Phenylene-bridged Polysilaalkane Macrocycles as Framed Molecular Rotor

Wataru Setaka,* Keisuke Sato, Atsushi Ohkubo, Chizuko Kabuto, and Mitsuo Kira*
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

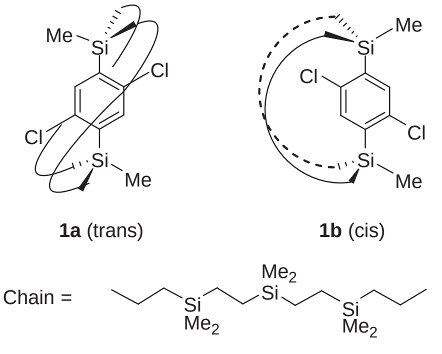
(Received February 23, 2006; CL-060223; E-mail: setaka@mail.tains.tohoku.ac.jp; mkira@mail.tains.tohoku.ac.jp)

Using ring-closing hydrosilylation, trans- and cis-isomers of 2,5-dichrolo-1,4-phenylene-bridged macrocyclic polysilaalkanes were synthesized as molecular tops with a frame and characterized by X-ray crystallography. Dynamic ^{1}H NMR analysis for the cis-isomers in toluene-d_8 showed the internal rotation of the phenylene ring in solution.

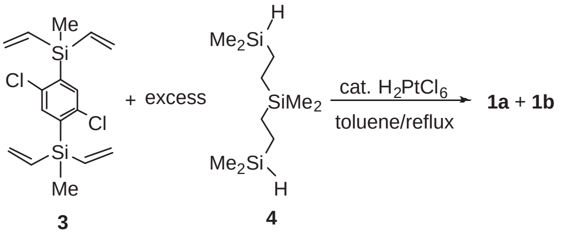
Macrocyclic compounds with bridged π-electronic systems have attracted current attention, because they are expected to have unique functions of framed molecular tops. Control of the motion of the π-systems in the solid state with external electric, magnetic, optical, and thermal stimuli may be the first step toward future molecular machines.[1] However, very few such macrocyclic systems have been synthesized so far.[2–4]

We report herein the synthesis, structure, and dynamics of the first silicon-based macrocycles bridged by a 1,4-phenylene group, trans- and cis-isomers of cyclooctasilatetracosanes bridged by 2,5-dichloro-1,4-phenylene groups **1a** and **1b**, which show characteristics of framed molecular tops in solution (Scheme 1). Dynamic ^{1}H NMR analysis for the cis-isomer in toluene-d_8 showed restricted internal rotation of the phenylene ring in solution, while the phenylene rotation is prevented in the solid state. Long carbosilane chains are relatively easily constructed, thermally stable, transparent for UV–vis light, and functionalized if necessary; they often facilitate the crystallization of the systems. The long carbosilane chains may be useful as a stator of a phenylene rotator.[5]

A mixture of **1a** and **1b** is obtained by ring-closing hydrosilylation between vinylsilane **3** and hydrosilane **4** in the presence of a catalytic amount of H_2PtCl_6 under high dilution conditions in 6% yield (Eq 1).[6] The isomer ratio **1a**/**1b** in the product mixture is determined by ^{1}H NMR to be about 1:1. While the yields are low because of the major formation of polymeric materials, separation of **1a** and **1b** is achieved by fractional crystallization or reversed-phase HPLC. The structures of these macrocyclic compounds are determined by ^{1}H NMR, MS, and X-ray crystallography.



Scheme 1.



(1)

Figure 1 shows the molecular structures of **1a** and **1b** determined by X-ray crystallography.[7] In the solid state, the internal rotation of the phenylene ring of two macrocycles **1a** and **1b** is prevented owing to the steric contact with neighboring molecules. As seen in Figures 1b and 1d, the environments around two chlorine atoms in **1a** are identical but those in **1b** are very different; a half of the phenylene ring is covered by the carbosilane framework but the other half is uncovered in **1b**. We may expect therefore that two singlets are observed for phenylene protons of **1b** by NMR in solution if the internal phenylene rotation is much slower than the NMR time scale, while two phenylene protons of **1a** should afford a sharp singlet even at low temperatures. Actually, the ^{1}H NMR spectra of **1b** in toluene-d_8 show two singlets at 7.49 and 7.59 ppm at 203 K. The two singlets are broadened with increasing temperatures and coalesced at around 220 K (Figure 2), while the singlet line for **1a** does not change in the temperature range of 203–273 K.

The dynamic ^{1}H NMR behavior of **1b** is explained by assuming an equilibrium between two equivalent conformations

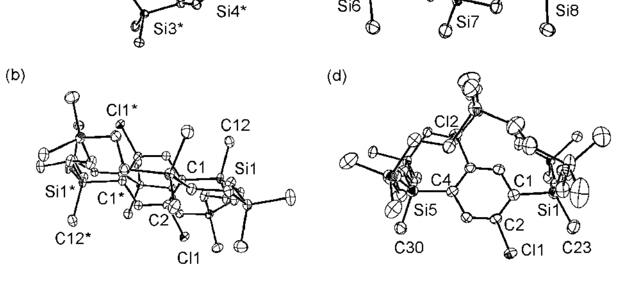


Figure 1. ORTEP drawings of **1a** (trans) and **1b** (cis) determined by X-ray crystallography. (a) **1a**, side view; (b) **1a**, top view; (c) **1b**, side view; (d) **1b**, top view. Selected bond lengths (Å) and dihedral angles (°). **1a**: C1–Si1 1.901(3); C2–Cl1 1.759(3); C2–C1–Si1–C12 −178.3(2). **1b**: C1–Si1 1.909(4); C4–Si5 1.897(4); C2–Cl1 1.751(4); C5–Cl2 1.759(4); C2–C1–Si1–C23 13.3(2); C23–Si1–Si5–C30 0.6(2).

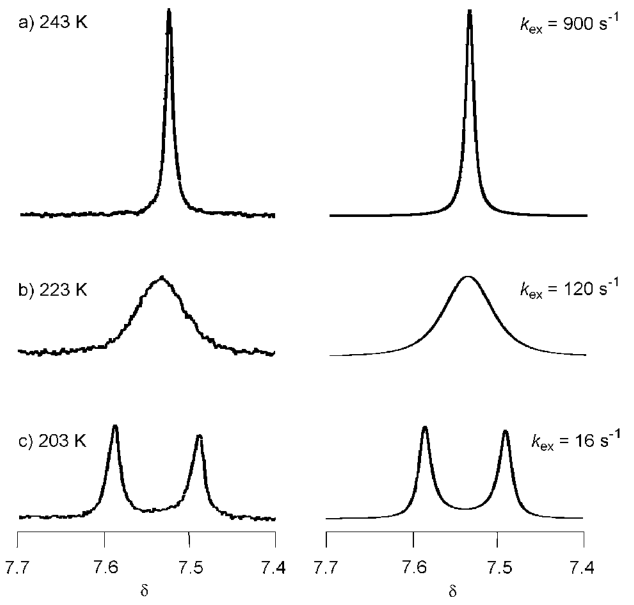
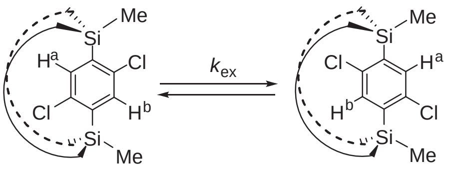


Figure 2. Temperature dependence of ^{1}H NMR spectra of **1b** (aromatic region). Left: observed spectra. Right: spectra simulated with designated exchange rate constants (k_{ex}).[8,9]



1b **1b'**

Figure 3. Schematic representation of phenylene rotation in **1b**.

1b and **1b′** shown in Figure 3. During the rotation of the phenylene ring around Si1–Si5 axis, both H^a and H^b experience covered and uncovered positions. The chemical shift difference between the covered and uncovered protons of **1b** in toluene would be caused by the solvation of aromatic solvents to the uncovered proton; in $CDCl_3$, two protons H^a and H^b of **1b** give a sharp singlet at 7.26 ppm even at low temperatures.[10]

The exchange rate constants (k_{ex}) between **1b** and **1b′** are determined by the line-shape analysis of the two-site model.[8] The Eyring parameters for the exchange determined using linear plots of $\ln(k_{ex}/T)$ vs $1/T$ are $\Delta H^{\neq} = 9.8 \pm 0.3\,\mathrm{kcal\,mol^{-1}}$ and $\Delta S^{\neq} = -4.2 \pm 1.3\,\mathrm{cal\,K^{-1}\,mol^{-1}}$ for **1b**.[11]

In summary, the rates for the internal rotation of a phenylene group bridging over a polysilaalkane macrocycle as molecular top were found by dynamic ^{1}H NMR spectroscopy to be controlled by temperature. The rates may also be controlled by UV irradiation and the chemical reduction giving the corresponding anion radicals and dianions.[12]

Further works including the rotational rate dependence on the substituents on the phenylene ring are now in progress.

References and Notes

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6 **1**: A toluene (250 mL) solution of **3** (1.07 g, 3.17 mmol) and **4** (4.09 g, 12.9 mmol) was released dropwise into a toluene (50 mL) solution of a catalytic amount of H_2PtCl_6 (0.05 mg) at reflux over 36 h and the solution was stirred for 5 days. The reaction mixture was treated by flash column chromatography. A 1:1 mixture of **1a** and **1b** (150 mg, 0.19 mmol) was obtained by preparative gel permeation chromatography in 6% yield. **1a/1b**: colourless crystals; HRMS (ESI negative) m/z calcd for $C_{36}H_{76}Cl_2Si_8 + Cl^-$: 837.3176, found: 837.3172. Compounds **1a** and **1b** were separated by reversed phase HPLC. **1a**: ^{1}H NMR (toluene-d_8, 293 K) δ 0.01 (s, 12H), 0.05 (s, 12H), 0.07 (s, 12H), 0.28 (s, 6H), 0.2–0.4 (m, 32H, methylenes), 7.47 (s, 2H). **1b**: ^{1}H NMR (toluene-d_8, 293 K) δ −0.03 (s, 12H), 0.02 (s, 6H), 0.09 (s, 12H), 0.13 (s, 6H), 0.28 (s, 6H), 0.3–0.5 (m, 32H, methylenes), 7.53 (s, 2H).

7 Crystal data for **1a**: $C_{36}H_{76}Cl_2Si_8$, M_r 804.59, colourless prism, $0.15 \times 0.15 \times 0.1\,\mathrm{mm^3}$, monoclinic, space group $P2_1/c$, $a = 10.499(3)$, $b = 19.559(6)$, $c = 12.370(4)$ Å, $\beta = 100.790(1)°$, $V = 2495.5(13)$ Å^3, $Z = 2$, $D_{calcd} = 1.071\,\mathrm{g\,cm^{-3}}$, Mo K$\alpha$ ($\lambda = 0.7107$ Å), $T = 173(2)$ K, 4809 unique reflections were collected, 3479 observed [$I > 2\sigma(I)$]. Final $Goof = 1.093$, $R1 = 0.0506$ [$I > 2\sigma(I)$], 208 parameters. Crystal data for **1b**: $C_{36}H_{76}Cl_2Si_8$, $M_r = 804.59$, colorless prism, $0.2 \times 0.2 \times 0.1\,\mathrm{mm^3}$, monoclinic, space group $P2_1/a$, $a = 12.264(1)$, $b = 32.600(2)$, $c = 13.203(1)$ Å, $\beta = 107.823(2)°$, $V = 5025.4(8)$ Å^3, $Z = 4$, $D_{calcd} = 1.063\,\mathrm{g\,cm^{-3}}$, Mo K$\alpha$ ($\lambda = 0.7107$ Å), $T = 173(2)$ K, 11392 unique reflections were collected, 7026 observed [$I > 2\sigma(I)$]. Final $Goof = 1.167$, $R1 = 0.0785$ [$I > 2\sigma(I)$], 444 parameters. Two parts of the ethylene chain (C11–C12 (sof = 0.697(15)) and C9 (sof = 0.808(13)) were included in a disorder model for alternate zigzag chains. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-287704 (**1a**) and CCDC-287705 (**1b**).

8 For the line-shape analysis, the NMR spectra were simulated using gNMR program (v.4.1.0) for Windows, Ivory Soft, 1999.

9 For the details of the dynamic NMR analysis of **1b**, see the Supporting Information.

10 The chemical shift difference between H^a and H^b in chloroform-d seems to be significantly smaller than that in benzene-d_6; the singlet aromatic proton signal in chloroform-d broadens at low temperatures but does not split into two singlets even at 213 K. For the details, see the Supporting Information. The origin of the solvent effects remains to be elucidated.

11 Errors are given by standard deviations.

12 Polysilylbenzenes are known to give the corresponding radical anions and dianions by the reduction with alkali metals. For our recent studies, see: a) W. Setaka, M. Kira, *Chem. Phys. Lett.* **2002**, *363*, 447. b) W. Setaka, K. Ebata, H. Sakurai, M. Kira, *J. Am. Chem. Soc.* **2000**, *122*, 7781. c) W. Setaka, C. Kabuto, M. Kira, *Chem. Lett.* **1999**, 317. d) K. Ebata, W. Setaka, T. Inoue, M. Kira, H. Sakurai, *J. Am. Chem. Soc.* **1998**, *120*, 1335.

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