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Stereochemistry of the reaction of *cis,trans,cis*-2,4,6,8-tetraisocyanato-2,4,6,8-tetramethylcyclotetrasiloxane with triphenylsilanol and 1,1,3,3-tetraphenyldisiloxane-1,3-diol

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ABSTRACT

All-*cis*-2,4,6,8-tetramethyl-2,4,6,8-tetrakis(triphenylsiloxy)cyclotetrasiloxane (**4**) and *syn*-1,3,9,11-tetramethyl-5,5,7,7,13,13,15,15-octaphenyltricyclo[9.5.1.1^{3,9}]octasiloxane (**5**) were synthesized by the reaction of *cis,trans,cis*-[MeSi(NCO)O]$_4$ (**1**) with Ph_3SiOH (**2**) and $[Ph_2Si(OH)]_2O$ (**3**), respectively, in the presence of pyridine for the sake of investigating the synthesis of ladder polysilsesquioxanes with perfect siloxane frameworks. Their stereostructures were confirmed by nuclear magnetic resonance spectra and X-ray crystallography, which revealed that **4** and **5** did not retain the stereostructure of the precursor **1**. This result was caused by the racemization of **1** with pyridine, and a subsequent nucleophilic substitution reaction of **1** with **2** or **3**, including inversion and retention of the configuration at the silicon atoms.

1. Introduction

Since the first report on the synthesis of ladder polyphenylsilsesquioxane (PSQ) by Brown et al. in 1960 [1], many scientists have been interested in such polymers due to their excellent chemical, physical, and electrical properties derived from the double-chained structure with the formula $(RSiO_{3/2})_n$ [2]. In 1971, however, Frye disputed the reported structure of PSQ, indicating that it was made up of not a linear double-chain ladder structure but instead partially opened polycyclic cages [3]. Based on these arguments, it appears that PSQ with a perfect siloxane framework has not yet been obtained. In order to design high-performance materials, a method must be developed to control the ladder siloxane backbone [4].

To date, synthesis of a novel precursor as a model compound for highly regulated PSQ and ladder oligosilsesquioxanes has been studied. PSQ consists of a unit structure such as a monomer ($RSiO_{3/2}$), disiloxane ($(RSiO)_2O_{2/2}$), or cyclotetrasiloxane ($(R_4Si_4O_4)O_{4/2}$), which is derived from sila-functional silane or siloxane. Due to the difficulty of obtaining a perfect ladder structure by a simple hydrolysis method of trifunctional silanes [5], sila-functional disiloxanes $[RSiX_2]_2O$ and cyclotetrasiloxanes $[RXSiO]_4$ should be considered as potential precursors for PSQ. In particular, sila-functional cyclotetrasiloxanes are considered to be desirable precursors of ladder and cage siloxane compounds because they have a tetrasiloxane ring system that is suitable for facile construction of rigid ladder and cage structures.

It is important that sila-functional cyclotetrasiloxane is a mixture of four stereoisomers: all-*cis*-, *cis,trans,cis*-, *cis,cis,trans*- and all-*trans*-configurations. From the perspective of controlling the structure of PSQ, all-*cis*- and *cis,trans,cis*-configurations are possible key intermediates for the formation of an ideal structure. Among the sila-functional tetramethylcyclotetrasiloxanes, $[MeSi(X)O]_4$ (X = H, Cl, Br, OEt) [6] are known compounds, and some of them are commercially available only as a mixture of four stereoisomers. Unno et al. have reported the synthesis of *cis,trans,cis*-$[MeSiBrO]_4$ as a sole isomer, but its high hydrolyzability causes difficulty in controlling the synthesis of silsesquioxanes [7]. In contrast, we have synthesized *cis,trans,cis*-[MeSi(NCO)O]$_4$ (**1**) [8] and shown that **1** is a suitable building block for the synthesis of ladder oligo- and polysilsesquioxanes [9]. Quite recently, we have succeeded in synthesizing highly soluble PSQ by the hydrolysis of $[MeSi(X)O]_4$ (X = H, OEt (a mixture of four stereoisomers)) or **1** [10]. PSQ synthesized from **1** has a highly regulated ladder structure with

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fewer defects in the siloxane framework than the hydrolyzate of X = H or OEt.

As it has been reported that all-*cis*-$[PhSi(OH)O]_4$ compounds in acetone give a mixture of four stereoisomers at room temperature in the presence of hydrochloric acid [11], we must consider not only their stereostructure and reactivity but also their isomerization when sila-functional cyclotetrasiloxanes are used as a precursor for ladder silsesquioxanes. As preferable synthetic methods for perfect PSQ have not been developed thus far, the synthesis of ladder oligosilsesquioxanes is focused on to provide a model compound to estimate the real and essential structures and properties of PSQ: the reaction of all-*cis*-$[PhSi(OH)O]_4$ with $[Me_2SiCl]_2O$ gives a mixture of *syn*- and *anti*-tricyclic ladder oligosilsesquioxanes [12]. *Syn*- (5%) and *anti*- (20%) tricyclic ladder oligomethylsilsesquioxanes were synthesized and separated by recycle-type high-performance liquid-phase chromatography after the heterofunctional condensation of **1** with $[MeSi(OBu^t)(OH)]_2O$ in the presence of triethylamine [9]. In both cases, the formation of a mixture suggested that the stereostructure of **1** was not retained in these reactions. On the other hand, cage and ladder siloxane derivatives were synthesized from all-*cis*-$[Pr^iSi(OH)O]_4$ by retaining its configuration [13]. As a result, the reaction mechanism and stereostructure of sila-functional cyclotetrasiloxane, in other words, the relationship of the structure of ladder oligosilsesquioxanes with PSQ was not fully investigated.

The mechanism of the nucleophilic substitution reaction at silicon has also been studied over many years. For example, hydrolysis of halosilanes can be accelerated by the addition of nucleophiles, and the predominant stereochemistry changes from an inversion of configuration at silicon to retention [14]. Similarly, chiral halosilanes are racemized by the addition of nucleophiles [14,15]. The most widely accepted racemization mechanism was proposed by Corriu [16,17]: a chiral chlorosilane $R^1R^2R^3SiCl$ reacts with a nucleophile to produce a pentacoordinate species that is activated for substitution. A second molecule of a nucleophile then attacks the pentacoordinated silicon to give a hexacoordinated silicon species, either an intermediate or a transition state, which collapses to another pentacoordinate species that has a plane of symmetry. Chiral memory is, therefore, lost, and racemization is inevitable.

Another mechanism was proposed by Chojnowski that involved displacement of halide by the nucleophile [18]: in the first step, there are double displacements in which the nucleophile displaces the leaving group with an inversion of configuration. Second, in the stereochemically determining step, is an attack by another nucleophile on the tetracoordinated silicon-nucleophile species, which again takes place with an inversion of configuration. Racemization is the eventual result, and a number of these inversions can occur before leaving group re-coordinates to the silicon. Bassindale has reported that a wide range of nucleophiles form five-coordinated complexes with Me_3SiX (X = I, OSO_2CF_3, Br), and has proved the racemization mechanism based on the NMR study [19]: he suggested that the four-coordinated silicon cation route is favored for the substitution of R_3SiX (R = alkyl), while a hyper-coordinated intermediate route is more common for R'_3SiX (R′ = O-alkyl, halide and other electron-withdrawing groups).

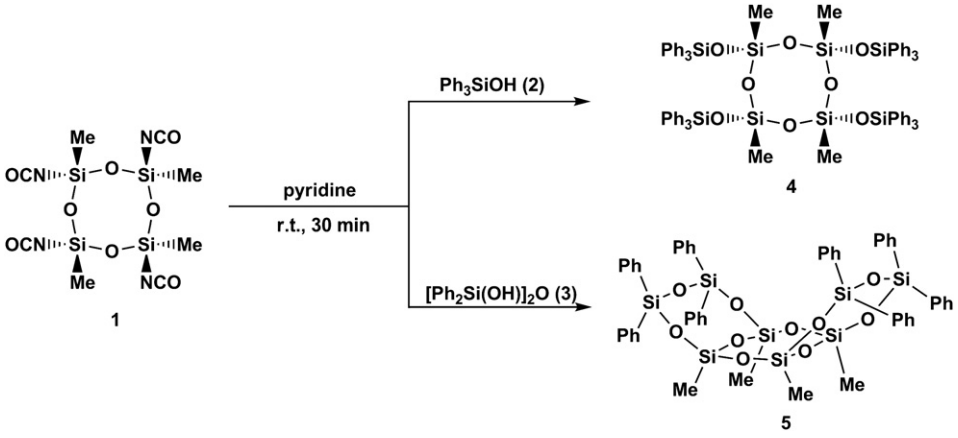
In this paper, therefore, we will report the reaction of **1** with triphenylsilanol (**2**) and 1,1,3,3-tetraphenyldisiloxane-1,3-diol (**3**) in the presence of pyridine, as shown in Scheme 1, to investigate the mechanism of the nucleophilic substitution reaction at sila-functional cyclotetrasiloxane in the synthesis of perfect ladder oligo- and polysilsesquioxanes. In addition, the structures of **4** and **5** and the relationship of the nucleophilic substitution reaction with the stereostructures of the products will be presented.

2. Results and discussion

2.1. Synthesis of *4* and *5*

1 was synthesized according to the literature [8] by a two-step vapor-phase hydrolysis started with triisocyanato(methyl)-silane via $[MeSi(NCO)_2]_2O$, followed by the liquid-phase hydrolysis of 1,1,3,5,7,7-hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane in tetrahydrofuran (THF). **3** was synthesized by the two-step hydrolysis starting with dichloro(diphenyl)silane via $[Ph_2SiCl]_2O$ in the presence of triethylamine.

All-*cis*-2,4,6,8-tetramethyl-2,4,6,8-tetrakis(triphenylsiloxy)cyclotetrasiloxane (**4**) and *syn*-1,3,9,11-tetramethyl-5,5,7,7,13,13,15,15-octaphenyltricyclo[9.5.1.1^{3,9}]octasiloxane (**5**) were synthesized by a heterofunctional condensation of **1** with **2** and **3**, respectively, in the presence of pyridine. A THF solution of **1** with pyridine was stirred at room temperature for 30 min, then **2** or **3** was added to the reaction mixture and subjected to reflux (for **2**) or stirring at room temperature (for **3**). After cyanuric acid was filtered out, **4** was isolated as a white solid in 57% yield by column chromatography separation (silica gel, hexane/$CHCl_3$ = 7/3), and **5** was obtained as a white solid in 52% yield by washing the crude product twice with methanol. Compounds **4** and **5** were the main products, and their stereostructures were determined by spectroscopic data and X-ray crystallography.



Scheme 1. Synthesis of cyclotetrasiloxane derivatives **4** and **5** by the reaction of **1** with **2** or **3**.

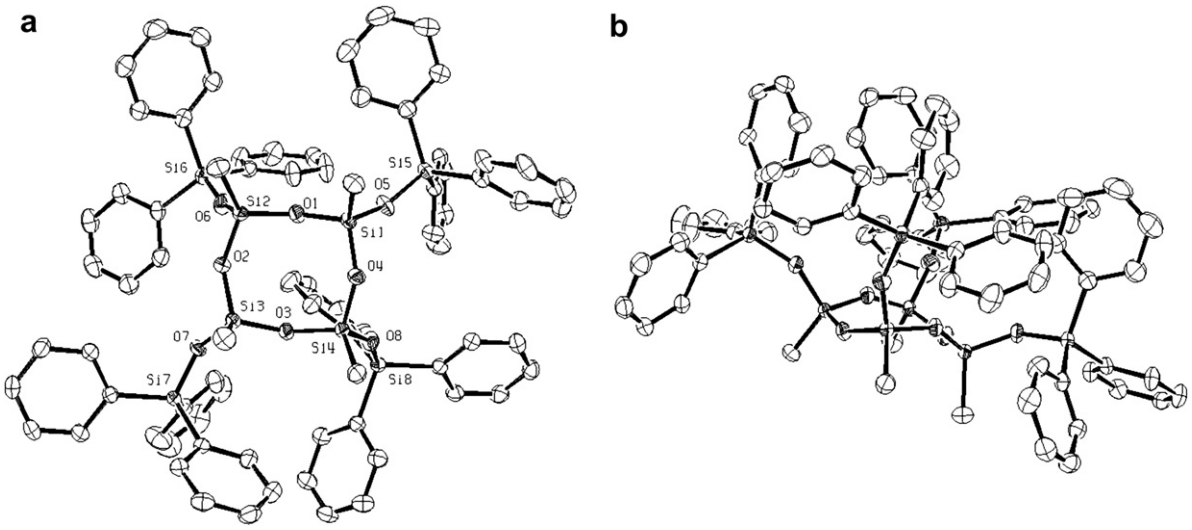


Fig. 1. Molecular structures of **4** (a: top view and b: side view). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

2.2. Structures of *4* and *5*

The X-ray crystallography of **4** and **5** revealed the molecular structures shown in Figs. 1 and 2, and the crystallographic data are summarized in Table 1. Suitable crystals for X-ray crystallography were obtained directly at room temperature by slow evaporation of the solution of chloroform/acetone = 1/1 (**4**) and diethyl ether/methanol = 2/1 (**5**).

The single crystal of **4** belonged to a monoclinic system ($P2_1/c$ group), with four molecules being included per unit cell. The structure was fully refined to the *R*-value of 5.2%. The average bond lengths and angles of the eight-membered rings were 1.62 Å for Si–O, 147.0° for Si–O–Si, and 109.5° for O–Si–O. As compared with the starting material **1**, the angle of Si–O–Si was decreased. Monocyclic **4** showed a distorted planar skeleton of Si atoms with a dihedral angle of the central eight-membered ring of 19.4° (Si1-Si2-Si3-Si4) compared with **1** (dihedral angles; 0°). The torsion angle between Si1–Si2 and Si3–Si4 lines was 13.8°. The conformation of the triphenylsiloxy groups bonded to a siloxane ring is clearly dictated by the need to minimize the mutual hindrance; the four triphenylsiloxy groups, therefore, have different angles combined with the Si_4O_4 average plane, being in the range of 119–150°. It is noteworthy that an all-*cis*-configuration was obtained, indicating that the configuration around the Si atoms was not retained under this condition. The configuration of **4** was also revealed by NMR spectrum. The ^{1}H NMR spectrum of **4** showed one sharp signal at −0.15 ppm due to the methyl group. The ^{29}Si NMR spectrum showed sharp signals at −20.5 and −65.7 ppm due to silicon atoms in the Ph_3SiO and $MeSiO_{3/2}$ units, respectively. These results indicate that **4** was isolated as the sole stereostructure.

On the other hand, the single crystal of **5** belonged to a monoclinic system (*C*2/c group), and four molecules were included in the unit cell. The structure was fully refined at an *R*-value of 3.1%. **5** is constructed of three eight-membered rings with Si–O–Si bonds. The central ring Si1-Si4^i-Si1^i-Si4 combines with the side rings Si1-Si2-Si3-Si4 at dihedral angles of 49.3°. The structure of **5** was, therefore, determined to be a *syn*-configuration, and the stereostructure of **1** was not retained. The torsion angles were 24.0° at the center ring and 5.2° at the terminal rings, for a total of 34.4°. This suggests that the side rings are under significant strain due to steric hindrance caused by the configuration of the phenyl groups, which are bonded to the silicon atoms. The average bond length for **5** is 1.63 Å for Si–O, and the bond angles are 142.3° for Si–O–Si and 108.7° for O–Si–O. As compared with other *syn*-type ladder oligosilsesquioxanes $Me_8Ph_4Si_8O_{10}$ [12b,12c] and *i*-$Pr_{12}Si_8O_{10}$ [13b] (Si–O: 1.61–1.64 Å, Si–O–Si: 147.9–157.9°, O–Si–O: 107.4–110.6°), the angle of Si–O–Si was decreased. Only one sharp signal due to a methyl group was detected at 0.14 ppm, and the other signal was not observed in the ^{1}H NMR spectrum. The ^{29}Si NMR spectrum showed sharp signals at −44.4 and −62.8 ppm due to the silicon atoms at the 5-, 7-, 13-, and

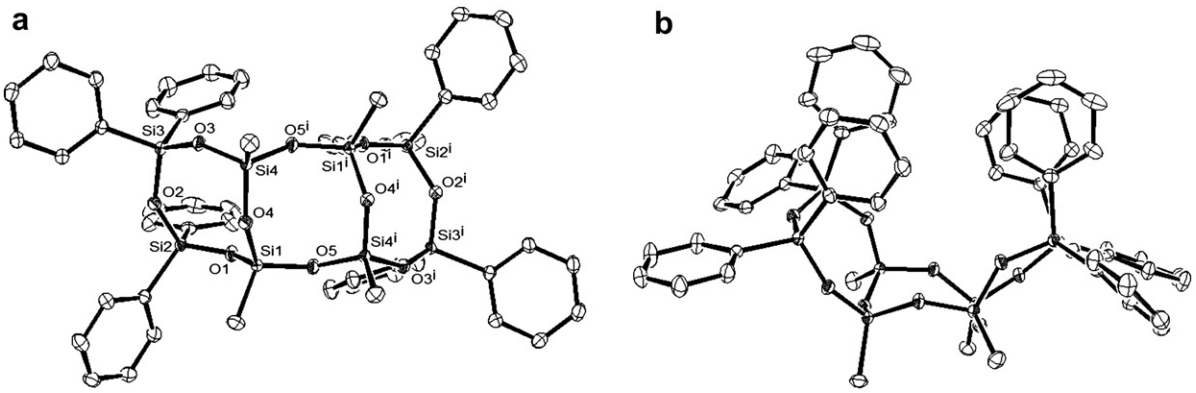


Fig. 2. Molecular structures of **5** (a: top view and b: side view). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1
Crystallographic data and structure refinement for **4** and **5**.

	4	**5**
Molecular formula	$C_{76}H_{72}O_8Si_8$	$C_{52}H_{52}O_{10}Si_8$
Fw	1338.06	1061.66
Temperature/K	103	90
Wavelength	Mo Kα	Mo Kα
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	13.9182 (12)	19.4454 (14)
b/Å	27.040 (2)	11.3032 (8)
c/Å	20.0733 (12)	24.7195 (18)
α/deg		
β/deg	108.1230 (10)	96.5760 (10)
γ/deg		
Volume Å^3	7179.7 (11)	5397.5 (7)
Z	4	4
Dcalc/g cm^{-3}	1.238	1.306
Absorption coefficient/mm^{-1}	0.204	0.255
Crystal size/mm	0.35 × 0.32 × 0.22	0.30 × 0.29 × 0.24
θ range/deg	1.31 to 27.59	2.11–27.49°
No. of reflections collected	49 750	16 023
No. of independent reflections	16 078	6041
Data/restraints/parameters	16 078/0/833	6041/0/318
Goodness-of-fit on F^2	1.042	0.609
R indices [I > 2σ (I)]	$R_1 = 0.0521$	$R_1 = 0.0311$
	$wR_2 = 0.1360$	$wR_2 = 0.0927$
R indices (all data)	$R_1 = 0.0599$	$R_1 = 0.0326$
	$wR_2 = 0.1433$	$wR_2 = 0.0949$

15-positions and at the 1-, 3-, 9-, and 11-positions, respectively. These results indicated that **5** was a *syn*-tricyclic ladder siloxane.

2.3. Isomerization of **1** in the presence of nucleophilic agents

The spectroscopic data and X-ray crystallographic analysis showed that **4** and **5** were constructed with an all-*cis*-configuration, and indicated that the nucleophilic substitution reaction of **1** with **2** or **3** caused inversion and retention of the stereochemical configuration around Si atoms of **1**.

In general, a nucleophilic substitution reaction of sila-functional silane $R_{4-n}SiX_n$ (X = H, OR, halogen) with alcohol or silanol gives inversion and retention of the stereostructure through an intermediate or transitional state depending on the functional group, solvent, and catalysis (acid or base). To our knowledge, however, the stereochemistry of isocyanatosilanes $R_{4-n}Si(NCO)_n$ has not yet been reported. We, therefore, studied in detail the reaction mechanism of the nucleophilic substitution reaction of **1**. The effects of base-catalyst and solvent were also studied because the reactivity of isocyanatosilane lay between that of chlorosilane and alkoxysilane, and substitution reactions are often accelerated by base-catalysts [20].

It is possible that the nucleophile changes the stereostructure of functional silane. We examined the behavior of **1** in the presence of nucleophilic agents such as hexamethylphosphoric triamide (HMPT), dimethyl formamide (DMF), pyridine, and acetonitrile, which are known to be racemization agents. The mixture of Me_3SiX (X = Br, OSO_2CF_3, and I) with nucleophiles such as HMPT and DMF gives a 1/1 ion complex, which is isolated as a solid [15]. Pyridine also forms a 2/1 adduct $[RSiH_2py_2]^+X^-$ (R = H, Me) with $SiXH_3$ or $MeSiH_2X$ (X = Br, I), but not with Me_3SiX [21]. When four equivalents of nucleophilic agents (HMPT, DMF, pyridine, and CH_3CN) were added to the diethyl ether solution of **1**, no precipitates were obtained. The signals due to HMPT and DMF in the ^{1}H NMR spectrum are expected to shift to high magnetic field upon the addition to Me_3SiX and are consistent with *O*-silylation. But no shifts to high magnetic field were observed over the mixing at room temperature for 1 h in our experiment, which indicates that **1** didn't form an ionic adduct with nucleophiles because the polarization of $Si^{\delta+}$–$NCO^{\delta-}$ was too weak to bring about the nucleophilic replacement of the Si–NCO bond.

Next, we undertook a preliminary study of the interaction of **1** with an equivalent amount of nucleophile in $CDCl_3$ at room temperature and monitored this interaction by ^{1}H NMR spectrum, as shown in Fig. 3. When an equivalent amount of pyridine was added to **1**, the signal intensity at 0.41 ppm due to the methyl group for *cis,trans,cis*-isomer was decreased, and new signals appeared at 0.36, 0.38, 0.40, 0.43, and 0.45 ppm (Fig. 3b). The observation of six signals can be explained by the isomerization of **1,** as shown in Scheme 2. After 20 min (Fig. 3c), the intensity of the six signals became constant, with a ratio of *cis,trans,cis*-: *cis,cis,trans*-: isomer a: isomer b (isomers a and b are all-*cis*- or all-*trans*-) = 2:4:1:1, similar to that of the statistical abundance. The signals at 0.38, 0.40, and 0.43 ppm could be assigned to *cis,cis,trans*- isomer due to three different silicon atoms with a 1:2:1 intensity ratio. The structures of the remaining two isomers, however, could not be determined by the ^{1}H NMR spectrum. In the ^{29}Si NMR spectrum, the signal became broad due to the loss of a sole configuration, but a change in chemical shift was not observed. Because the signals didn't shift to high magnetic field, it was concluded that **1** did not form an ion adduct. On the other hand, the racemization of **1** was very slow in

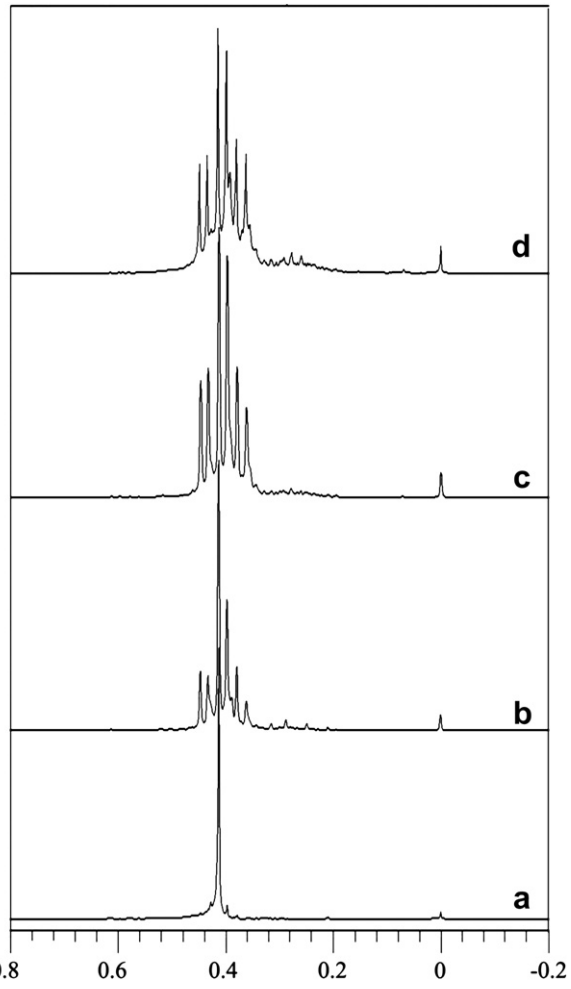
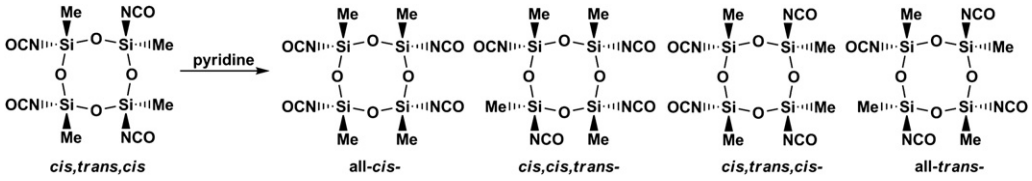


Fig. 3. ^{1}H NMR spectra of a mixture of **1** and pyridine (1:1). Before addition of pyridine (a), 5 min after addition (b), 20 min after addition (c), and after the removal of pyridine (d) (Solvent; $CDCl_3$, Temperature; 25 °C).



Scheme 2. Formation of four isomers by the reaction of **1** with pyridine.

HMPT, but it was not measured for DMF and triphenylphosphine, which are known to be strong racemization agents by *O*-silylation. The isomerization of **1** is, therefore, caused by *N*-addition with HMPT. These results showed that the racemization of **1** in the presence of nucleophile was caused by an extension of coordination with *N*-addition at Si atoms (Scheme 3).

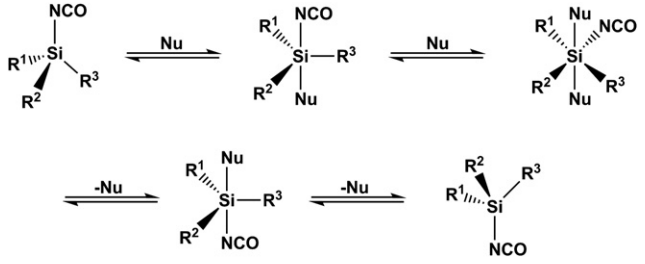
The reaction of all-*cis*-[4-$RC_6H_4Si(OR')O]_4$ (R = H, R′ = H [22], R = Cl, Br, CH=CH_2, and CH_2Cl, R′ = Na [23]) with Me_3SiCl in the presence of pyridine gave all-*cis*-tetrakis(trimetylsiloxy)cyclotetrasiloxane in an excellent yield. Other isomers were not obtained due to the bulkiness of the substituent affecting the stability against racemization. On other hand, methyl-substituted cyclotetrasiloxane is unstable against racemization agents.

2.4. Formation of *4* and *5* followed by isomerization of *1*

As mentioned in the previous section, the structures of cyclic siloxanes **4** and **5** didn't reflect the stereostructure of **1**, which suggests that there is retention and inversion in the reaction pathway. Because this reaction is carried out under the condition to form an isomer mixture of **1**, the *cis,cis,trans*-formed compound is expected to be a major product of the reaction of **1** with **2** in the presence of pyridine. The all-*cis*-formed compound was, however, isolated in 57% yield, which suggests the formation of all-*cis*-formed compound by the retention and inversion of **1**. This result is in good agreement with the calculated structures based on MM2 [24] that predicted that the all-*cis*-configuration would be slightly more stable than the other isomers by 2.7–5.2 kcal/mol. In addition, the formation of the all-*cis*-formed compound would be accelerated by a π–π interaction of the phenyl group to produce dense packing. Similarly, the formation of a *syn*-formed compound in **5** would be favored by an interaction of phenyl groups on the axial and equatorial positions in the boat-formed tricycles.

3. Conclusions

We studied the isomerization behavior of the nucleophilic substitution reaction of *cis,trans,cis*-[MeSi(NCO)O]$_4$ (**1**) in the presence of pyridine as a basic catalyst. ^{1}H and ^{29}Si NMR spectra showed that **1** was isomerized by pyridine to four stereoisomers (all-*cis*-:*cis,cis,trans*-:*cis,trans,cis*-:all-*trans*- = 1:4:2:1). The reaction of **1** with Ph_3SiOH (**2**) or $[Ph_2Si(OH)]_2O$ (**3**) in the presence of pyridine gave all-*cis*-2,4,6,8-tetramethyl-2,4,6,8-tetrakis(triphenylsiloxy)-cyclotetrasiloxane (**4**) or *syn*-1,3,9,11-tetramethyl-5,5,7,7,13,13,15,15-octaphenyltricyclo[9.5.1.1^{3,9}]octasiloxane (**5**), respectively, due to the inversion and retention of the stereochemical configuration during the production of an intermediate with a penta- and/or hexacoordinated silicon atom formed by the addition of base as a nucleophile to the silicon atom. As a result, the importance of the molecular design on the structure of the precursor and reaction conditions was concretely suggested as a factor in obtaining a ladder polysilsesquioxane with a perfect siloxane framework.



Scheme 3. Isomerization processes in the substitution reaction of R_3SiNCO.

4. Experimental section

4.1. General experimental procedures

All reagents were commercially available. THF, triethylamine, pyridine, and dichloro(diphenyl)silane were purified by distillation, and other reagents were used without further purification. Fourier transform NMR spectra were obtained by JEOL ECP-300 (^{1}H at 300 MHz, ^{13}C at 75 MHz, and ^{29}Si at 60 MHz). Chemical shifts were reported as δ units (ppm) relative to $SiMe_4$, and/or the residual solvent peaks were used as a standard. ^{29}Si NMR spectra were obtained on samples with chromium(III) acetylacetonate as a relaxation agent. FTIR spectra were measured using a JASCO FT-IR-6100 IR spectrophotometer by means of a carbon tetrachloride solution method, KBr disk method, and neat method. The mass spectra (FAB) were obtained on a JEOL JMS-700 spectrometer. The mass spectra (ESI) were obtained on a JEOL JMS-T100CS spectrometer.

4.2. X-ray crystallography

A single crystal was attached to the top of a glass fiber with a cold nitrogen gas stream at 90 or 103 K, and measured using a Bruker SMART APEX equipped with a CCD diffractometer (λ(Mo Kα) = 0.71073 Å, 25 ± 2 °C). The structure was solved by SHELXL-97 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.

4.3. Preparation of cis,trans,cis-2,4,6,8-tetraisocyanato-2,4,6,8-tetramethylcyclotetrasiloxane (*1*)

1,1,3,5,7,7-Hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane was synthesized according to the literature [8]. A solution of water (0.54 g, 30 mmol) in THF (100 mL) was slowly added to a vigorously stirred and ice-cooled (0 °C) solution of 1,1,3,5,7,7-hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane (14.2 g, 30 mmol) in THF (20 mL), and the mixture was then stirred for 2 h. The solvent was removed, and the residue was distilled *in vacuo* to give **1** as a white solid (49% yield, b.p. 110–112 °C/1.0 Torr).

^{1}H NMR ($CDCl_3$) δ 0.41 (s, 12H). ^{13}C NMR ($CDCl_3$) δ −2.20, 122.8. ^{29}Si NMR ($CDCl_3$) δ −60.0. MS (70 eV) m/z 389 (M^+−Me, 15). IR (CCl_4 solution) 2975, 2290, 1270, 1110 cm^{-1}.

4.4. Preparation of 1,1,3,3-tetraphenyldisiloxane-1,3-diol (**3**)

A solution of water (3.60 g, 0.20 mol) in THF (70 mL) was slowly added to a vigorously stirred and ice-cooled (0 °C) solution of dichloro(diphenyl)silane (100.8 g, 0.40 mol) in THF (70 mL), and the mixture was then refluxed for 3 h. The solvent was removed, and the residue was distilled *in vacuo* to give 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane as a colorless liquid in 41% yield (b.p. 215–224 °C/0.12 Torr).

A solution of 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane (9.02 g, 20 mmol) in diethyl ether (80 mL) was added to a vigorously stirred and ice-cooled (0 °C) mixture of water (0.72 g, 40 mmol), triethylamine (4.04 g, 40 mmol), diethyl ether (100 mL), and acetone (25 mL), followed by stirring at room temperature for 30 min. Triethylamine hydrogen chloride was filtered out, and solvent was evaporated. The solution was poured into hexane with vigorous stirring, and the precipitate was filtered. The precipitate was subjected to recrystallization from benzene/petroleum ether to give **3** as a white plate (81% yield, 6.72 g).

M.p. 111.9–112.6 °C ^{1}H NMR (acetone-d_6/ppm) δ 4.06 (s, 2H), 7.23 (t, 7.0 Hz, 8H), 7.34 (t, 7.0 Hz, 4H), 7.55 (d, 7.0 Hz, 8H). ^{13}C NMR (acetone-d_6/ppm) δ 128.4, 130.5, 135.2, 137.3. ^{29}Si NMR (acetone-d_6/ppm) δ −39.5. IR (KBr disk) 3425, 3071, 1429, 1126, 1089, 886, 847, 697, 512 cm^{-1}.

4.5. Synthesis of 1/1 adduct of **1** with nucleophile

Typically, four equivalents of nucleophile (HMPT, DMF, pyridine, and triphenylphosphine) were added to a diethyl ether solution of **1,** and the mixture was cooled to 0 °C. No precipitates were formed till 1 day.

4.6. NMR studies of **1** with nucleophiles

Typically, an equivalent nucleophile (HMPT, DMF, pyridine, and acetonitrile) and **1** were added together in $CDCl_3$. Measurements were recorded at appropriate intervals at room temperature.

4.7. Synthesis of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(triphenylsiloxy)cyclotetrasiloxane (**4**)

A two-necked flask equipped with a reflux condenser was charged with **1** (0.20 g, 0.50 mmol) and THF 2 mL, while pyridine (80 μL, 1.0 mmol) was added to the flask and subjected to stirring at room temperature for 30 min. Triphenylsilanol (0.69 g, 2.5 mmol) was added to the mixture and refluxed for 12 h. Diethyl ether was added and washed with diluted hydrochloric acid two times. The organic layer was washed with water two times and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed *in vacuo,* affording the product as an oil. The compound was purified by column chromatography (silica gel, hexane/$CHCl_3$ = 7/3), affording **4** as a white solid (0.38 g, 57% yield). Recrystallization by the solvent evaporation method using $CHCl_3$/acetone = 1/1 gave a single crystal as a colorless plate.

M.p. 194.5–195.1 °C ^{1}H NMR ($CDCl_3$/ppm) δ −0.15 (s, 12H), 7.03 (t, J = 7.6 Hz, 24H), 7.21 (tt, J = 7.8, 1.5 Hz, 12H), 7.50 (dd, J = 7.6, 1.5 Hz, 24H). ^{13}C NMR ($CDCl_3$/ppm) δ −2.5, 127.6, 129.6, 135.0, 135.3. ^{29}Si NMR ($CDCl_3$/ppm) δ −20.5, −65.7. MS-ESI$^+$ m/z = 1360.3 $[M + Na]^+$. IR (CCl_4/cm^{-1}) 3071, 3052, 1429, 1271, 1119, 1052, 713, 700, 515. Anal. Calcd. for $C_{76}H_{72}O_8Si_8$; C, 68.22; H, 5.42. Found; C, 68.07; H, 5.38.

4.8. Synthesis of syn-1,3,9,11-tetramethyl-5,5,7,7,13,13,15,15-octaphenyltricyclo[9.5.1.1^{3,9}]octasiloxane (**5**)

A two-necked flask equipped with a reflux condenser was charged with **1** (0.40 g, 1.0 mmol) and THF 5 mL, while pyridine (0.32 g, 4.0 mmol) was added to the flask and subjected to stirring at room temperature for 30 min. A solution of **3** (0.82 g, 2.0 mmol) in THF 5 mL was added to the mixture and subjected to stirring at room temperature for 6 h. Cyanuric acid was filtered out, and the organic layer was then washed with diluted hydrochloric acid two times. The organic layer was then washed with water two times and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed *in vacuo* and washed with methanol two times. The product was dried under reduced pressure to give **5** as a white solid (52% yield, 0.55 g). Recrystallization by the solvent evaporation method using diethyl ether/acetone = 2/1 gave a single crystal as a colorless plate.

M.p. 170.2–170.7 °C ^{1}H NMR (acetone-d_6/ppm) δ 0.14 (s, 12H), 6.95–7.67 (m, 40H). ^{13}C NMR (acetone-d_6/ppm) δ −3.3, 128.5, 128.7, 130.8, 131.1, 134.8, 134.9, 135.7. ^{29}Si NMR (acetone-d_6/ppm) δ −44.4, −62.8. IR (CCl_4 solution/cm^{-1}) 3073, 3052, 2971, 1593, 1430, 1270, 1128, 1055, 1027, 865, 521. MS (FAB^+) m/z 1061 $[M + H]^+$ Anal. Calcd. for $C_{52}H_{52}O_{10}Si_8$; C, 58.83; H, 4.94. Found; C, 58.87; H, 5.00.

Appendix A. Supplementary material

CCDC 794551, and 794552 contain the supplementary crystallographic data for **4**, and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.10.013.

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