Hexa-, Hepta-, and Octacyclic Ladder Polysilanes

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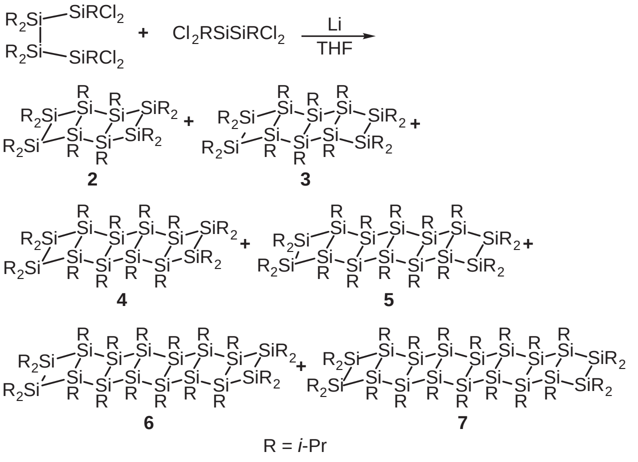
Hexa-, hepta-, and octacyclic ladder polysilanes (**5**–**7**) were synthesized, and their structures were determined by X-ray crystallography. These compounds have the double helix structure consisting of two linear polysilane chains. In the UV–visible spectra, the lowest energy absorption maxima of **5**–**7** shift bathochromically as the number of cyclotetrasilane rings progressively increases.

Ladder polysilanes have been studied by our group as our original systems with unique structures and properties.[1,2] The ladder polysilanes with two to five rings have so far been synthesized, and their structures and properties have been studied. We found that the properties of ladder polysilanes highly depend on the number of cyclotetrasilane rings. For example, the radical anion of decaisopropylbicyclo[2.2.0]hexasilane (**1**) can be observed only at low temperatures, while the radical anion of a pentacyclic ladder polysilane persists for several months at room temperature.[2j] The construction of longer ladder polysilanes seems to disclose different properties which shorter ladder polysilanes do not exhibit. We report herein the synthesis of hexa-, hepta-, and octacyclic ladder polysilanes. We also report the structures and electronic properties of these ladder polysilanes.

The ladder polysilanes with two to five rings were synthesized for the first time by the condensation of $\mathrm{Cl}(i\text{-Pr})_2\mathrm{SiSi}(i\text{-Pr})_2\mathrm{Cl}$ and $\mathrm{Cl}_2(i\text{-Pr})\mathrm{SiSi}(i\text{-Pr})\mathrm{Cl}_2$ with lithium.[2a] In order to synthesize longer ladder polysilanes, we selected another combination of the precursors. Thus, the condensation of $\mathrm{Cl}_2(i\text{-Pr})\mathrm{Si}[\mathrm{Si}(i\text{-Pr})_2]_2\mathrm{Si}(i\text{-Pr})\mathrm{Cl}_2$ and $\mathrm{Cl}_2(i\text{-Pr})\mathrm{SiSi}(i\text{-Pr})\mathrm{Cl}_2$ with lithium gave the hexa-, hepta-, and octacyclic ladder polysilanes (**5**–**7**) in addition to the tri- to pentacyclic ladder polysilanes (**2**–**4**).[3] In this reaction, $\mathrm{Cl}_2(i\text{-Pr})\mathrm{Si}[\mathrm{Si}(i\text{-Pr})_2]_2\mathrm{Si}(i\text{-Pr})\mathrm{Cl}_2$ formed both terminal rings, and $\mathrm{Cl}_2(i\text{-Pr})\mathrm{SiSi}(i\text{-Pr})\mathrm{Cl}_2$ formed the interposed Si–Si rungs (Scheme 1).



Scheme 1.

The structures of **5**–**7** were determined by X-ray crystallography (Figure 1).[4–7] These ladder polysilanes have the rod-like silicon skeletons with the lengths of 1.2 (**5**), 1.4 (**6**), and 1.6 nm (**7**). Each compound has the double helix structure consisting of two linear polysilane chains. The twist angles between the terminal Si–Si rungs are 96.2° (**5** (molecule A)), 101.1° (**5** (molecule B)), 119.6° (**6**), and 128.5° (**7**).[8] The helical structures arise from the systematic folding of cyclotetrasilane rings: the folding of cyclotetrasilane rings all upward or all downward along diagonals leads to right-handed or left-handed helical structures as described previously.[1b] The dihedral angles of the folded cyclotetrasilane rings are 22.8–29.8° (**5** (molecule A)), 24.2–32.4° (**5** (molecule B)), 23.9–31.7° (**6**), and 24.6–28.2° (**7**). The bond lengths of Si–Si rungs (**5** (molecule A): 2.388–2.415 Å, average 2.401 Å, **5** (molecule B): 2.380–2.416 Å, average 2.399 Å, **6**: 2.379–2.415 Å, average 2.392 Å, **7**: 2.394–2.409 Å, average 2.399 Å) are slightly longer than those of peripheral Si–Si bonds (**5** (molecule A): 2.359–2.425 Å, average 2.391 Å, **5** (molecule B): 2.352–2.422 Å, average 2.390 Å, **6**: 2.355–2.417 Å, average 2.389 Å, **7**: 2.359–2.411 Å, average 2.385 Å).

The molecular packing of **7** is shown in Figure 2. Both right-handed (*P*) and left-handed (*M*) double helix molecules are

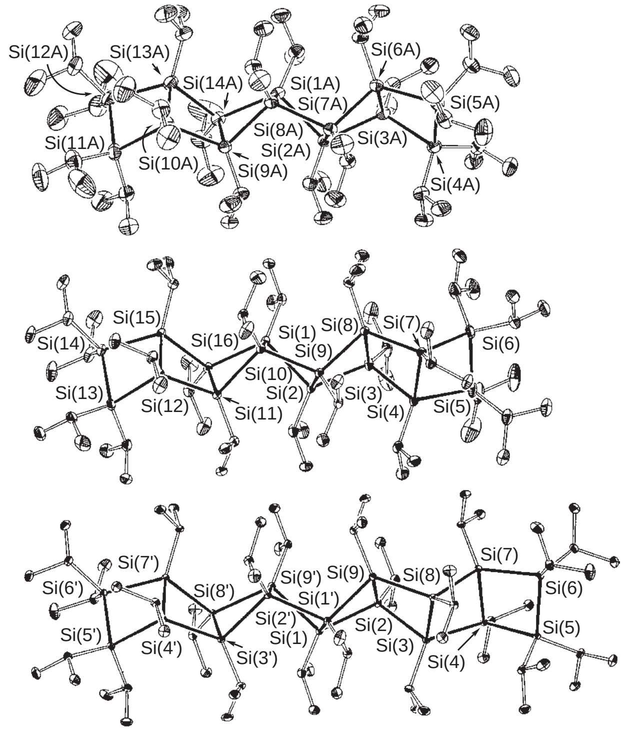


Figure 1. Molecular structures of **5** (molecule A, top), **6** (middle), and **7** (bottom). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

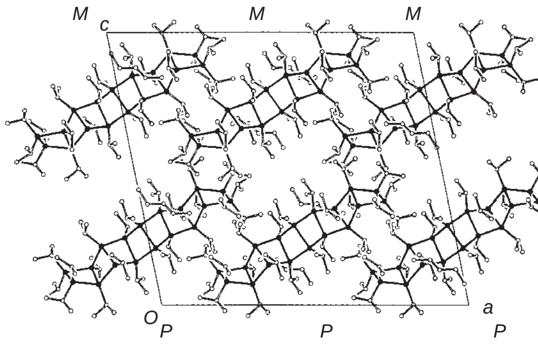


Figure 2. Molecular packing of **7** viewed along the *b* axis.

packed in a unit cell since the crystals have a centrosymmetric space group ($C2/c$). Similarly, the crystals of **5** and **6** have centrosymmetric space groups $P2_1/n$ and $P\bar{1}$, respectively, and the unit cell contains both right-handed and left-handed double helix molecules. Therefore, the crystals of **5**–**7** are racemates of chiral helical molecules.

The ladder polysilanes **5**–**7** show absorption bands in the UV–visible region (Figure 3). The lowest energy absorption maxima of **5**, **6**, and **7** exist at 440, 464, and 483 nm, respectively. As reported previously, the lowest energy absorption maxima of **1**, **2**, **3**, and **4** exist at 310, 345, 380, and 414 nm.[1] These results show that the lowest energy absorption maximum shifts bathochromically as the number of cyclotetrasilane rings progressively increases. Molecular orbital calculations of methyl-substituted ladder polysilanes at the B3LYP/6-31G* level show that the highest occupied molecular orbital (HOMO) is destabilized and the lowest unoccupied molecular orbital (LUMO) is stabilized as the number of cyclotetrasilane rings increases. The destabilization of the HOMO is due to the extension of σ conjugation of Si–Si bonds, while the stabilization of the LUMO arises from the interaction between the Si–C σ^* orbitals at the opposite bridgehead positions.

In summary, we have demonstrated the synthesis, structures, and electronic properties of compounds **5**–**7** which represent the first examples of nanometer-sized polycyclopolysilanes with two-dimensional frameworks.

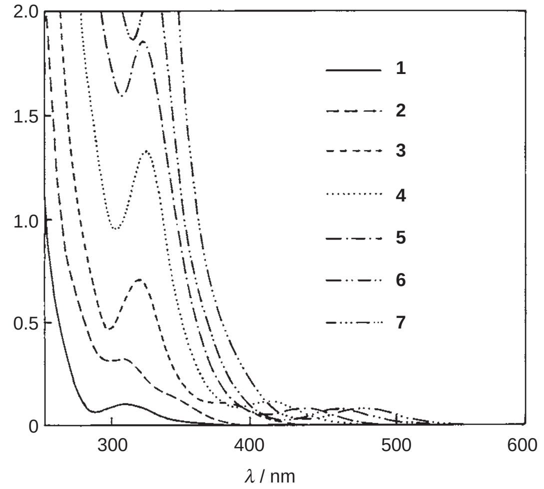


Figure 3. UV–visible spectra of **1**–**7** in hexane at room temperature.

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References and Notes

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3 A solution of 1,1,4,4-tetrachloro-1,2,2,3,3,4-hexaisopropyltetrasilane (2.47 g, 4.82 mmol) and 1,1,2,2-tetrachloro-1,2-diisopropyldisilane (2.77 g, 9.75 mmol) in THF (30 mL) was added dropwise to a mixture of lithium (0.39 g, 56 mmol) and THF (90 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 day. After the solvent was removed by evaporation, the residue was dissolved in hexane, and the mixture was filtered through a short column of silica gel. The filtrate was evaporated, and the residue was separated by recycle-type HPLC (ODS, methanol–THF (55:45)) to give **2** (32.2 mg, 1.2%), **3** (50.5 mg, 2.0%), **4** (63.9 mg, 2.6%), **5** (19.1 mg, 0.8%), **6** (8.1 mg, 0.3%), and **7** (3.9 mg, 0.2%).

4 Crystal data for **5**: $C_{54}H_{126}Si_{14}$, fw 1168.78, monoclinic, space group $P2_1/n$, $a = 19.5865(5)$, $b = 19.7470(7)$, $c = 42.535(1)$ Å, $\beta = 90.973(1)^\circ$, $V = 16449.0(8)$ Å^3, $T = 273$ K, $Z = 8$, $D_{\mathrm{calcd}} = 0.944\ \mathrm{g\,cm^{-3}}$, $R1 = 0.066$ ($I > 2\sigma(I)$), $wR2 = 0.208$ (all data).

5 Crystal data for **6**: $C_{60}H_{140}Si_{16}\cdot C_5H_{12}$, fw 1383.27, triclinic, space group $P\bar{1}$, $a = 11.1272(9)$, $b = 20.072(1)$, $c = 21.295(2)$ Å, $\alpha = 103.002(8)$, $\beta = 103.312(8)$, $\gamma = 76.488(8)^\circ$, $V = 4425.8(6)$ Å^3, $T = 153$ K, $Z = 2$, $D_{\mathrm{calcd}} = 1.038\ \mathrm{g\,cm^{-3}}$, $R1 = 0.089$ ($I > 2\sigma(I)$), $wR2 = 0.246$ (all data).

6 Crystal data for **7**: $C_{66}H_{154}Si_{18}\cdot 2C_5H_{12}$, fw 1597.77, monoclinic, space group $C2/c$, $a = 27.053(2)$, $b = 16.1238(8)$, $c = 24.232(2)$ Å, $\beta = 101.628(2)^\circ$, $V = 10353(1)$ Å^3, $T = 113$ K, $Z = 4$, $D_{\mathrm{calcd}} = 1.025\ \mathrm{g\,cm^{-3}}$, $R1 = 0.045$ ($I > 2\sigma(I)$), $wR2 = 0.144$ (all data).

7 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-290140 (**5**), CCDC-290139 (**6**), and CCDC-290138 (**7**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

8 Molecular A and molecular B denote two independent molecules present in a unit cell of the crystal of **5**.

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