Synthesis and Structure of *cis*-*trans*-*cis*-1,3,5,7-Tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane

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The controlled hydrolysis of 1,1,3,5,7,7-hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane in tetrahydrofuran gave the desired cyclotetrasiloxane which is expected to be a building block for novel ladder oligosiloxanes with *anti* configuration, in contrast to the conventional ladder oligosiloxanes with *syn* configuration.

Silicone representative of polysiloxanes is well-known as unique and versatile materials with excellent chemical, physical, and electrical properties. Polyphenylsilsesquioxane, first reported by Brown in 1965, was believed to show properties superior to silicone because of ladder frameworks.[1] To date, however, the results on the spectroscopic and X-ray analysis of polyphenylsilsesquioxane reveal that the structure is not perfect ladder but irregular ladder.[2] Perfect ladder polysiloxanes should be expected to provide high performance materials, and thus the syntheses have attracted continuous attentions as a fascinating research challenge.

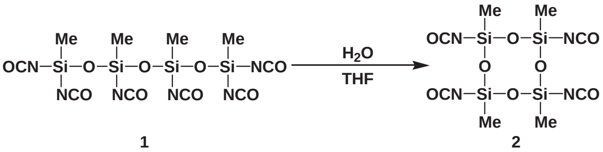
Since no preferable synthetic methods for perfect ladder polysiloxanes have been developed so far, the synthesis of ladder oligosiloxanes has been a serious target to investigate the real and essential properties of ladder polysiloxanes. Currently, tri- and pentacyclic ladder oligosiloxanes have been synthesized by heterofunctional condensation reactions of sila-functional oligosiloxanes such as chlorodisiloxanes, disiloxanepolyols, and cyclotetrasiloxanetetraols with sterically bulky groups of phenyl, isopropyl, and cyclohexyl group.[3]

One of the key process to obtain ladder oligosiloxanes is the synthesis of precursors as building blocks: trifunctional silane $RSiX_3$, disiloxane $(RX_2Si)_2O$, and cyclotetrasiloxane $(RXSiO)_4$ ($X = H$, OH, Cl, and OR) which are the constituents of ladder polysiloxanes. Of these, the cyclotetrasiloxane is a key material for ladder oligosiloxanes. At present, sila-functional cyclotetrasiloxanes such as 1,3,5,7-tetrachloro-1,3,5,7-tetra-R substituted cyclotetrasiloxanes ($R = Me$[4], Vi,[4] and Ph[5]) or 1,3,5,7-tetrahydroxy-1,3,5,7-tetra-R substituted cyclotetrasiloxanes have been reported, of which the former was obtained as a by-product and the latter was prepared by hydrolysis of $RSiCl_3$ ($R = Ph$[6] and *i*-Pr[7]). The hydroxy groups of siloxanetetraols have been confirmed to be arranged all-*cis* by X-ray crystallography. In the usual method to synthesize sila-functional oligosiloxanes selectively, it is the key factor that the starting materials bear sterically bulky organic groups. Therefore, it is of significance and practical importance to develop the synthetic routes of sila-functional oligosiloxanes as the building block for not only ladder oligo- and even polysiloxanes but also cube siloxanes, using versatile silanes with sterically less hindered methyl and vinyl groups.[8]

From the above point of view, we have investigated the synthesis, reaction, and properties of sila-functional silanes and oligosiloxanes, especially those with isocyanato group. Isocyanatosilane is a pseudo halosilane being less reactive than chlorosilane but more reactive compared with alkoxysilane on nucleophilic substitution reactions such as alcoholysis, hydrolysis, and condensation, which means that the reactions can easily be controlled to give the substitution products selectively.[9] This was realized by investigating the reaction of triisocyanato(methyl)silane with alcohols and amines to give alkoxyisocyanato(methyl)silanes or aminosilanes.[10] The results also led to the synthesis of oligoisocyanato(methyl)siloxanes as the building block for ladder oligo(methyl)siloxanes; a vapor phase hydrolysis of triisocyanato(methyl or vinyl)silane was found to provide corresponding oligoisocyanatodi- and tetrasiloxanes in high yields,[11] of which the former provided disiloxanediols.[12] Furthemore, a series of linear and cyclic isocyanatosiloxanes was successfully synthesized.[13] Recently, we have reported the synthesis of 1,3,5,7-tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane, but the real structure have not been clarified yet.[14] In this work, we wish to report the result of the X-ray crystallography.

1,3,5,7-Tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane **2** was synthesized by the two-step vapor-phase hydrolysis[11] started with triisocyanato(methyl)silane via 1,1,3,3-tetraisocyanato-1,3-dimethyldisiloxane followed by the liquid-phase hydrolysis of 1,1,3,5,7,7-hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane **1** in tetrahydrofuran (THF) according to Scheme 1. Since the yield of **2** formed by intramolecular condensation reaction depends on the molar concentration of substrates of **1** and water, it was investigated in the various molar water concentrations of 0.01 to 0.10%; a stoichiometric amount of water diluted with THF was dropped into **1** dissolved in THF with stirring at room temperature for a certain time. The solvent was removed, and the residue was distilled in vacuo to give **2**. As the molar concentration decreased 0.01%, the yield increased up to 49%. **2** was obtained as a colorless liquid (bp 110–112 °C/133 Pa) but solidified at room temperatures after distillation.[15]

In the infrared absorption spectra, the absorption peaks were observed at 2240 and $1110\,cm^{-1}$ due to Si–NCO and Si–O–Si, respectively. The ^{1}H NMR spectrum showed the single signal at 0.63 ppm, and the ^{13}C NMR spectrum indicated the signals at 123.0 and −2.2 ppm ascribed to isocyanato group and methyl group, respectively, while the single signal at −60.0 ppm was



1 **2**

Scheme 1.

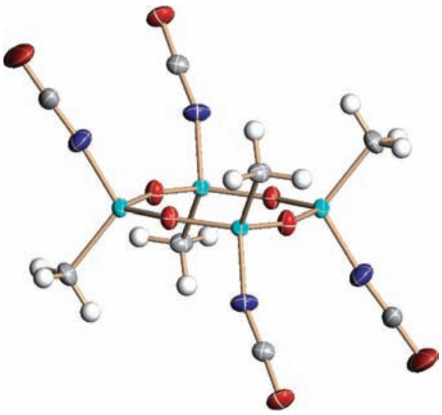


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawing at the 50% probability level. Cyan: silicon, red: oxygen, blue: nitrogen, gray: carbon, white: hydrogen atoms.

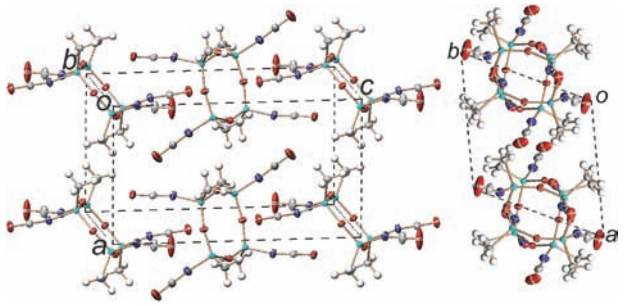


Figure 2. Packing diagram of **2**. The average distance between adjacent planar rings along the *c* axis in the crystal is 4.62 Å. Thus the isocyanato groups of each molecule are arranged alternately because the length of isocyanato groups is 4.02 Å.

detected with the ^{29}Si NMR spectrum, indicating that isocyanato(methyl)siloxane **2** was provided.

On heating **2** at 120 °C and then gradually cooling down to the melting point, a colorless plate crystal was formed. The X-ray crystallography was performed at 90 K.[16] The space group was found to be triclinic system $P\bar{1}$ and the unit lattice cell was consisted of two molecules of **2**. The R factor was 3% and the structure was sufficiently refined. The molecular structure of **2** is shown in Figure 1. The average bond lengths and bond angles were 1.61 Å for Si–O, 156.8° for Si–O–Si, and 110.9° for O–Si–O. They are close to the typical values for siloxane compounds.

An eight-membered ring formed by siloxane bonds has a plane of symmetry at its center, and is approximately planar because the dihedral angle is zero degree. The isocyanato and methyl groups were arranged *cis-trans-cis*, which was also supported by the spectral data. Figure 2 shows the crystal packing of **2**. The molecules are aligned along the *c* axis where isocyanato groups are arranged alternately. The view of the molecular row show that **2** consists of a chain-like structure, as four of the isocyanato groups are used to form a joint, and the chains mutually lengthen in parallel.

In conclusion, we have succeeded in not only the structure determination but also the simple and first synthesis of **2** with less sterically hindered methyl group arranged in a *cis-trans-cis* configuration as well as isocyanato groups, compared with conventional sila-functional cyclotetrasiloxanes with bulky organic groups. **2** is expected to be a building block for novel ladder oligosiloxanes with *anti* configuration, as has been reported in the meeting,[17] in contrast to the conventional ladder oligosiloxanes with *syn* configuration.

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15 Melting point and spectral data of **2**: mp 50.0–52.5 °C. ^{1}H NMR (CDCl$_3$) δ 0.36 (s, 1H) ppm. ^{13}C NMR (CDCl$_3$) δ 123.0, −2.2 ppm. ^{29}Si NMR (CDCl$_3$) δ −60.6 ppm. IR (CCl$_4$ solution) 2975, 2290, 1270, 1110 cm^{-1}.

16 Crystallographic data for **2**: colorless plate, molecular formula $C_8H_{12}N_4O_8Si_4$, fw = 404.58, $T = 90$ K, triclinic, $P\bar{1}$, $a = 8.200(7)$ Å, $b = 8.346(7)$ Å, $c = 14.384(16)$ Å, $\alpha = 98.923(10)^\circ$, $\beta = 92.316(10)^\circ$, $\gamma = 114.996(10)^\circ$, $V = 875.3(14)$ Å^3, $Z = 2$, $R1 = 0.0274$, $wR2 = 0.0681$ for all 4107 data with 221 parameters.

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