Synthesis and Structure of Ladder Oligosilsesquioxanes: Tricyclic Ladder Oligomethylsilsesquioxanes

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Novel tricyclic ladder oligomethylsilsesquioxanes were prepared by heterofunctional condensation of *cis-trans-cis*-1,3,5,7-tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane with 1,3-di-*tert*-butoxy-1,3-dimethyldisiloxane-1,3-diol in the presence of triethylamine in THF. A mixture of stereoisomers of the tricyclic oligomethylsilsesquioxanes was obtained. Two of the isomers were separated as white solids by recycle-type high-performance liquid-phase chromatography. They were determined by X-ray crystallography to be tricyclic ladder oligomethylsilsesquioxanes consisting of three eight-membered rings arranged in *syn*- and *anti*-configurations.

Introduction

Recent studies of polysiloxanes have focused on the synthesis of cage and ladder polysilsesquioxanes because they consist of unique two- and three-dimensional structures and because of their potential application as materials with better chemical, physical, and electrical properties compared to those of silicones.

Because of their ladder structures and high thermal stability, much attention has focused on the polyphenylsilsesquioxanes (PPSQs), which were first prepared in 1960 by Brown.[1] High molecular weight PPSQs are prepared by the hydrolysis of trichloro(phenyl)silane ($PhSiCl_3$) followed by an equilibration reaction of the hydrolyzate with potassium hydroxide. In addition, many investigations concerning the synthesis of PPSQs have been carried out using the equilibration method as well as similar hydrolysis processes of $PhSiCl_3$, followed by condensation of the hydrolyzates with or without various solvents in the presence of bases to give the PPSQs.[2] Furthermore, the acid-catalyzed hydrolysis of trimethoxy(phenyl)silane followed by an alkali equilibration reaction produced the PPSQ.[3] The condensation of phenylsilanetriol in a two-phase solvent system in the presence of tetramethylammonium hydroxide has been reported to generate a PPSQ, which showed a characteristic sharp ^{29}Si NMR signal.[4]

Although PPSQs have been synthesized by various methods, there have been problems in establishing the structures. Brown reported the advantages of infrared (IR) analysis for identifying the ladder structure; cage silsesquioxanes gave a single absorption peak at 1121−1129 cm^{-1} due to the siloxane bond, while the IR spectra of the ladder silsesquioxanes consisting of at least 22−24 siloxane units showed two absorption peaks at 1135−1150 and 1045−1060 cm^{-1}.[5] Conventional PPSQs are classified as ladder polymers on the basis of the IR spectral analysis. The real structure of PPSQ, however, has not been identified to date because the absorption peak due to the T^3 ($PhSiO_{3/2}$) structural unit of the perfect ladder PPSQ has not been clarified. In addition, the ^{29}Si NMR spectra of the conventional PPSQs show a broad signal at around −80 ppm due to T^3, which suggests the presence of irregular ladder structures.[6]

In contrast to the reports in 1960 related to the PPSQ,[1] a high molecular weight and soluble polymethylsilsesquioxane (PMSQ) stable to self-condensation has been reported in 1978 in a patent.[7] The hydrolytic polycondensation of $MeSiX_3$ (X = Cl, OR) was more loosely controlled compared to that of $PhSiX_3$ due to the easy gel formation. Thus, the PMSQs were synthesized by the hydrolysis of $MeSiCl_3$ or *N*,*N*-bis(dichloro(methyl)silyl)ethylenediamine under various conditions.[8] Furthermore, we reported the facile one-pot synthesis of soluble PMSQ stable to self-condensation by the acid-catalyzed controlled hydrolytic polycondensation of $MeSi(OMe)_3$.[9]

As preferred methods for the synthesis of the perfect ladder polysilsesquioxanes have yet to be developed, more focus is on the development of a method for the synthesis of the ladder oligosilsesquioxanes as a model compound to investigate the real and essential structure and properties of the ladder polysilsesquioxanes. Currently, tri- and pentacyclic ladder oligosilsesquioxanes have been synthesized by heterofunctional condensation of sila-functional oligosiloxanes such as chlorodisiloxanes, disiloxanepolyols, and cyclotetrasiloxanetetraols with sterically bulky phenyl, isopropyl, and cyclohexyl groups.

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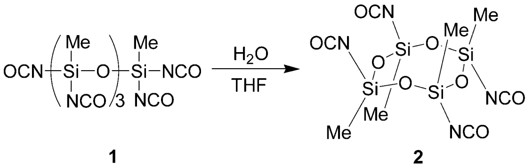
In 1965, Brown first reported the synthesis of a tricyclic ladder oligosilsesquioxane, 1,1,3,3,9,9,11,11-octamethyl-5,7,-13,15-tetraphenyltricyclo[9.5.1.1^{3,9}]octasiloxane, obtained by the reaction of the all-*cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane $[PhSi(OH)O]_4$ with 1,3-dichloro-1,1,3,3-tetramethyldisiloxane in pyridine.[10] Its structure was confirmed to have the *syn*- and *anti*-configurations in 1981.[11] In 1995, the tricyclic ladder oligosilsesquioxanes, 1,3,9,11-tetramethyl-1,3,9,-11-tetravinyl-5,7,13,15-tetraphenyltricyclo[9.5.1.1^{3,9}]-octasiloxane and 1,1,3,3,9,9,11,11-octamethyl-5,7,13,15-tetraphenyltricyclo[9.5.1.1^{3,9}]octasiloxane, were synthesized by the reaction of the all-*cis*-$[PhSi(OH)O]_4$ with 1,3-dichloro-1,3-divinyl-1,3-dimethyldisiloxane and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane in 1:1 molar ratio.[12] The ^{1}H NMR spectra of the product showed a multiplet signal due to the vinyl group, suggesting that it was a mixture of stereoisomers. However, the IR spectroscopic data suggested that its structure was that of a tricyclic ladder oligosilsesquioxanes. The absorption due to the siloxane bond was split into peaks at 1050 and 1080 cm^{-1}, which is characteristic of silsesquioxanes having a ladder framework. In 2002, an interesting study was reported on a pentacyclic ladder oligosilsesquioxane obtained by the stepwise synthesis starting with the heterofunctional condensation of the all-*cis*-1,3,5,7-tetraisopropoxycyclotetrasiloxane-1,3,5,7-tetra-ol with 1,3-dichloro-1,3-diisopropoxy-1,3-diphenyldisiloxane, followed by dearylchlorination, hydrolysis, and condensation. The formed stereoisomers were purified by recycle-type high-performance liquid-phase chromatography (HPLC) and confirmed to consist of a pentacyclic ladder structure by X-ray analysis.[13]

In the approach to a selective synthesis of sila-functional oligosiloxanes, such as $(RSiCl_2)_2O$ (R = Ph) and $[RSi(OH)O]_4$ (R = Ph, *i*-Pr), it is important that the starting materials bear sterically bulky organic substituents. Oligosiloxanes, such as sila-functional disiloxane and tetrasiloxane synthesized from methylsilane compounds ($MeSiX_3$), are the key materials for the synthesis of not only polysiloxanes but also cage siloxanes and oligo- and polysilsesquioxanes. However, no practical routes for the synthesis of such siloxanes have been developed thus far.

Isocyanatosilanes are heterocumulene-type pseudo-halosilanes that are less reactive than the corresponding chlorosilanes but more reactive than alkoxysilanes, so that their reactions with alcohols and amines provide products with different degrees of substitution.[14] Practical uses of isocyanatosilanes as vulcanizers or cross-linking agents for resins, as surface-treatment agents, as coupling agents for organic and inorganic materials, and as precursors for polysiloxanes have been developed.[15] We have developed a simple and convenient synthesis route for a series of isocyanatooligosiloxanes $(NCO)_2RSiO[-RSi(NCO)O-]_nSiR(NCO)_2$ (R = Me, n = 0−6; R = Vi, n = 0−4)[16] and, furthermore, succeeded in the synthesis and X-ray crystallographic structure determination of the cyclotetrasiloxane $[MeSi(NCO)O]_4$.[17] On the basis of these experimental results, we have prepared a novel ladder oligomethylsilsesquioxanes using $[MeSi(NCO)O]_4$ as a building block.

Scheme 1. Synthesis of *cis,trans,cis*-$[MeSi(NCO)O]_4$, 2



Results and Discussion

Synthesis of Tricyclic Ladder Methylsilsesquioxane and Separation of Isomers. 1,3,5,7-Tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane (**2**) was synthesized according to Scheme 1 by the reaction of a THF solution containing a stoichiometric amount of water at 0 °C. The yield of **2** depended on the molar concentration of water, increasing up to 49% when the concentration decreased from 0.10 to 0.01%. IR, NMR (^{1}H, ^{13}C, ^{29}Si), mass spectroscopy, and ultimately X-ray crystallography were applied in the determination of the structure of **2**.[17] The methyl and isocyanato groups were shown to be arranged in a *cis-trans-cis* configuration, by the fact that there is only a singlet signal at −60.0 ppm in the ^{29}Si NMR spectrum. Since **2** is expected to be a potential building block for oligo- and polysilsesquioxanes with an *anti*-configuration, the synthesis of the ladder oligomethylsilsesquioxane using **2** was investigated according to Scheme 2.

The reaction of **2** with 2 molar equiv of 1,3-di-*tert*-butoxy-1,3-dimethyldisiloxane-1,3-diol (**3**) in THF at room temperature or at reflux gave only the bicyclic oligosilsesquioxane **4**, isolated in 50% yield as a colorless, viscous liquid. Its ^{1}H NMR spectrum showed signals at 1.31 and 0.15−0.30 ppm, which are ascribed, respectively, to the *tert*-butoxy and methyl groups. The ^{13}C NMR spectrum showed a signal at 123 ppm, the IR spectrum showed an absorption at 2285 cm^{-1} due to the isocyanato groups, while the ^{29}Si NMR spectrum showed split signals centering at −61.5, −63.7, and −64.6 ppm, which were assigned to the silicon atoms at the 3,5-, 9,11-, and 1,7-positions, respectively. The mass spectrum indicated a molecular weight of 600 (m/z = 585 ($M^+ - Me$, 15)), which indicated the composition $(t\text{-}BuO)_2Me_6(NCO)_2Si_6O_7$.

The same reaction carried out in the presence of an equimolar amount of triethylamine resulted in the formation of the tricyclic oligosilsesquioxane **5**. This reaction was monitored by gas chromatography; it was found that **5** is formed by the stepwise reaction of **2** with **3**, followed by the further reaction of **3** with **4**. As the concentration of **2** and **3** decreased with increasing reaction time, **4** increased. This was followed by the further reaction of **4** with **3** to form **5** with the corresponding decrease in **4**. Thus, **5** formed in this way was isolated by distillation in vacuo in 52% yield as a colorless, viscous liquid (bp 145−150 °C/0.6 mmHg). The distillation provided a residual solid insoluble in various solvents. In the IR spectrum of **5**, no absorption peaks due to the Si−NCO and Si−OH groups were detected, while those due to the Si−O−Si bonds were observed at 1054 and 1119 cm^{-1}. In the ^{1}H NMR spectrum, the signals

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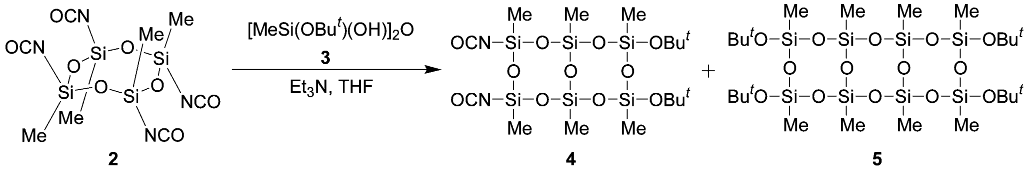
Scheme 2. Synthesis of Bi- and Tricyclic Oligosilsesquioxanes



due to the methyl and *tert*-butyl groups appeared at 1.33 and 0.14 ppm, respectively, with an integration ratio of Me:Bu^t = 2:3. The ^{29}Si NMR spectrum showed split signals centering at −62.5 and −65.1 ppm, respectively. These data suggest that **5** was obtained as a mixture of stereoisomers.

The stereoisomers of the ladder oligosilsesquioxane have been reported to be obtained as a crystal when separated, even if they are a liquid product before purification.[13] Figure 1 shows a chromatogram of the separation of the stereoisomers of **5** by recycle-type reverse-phase HPLC. The product was separated into **5a** (1.2%), **5b** (14.8%), **5c** (3.7%), **5d** (19.7%), and **5e** (8.6%) in a total yield of 48%. After separation, **5a** and **5d** were obtained as white solids. Recrystallization of these compounds by the solvent evaporation method using diethyl ether (Et$_2$O) produced single crystals of colorless plates (**5a**) and blocks (**5d**).

Structure of 5a and 5d. The X-ray crystallography of **5a** and **5d** revealed the molecular structures shown in Figures 2 and 3. Table 1 summarizes the crystallographic data.

As Figure 2 shows, **5a** is constructed of three eight-membered rings with Si−O−Si bonds. The central ring Si1A−Si2A−Si5A−Si6A combines with the side rings Si1A−Si6A−Si7A−Si8A and Si2A−Si3A−Si4A−Si5A at dihedral angles of 56.4° and 44.7°, respectively. The structure of **5a** was, therefore, determined to be the *syn*-configuration ladder oligosilsesquioxane. The average bond lengths and angles of the central eight-membered ring are 1.62 Å for Si−O, 147.7° for Si−O−Si, and 109.5° for O−Si−O. As compared with the starting material **2**, the angle of Si−O−Si becomes acute, which means that the siloxane rings formed by the condensation reaction of **3** with **2** are more rigid or fixed (the average bond lengths and angles of **2** were 1.61 Å for Si−O, 156.8° for Si−O−Si, and 110.9° for O−Si−O). The dihedral angles of the central eight-membered ring and the others are 1.40° (Si1A−Si2A−Si5A−Si6A), 6.55° (Si1A−Si6A−Si7A−Si8A), and 13.67° (Si2A−Si3A−Si4A−Si5A). This suggests that the side rings are under significant strain due to steric hindrance caused by the configuration of the *tert*-butoxy groups, which are bonded to the silicon atoms (Si(4A), Si(8A)) and located on the plane of the central eight-membered ring. Although the three eight-membered rings are distorted, the bond lengths and angles in the siloxane rings are close to the typical values for Si−O−Si bonds. The average bond for **5a** is 1.62 Å for Si−O, and the bond angles are 149.3° for Si−O−Si and 109.2° for O−Si−O. These values are comparable to those found in the *syn*-type ladder oligosilsesquioxanes Me$_8$Ph$_8$Si$_8$O$_{10}$[11] and *i*-Pr$_{12}$Si$_8$O$_{10}$[13a] (Si−O: 1.61−1.64 Å, Si−O−Si: 147.9−157.9°, O−Si−O: 107.4−110.6°).

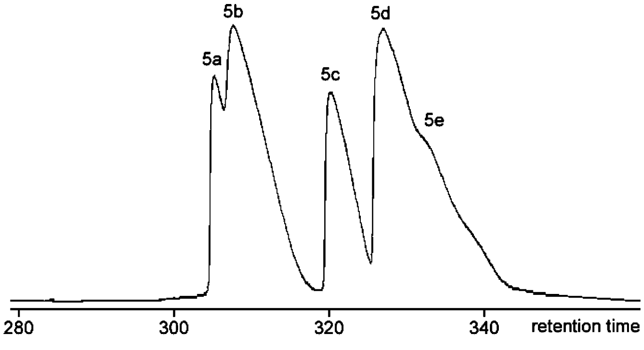


Figure 1. HPLC of the mixture of isomers after six cycles (ODS, MeOH).

As Figure 3 shows, **5d** is the ladder oligosilsesquioxane constructed of three eight-membered rings with the side rings arranged *trans* to the central ring. It is a ladder oligomethylsilsesquioxane with the *anti*-type stereostructure, which has not been previously reported. **5d** is characterized by a symmetry plane passing through the Si(2D) and Si(6D) atoms, and the dihedral angles of either side ring to the central ring are 85.7°, which is obviously greater than those of the *syn*-type **5a** (56.4°, 44.7°). In addition, the central eight-membered ring, Si1D−Si2D−Si5D−Si6D, of **5d** is planar, while the dihedral angles of either side ring, Si1D−Si6D−Si7D−Si8D and Si2D−Si3D−Si4D−Si5D, were found to be 23.0°, indicating that the rings are more distorted than those of the *syn*-type **5a**.

A significant difference in the dihedral angles of the side rings may depend on the configuration of the *tert*-butoxy groups attached to either ring arranged *syn* and *anti*. As indicated by the schematic drawing of **5a** in Figure 2, the *tert*-butoxy groups bonded to both side rings (**5a**) are arranged such that they extend along the plane of the central ring, which suggests an appreciable interaction occurring between the substituents or between these and the rings, leading to a decrease in the flexibility of the ring and/or the dihedral angle. As is shown by the drawing of **5d** in Figure 3, however, the *tert*-butoxy groups are located not only outside the central ring but also *trans* to the adjacent groups, which results in the least possible interaction, thus allowing an increase in the flexibility of the ring and/or the dihedral angle. In other words, the side rings can be less fixed and involved in various conformations by bending and twisting compared with that of the *syn*-type isomers (**5a**).

In the central eight-membered ring of **5d**, the average bond length was 1.62 Å for Si−O, and the bond angles were 146.0° for Si−O−Si and 109.3° for O−Si−O, which are comparable to the values for **2**. The *anti*-type structure of **5d** is possibly derived from the *cis-trans-cis* configuration of the isocyanato group of **2**. The *syn*-type ladder oligosilsesquioxane[13] has been reported to have a double-helix structure. Since **5d** is confirmed to be a linear ladder structure, it is expected to provide a representative model compound for the *anti*-type and/or *cis*-syndiotactic ladder polysilsesquioxanes.

Reaction and Structure. The nucleophilic substitution reaction (S$_N$) of the isocyanatosiloxane **2** with the silanol **3** resulted in the production of the *syn*- and *anti*-type ladder oligosilsesquioxanes. Since the isocyanato groups of **2** are arranged in a *cis-trans-cis* configuration, only the *anti*-type should be formed, provided that the reaction proceeds according to the S$_N$2(Si) type. However, the reaction produced the *syn*- and *anti*-types, suggesting that inversion and retention of the stereochemical configuration take place during the reaction. Analogous to chlorosilane, the hydrolytic condensation of an isocyanatosilane is known to proceed with the inversion of stereochemical

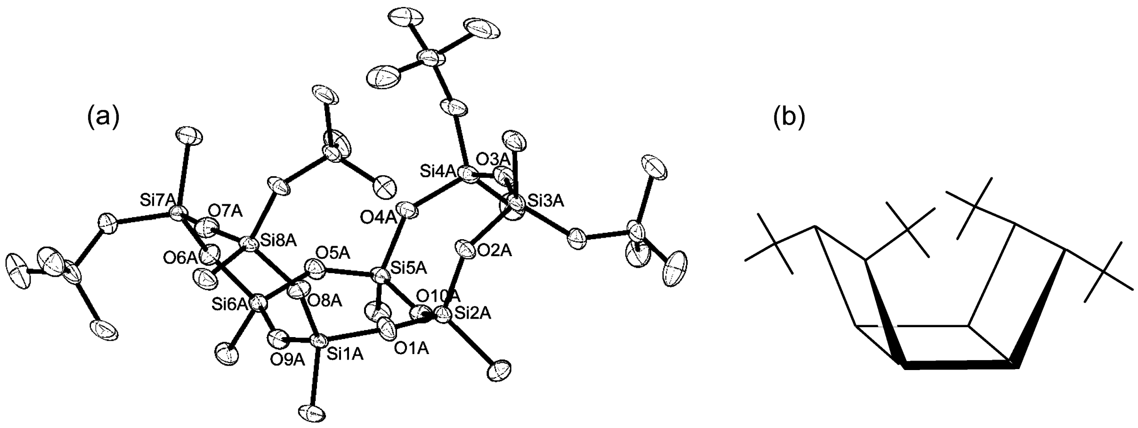


Figure 2. ORTEP drawing (a) and schematic drawing (b) of **5a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

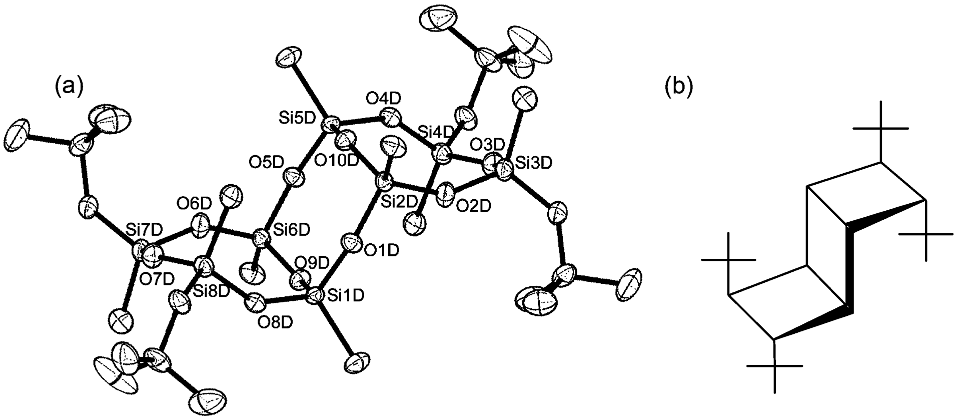


Figure 3. ORTEP drawing (a) and schematic drawing (b) of **5d**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for 5a and 5d

	5a	5d
formula	$C_{24}H_{60}O_{14}Si_8$	$C_{24}H_{60}O_{14}Si_8$
fw	797.44	797.44
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.6034(16)	8.5654(14)
b, Å	13.100(2)	13.721(2)
c, Å	19.985(4)	19.278(3)
α, deg	103.091(3)	76.599(2)
β, deg	101.413(4)	78.407(2)
γ, deg	96.798(4)	83.239(2)
V, Å3	2118.7(7)	2153.0(6)
Z	2	2
μ, mm^{-1}	0.333	0.302
θ range, deg	1.08 to 28.46	1.53 to 27.93
no. of indep reflns	10 340	10 054
no. of reflns collected	15 064	27 810
solution	SHELXL-97	SHELXL-97
R1	0.0580	0.0554
wR2	0.1729	0.1225
S	1.104	1.153
no. of params	435	435

configuration.[18] However, in 1978, Corriu reported that the hydrolytic condensation and alcoholysis of a chlorosilane in the presence of a base catalyst leads to racemization due to the inversion and retention of the stereochemical configuration during the production of an intermediate with a five-coordinated silicon atom formed by the addition of base as a nucleophile to the silicon atom.[19] Since then, many investigations of five-coordinated silicon atoms have been performed. Recently, Bassindale realized the presence of a five-coordinated silicon atom by ^{29}Si NMR spectroscopy.[20] In our investigation, triethylamine was found to be essential to the formation of the tricyclic ladder silsesquioxane and to possibly act as a base to form a five-coordinated intermediate that can produce *syn*- and *anti*-type products resulting from the retention and inversion of the stereochemical configuration.

NMR Spectra and Structure. The ^{29}Si and ^{1}H NMR spectra of **5a** and **5d** are shown in Figures 4−7. The ^{29}Si NMR spectrum of **5a** (Figure 4) showed sharp signals at −62.8 and −63.2 ppm due to the $CH_3Si(Ot\text{-}Bu)O_{2/2}$ (T^2) silicon atoms at the 5-, 7-, 13-, and 15-positions and −64.4 and −64.8 ppm due to $CH_3SiO_{3/2}$ (T^3) silicon atoms at the 1-, 3-, 9-, and 11-positions. The splitting of these signals may be caused by the appreciable bending of the side rings, Si1A−Si6A−Si7A−Si8A and Si2A−Si3A−Si4A−Si5A, as suggested by the dihedral angles of the side rings (6.55°, 13.67°) and central ring (1.40°), resulting from the configuration of the *tert*-butoxy groups in the *syn*-type structure, where they meet or entangle above the central ring (Figure 2). In other words, the conformation of the side rings is rather fixed. The same is true in the ^{1}H NMR spectrum of **5a** in Figure 5, which shows two fine signals at 1.26 and 1.28 ppm because of the *tert*-butoxy groups attached to the silicon atoms, SiA3−SiA7 and SiA4−SiA8.

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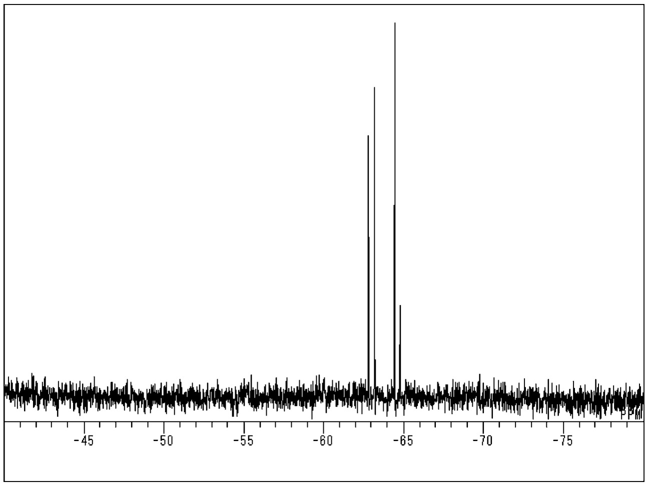

Figure 4. ^{29}Si NMR spectrum of **5a**.

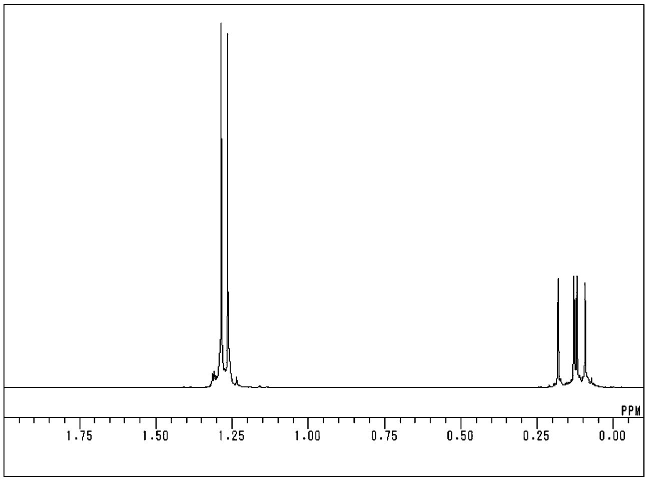

Figure 5. ^{1}H NMR spectrum of **5a**.

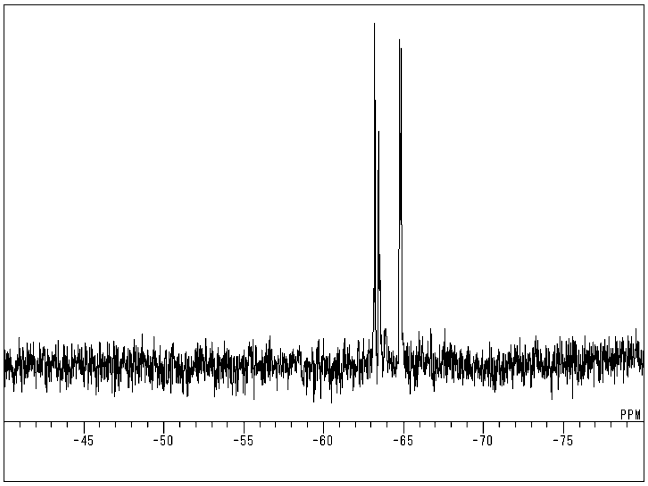

Figure 6. ^{29}Si NMR spectrum of **5d**.

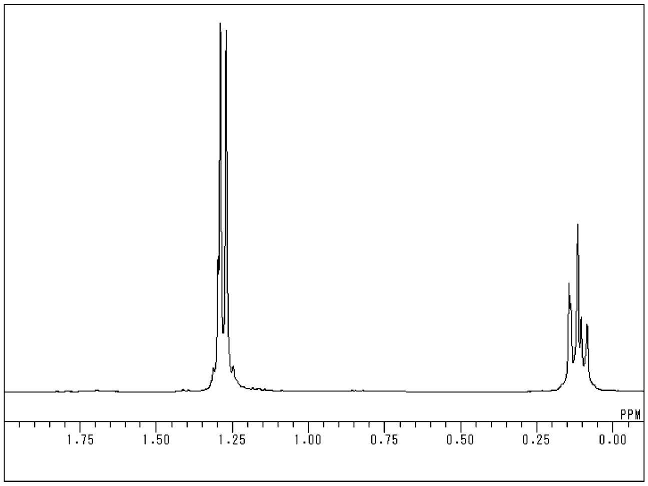

Figure 7. ^{1}H NMR spectrum of **5d**.

On the other hand, in the ^{29}Si NMR spectrum of **5d**, the difference in the chemical shifts due to the T^2 and T^3 silicon atoms decreased when compared with that of **5a**; the ^{29}Si NMR spectrum of **5d** showed signals at −63.2 and −63.4 ppm due to the T^2 silicon atoms and at −64.7 and −64.8 ppm due to the T^3 silicon atoms (Figure 6), while the two broad signals at 1.27 and 1.29 ppm were observed in the ^{1}H NMR spectrum of **5d** (Figure 7). The spectral aspect of **5d** compared to **5a** could reasonably be correlated with the structure; the *anti*-configuration of the side rings with *tert*-butoxy groups arranged *trans* results in the least possible interaction of the substituents, and the rings are subsequently less fixed and can assume various conformations. In addition, this finding is supported by the dihedral angles of the side rings, having been measured to be 23.0°, which is greater than those of **5a**, although the central ring is almost entirely planar. Furthermore, it was observed that the signals due to the siloxane unit structures T^2 and T^3 of the *anti*-type **5d** shift to higher fields than those of the *syn*-type **5a**. This finding and the previous results imply a significant relationship between the ^{29}Si NMR spectra and the structure of the *syn*- and *anti*-ladder oligosilsesquioxanes because it may allow us not only to assign the *syn*- and *anti*-structures but also to predict the chemical shift for the ^{29}Si NMR spectra of the *anti*-type and/or *cis*-syndiotactic ladder polysilsesquioxane.

In contrast to PPSQ, no detailed investigation has been reported regarding the structure of PMSQ. The ^{29}Si CP/MAS NMR spectroscopy of the white solid that was prepared by the hydrolytic condensation reaction of $MeSiCl_3$ or $MeSi(OEt)_3$ using an excess amount of water was reported.[21] PMSQ synthesized from $MeSiCl_3$ showed a strong and broad signal at −65 ppm and a weak signal at −55 ppm, which were assigned to $CH_3SiO_{3/2}$ (T^3) and $CH_3Si(OH)O_{2/2}$ (T^2), respectively. On the other hand, PMSQ synthesized from $MeSi(OEt)_3$ showed a broad signal with a shoulder peak at −65 ppm, which was assigned to $CH_3Si(OC_2H_5)O_{2/2}$. The ^{29}Si NMR spectrum of the methylsilicone resin was reported to show a signal due to $CH_3SiO_{3/2}$ (T^3) at −65.6 ppm in the solid state and at −65.3 ppm in a chloroform solution.[22] In addition, the ^{29}Si NMR spectra of PMSQ ($M_n = 10^5-10^6$) described above showed broad signals at −55.3 and −64.8 ppm.[8b] In our study, the T^3 silicon signals of the tricyclic ladder oligomethylsilsesquioxanes were observed from −64.3 to −64.8 ppm; in particular, the T^3 silicon signals of **5d** appeared at approximately −65 ppm. Consequently, the ladder polymethylsilsesquioxane with an *anti*-configuration (i.e., *cis*-syndiotactic) may be expected to show a finer signal at around −65 ppm due to the T^3 silicon atom.

Conclusion

We have synthesized novel tricyclic ladder oligosilsesquioxanes with methyl groups by the heterofunctional condensation

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[21] Maciel, G. E.; Sullivan, M. J.; Sindorf, D. W. *Macromolecules* **1981**, *14*, 1607.

[22] Engelhardt, G.; Jancke, H.; Lippmaa, E.; Samoson, A. *J. Organomet. Chem.* **1981**, *210*, 295.

reaction of the *cis-trans-cis*-1,3,5,7-tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane with 1,3-di-*tert*-butoxy-1,3-dimethyldisiloxane-1,3-diol. The reaction product obtained as a liquid was a mixture of stereoisomers. The separation of the isomers by recycle-type HPLC gave two ladder oligomethylsilsesquioxanes as crystals. The X-ray crystallography showed that they were *syn*- and *anti*-type ladder oligosilsesquioxanes constructed of three eight-membered rings. Compared to the *syn*-type oligomethylsilsesquioxane, the *anti*-type provides a suitable model compound for the *cis*-syndiotactic ladder polysilsesquioxane.

Experimental Section

General Experimental Procedures. Triisocyanato(methyl)silane (Matsumoto Chemical Industry Co., Ltd.), triethylamine (Wako Pure Chemical Industries, Ltd.), and THF (Wako Pure Chemical Industries, Ltd.) were purified by distillation. All other reagents were obtained from commercial sources and used without additional purification. The gas chromatography was performed using a GL Science GC-390 with a column (SE-30, 3.0 m × 3.0 mm). The mass spectra were obtained using a Shimadzu GCMS-QP2000A (column: OV-1, 50 m × 0.25 mm) equipped with a direct insertion apparatus. Recycle-type HPLC was carried out using a Shimadzu CBM-10A with two YMC 250 mm × 20 mm ODS S-5 columns. Fourier transform nuclear magnetic resonance spectra were obtained using a JEOL ECP-500 (^{1}H at 500.00 MHz, ^{13}C at 125.00 MHz, and ^{29}Si at 99.00 MHz). The chemical shifts were reported as δ units (ppm) relative to $SiMe_4$, and/or the residual solvent peaks were used as the standard. The Fourier transform infrared spectra were measured using a JEOL FT-IR-400 IR spectrophotometer with a carbon tetrachloride solution method. The X-ray crystallography was performed as follows: A single crystal was attached to the top of a glass fiber and measured by a Bruker SMART APEX equipped with a CCD diffractometer (λ(Mo Kα) = 0.71073 Å; 25 ± 2 °C) in a nitrogen gas stream at 90 K. The structure was solved by SHELXL-97 and refined by a full-matrix least-squares technique.

Preparation of 1,1,3,5,7,7-Hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane (1). In a four-necked flask equipped with a reflux condenser and a flow meter connected to the flask, triisocyanato(methyl)silane was added, while a stoichiometric amount of water and 1,4-dioxane were added to the flask. Upon refluxing triisocyanato(methyl)silane under reduced pressure, a mixed vapor of 1,4-dioxane and water was introduced into a 200 mL four-necked flask to hydrolyze triisocyanato(methyl)silane. The reaction mixture was distilled to give 1,1,3,3-tetraisocyanato-1,3-dimethyldisiloxane in an 80% yield. Furthermore, vapor-phase hydrolysis of 1,1,3,3-tetraisocyanato-1,3-dimethyldisiloxane gave **1** in 68% yield (colorless liquid, bp 141−143 °C/2 mmHg). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.48 (s, 6H); ^{13}C NMR ($CDCl_3$) δ −3.76, −0.51, 123; ^{29}Si NMR ($CDCl_3$) δ −61.8, −60.1; MS (70 eV) *m/z* (%) 457 (M^+ − Me, 15); IR (CCl_4 solution) 2970, 2280, 1275, 1110 cm^{-1}.

Preparation of 1,3,5,7-Tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane (2). A solution of water (0.54 g, 0.03 mol) in THF (100 mL) was slowly added to a vigorously stirred and ice-cooled (0 °C) solution of **1** (14.2 g, 0.03 mol) 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 **2** in 49% yield (bp 110−112 °C/1.0 mmHg). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.36 (s, H); ^{13}C NMR ($CDCl_3$) δ −2.20, 123; ^{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}.

Preparation of 1,3-Di-*tert*-butoxy-1,3-dimethyldisiloxane-1,3-diol (3). According to the literature,[23] a solution of *tert*-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 °C) solution of 1,1,3,3-tetraisocyanato-1,3-dimethyldisiloxane (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-*tert*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane in 70% yield (bp 92.0−92.5 °C/1.7 mmHg). A solution of water (0.72 g, 0.04 mol) and triethylamine (4.04 g, 0.04 mol) was added to a vigorously stirred and ice-cooled (0 °C) solution of 1,3-di-*tert*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane (6.64 g 0.02 mol), and the mixture was refluxed for 2 h, filtered, and evaporated to give a crude product. Recrystallization of the product from pentane (50 mL) produced **3** in 65% yield (mp 90.7−91.3 °C (dec)). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 3H), 1.33 (s, 9H), 4.40 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −1.89, 31.6, 73.0; ^{29}Si NMR ($CDCl_3$) δ −53.1; MS (70 eV) *m/z* (%) 267 (M^+ − Me, 15); IR (CCl_4 solution) 3250, 2980, 1280, 1060, 1020 cm^{-1}.

Synthesis of 9,11-Di-*tert*-butoxy-3,5-diisocyanato-1,3,5,7,9,11-hexamethylbicyclo[5.5.1]hexasiloxane (4). A solution of **3** (2.82 g, 0.01 mol) in THF (10 mL) was slowly added to a vigorously stirred and ice-cooled (0 °C) solution of **2** (4.04 g, 0.01 mol) in THF (10 mL), and the mixture was stirred at room temperature for 2 h. After filtration of cyanuric acid as a precipitate followed by removal of THF, the residue was distilled in vacuo to give **4** in 52% yield (bp 148−150 °C/3.0 mmHg). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.15 (m, 12H), 0.30 (m, 6H), 1.31 (m, 18H); ^{13}C NMR ($CDCl_3$) δ −3.8, −1.9, −1.8, 31.5, 73.1, 123.0; ^{29}Si NMR ($CDCl_3$) δ −61.5 to −64.6; MS (70 eV) *m/z* (%) 585 (M^+ − Me, 15); IR (CCl_4 solution) 2977, 2285, 1366, 1270, 1097, 1062 cm^{-1}.

Synthesis of 5,7,13,15-Tetra-*tert*-butoxy-1,3,5,7,9,11,13,15-octamethyltricyclo[9.5.1.1^{3,9}]octasiloxane (5). A solution of **3** (5.64 g, 0.02 mol) and triethylamine (2.02 g, 0.02 mol) in THF (20 mL) was slowly added to a vigorously stirred and ice-cooled (0 °C) solution of **2** (4.04 g, 0.01 mol) in THF (10 mL), and the mixture was then stirred at room temperature for 2 h. After filtration of the cyanuric acid as a precipitate followed by removal of the THF, the residue was distilled in vacuo to give **5** (bp 145−150 °C/0.6 mmHg, 4.10 g). The isomeric mixture of **5** was separated by recycle-type HPLC (ODS, MeOH) to afford **5a** (0.096 g, 1.2%), **5b** (1.18 g, 14.8%), **5c** (0.290 g, 3.7%), **5d** (1.57 g, 19.7%), and **5e** (0.685 g, 8.6%). Spectral data of **5** (mixture of isomers): ^{1}H NMR ($CDCl_3$) δ 0.059−0.133 (m, 24H), 1.25−1.31 (m, 36H); ^{13}C NMR ($CDCl_3$) δ −3.8, −1.8, 31.5, 72.7; ^{29}Si NMR ($CDCl_3$) δ −63.8 to −65.3; MS (70 eV) *m/z* (%) 782 (M^+ − Me, 15); IR (CCl_4 solution) 2977, 1365, 1268, 1119, 1054 cm^{-1}; Spectral data of **5a**: ^{1}H NMR ($CDCl_3$) δ 0.071 (s, 6H), 0.098 (s, 6H), 0.107 (s, 6H), 0.159 (s, 6H), 1.24 (s, 18H), 1.26 (s, 18H); ^{13}C NMR ($CDCl_3$) δ −3.59, −1.46, −1.39, 31.6, 31.7, 72.9, 73.0; ^{29}Si NMR ($CDCl_3$) δ −64.75, −64.43, −63.17, −62.80; MS (70 eV) *m/z* (%) 782 (M^+ − Me, 15); IR (CCl_4 solution) 2977, 1365, 1268, 1119, 1054 cm^{-1}. Anal. Calcd for $C_{24}H_{60}O_{14}Si_8$: C, 36.15; H, 7.58. Found: C, 36.07; H, 7.93. Spectral data of **5b**: ^{1}H NMR ($CDCl_3$) δ 0.069−0.176 (m, 24H), 1.25−1.29 (m, 36H); ^{13}C NMR ($CDCl_3$) δ −3.92, −3.87, −2.00, −1.84, −1.80, −1.70, 31.2, 31.3, 72.2, 72.6, 72.7; ^{29}Si NMR ($CDCl_3$) δ −64.97, −64.77, −64.66, −64.58, −64.56, −64.48, −64.24, −64.05, −63.24, −63.03, −62.86, −62.61; MS (70 eV) *m/z* (%) 782 (M^+ − Me, 15); IR (CCl_4 solution) 2977, 1365, 1268, 1119, 1054 cm^{-1}. Spectral data of **5c**: ^{1}H NMR ($CDCl_3$) δ 0.097 (s, H), 0.111 (s, H), 0.145 (s, H), 0.166 (s, H), 1.29 (s, H), 1.30 (s, H), 1.32 (s, H), 1.33 (s, H); ^{13}C NMR ($CDCl_3$) δ −3.59, −1.46, −1.39, 31.6, 31.7, 72.9, 73.0; ^{29}Si NMR ($CDCl_3$) δ −64.91, −64.82, −64.72, −64.63, −64.57, −64.42, −63.44, −63.38, −63.32, −63.23, −63.14, −62.92, −62.83; MS (70 eV) *m/z* (%) 782 (M^+ − Me, 15); IR (CCl_4 solution) 2979, 1368, 1268, 1119, 1055 cm^{-1}. Spectral data of **5d**: ^{1}H NMR ($CDCl_3$) δ 0.085 (s, 3H), 0.105 (s, 3H), 0.116 (s, 9H), 0.144 (s, 9H), 1.27 (s, 18H), 1.29 (s, 18H); ^{13}C NMR ($CDCl_3$) δ −3.63, −1.79, 31.6, 72.7, 72.9; ^{29}Si NMR ($CDCl_3$) δ −64.82, −64.72, −63.42, −63.17; MS (70 eV) *m/z* (%) 782 (M^+

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− Me, 15); IR (CCl_4 solution) 2977, 1365, 1268, 1119, 1054 cm^{-1}. Anal. Calcd for $C_{24}H_{60}O_{14}Si_8$: C, 36.15; H, 7.58. Found: C, 36.16; H, 7.79. Spectral data of **5e**: ^{1}H NMR ($CDCl_3$) δ 0.068−0.143 (m, 24H), 1.27−1.31 (m, 36H); ^{13}C NMR ($CDCl_3$) δ −3.73, −3.65, −1.94, −1.89, −1.85, −1.81, −1.74, −1.67, 31.5, 31.6, 72.8, 72.9; ^{29}Si NMR ($CDCl_3$) δ −65.11, −64.88, −64.74, −64.45, −63.96, −63.87, −63.75, −63.59, −63.50, −63.28, −63.24; MS (70 eV) *m*/*z* (%) 782 ($M^+ - Me$, 15); IR (CCl_4 solution) 2977, 1365, 1268, 1119, 1054 cm^{-1}.

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Note Added after ASAP Publication. In the version of this paper that was posted on the Web Sept 23, 2006, the author affiliations were incorrect. The affiliations that now appear are correct.

Supporting Information Available: Molecular structure of **5c**, selected bond lengths and angles data (PDF), and crystallographic information for **5a** and **5d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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