

Molecular Gyroscope Having a Halogen-substituted *p*-Phenylene Rotator and Silaalkane Chain Stators

Wataru Setaka,^{*1,3} Soichiro Ohmizu,² and Mitsuo Kira^{*2}

¹Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki 769-2193

²Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

³PRESTO, JST, 4-1-8 Honcho, Kawaguchi 332-0012

(Received February 22, 2010; CL-100172; E-mail: setaka@kph.bunri-u.ac.jp, mkira@m.tains.tohoku.ac.jp)

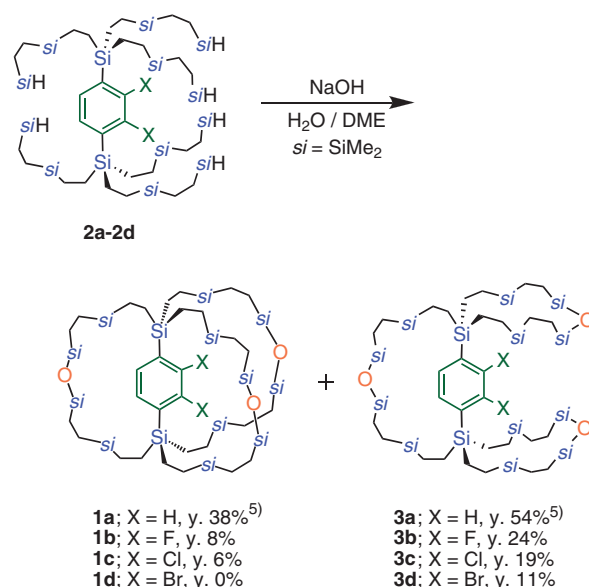
2,3-Halophenylene-bridged polysilaalkane macrocages **1b** and **1c** were synthesized as novel molecular gyroscopes. X-ray crystallographic data showed that the structures of the macrocages were deformed to avoid contact between the halogens and the silaalkane cage. The 2,3-dichlorophenylene derivative **1c** shows restricted rotation of the phenylene in solution as observed by variable temperature ¹H NMR spectroscopy.

Macrocyclic molecules having bridged π -electron systems have attracted much attention in terms of their unique structures, dynamics, and functions.^{1–5} Especially phenylene-bridged macrocages are expected to have functions of gyroscopes and compasses as first proposed by Garcia-Garibay et al.³ Recently, such cage molecules were reported as molecular gyroscopes.^{3–5}

We have applied polysilaalkane chains of novel cyclophanes.^{2a,5} These chains are easily constructed, chemically stable, and exhibit good crystallinity. Recently we reported the synthesis and structure of a molecular gyroscope having a bridged phenylene encased in a large silaalkane cage.⁵ Cage compound **1a** was found by X-ray crystallography to show remarkable disorder at 30 °C. The phenylene ring was observed at three positions around the threefold molecular axis, suggesting the phenylene rotates around the axis even in crystals. We report herein the synthesis and structure of 2,3-halophenylene-bridged polysilaalkane macrocages **1b** and **1c** and reveal steric effects on the structure and dynamics of the corresponding macrocages.

The 2,3-halophenylene-bridged molecular gyroscopes were synthesized by hydrolysis reactions of hydrosilanes **2a–2d** (Scheme 1).^{6,7} Statistically, the ratio of the formation of a cage structure to its isomer is calculated to be 1:3; therefore, the yield of the cage structure is lower than that of the isomer. In this reaction, a remarkable dependence of the yields on the bulkiness of the internal rotator was observed. The yields of the cage compounds decreased with increasing atomic size of the halogens on the rotator. Indeed, there was no observation of a 1,2-dibromophenylene-bridged molecular gyroscope **1d** due to the steric hindrance in the reaction. Compounds **1b** and **1c** were identified by ¹H, ²⁹Si, and ¹³C NMR spectroscopy, and mass spectrometry.

The molecular structures of the molecular gyroscopes **1b** and **1c** were confirmed by X-ray crystallography (Figure 1).⁸ In the 2,3-difluorophenylene-bridged molecular gyroscope **1b**, the shape of the frame was slightly deformed from that of the phenylene-bridged derivative, and the molecule **1b** has C₂ symmetry. This deformation was most likely due to steric hindrance of the fluorines on the phenylene ring. The phenylene ring was observed at two positions around the molecular axis.



Scheme 1.

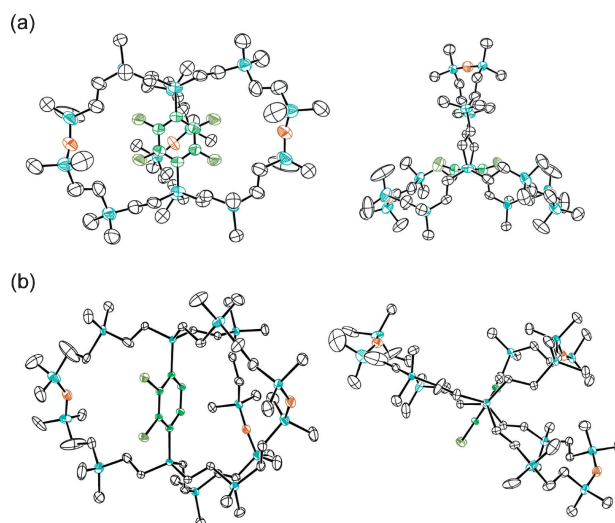


Figure 1. Molecular structure of (a) compound **1b** at 0 °C and (b) compound **1c** at –120 °C. Left: equatorial view with 30% thermal probability ellipsoid; Right: axial view. Hydrogen atoms and structural disorder on the side chains are omitted for clarity. Structural disorder of phenylene ring in **1b** is shown, and ratio of occupancy factor is 0.5:0.5.

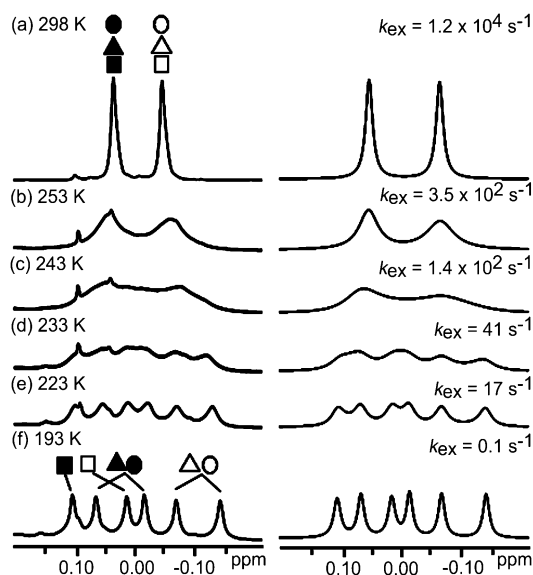


Figure 2. Temperature dependence of ^1H NMR spectra of **1c** (methyl region). Left: observed spectra. Right: spectra simulated with designated exchange rate constants (k_{ex}).

The frame structure of the 2,3-dichlorophenylene-bridged derivative **1c** was significantly deformed and has no symmetry. The silaalkane chains of the frame were separated from each other to avoid steric contact between the chains and chlorines on the phenylene. The phenylene ring was observed at only one position around the molecular axis.

Internal rotation of the phenylenes in solution is one of the most important properties of molecular gyroscopes. The dynamic behavior of ^1H NMR spectra of **1b** and **1c** in solution were investigated. NMR spectra of **1b** and **1c** in solution at room temperature (298 K) show only two methyl signals with a highly symmetric (D_3) pattern. This indicates that the phenylene group of **1b** and **1c** rotates rapidly in solution. The two methyl signals of the 2,3-difluorophenylene-bridged derivative **1b** do not change even at low temperature.⁷ However the two methyl singlets in the 2,3-dichlorophenylene-bridged derivative **1c** are broadened with decreasing temperatures, coalesce at around 220 K, and then separate into six singlets at 193 K (Figure 2), indicating the internal phenylene rotation is much slower than the NMR time scale. The dynamic ^1H NMR behavior of **1c** is explained by assuming a three-site exchange model as shown in Figure 3. The exchange rate constants (k_{ex}) were determined by line-shape analysis. The Eyring parameters for the exchange determined using linear plots of $\ln(k_{\text{ex}}/T)$ vs. $1/T$ are $\Delta H^\ddagger = 12.8 \pm 0.47 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -4.61 \pm 2.02 \text{ cal mol}^{-1} \text{ K}^{-1}$ for **1c**.⁷

In summary, 2,3-halophenylene-bridged polysilaalkane macrocages **1b** and **1c** were synthesized as novel molecular gyroscopes. Deformation of the frame structures in the crystal and rate of the phenylene rotation in solution were dependent on steric hindrance of the phenylene rotator with halogens.

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [Grant-in-Aid for Scientific Research on Specially Promoted Research (No. 17002005)].

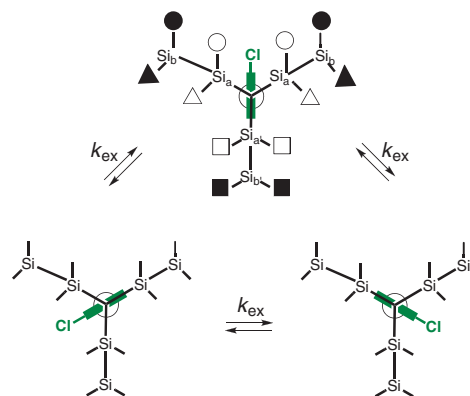


Figure 3. Schematic representation of phenylene rotation in **1c**.

References and Notes

- a) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH Verlag, Weinheim, Germany, **2003**. b) *Molecular Machines in Topics in Current Chemistry*, ed. by T. R. Kelley, Springer, New York, **2005**. c) *Modern Cyclophane Chemistry*, ed. by R. Gleiter, H. Hopf, Wiley-VCH Verlag, Weinheim, Germany, **2004**. d) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. e) G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl, *Chem. Rev.* **2005**, *105*, 1281. f) M. A. Garcia-Garibay, *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10771. g) S. D. Karlen, M. A. Garcia-Garibay, *Top. Curr. Chem.* **2005**, *262*, 179. h) T.-A. V. Khuong, J. E. Nuñez, C. E. Godinez, M. A. Garcia-Garibay, *Acc. Chem. Res.* **2006**, *39*, 413.
- a) W. Setaka, K. Sato, A. Ohkubo, C. Kabuto, M. Kira, *Chem. Lett.* **2006**, *35*, 596. b) S. T. Phan, W. Setaka, M. Kira, *Chem. Lett.* **2007**, *36*, 1180. c) S. T. Phan, W. Setaka, M. Kira, *Chem. Lett.* **2008**, *37*, 976. d) T. C. Bedard, J. S. Moore, *J. Am. Chem. Soc.* **1995**, *117*, 10662. e) A. Lüttringhaus, H. Simon, *Justus Liebig's Ann. Chem.* **1947**, *557*, 120. f) G. Schill, K. Rißler, H. Frits, *Chem. Ber.* **1983**, *116*, 1866. g) G. Schill, H. Neubauer, *Justus Liebig's Ann. Chem.* **1971**, *750*, 76.
- a) J. E. Nuñez, A. Natarajan, S. I. Khan, M. A. Garcia-Garibay, *Org. Lett.* **2007**, *9*, 3559. b) Z. Dominguez, H. Dang, M. J. Strouse, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, *124*, 7719. c) C. E. Godinez, G. Zepeda, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, *124*, 4701.
- a) T. Shima, F. Hampel, J. A. Gladysz, *Angew. Chem., Int. Ed.* **2004**, *43*, 5537. b) T. Shima, E. B. Bauer, F. Hampel, J. A. Gladysz, *Dalton Trans.* **2004**, 1012. c) A. J. Nawara, T. Shima, F. Hampel, J. A. Gladysz, *J. Am. Chem. Soc.* **2006**, *128*, 4962. d) L. Wang, F. Hampel, J. A. Gladysz, *Angew. Chem., Int. Ed.* **2006**, *45*, 4372. e) L. Wang, T. Shima, F. Hampel, J. A. Gladysz, *Chem. Commun.* **2006**, 4075. f) G. D. Hess, F. Hampel, J. A. Gladysz, *Organometallics* **2007**, *26*, 5129. g) K. Skopek, J. A. Gladysz, *J. Organomet. Chem.* **2008**, *693*, 857. h) K. Skopek, M. Barbasiewicz, F. Hampel, J. A. Gladysz, *Inorg. Chem.* **2008**, *47*, 3474.
- W. Setaka, S. Ohmizu, C. Kabuto, M. Kira, *Chem. Lett.* **2007**, *36*, 1076.
- 1b**: colorless crystals; mp 99–100 °C; ^1H NMR (400 MHz, CDCl_3): δ -0.08 (s, 36H), 0.00 (s, 36H), 0.32–0.34 (m, 24H), 0.36–0.41 (m, 12H), 0.68–0.73 (m, 12H), 7.06 (s, 2H, aromatic protons); ^{13}C NMR (100 MHz, CDCl_3): δ -4.3, -0.6, 4.8, 5.8, 6.9, 10.1, 127.0 (dd, $^2J_{\text{C-F}} = 16.3 \text{ Hz}$, $^3J_{\text{C-F}} = 10.6 \text{ Hz}$, aromatic C-H), 130.2 (dd, $^3J_{\text{C-F}} = ^4J_{\text{C-F}} = 6.6 \text{ Hz}$, C_{ipso}), 154.1 (dd, $^1J_{\text{C-F}} = 245.6 \text{ Hz}$, $^2J_{\text{C-F}} = 18.1 \text{ Hz}$, C-F); ^{29}Si NMR (79 MHz, CDCl_3): δ 5.4 (br), 5.7, 8.1; HRMS (ESI) calcd for $\text{C}_{54}\text{H}_{122}\text{Si}_{14}\text{O}_3\text{F}_2\text{I}$, 1375.5182 ($[\text{M} + \text{I}]^-$); found, 1375.5173 ($[\text{M} + \text{I}]^-$). **1c**: colorless crystals; mp 86–87 °C; ^1H NMR (400 MHz, CDCl_3 , 298 K): δ -0.08 (s, 36H), 0.00 (s, 36H), 0.29–0.37 (m, 36H), 0.74–0.82 (m, 12H), 7.25 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ -4.3, -0.5, 4.8, 6.0, 7.1, 10.2, 134.2, 138.7, 139.1; ^{29}Si NMR (79 MHz, CDCl_3 , 298 K): δ 5.6, 7.9, 8.1; HRMS (ESI) m/z ; calcd for $\text{C}_{54}\text{H}_{122}\text{Si}_{14}\text{O}_3\text{Cl}_2\text{Na}$, 1303.5433 ($[\text{M} + \text{Na}]^+$); found, 1303.5439 ($[\text{M} + \text{Na}]^+$); Anal. Calcd for $\text{C}_{54}\text{H}_{124}\text{Si}_{14}\text{O}_3\text{Cl}_2$: C, 50.53; H, 9.58%. Found: C, 50.23; H, 9.50%.
- See the Supporting Information for the details of the synthesis of **1b** and **1c**, temperature-dependent NMR data. Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- Crystal data for **1b** (273 K): orthorhombic, space group *Pbcn*, $R1 = 0.128$ ($I > 2\sigma(I)$), $wR2 = 0.343$ for all data, 9803 unique reflections. CCDC-716908; Crystal data for **1c** (150 K): monoclinic, space group *P21*, $R1 = 0.0556$ ($I > 2\sigma(I)$), $wR2 = 0.1510$ for all data, 9671 unique reflections. CCDC-716909.