (0.0000)
Completeness to $\theta_{\max}$ (%)	99.1
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
Number of data/restraints/parameters	8546/0/412
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.125
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0964, <i>wR</i> <sub>2</sub> = 0.1710
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1906, <i>wR</i> <sub>2</sub> = 0.2271

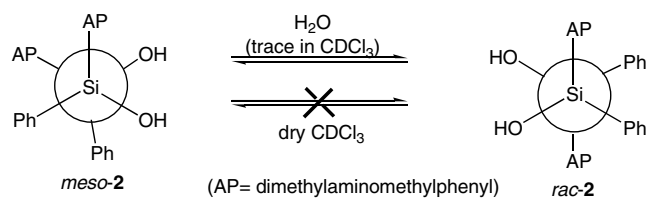
Table 4  
Selected bond distances (Å) and angles (°) for compounds **2** and **3**

	<i>meso-2</i>	<i>rac-2a</i>	<i>rac-2b</i>	<b>3</b>
Si–O of Si–O–Si	1.626(2)	1.618(3)	1.6224(13)	1.617(3)
	1.620(2)	1.610(3)		1.624(3)
Si–O of Si–OH	1.608(2)	1.612(4)	1.618(3)	1.622(3)
	1.617(2)	1.612(4)		1.620(4)
Si–O–Si	152.27(14)	159.3(2)	152.1(2)	174.4(2)
N–O	2.692(3)	2.661(6)	2.651(4)	2.646(5)
	2.745(3)	2.696(7)		2.731(5)
N–H–O	172(3)	166(6)	175(5)	171(6)
	163(3)	160(5)		172(6)
H–O	1.817(18)	1.89(5)	1.69(6)	1.89(6)
	1.82(3)	1.92(5)		1.92(6)

of *rac-2* and **3** are in the range of the normal hydrogen bonding distance.

### 2.3. Isomerization of **2**

We observed that the diastereomeric isomerization of *meso-2* in non-dried CDCl<sub>3</sub> solvent occurred to result in the 55:45 equilibrium mixture of *meso-2* and *rac-2* and vice versa, which was monitored by <sup>1</sup>H NMR, as was the case for isomerization of *meso-1* to *rac-1* [8].

Fig. 5. Isomerization of **2**.

On the other hand, in dry  $\text{CDCl}_3$ , *meso-2* or *rac-2* was stereochemically rigid and did not isomerize (Fig. 5). An isotope experiment using  $\text{H}_2^{18}\text{O}$  was conducted in order to prove the mechanism of the isomerization. The isomerization of *meso-2* in the presence of  $\text{H}_2^{18}\text{O}$  occurred to give partly  $^{18}\text{O}$  labeled disiloxane-1,3-diol identified by FAB MS. This indicates that *meso-2* isomerization is induced by nucleophilic attack by water at silicon. It is rare that the hydrolysis of silanol occurred by water under a neutral condition in the absence of a base or an acid. The detailed discussion about the isomerization of silanol was reported in our previous paper [8].

### 3. Conclusion

In this work, we have observed that an introduction of intramolecular donor atom provided a convenient way to synthesize disiloxane-1,3-diols,  $[(\text{OH})o\text{-}\{(\text{CH}_3)_2\text{NCH}_2\text{-C}_6\text{H}_4\}\text{RSi}]_2\text{O}$  ( $\text{R} = \text{CH}_2=\text{CH}$  (**1**)  $\text{C}_6\text{H}_5$  (**2**),  $o\text{-}\{(\text{CH}_3)_2\text{NCH}_2\}\text{C}_6\text{H}_4$  (**3**),  $\text{Me}$  (**4**)), in high yields. In the structural studies of *meso-2*, *rac-2a*, *rac-2b* and **3**, we found strong intramolecular hydrogen bondings between the hydroxy group and the nitrogen atom, which is consistent with the  $^1\text{H}$  NMR resonances of hydroxyl groups observed at down fields. We have also observed that the diastereomeric isomerization of *meso-2* in  $\text{CDCl}_3$  solvent containing moisture occurred to result in the 55:45 equilibrium mixtures of *meso-2* and *rac-2*, as was the case for the isomerization of *meso-1* to *rac-1*.

## 4. Experimental

### 4.1. General comments

In all reactions where air-sensitive chemicals were used, the reagents and solvents were dried prior to use. Diethylether was distilled from  $\text{Na}/\text{Ph}_2\text{CO}$ . Other starting materials were purchased in reagent grade and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 250 FT-NMR spectrometer and Bruker AMX 500 NMR spectrometer and referenced to residual protons of the solvent with chemical shifts being reported as  $\delta$  ppm.

### 4.2. Synthesis of **2**

To a mixture of  $\text{H}_2\text{O}$  (1.8 ml, 0.10 mol) and triethylamine (14 ml, 0.10 mol) in  $\text{Et}_2\text{O}$  was added slowly [2-(dimethylaminomethyl)phenyl]phenyldichlorosilane (15 g, 0.049 mol) in  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$  during 50 min. The reaction mixture was allowed to warm slowly to room temperature and stirred for 1 h. After filtration of the precipitated  $\text{Et}_3\text{NHCl}$ , volatiles were distilled under vacuum. The residue was recrystallized to give *meso-2* and *rac-2* (55:45) as colorless crystals (9.3 g, 72%). *Meso-2*: m.p.:  $137\text{--}138^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  2.13 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 3.23, 3.62 (AB-system,  $^2J(\text{H}, \text{H}) = 12.4$  Hz, 4H,  $\text{PhCH}_2$ ), 7.08–7.73 (m, 18H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ), 10.37 (s, 2H, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  43.93 ( $\text{NMe}_2$ ), 64.65 ( $\text{CH}_2\text{N}$ ), 126.97, 127.51, 129.35, 129.62, 130.81, 134.78, 135.66, 136.27, 137.82, 142.06 ( $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ). IR (film,  $\text{cm}^{-1}$ , KBr): 3420 (OH), 1094 (Si–O–Si). *Anal.* Calc. for  $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_3\text{Si}_2$ : C, 68.14; H, 6.86; N, 5.30. Found: C, 68.17; H, 6.86; N, 5.34. *Rac-2*: m.p.:  $145\text{--}146^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  2.20 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 3.17, 3.52 (AB-system,  $^2J(\text{H}, \text{H}) = 12.4$  Hz, 4H,  $\text{PhCH}_2$ ), 7.07–7.72 (m, 18H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ), 10.37 (s, 2H, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  43.83 ( $\text{NMe}_2$ ), 64.58 ( $\text{CH}_2\text{N}$ ), 126.94, 127.48, 129.34, 129.56, 130.74, 134.68, 135.67, 136.23, 137.77, 142.06 ( $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ). IR (film,  $\text{cm}^{-1}$ , KBr): 3420 (OH), 1094 (Si–O–Si).

### 4.3. Synthesis of **3**

To a mixture of  $\text{H}_2\text{O}$  (0.11 ml, 6.1 mmol) and triethylamine (0.90 ml, 6.5 mmol) in  $\text{Et}_2\text{O}$  was added slowly bis[2-(dimethylaminomethyl)phenyl]dichlorosilane (1.10 g, 3.0 mmol) in  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$ . In similar manners to synthesis of **2**, **3** as colorless crystals was obtained in 65% yield (0.63 g). **3**: m.p.:  $111\text{--}112^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  2.20 (s, 24H,  $\text{NMe}_2$ ), 3.32, 3.58 (AB-system,  $^2J(\text{H}, \text{H}) = 13.0$  Hz, 8H,  $\text{PhCH}_2$ ), 7.12–7.76 (m, 16H,  $\text{C}_6\text{H}_4$ ), 9.98 (s, 2H, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  41.1 ( $\text{NMe}_2$ ), 61.1 ( $\text{PhCH}_2$ ), 126.6, 128.6, 129.5, 133.5, 135.5, 143.6 ( $\text{C}_6\text{H}_4$ ). *Anal.* Calc. for  $\text{C}_{36}\text{H}_{50}\text{N}_4\text{O}_3\text{Si}_2$ : C, 67.25; H, 7.84; N, 8.71. Found: C, 67.25; H, 7.79; N, 8.68%.

### 4.4. Synthesis of **4**

To a mixture of  $\text{H}_2\text{O}$  (0.11 ml, 6.1 mmol) and triethylamine (0.85 ml, 6.1 mmol) in  $\text{Et}_2\text{O}$  was added slowly [2-(dimethylaminomethyl)phenyl]methylchlorosilane [23] (0.74 g, 3.0 mmol) in  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$ . In similar manners to synthesis of **2**, **4** was obtained in 68% yield (0.41 g). **4**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  0.27, 0.30 (s, 6H,  $\text{SiCH}_3$ ), 2.05, 2.06 (s, 12H,  $\text{NMe}_2$ ), 3.06–3.66, 3.06–3.71 (m, 4H,  $\text{PhCH}_2$ ), 7.01–7.55 (m, 8H,  $\text{C}_6\text{H}_4$ ), 9.53 (s, 2H, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  -1.34, -1.32 ( $\text{SiCH}_3$ ), 43.91 ( $\text{NMe}_2$ ), 64.65, 64.66 ( $\text{PhCH}_2$ ), 127.0, 129.2, 130.8,

134.8, 134.9, 139.2, 141.7 (C<sub>6</sub>H<sub>4</sub>). Anal. Calc. for C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub>: C, 59.36; H, 7.97; N, 6.92. Found: C, 59.32; H, 8.02; N, 6.90%.

#### 4.5. Isomerization of **2** in the presence of H<sub>2</sub><sup>18</sup>O

To *meso*-**2** (30 mg) in 1.0 ml of CDCl<sub>3</sub> in an NMR tube was added 3.0 μl of H<sub>2</sub><sup>18</sup>O at room temperature. The isomerization of *meso*-**2** to *rac*-**2** was monitored by <sup>1</sup>H NMR spectroscopy. It took about 10 days to reach the equilibrium (55:45). The partly <sup>18</sup>O labeled disiloxane-1,3-diol **2** was identified by FAB-MS and compared with the FAB-MS of *meso*-**2**. FAB-MS: *m/z* (relative intensity) <sup>18</sup>O labeled **2**: 528 (100), 530 (55); *meso*-**2**: 528 (100), 530 (22).

#### 4.6. Crystallographic experimental section

Crystals (compound **2**) were selected and attached to the tip of a glass fiber, transferred to a Bruker SMART diffractometer/CCD area detector and centered under liquid nitrogen in the beam at 233(2) K. The crystal evaluation and data collection were performed on a Bruker CCD diffractometer with Mo Kα (λ = 0.71073 Å) radiation employing 2 kW sealed tube X-ray source operating at 1.6 kW and the diffractometer to crystal distance of 4.9701 cm. Preliminary orientation matrix and cell constants were determined from three series of ω scans at different starting angles. Each series consisted of 10 frames collected at intervals of 0.3° ω scan with the exposure time of 10 s per frame. A single crystal (compound **3**) was used for data collections on a STOE STADI4 four-circles-diffractometer with graphite monochromatized Mo Kα radiation at room temperature. Cell parameters and an orientation matrix for data collections were obtained from least-squares refinement, using the 36 reflections in 19.0 < 2θ < 21.5. Intensities were collected ω–2θ scan technique. During data collection three standard reflections were measured every hour and showed no significant. The intensity data were collected for Lorentz and polarization effect, and absorption correction was not applied.

The systematic absences in the diffraction data were consistent for the space group that yielded chemically reasonable and computationally stable results of refinement [24]. A successful solution was obtained the direct methods from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms bonded to carbon atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The hydrogen atoms bonded to O were found on the difference Fourier map and refined isotropically.

## 5. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 215352 for compound *meso*-**2**, No. 215353 for compound *rac*-**2a**, No. 215354 for compound *rac*-**2b**, and No. 215355 for compound **3**. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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