Bicyclic and Tricyclic Ladder Compounds Consisting of Two Oligosiloxane Chains Bridged by Si–Si Rungs

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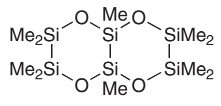
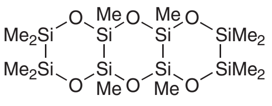
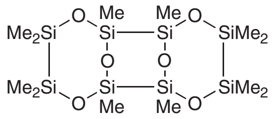
(Received September 16, 2003; CL-030863)

The bicyclic and tricyclic ladder compounds consisting of two oligosiloxane chains bridged by Si–Si rungs were synthesized by the condensation of 1,2-dihydroxy-1,1,2,2-tetraisopropyldisilane and 1,1,2,2-tetrachloro-1,2-diisopropyldisilane with aniline. The structures of these compounds were confirmed by X-ray crystallography.

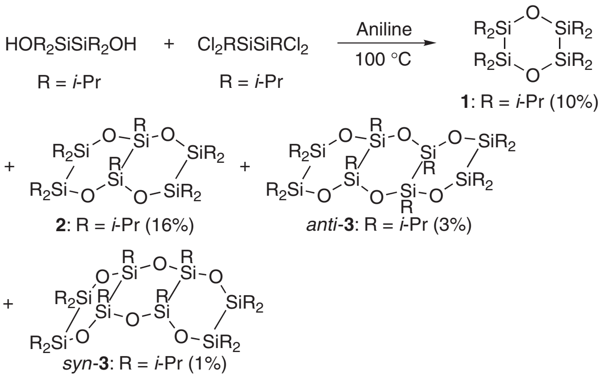
The ladder-shaped organosilicon compounds such as ladder oligosilanes[1,2] and ladder oligosiloxanes[3] are a unique class of compounds. Among several types of ladder compounds, the bicyclic and tricyclic ladder compounds consisting of two oligosiloxane chains bridged by Si–Si rungs have been reported as early as 1963 by Kumada and co-workers.[4] The authors proposed the ladder structures **A** and **B**, but later in 1967, the X-ray crystallographic study on the tricyclic compound showed that the correct structure corresponded to the isomer **C**, where two oxygen atoms are located in the bridgehead bonds.[5] As no X-ray crystallographic study on the bicyclic compound has been reported, the possibility of other isomeric structures remains. Recently we have found that the compounds of types A and B can be synthesized by the condensation of two kinds of disilanes with a base. We report herein the synthesis and structures of the bicyclic and tricyclic ladder compounds.


A


B


C

The condensation of 1,2-dihydroxy-1,1,2,2-tetraisopropyldisilane and 1,1,2,2-tetrachloro-1,2-diisopropyldisilane with aniline gave 1,3,3,4,4,6,8,8,9,9-decaisopropyl-2,5,7,10-tetraoxabicyclo[4.4.0]decasilane (**2**) and *anti*- and *syn*-1,3,5,5,6,6,8,10,12,12,13,13-dodecaisopropyl-2,4,7,9,11,14-hexaoxatricyclo[8.4.0.0^{3,8}]tetradecasilanes (*anti*-**3** and *syn*-**3**) together with the monocyclic compound **1**.[6] These compounds were separated by recycle-type HPLC (ODS, MeOH–THF (8:2)). In the tricyclic compounds, *anti*-**3** was a superior product to *syn*-**3**, and this result seems to reflect the strain of these molecules. Comparison of our results with Kumada's ones shows that the reaction conditions affect the structures of products. However, the effects of substituents cannot be excluded completely because the ready formation of the seven-membered ring structure has been demonstrated in methyl-substituted siloxanes.[5]



The structures of **2**, *anti*-**3**, and *syn*-**3** were determined by X-ray crystallography (Figures 1–3).[7–10] Compound **2** has a twisted ladder structure of C_2 symmetry. The twist angle between the terminal Si–Si rungs is 26.9°. Each 1,4-dioxacyclohexasilane ring has a unique structure, where the Si(1′)–Si(1)–O(1)–Si(2) atoms and the Si(1)–Si(1′)–O(2)–Si(3) atoms construct planes, and the dihedral angle of both planes is 11.9°. The terminal Si–Si rungs (2.390(2) Å) are significantly longer than that of the central Si–Si rung (2.360(2) Å). The twisted structure and the longer terminal Si–Si rungs are favorable for reducing the steric repulsion between the bulky diisopropylsilyl groups in the terminal rungs. The Si–O–Si bond angles (146.4(2) and 146.3(2)°) are normal compared with that of $Me_3SiOSiMe_3$ (148.8(2)°).[11] The dihedral angle between the cis-fused six-membered rings is 117.4°.

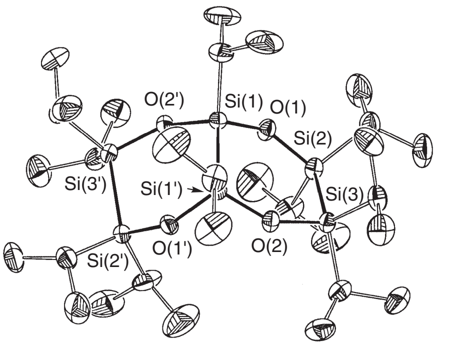


Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Compound *anti*-**3** has a slightly twisted ladder structure (Figure 2). Since the central six-membered ring has a planar structure, and the Si(2)–O(2) and Si(5)–O(3) bonds (also Si(1)–O(6) and Si(6)–O(5) bonds) adopt an eclipsed form, the twisted structure is ascribed to the terminal Si–Si rungs. The twist angle between the terminal Si–Si rungs is 14.9°. This compound has similar structural features to **2**: the terminal Si–Si rungs (2.394(2) and 2.382(2) Å) are significantly longer than those of the central Si–Si rungs (2.371(2) and 2.366(2) Å). The Si–O–Si bond angles are 144.5(2)–147.2(2)° (average 145.9°). The dihedral angles between the neighboring six-membered rings are 117.4 and 115.5°.

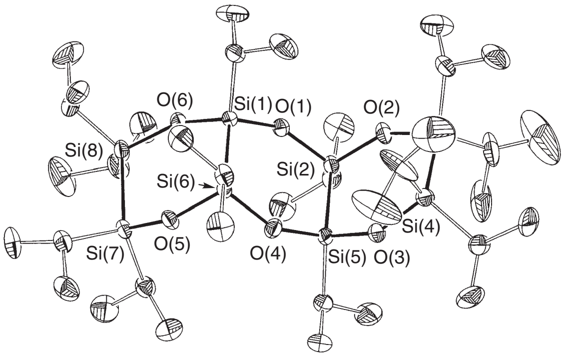


Figure 2. Molecular structure of *anti*-**3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

The structure of *syn*-**3** is shown in Figure 3. Three six-membered rings have slightly twisted structures. The twist angle between the Si(2)–Si(1′) and Si(3)–Si(4) bonds is 13.3°, and that between the Si(1)–Si(2′) and Si(2)–Si(1′) bonds is 7.6°. The steric repulsion between the facing endo isopropyl groups on the terminal Si–Si rungs is reduced by the twisted structure. The terminal Si–Si rungs (2.392(1) Å) are significantly longer than those of the central Si–Si rungs (2.379(1) Å). The Si–O–Si bond angles are 139.6(1)–143.6(2)° (average 142.3°). The dihedral angle between the neighboring six-membered rings is 116.3°.

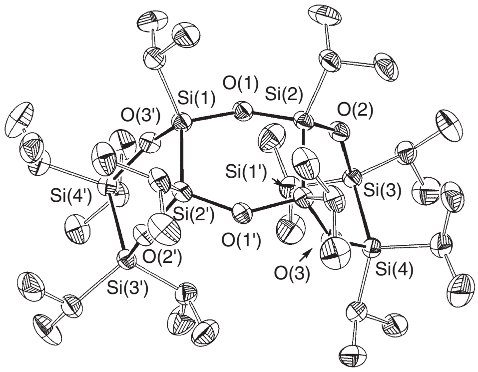


Figure 3. Molecular structure of *syn*-**3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

This work was supported in part by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science and the Toray Science Foundation.

References and Notes

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6 **2**: mp 172–173 °C; ^{1}H NMR (C_6D_6, δ): 0.91 (sep, 2H, $J = 7.5$ Hz), 1.12–1.21 (m, 52H), 1.27–1.35 (m, 16H); ^{13}C NMR (C_6D_6, δ): 16.1, 16.5, 17.4, 18.0, 18.6, 18.7; ^{29}Si NMR (C_6D_6, δ): −24.7, 7.3; IR (NaCl, cm^{-1}): 2940, 2860, 1460, 1030, 1000, 880, 650; MS m/z (%): 662 (M$^+$, 31), 619 (100), 577 (19). *anti*-**3**: mp 169–170 °C; ^{1}H NMR (C_6D_6, δ): 0.99 (sep, 4H, $J = 7.4$ Hz), 1.13–1.30 (m, 80H); ^{13}C NMR (C_6D_6, δ): 15.9, 16.2, 16.3, 16.7, 17.4, 17.9, 18.1, 18.3, 18.6; ^{29}Si NMR (C_6D_6, δ): −24.0, 7.7; IR (NaCl, cm^{-1}): 2940, 2860, 1460, 1070, 1020, 1000, 880, 650; MS m/z (%): 836 (M$^+$, 40), 793 (100), 751 (19). *syn*-**3**: ^{1}H NMR (C_6D_6, δ): 0.88 (sep, 4H, $J = 7.3$ Hz), 1.14–1.22 (m, 66H), 1.32–1.40 (m, 14H); ^{13}C NMR (C_6D_6, δ): 15.7, 16.1, 16.5, 16.6, 17.4, 18.1, 18.2, 18.8; ^{29}Si NMR (C_6D_6, δ): −25.1, 8.0; IR (NaCl, cm^{-1}): 2940, 2860, 1460, 1040, 990, 880, 660; MS m/z (%): 836 (M$^+$, 39), 793 (100), 751 (19).

7 Crystal data for **2**: $C_{30}H_{70}O_4Si_6$, fw 663.39, monoclinic, space group $C2/c$, $a = 10.275(2)$, $b = 18.33(1)$, $c = 22.436(2)$ Å, $\beta = 95.97(1)°$, $V = 4203(2)$ Å^3, $T = 295$ K, $Z = 4$, $D_{\rm calcd} = 1.048$ g cm^{-3}, $R = 0.052$, $R_{\rm w} = 0.039$ ($I > 3\sigma(I)$) for 2759 observed reflections.

8 Crystal data for *anti*-**3**: $C_{36}H_{84}O_6Si_8$, fw 837.73, triclinic, space group $P\bar{1}$, $a = 15.7941(2)$, $b = 18.0447(5)$, $c = 10.3704(4)$ Å, $\alpha = 97.137(6)$, $\beta = 108.548(5)$, $\gamma = 67.333(4)°$, $V = 2585.6(2)$ Å^3, $T = 223$ K, $Z = 2$, $D_{\rm calcd} = 1.076$ g cm^{-3}, $R = 0.074$, $R_{\rm w} = 0.089$ ($I > 3\sigma(I)$) for 5514 observed reflections.

9 Crystal data for *syn*-**3**: $C_{36}H_{84}O_6Si_8$, fw 837.73, monoclinic, space group $C2/c$, $a = 26.575(3)$, $b = 10.640(1)$, $c = 19.305(2)$ Å, $\beta = 113.227(3)°$, $V = 5016.3(8)$ Å^3, $T = 295$ K, $Z = 4$, $D_{\rm calcd} = 1.109$ g cm^{-3}, $R = 0.076$, $R_{\rm w} = 0.093$ ($I > 3\sigma(I)$) for 3787 observed reflections.

10 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-223181 (**2**), CCDC-223182 (*anti*-**3**), and CCDC-223183 (*syn*-**3**).

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Published on the web (Advance View) December 15, 2003; DOI 10.1246/cl.2004.24