Silicon-based Synthesis of [2]Rotaxanes without Polar Functional Groups

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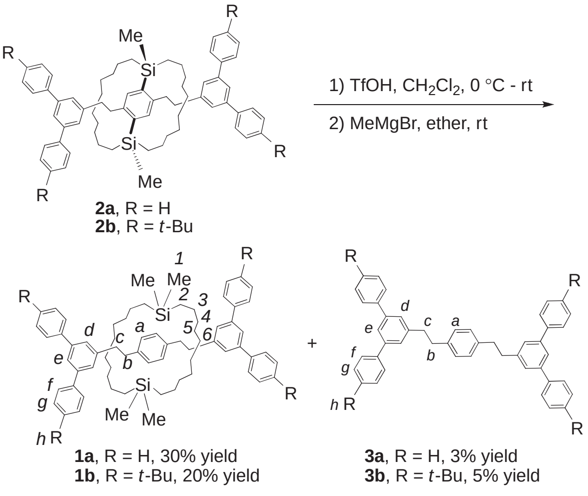
The synthesis of [2]rotaxanes without polar functional groups was achieved by protodesilylation of the corresponding phenylene-bridged 1,12-disilacyclodocosanes in 20–30% isolated yields. The molecular structure of rotaxane **1a** showed that the wheel is not at the center of the rod but on a dimethylene group of the dumbbell. By detailed NMR analyses, facile shuttling of the wheel was found to control the geometry of the dumbbells in the rotaxanes.

Rotaxanes which are interlocked molecular architectures composed of a dumbbell-shaped component and one or more macrocyclic components (wheels) encircling the rod of the dumbbell (axle) have attracted much attention because of their potential applications to molecular machines using control of the motion of the wheels along the axle.[1] Although a number of rotaxanes have been synthesized to date, none of them are *parent* hydrocarbon rotaxanes without heteroatoms. Among three synthetic methods, statistical, directed, and template,[1c] the latter two methods are the most popular for the synthesis of rotaxanes. However, the methods utilize functional group transformations and attractive interactions between wheel and axle, and hence, the rotaxanes synthesized by these methods inevitably contain polar functional groups. The statistic methods using thermodynamic threading may be applied for the synthesis of hydrocarbon rotaxanes but in despairingly low yields. Herein we would like to report a silicon-based directed synthesis of [2]rotaxanes composed of carbon, hydrogen, and silicon atoms, and hence, without polar functional groups. Facile shuttling of the wheel was observed to control the axle conformation in solution.



2a, R = H
2b, R = *t*-Bu

1a, R = H, 30% yield
1b, R = *t*-Bu, 20% yield

3a, R = H, 3% yield
3b, R = *t*-Bu, 5% yield

Scheme 1.

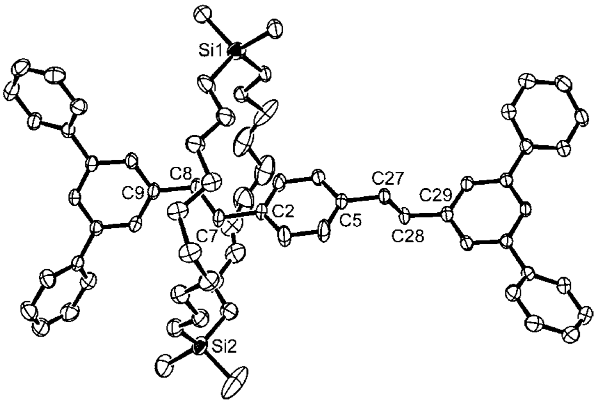


Figure 1. Molecular structure of **1a**. Thermal ellipsoids are drawn at the 50% probability level. One of the two crystallographically independent molecules that exist with similar geometrical parameters in an asymmetric unit is shown. Selected dihedral angles (°): C2–C7–C8–C9 171.5(2); C5–C27–C28–C29 172.8(2).

The syntheses of [2]rotaxanes **1a** and **1b** were achieved by the selective cleavage of Si–C(Ar) bonds of prerotaxanes, phenylene-bridged 1,12-disilacyclodocosanes **2a** and **2b**,[2] using triflic acid followed by the methylation of intermediary silyl triflates with methylmagnesium bromide, as shown in Scheme 1.[3] Rotaxanes **1a** and **1b** were obtained in 30% and 20% isolated yields, respectively,[4] together with the corresponding free dumbbells **3a** and **3b** as minor side products.[3,5]

Rotaxanes **1a** and **1b** are thermally very stable; no dethreading of the wheel from the dumbbell occurs up to 140 °C.

The molecular structure of rotaxane **1a** determined by X-ray crystallography is shown in Figure 1.[6] Rotaxane **1a** consists of a simple disilacycloalkane wheel threading a stretched dumbbell-shaped axle. In the solid state, the wheel is not at the center of the axle but on a dimethylene group of the dumbbell.[3]

The NMR patterns of **1a** and **1b** are similar and highly symmetric even at −50 °C,[3] indicating that the wheel is mostly localized on the central phenylene group or facilely shuttling between two dimethylene stations in the dumbbell in solution. The latter aspect is evidenced by the ROESY experiments of rotaxanes **1a** and **1b**.[3] The enhancement of signals of aromatic protons *a* and *d* (Scheme 1) together with those of benzylic protons *b* and *c* was observed when CH_2Si proton signals at ca. 0.5 ppm were irradiated. Increase of %NOE of these signals with lowering temperatures implies the decrease of the shuttling frequency with lowering temperature. The present view is compatible with the smaller steric bulk of the dimethylene moiety than that of the phenylene group.

The ^1H NMR spectrum of rotaxane **1a** is compared with that of the corresponding free dumbbell **3a** in Figure 2. The spectral

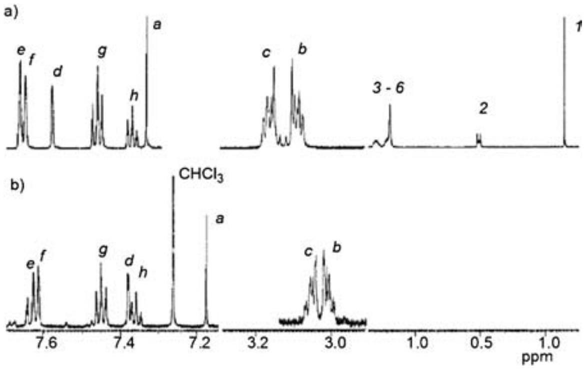


Figure 2. ^{1}H NMR spectral characteristics of (a) rotaxane **1a** and (b) dumbbell **3a** at 600 MHz, rt; All signals were assigned with the assistance of 2D NMR, HMBC, and HMQC experiments. Labeling of protons is given in Scheme 1.

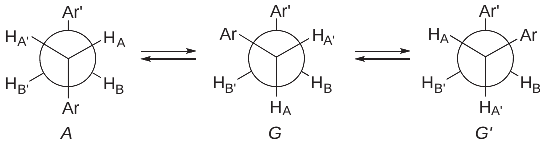


Figure 3. Newman projection of three conformers around a dimethylene C–C bond of the dumbbell in **1a** and **3a** with labeling scheme for the four protons.

pattern of the axle in **1a** is significantly different from that of **3a**; the deshielding of protons $a - d$ of **1a** and the difference in the coupling patterns of dimethylene protons (b and c) between **1a** and **3a** are remarkable. Apparently, the axle in the rotaxane feels the existence of the wheel, and the geometry of the axle in the rotaxane is modified by the steric effects of the wheel.[7]

To further elucidate the difference of rotational conformation around dimethylene C–C bonds between **1a** and **3a**, the coupling patterns for AA′BB′ spin systems of $\text{–CH}^{\text{A}}\text{H}^{\text{B}}\text{–CH}^{\text{A}'}\text{H}^{\text{B}'}\text{–}$ moieties at 303 K are analyzed by spectral simulation.[3] The proton labeling scheme is shown in Figure 3. The observed spectral pattern of rotaxane **1a** is reproduced using δ_{A} and δ_{B} of 3.089 and 3.161, germinal couplings $J_{\text{AA}'}$ ($=J_{\text{BB}'}$) of -14.00 Hz, and vicinal couplings J_{AB} ($=J_{\text{A}'\text{B}'}$) and $J_{\text{AB}'}$ ($=J_{\text{A}'\text{B}}$) of 5.00 and 11.90 Hz and for dumbbell **3a**, the parameters are δ_A, 3.008; δ_B, 3.049; J_{AB} ($=J_{\text{A}'\text{B}'}$), -14.00 Hz; J_{AB} ($=J_{\text{A}'\text{B}'}$), 6.00; $J_{\text{AB}'}$ ($=J_{\text{A}'\text{B}}$), 9.80.

It is expected according to the Karplus equation that the J_{AB} decreases and the $J_{\text{AB}'}$ increases with increasing the population of anti conformation (A) among three conformations A, G, and G' shown in Figure 3. The difference in the coupling patterns observed between **1a** and **3a** is in accord with the population of conformer A in **1a** is much larger than that for **3a**.[8] The dumbbell geometry in **1a** is suggested to be more stretched as an average than that in **3a** owing to the steric effects of the wheel shuttling in **1a**. In other words, dynamic steric effects due to the rapid one-dimensional Brownian motion[1i] of the wheel regulates the slower conformational change of the axle.[7,9]

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References and Notes

1 For recent reviews of molecular machines and rotaxanes, see: a) D. B. Amabilino, J. K. Stoddart, *Chem. Rev.* **1995**, *95*, 2725. b) V. Balzani, M. Gomez-Lopez, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405. c) M. J. Blanco, M. C. Jimenez, J. C. Chambron, V. Heitz, M. Linke, J. P. Sauvage, *Chem. Soc. Rev.* **1999**, *28*, 293. d) F. M. Raymo, J. F. Stoddart, *Chem. Rev.* **1999**, *99*, 1643. e) A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456. f) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH Verlag, Weinheim, Germany, **2003**. g) T. R. Kelley, *Molecular Machines. Topics in Current Chemistry*, Springer, Berlin, Heidelberg, New York, **2005**. h) G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl, *Chem. Rev.* **2005**, *105*, 1281. i) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem., Int. Ed.* **2007**, *46*, 72.

2 Prerotaxanes **2a** and **2b** were synthesized using ring-closing methathesis of the corresponding 1,4-bis[di-ω-hexenyl(methyl)-silyl]benzene derivatives: S. T. Phan, W. Setaka, M. Kira, *Chem. Lett.* **2007**, *36*, 1180.

3 See the Supporting Information for the details of the synthesis of **1a**, **1b**, **2a**, and **2b**, detailed NMR analysis of **1a** and **1b**, and X-ray structures of **1a**. Supporting Information is available electronically on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/index.html.

4 **1a**: colorless crystals, mp: 99–100 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ -0.17 (s, 12H, SiCH$_3$), 0.47–0.51 (m, 8H, H$_{\text{ring}}$), 1.17–1.28 (m, 32H, H$_{\text{ring}}$), 3.02–3.18 (m, 8H, CH_2Ar), 7.32 (s, 4H, PhH), 7.36 (t, $J = 7.4$ Hz, 4H, aryl), 7.45 (t, $J = 7.6$ Hz, 8H, aryl), 7.57 (d, $J = 1.2$ Hz, 4H, aryl), 7.64 (d, $J = 7.2$ Hz, 8H, aryl), 7.66 (s, 2H, aryl); ^{13}C NMR (100 MHz, CDCl$_3$) δ -3.25, 16.25, 24.50, 28.95, 29.17, 34.23, 36.92, 37.35, 124.19, 126.82, 127.43, 127.44, 128.72, 128.83, 139.00, 141.45, 142.05, 142.77; ^{29}Si NMR (79 MHz, CDCl$_3$) δ 1.70; Anal. Calcd for $C_{70}H_{90}Si_2$ (MW: 987.63): C, 85.13; H, 9.19%. Found: C, 84.85; H, 8.90%. HR-MS (ESI) calcd for $C_{70}H_{90}Si_2Na$: $[M + Na]^+$ 1009.6473, found 1009.6481.

5 Because the cleavage of Si–C(Ar) bonds by an acid (protodesilylation) is known to be highly efficient and selective, the low yield of **1a** and **1b** as well as the formation of side-products **3a** and **3b** is rather unexpected. Effective steric protection of Si-C(Ar) bonds in the prerotaxanes may reduce the selectivity of the protodesilylation. The protodesilylation of a similar prerotaxane having 3,5-di-*tert*-butylphenyl groups as terminal groups followed by the methylation gave only the corresponding free dumbbell in 33% yield. In this case, bulkiness of the terminal group would not be enough to prevent thermal dethreading.

6 Structure refinement was performed using SHELX-97: A. M. Sheldrick, *SHELX 97-Programs for Crystal Structure Analysis*, Göttingen, Germany, **1998**. Crystal data for **1a**: $C_{70}H_{90}Si_2$, $M_r = 987.60$, colorless prism, $0.4 \times 0.2 \times 0.05\,\text{mm}^3$, monoclinic, space group $P2_1/n$, $a = 25.618(11)$, $b = 17.857(8)$, $c = 27.997(12)$ Å, $\beta = 106.366(5)°$, $V = 12288(9)$ Å^3, $Z = 8$, $D_{\text{calc}} = 1.068\,\text{g cm}^{-3}$, Mo K$\alpha$ ($\lambda = 0.7107$ Å), $T = 173$ K, 28781 unique reflections were collected, 18022 observed [$I > 2\sigma(I)$]. Final $Goof = 1.022$, $R1 = 0.0676$ [$I > 2\sigma(I)$], 1359 parameters. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-694109.

7 Similar behavior was observed for **2b**.[3]

8 The population of anti conformation (%A) is not able to be determined uniquely. If J_{AB} for the anti conformation of **1a** and **3a** is assumed to be roughly 12.0 Hz, the %A value is estimated to be 98 and 69% for **1a** and **3a**, respectively. For the value of J_{AB}(anti) of similar spin systems, see: O. Takahashi, K. Saito, Y. Kohno, H. Suezawa, S. Ishihara, M. Nishio, *Eur. J. Org. Chem.* **2004**, 2398.

9 The static steric effect of the wheel on the axle conformation in a rotaxane has been investigated: cf. Y. Tachibana, H. Kawasaki, N. Kihara, T. Takata, *J. Org. Chem.* **2006**, *71*, 5093.

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