A Molecular Gyroscope Having Phenylene Rotator Encased in Three-spoke Silicon-based Stator

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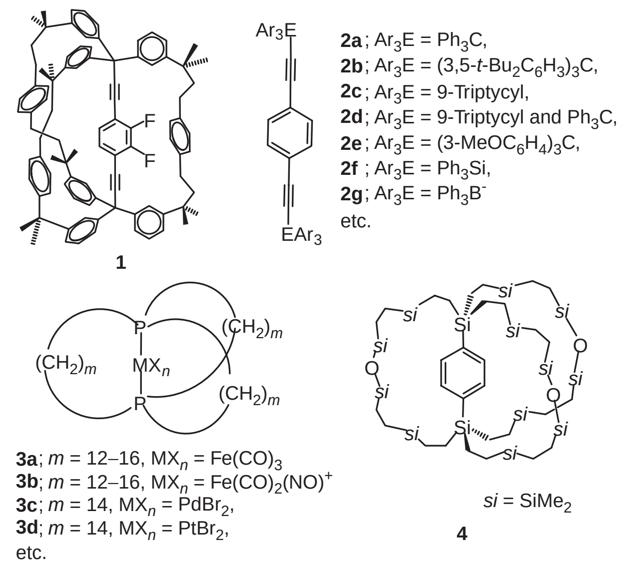
A molecular gyroscope which has a phenylene rotator encased in three long siloxaalkane spokes was synthesized. The phenylene ring is observed by X-ray crystallography at three rotational positions around the 1,4-axis between 223–303 K. The area in which the phenylene ring is found is significantly reduced at 173 K owing to the deformation of a siloxaalkane spoke; the temperature-dependent phenylene disorder is reversible.

As a class of molecular machines,[1] much attention has been focused on macrocyclic molecules with bridged phenylene groups, because they are expected to demonstrate functions of molecular gyroscopes and compasses, whose interior rotator (phenylene) is protected by an exterior framework. The rotation or orientation of a bridged phenylene group in these molecules could be controlled by external electric and magnetic fields, thermal stimulus, etc., as first proposed by Garcia-Garibay et al.[2] As a solid-state molecular gyroscope, they proposed a triply bridged 1,4-bis[(tritylethynyl)-2,3-difluorobenzene (**1** in Chart 1). Whereas the synthesis of **1** has not yet been achieved, the dynamic behavior in the solid state of related 1,4-bis[(3,3,3-triarylpropynyl)benzenes **2a**–**2f** and an ionic boron congener **2g** have been investigated by Garcia-Garibay et al.[2] and Gardinier et al.,[3] respectively.[4] Recently, Gladysz et al.[5] have reported the synthesis of molecular gyroscope-type compounds having transition metal rotators **3a**–**3d**. During the course of our studies in this direction,[6] we have achieved the synthesis and structural characteristics of a novel molecular gyroscope having a phenylene rotator **4**, which is encased in three long siloxaalkane spokes.



2a; Ar$_3$E = Ph$_3$C,
2b; Ar$_3$E = (3,5-t-Bu$_2$C$_6$H$_3$)$_3$C,
2c; Ar$_3$E = 9-Triptycyl,
2d; Ar$_3$E = 9-Triptycyl and Ph$_3$C,
2e; Ar$_3$E = (3-MeOC$_6$H$_4$)$_3$C,
2f ; Ar$_3$E = Ph$_3$Si,
2g; Ar$_3$E = Ph$_3$B$^-$
etc.

3a; m = 12–16, MX$_n$ = Fe(CO)$_3$
3b; m = 12–16, MX$_n$ = Fe(CO)$_2$(NO)$^+$
3c; m = 14, MX$_n$ = PdBr$_2$,
3d; m = 14, MX$_n$ = PtBr$_2$,
etc.

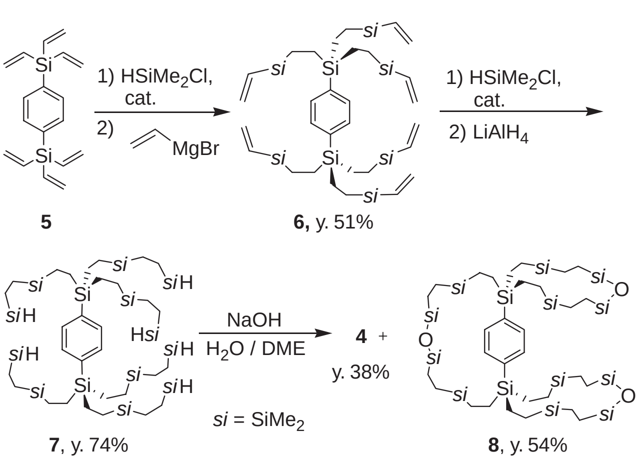
Chart 1.

Compound **4** was synthesized as shown in Scheme 1.[7] The isomers **4** and **8** were separated from each other by recycle reversed phase HPLC and purified by recrystallization.[7]

NMR spectra of **4** in CDCl$_3$ show highly symmetric (D_3) pattern between 173 and 300 K, indicating that the phenylene group of **4** rotates rapidly in solution in the temperature range.

The molecular structure of **4** and its packing diagram in a single crystal are shown in Figure 1.[8] All the phenylene 1,4-axes are parallel in the single crystal of **4**. In a molecule of **4**, the phenylene ring is observed at three positions A, B, and C with the occupancy factors of 0.25, 0.50, and 0.25, respectively, between 223 and 303 K, as shown in Figure 2. At 173 K, the conformation of a siloxaalkane spoke of **4** largely deforms from that found at 223 K with slight reduction of the unit cell volume. This deformation causes significant modification of the phenylene disorder due to the increase of steric contact between phenylene and siloxaalkane chains in **4**;[9] the phenylene ring is observed at D, E, and F positions with the occupancy factors of 0.29, 0.42, and 0.29 at 173 K (Figure 2b). The phase transition was observed reversibly. No such disorder has been observed in the crystals of **8** or other known gyroscope-type molecules.[2,3] The area in which the phenylene ring is observed in the molecule is significantly reduced at 173 K compared with the area at 223 K, suggesting that the phenylene ring rotates smoothly at >223 K but flips in a confined area at <173 K.[10] Using flexible siloxaalkane side chains, phenylene rotation of molecular gyroscopes is expected to be temperature-controlled.

In the ^{13}C CP/MAS spectrum of **4**, aromatic CH carbons were observed as a sharp singlet between 173 and 323 K. The



Scheme 1.

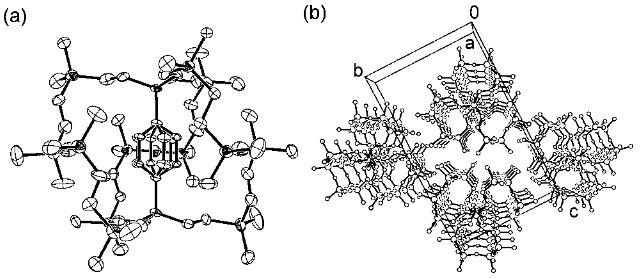


Figure 1. (a) Molecular structure of compound **4** at 223 K (30% thermal probability ellipsoid). Hydrogen atoms are omitted for clarity. (b) Crystal packing diagram of **4**.

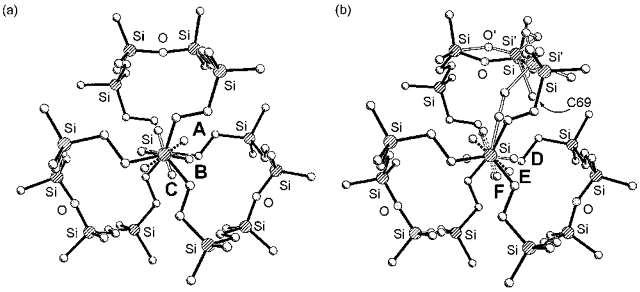


Figure 2. Temperature dependence of structural disorder in **4**: (a) 303 K, (b) 173 K. The ratio of accented and unaccented side chains is 0.328(5):0.672(5).

aromatic CH carbon signal was intense even with a 100-μs dipolar dephasing delay, while in a reference compound, 1,4-bis(trimethylsilyl)benzene, in the solid state, the corresponding ^{13}C signal disappeared rapidly by the dipolar dephasing at 298 K, indicating facile phenylene rotation of **4** in the solid state.[11]

Because the siloxaalkane spokes are not only robust and relatively easily constructed but transparent for UV–vis light and functionalized if necessary, optical control of the rotation may be feasible by introducing polar substituents on the molecule.[12]

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7 For the synthetic details, see Supporting Information, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett. **4**: colorless crystals; mp 113–114 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ) −0.09 (s, 36H), 0.01 (s, 36H), 0.32–0.34 (m, 24H), 0.39–0.43 (m, 12H), 0.62–0.67 (m, 12H), 7.43 (s, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, δ) −4.2, −0.5, 4.5, 5.9, 6.9, 10.2, 133.7, 137.0; ^{29}Si NMR (79 MHz, CDCl$_3$, δ) 2.1, 5.6, 8.1; Anal. Calcd for $C_{54}H_{124}Si_{14}O_3$: C, 53.39; H, 10.29. Found: C, 53.60, H. 9.87. **8**: colorless crystals; mp 151–152 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ) −0.12 (s, 12H), −0.06 (s, 12H), −0.04 (s, 12H), −0.01 (s, 12H), 0.02 (s, 12H), 0.03 (s, 12H), 0.18–0.23 (m, 4H), 0.25–0.26 (m, 8H), 0.40–0.41 (m, 16H), 0.44–0.50 (m, 8H), 0.56–0.60 (m, 4H), 0.69–0.75 (m, 8H), 7.44 (s, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, δ) −4.6, −4.2, −4.0, −0.43, −0.36, −0.3, 3.1, 3.9, 6.2, 6.28, 6.31, 6.5, 10.1, 10.7, 133.5, 138.0; ^{29}Si NMR (79 MHz, CDCl$_3$, δ) 2.6, 5.7, 5.8, 8.0, 8.4; Anal. Calcd for $C_{54}H_{124}Si_{14}O_3$: C, 53.39; H, 10.29%. Found: C, 53.39, H. 10.37%.

8 Crystal data for **4** (223 K): $C_{54}H_{124}O_3Si_{14}$; fw 1214.79; monoclinic; space group Pn; $a = 11.840(4)$, $b = 14.619(5)$, $c = 24.188(9)$ Å, $\beta = 99.240(2)°$, $V = 4133(3)$ Å^3, $D_{\text{calcd}} = 0.976$ Mg/m^3, $Z = 2$, 715 parameters. Final R indices $R1 = 0.0718$ [$I > 2\sigma(I)$], $wR2 = 0.195$ for all data, 9455 unique reflections. Crystal data for **8** (223 K): $C_{54}H_{124}O_3Si_{14}$; fw 1214.79; triclinic; space group $P\bar{1}$; $a = 6.705(4)$, $b = 21.506(13)$, $c = 28.471(17)$ Å, $\alpha = 81.316(14)°$, $\beta = 88.504(16)°$, $\gamma = 88.278(16)°$, $V = 4056(4)$ Å^3, $D_{\text{calcd}} = 0.995$ Mg/m^3, $Z = 2$, 678 parameters. Final R indices $R1 = 0.1195$ [$I > 2\sigma(I)$], $wR2 = 0.3903$ for all data, 11357 unique reflections. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-643544 (**4** at 173 K), CCDC-643545 (**4** at 223 K), and CCDC-643546 (**8** at 223 K).

9 The shortest distance between the phenylene center and a methyl carbon in the deformed chain is only 3.64 Å (center–C69) at 173 K.

10 Interestingly only the siloxaalkane chain in **4** that is perpendicular to the plane of phenylene with the largest occupancy factor at higher temperatures deforms significantly at low temperatures, while the reason remains to be investigated.

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