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Synthesis and Structure of *syn*,*anti*,*syn*-Pentacyclic Ladder Oligomethylsilsesquioxane

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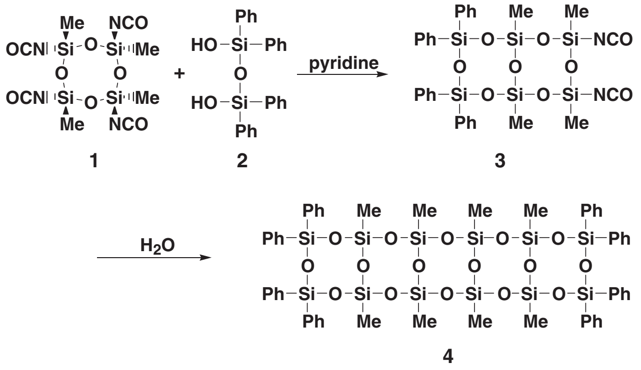
Novel pentacyclic ladder oligomethylsilsesquioxane was synthesized using *cis*,*trans*,*cis*-$[MeSi(NCO)O]_4$ as a building block. This compound was isolated in 13% yield by reprecipitation from the reaction mixture. X-ray crystallography revealed that pentacyclic rings assume a *syn*,*anti*,*syn*-configuration, resulting in the tube-like structure.

Ladder polymethylsilsesquioxanes (PMSQs) have become of growing interest in polymer chemistry due to their excellent chemical, physical, and electrical properties resulting from the double-chained siloxane linkage with the formula $(MeSiO_{3/2})_n$. The structure of PMSQ prepared by the hydrolysis of trifunctional silane, however, was suggested to have an irregular ladder structure, based on ^{29}Si NMR and GC-MS analyses.[1] Because the methyl group is useless by preventing the construction of a three-dimensional structure or cage-type silsesquioxane due to its bulkiness, PMSQ with a perfect siloxane framework has not yet been obtained. It is, therefore, difficult to obtain PMSQ with a highly regulated ladder structure by hydrolysis of trifunctional silanes. In order to design materials with high performance, a method must be developed to control the ladder siloxane backbone.[2]

On the other hand, many scientists have tried to estimate the ladder structure by powder X-ray diffraction, IR spectra, and calculation of the *a* value in the Sakurada–Mark–Houwink equation. The evidence is, however, not universally accepted.[3] As preferable synthetic methods for perfect PMSQs have not been developed thus far, the synthesis of ladder oligosilsesquioxanes has been focused on to provide a model compound to estimate the real and essential structure and properties of the ladder polysilsesquioxanes. Tri-, penta-, and heptacyclic ladder oligosilsesquioxanes have been synthesized by heterofunctional condensation reactions of sila-functional cyclotetrasiloxane with bulky groups such as phenyl and isopropyl groups.[4] There have been few reports regarding the synthesis of ladder oligosilsesquioxanes with a sterically less hindered group such as methyl.[5,6] The importance of the molecular design in relation to the structure of the precursor and reaction conditions has been suggested to be a factor in obtaining a ladder polysilsesquioxane with a perfect siloxane framework.

We have synthesized *cis*,*trans*,*cis*-$[MeSi(NCO)O]_4$ (**1**) and shown that **1** is a suitable building block for the synthesis of ladder oligo- and polysilsesquioxanes.[5–7] Quite recently, we have succeeded in synthesizing highly soluble PMSQ by the hydrolysis of $[MeSi(X)O]_4$ [X = H, OEt (a mixture of four stereoisomers)] or **1**.[8] PMSQ synthesized from **1** has a highly regulated ladder structure with fewer defects in the siloxane framework than the hydrolyzate of X = H or OEt. We therefore report herein the synthesis of novel pentacyclic ladder oligomethylsilsesquioxane **4** according to Scheme 1 using **1** as a building block.



Scheme 1.

1 was synthesized according to the literature[7] 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). 1,1,3,3-Tetraphenyldisiloxane-1,3-diol (**2**) was synthesized by a two-step hydrolysis started with dichloro(diphenyl)silane via $[Ph_2SiCl]_2O$ in the presence of triethylamine. A THF solution of **1** with pyridine was stirred at rt for 30 min. A stoichiometric amount of **2** in THF was then added to the reaction mixture and stirred at rt for 9 h. Bicyclic oligosilsesquioxane **3** was not isolated because **3** was highly hydrolyzable in air. The formation of **3** was estimated by the following three reasons, (1) **3** is expected to be an intermediate in the synthesis of tricyclic ladder silsesquioxane by the reaction of **1** with **2** in a molar ratio of 1:2.[6] (2) **2** is stable against self-condensation to form water. (3) The yield of **4** was increased with the increase of the molar ratio of water to **1** up to 8 to support the formation of **4** by the hydrolytic condensation of **3**. Then, the reaction mixture of **1** and **2** was directly treated with water at rt overnight. After cyanuric acid was filtered out, **4** was isolated as a white solid in 13% yield when methanol was added to the reaction mixture.[9] Surprisingly, ladder oligosilsesquioxane **4** was isolated in relatively good yield by a simple unit operation, reprecipitation, as a major product because we can expect a lower solubility than other stereoisomers due to the highly regulated structure for **4**. In the ^{1}H NMR spectrum, two sharp signals due to methyl groups were detected at 0.01 and 0.15 ppm. The ^{29}Si NMR spectrum showed sharp signals at −45.2, −64.1, and −64.2 ppm due to the silicon atoms at the 9-, 11-, 21-, and 23-potitions, at the 3-, 5-, 15-, and 17-positions,

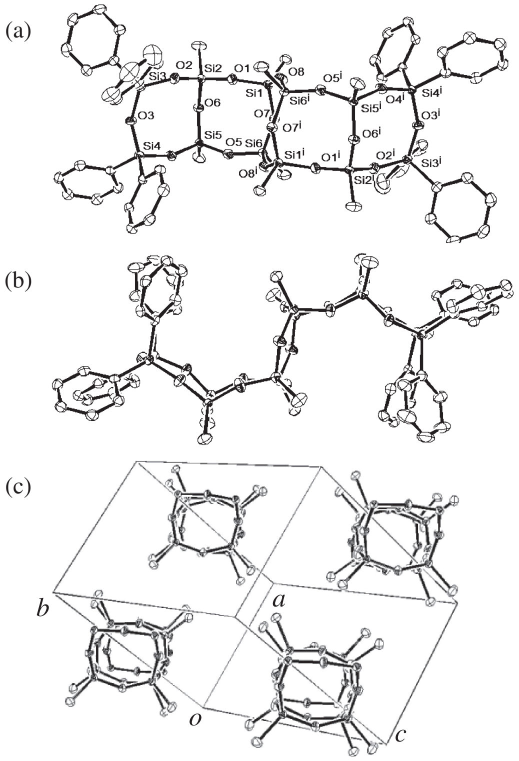


Figure 1. Molecular structures of **4** (a: top view, b and c: side view). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and carbon atoms of phenyl groups (1c) are omitted for clarity.

and at the 1-, 7-, 13-, and 19-positions. In the IR spectrum, no absorption peaks due to the Si–NCO and Si–OH groups were observed. Two sharp Si–O–Si stretching bands corresponding to a ladder structure were observed at 1047 and 1129 cm^{-1}. These bands were comparable to those found in other ladder oligo-[4f,5,6] and polysilsesquioxanes.[8,10] The positive MS-ESI spectrum showed a peak at m/z 1352.1 ($[M + Na]^+$). These results indicated that **4** was a pentacyclic ladder oligomethylsilsesquioxane.

The X-ray crystallography[11] of **4** revealed the molecular structures shown in Figure 1. Suitable crystals for X-ray crystallography were obtained directly by slow evaporation of a solution of chloroform/methanol (1/1) at rt. The single crystal of **4** belongs to a triclinic system ($P\bar{1}$ group), with one molecule being included per unit cell. The structure was fully refined to the R value of 4.8%. **4** is constructed of five eight-membered rings with a *syn*,*anti*,*syn*-configuration (Figure 1b) with a tube-like structure (Figure 1c). The torsion angles of the siloxane rings were 1.7° for Si3–Si4–Si2 to Si2–Si5–Si4, −8.6° for Si2–Si5–Si1 to Si1–Si1^{i}–Si5, and 0° for Si1–Si6^{i}–Si1^{i} to Si1^{i}–Si6–Si1. The dihedral angles were 2.4° for Si3–Si4–Si5–Si2, 12.1° for Si2–Si5–Si6–Si1, and 0° for Si1–Si6–Si1^{i}–Si6^{i} rings. These values were smaller than those for the other tricyclic ladder oligomethylsilsesquioxanes[5,6] because a sterically less hindered methyl group gives enough volume to arrange a relative methyl or phenyl group. To date, the steric structures of ladder eight-membered rings have been reported as a *cis-syndiotactic*[12] or double helix structure.[4f,13] In this study, we present the first synthesis of ladder backbone as a *syn*,*anti*,*syn*-configuration. The average bond length for **4** is 1.63 Å for Si–O, and the average bond angles are 142.3° for Si–O–Si and 108.7° for O–Si–O. The structure of **4** did not reflect the stereostructure of **1**, and siloxane rings with methyl groups were arranged in an all-*cis*-configuration, which was similar to our previous study.[6] This was caused by 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 a base as a nucleophile to the silicon atom.[14]

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9 Mp and spectral data of **4**: mp 238.3–238.8 °C. ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 12H), 0.15 (s, 12H), 7.23 (t, $J = 7.3$ Hz, 8H), 7.29–7.38 (m, 12H), 7.45 (tt, $J = 7.3$, 2.0 Hz, 4H), 7.56 (dd, $J = 8.0$, 1.4 Hz, 8H), 7.66 (dd, $J = 8.0$, 1.4 Hz, 8H). ^{13}C NMR ($CDCl_3$): δ −3.9, −3.5, 127.5, 127.7, 129.8, 130.0, 134.2, 134.3, 134.8. ^{29}Si NMR ($CDCl_3$): δ −45.2, −64.1, −64.2. MS-ESI m/z: 1352.1 $[M + Na]^+$. IR (CCl_4/cm^{-1}): 3073, 3052, 2971, 1592, 1429, 1270, 1129, 1047, 864, 522. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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11 A single crystal was attached to the top of a glass fiber with a cold nitrogen gas stream at 103 K, and measured using a Bruker SMART APEX equipped with a CCD diffractometer ($\lambda(\mathrm{Mo\,K}\alpha) = 0.71073$ 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. Crystallographic data for **4**: colorless plate, molecular formula $C_{56}H_{64}O_{16}Si_{12}$, $Mr = 1330.15$, $T = 103$ K, triclinic, $P\bar{1}$, $a = 9.1333(7)$ Å, $b = 12.8525(10)$ Å, $c = 14.0769(11)$ Å, $\alpha = 92.1960(10)°$, $\beta = 91.1030(10)°$, $\gamma = 94.9150(10)°$, $V = 1644.7(2)$ Å^3, $Z = 1$, $R1 = 0.0498$, $wR2 = 0.1258$ for all 7077 data points with 383 parameters. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-823965. Copies of the 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, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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