Shuttlecock-Like Arrangement of a Tweezer-Type Cavitand in the Crystalline State

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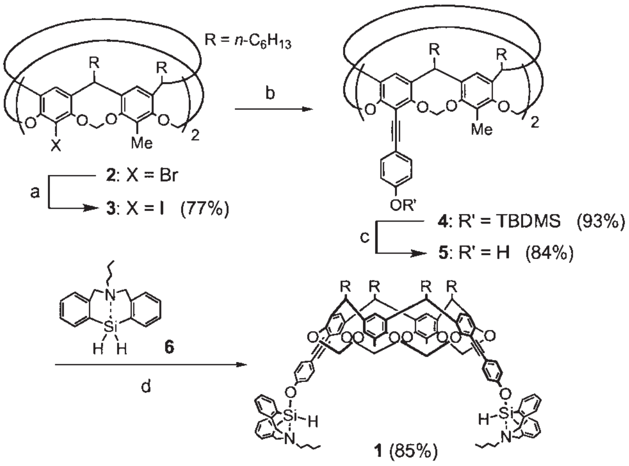
A tweezer-type cavitand bearing highly coordinated hydrosilane units at the pincer moieties was synthesized and its crystal structure was elucidated. It was found that the cavitand molecules and the hexane molecules included in their cavities form a unique shuttlecock-like columnar arrangement in the crystalline state.

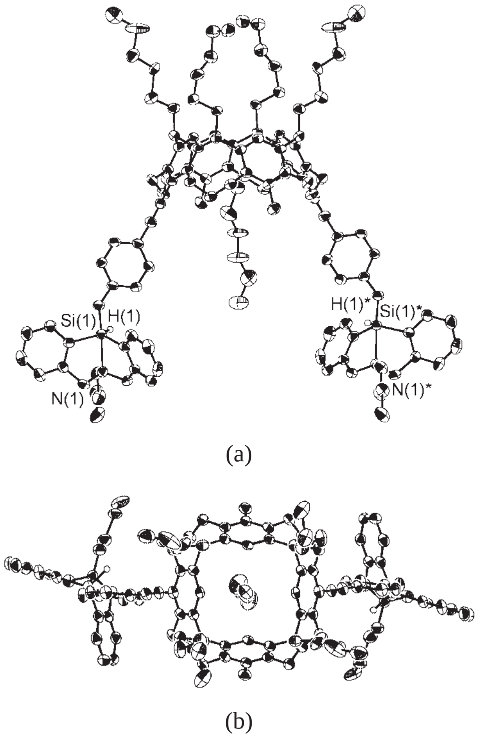
Resorcin[4]arene cavitands have been utilized as a versatile molecular platform for complexing agents for organic compounds and ions.[1] While various cavitands with a larger and deeper cavity have been developed to date, there have been only a few examples of tweezer-type cavitands utilizing resorcinarene as a spacer unit between pincers.[2] Pentacoordinate hydrosilanes have been reported to show high reactivity towards hydroxy compounds as well as carbonyl compounds.[3] We designed the novel cavitand-based molecular tweezers **1**, which have two intramolecularly coordinated hydrosilane units at both ends of the pincers for capturing various molecules. In the course of its synthesis, it was found that **1** shows a unique columnar arrangement in the crystalline state. Here, we report the details of the synthesis and crystal structure of **1**.

Cavitand **1** was synthesized by the route shown in Scheme 1. Dibromide **2**[4] was treated with n-BuLi, and quenched with a solution of iodine to give diiodide **3**. The Sonogashira coupling reaction of iodide **3** and 4-(t-butyldimethylsiloxy)phenylacetylene was carried out by using $[PdCl_2(PPh_3)_2]$, CuI, PPh_3, and triethylamine to give **4** in high yield of 93%. Cavitand diol **5** was prepared by deprotection using tetrabutylammonium fluoride. Heating of **5** with dihydrosilane **6**[5] in $CHCl_3$ afforded bis(monohydrosilane) **1**, which was isolated in 85% yield.

Single crystals of **1**•hexane were obtained from hexane/chloroform. X-ray crystallographic analysis established the tweezer-type structure of **1** as shown in Fig. 1. It belongs to the monoclinic space group $C2/c$ with $Z = 4$, and the molecules of **1** and hexane lie on a twofold crystallographic axis. The silicon atoms of **1** adopt the pentacoordinate state with intramolecular coordination of nitrogen; the Si···N distance (2.226(4) Å) is much shorter than the sum of van der Waals radii (3.65 Å) although longer than the sum of covalent radii (1.92 Å). The Si–H hydrogen atoms occupy the equatorial position of the distorted trigonal bipyramidal geometry, facing each other like tips of tweezers.



Scheme 1. Synthesis of tweezer-type cavitand **1**. Reagents and conditions: (a) (i) n-BuLi, THF, (ii) I_2, THF; (b) $[PdCl_2(PPh_3)_2]$, PPh_3, CuI, p-$(TBDMSO)C_6H_4C{\equiv}CH$, Et_3N, THF; (c) $(n\text{-}Bu)_4N^+F^-$, THF; (d) $CHCl_3$, 70 °C, 1.5 d.



(a)

(b)

Fig. 1. ORTEP drawings of **1**•hexane (50% probability). (a) Side view and (b) top view.

The main feature of the crystal packing is the shuttlecock-like columnar arrangement of **1** and hexane along the b direction (Fig. 2). The bowl-shaped resorcinarene unit, pincers units, and the four hexyl chains of the neighboring molecule form an oval cavity, the size and shape of which are appropriate for encapsulation of the hexane molecule. One of the two aromatic rings and the butyl group of the hydrosilane units pinch the neighboring resorcinarene unit, supporting the col-

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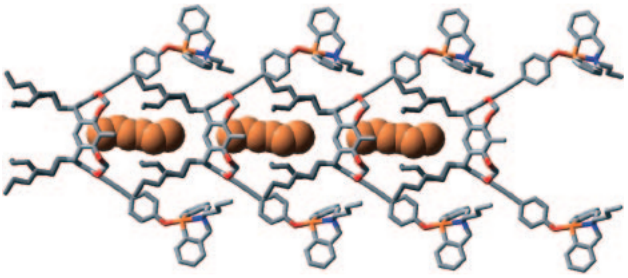

Fig. 2. View of the crystal packing of **1**•hexane along the *c* axis.

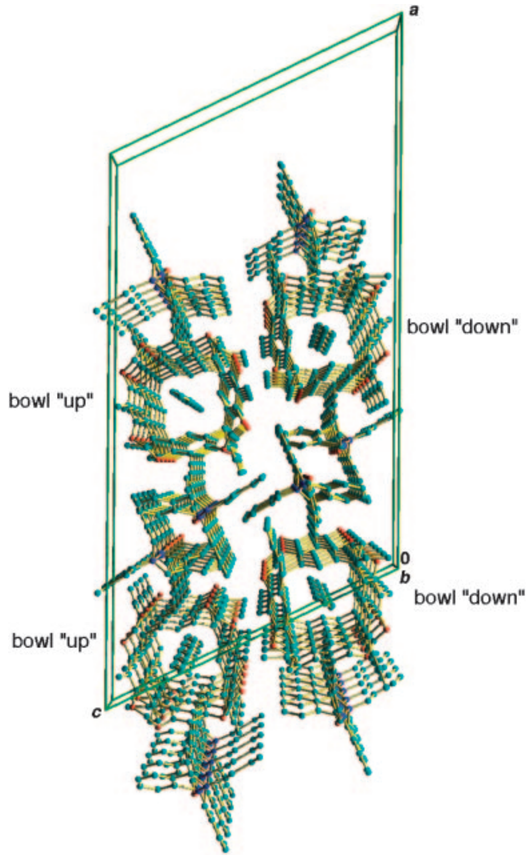

Fig. 3. View of the crystal packing of **1**•hexane down to the *b* axis. The hexyl groups are omitted for clarify.

umnar structure. While there have been several examples of resorcinarene derivatives that form a columnar structure in the crystalline state,[6] the formation of such chains of closed cavities that can include an organic guest is rare. When the packing is seen along the *c* axis, the bowls of the resorcinarenes in the neighboring columns point to the same direction, while the columns alternating "up" and "down" are observed in the view along the *a* axis (Fig. 3).

In the columns of **1**•hexane, the hexane molecules are linearly arranged at an interval of 12.8 Å. Unlike infinite channel structures, where the included molecules are liable to slide and are often disordered severely, the chain of the closed cavity observed here is considered to be useful for the arrangement of the guest molecules in a well-defined order. Actually, the single crystals of **1**•hexane are quite stable and no decomposition of the crystals due to the loss of solvent was observed at room temperature. It is expected that other guests with a linear shape will also be included in the cavity and ordered in the columns.

Experimental

All reactions were carried out under an argon atmosphere. Melting points were determined on a Yanaco micro melting point apparatus. The melting points were not corrected. THF was purified by distillation from sodium diphenylketyl under an argon atmosphere before use. Chloroform was distilled from calcium hydride before use. Triethylamine was purified by distillation. Column chromatography was carried out with Wakogel C-200. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded on Bruker DRX-500, JEOL α500, and JEOL AL400 spectrometers. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, the University of Tokyo.

Preparation of Diiodide 3. To a solution of dibromide **2**[4] (529.5 mg, 0.5 mmol) in THF (30 mL) was added *n*-butyllithium (1.60 M in hexane, 1.88 mL, 3.0 mmol) at −78 °C, and the reaction mixture was stirred for 30 min. After the addition of a solution of iodine (1.27 g, 5.0 mmol) in THF (5.0 mL), the reaction mixture was warmed to room temperature and then stirred for 1.5 h. The reaction mixture was treated with saturated aq Na_2SO_3 at 0 °C, extracted with ether, washed with brine, and dried over $MgSO_4$. The organic layer was filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2/hexane:$CHCl_3$ = 3:1) to afford **3** (442.6 mg, 0.37 mmol, 76.8%). **3**: white solid, mp 124.3–127.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, $J = 6.9$ Hz, 12H), 1.29–1.42 (m, 32H), 1.97 (s, 6H), 2.16–2.21 (m, 8H), 4.27 (d, $J = 7.3$ Hz, 4H), 4.79 (t, $J = 8.2$ Hz, 4H), 5.92 (d, $J = 7.3$ Hz, 4H), 6.92 (s, 2H), 7.09 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.41 (q), 14.11 (q), 22.63 (t), 27.80 (t), 29.43 (t), 30.08 (t), 31.84 (t), 37.44 (d), 92.33 (s), 98.59 (t), 117.37 (d), 120.84 (d), 124.28 (s), 137.66 (s), 139.04 (s), 153.30 (s), 154.70 (s). Found: C, 60.23; H, 6.67%. Calcd for $C_{58}H_{74}I_2O_8$: C, 60.42; H, 6.47%.

Preparation of Bis(silane) 4. To a solution of diiodide **3** (576.5 mg, 0.50 mmol), dichlorobis(triphenylphosphine)palladium(II) (17.5 mg, 25 µmol), triphenylphosphine (29.5 mg, 113 µmol), and copper(I) iodide (28.6 mg, 150 µmol) in triethylamine (10 mL) was added a solution of 4-(*t*-butyldimethylsiloxy)phenylacetylene (348.6 mg, 1.50 mmol) in triethylamine and THF (5 mL). The reaction mixture was heated at 50 °C for 12 h. After cooling to room temperature, the mixture was treated with water and 1 M aq HCl, extracted with ether, and washed with 1 M aq HCl and then with brine. The organic layer was dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The crude product was separated by column chromatography (SiO_2/hexane:$CHCl_3$ = 1:1, $CHCl_3$ then ethyl acetate) to give **4** (632.0 mg, 0.46 mmol, 92.9%). **4**: pale yellow solid, mp 136.0–138.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 12H), 0.89 (t, $J = 6.9$ Hz, 12H), 0.96 (s, 18H), 1.29–1.43 (m, 32H), 1.98 (s, 6H), 2.18–2.21 (m, 8H), 4.43 (d, $J = 6.9$ Hz, 4H), 4.80 (t, $J = 8.2$ Hz, 4H), 5.94 (d, $J = 6.9$ Hz, 4H), 6.75–6.78 (m, 4H), 6.95 (s, 2H), 7.07 (s, 2H), 7.30–7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.74 (q), 0.69 (s), 10.08 (q), 13.76 (q), 22.34 (t), 25.28 (q), 27.50 (t), 29.13 (t), 29.51 (t), 31.55 (t), 36.40 (d), 79.78 (s), 97.08 (s), 98.11 (t), 112.60 (s), 115.55 (s), 117.05 (d), 119.64 (d), 119.84 (d), 123.83 (s), 132.70 (d), 137.51 (s), 138.13 (s), 152.99 (s), 154.72 (s), 155.82 (s). Found: C, 75.67; H, 8.52%. Calcd for $C_{86}H_{112}O_{10}Si_2$: C, 75.84; H, 8.29%.

Preparation of Diol 5. To a solution of **4** (340.3 mg, 0.25 mmol, dried at 50 °C for 2 d in vacuo before use) in THF (10 mL) was added tetrabutylammonium fluoride (1.0 M in THF, 1.0 mL, 10 mmol) at 0 °C. After being stirred for 3 h, the reaction mixture was treated with water, extracted with ethyl acetate, and washed with brine. The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography ($SiO_2/CHCl_3$:ethyl acetate = 2:1) and then recrystallized from hexane/$CHCl_3$ to give **5** (237.1 mg, 0.21 mmol, 83.7%). **5**: white solid, mp 163.0–164.7 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.89 (t, $J = 6.8$ Hz, 12H), 1.30–1.42 (m, 32H), 1.99 (s, 6H), 2.33–2.38 (m, 8H), 4.44 (d, $J = 7.4$ Hz, 4H), 4.80 (t, $J = 8.1$ Hz, 4H), 6.00 (d, $J = 7.4$ Hz, 4H), 6.83 (d, $J = 8.3$ Hz, 4H), 7.36 (d, $J = 7.4$ Hz, 4H), 7.45 (s, 2H), 7.58 (s, 2H), 8.84 (brs, 2H); ^{13}C NMR (126 MHz, acetone-d_6) δ 10.35 (q), 14.33 (q), 23.32 (t), 28.75 (t), 30.15 (t), 30.27 (t), 32.66 (t), 37.85 (d), 80.37 (s), 98.52 (s), 99.38 (t), 113.85 (s), 114.84 (s), 116.39 (d), 119.51 (d), 122.20 (d), 125.54 (s), 134.04 (d), 138.76 (s), 139.58 (s), 154.16 (s), 155.91 (s), 158.89 (s). Found: C, 77.39; H, 7.49%. Calcd for $C_{74}H_{84}O_{10}\cdot H_2O$: C, 77.19; H, 7.53%.

Synthesis of Bis(hydrosilane) 1. A solution of diol **5** (45.3 mg, 40.0 µmol) and dihydrosilane **6**[5] (28.1 mg, 0.10 mmol) in $CHCl_3$ (3.0 mL) was heated at 70 °C for 1.5 d. The reaction mixture was separated by gel permeation liquid chromatography to give **1** (57.7 mg, 34.0 µmol, 85.2%). **1**: colorless crystals, mp 182.4–185.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88–0.93 (m, 18H), 1.26–1.43 (m, 32H), 1.56–1.63 (m, 8H), 1.98 (s, 6H), 2.18–2.21 (m, 8H), 2.75 (t, $J = 8.0$ Hz, 4H), 3.81 (d, $J = 14.9$ Hz, 4H), 3.92 (d, $J = 14.9$ Hz, 4H), 4.43 (d, $J = 7.2$ Hz, 4H), 4.80 (t, $J = 7.7$ Hz, 4H), 5.18 (s, $J_{SiH} = 250$ Hz, satellite, 2H), 5.94 (d, $J = 7.2$ Hz, 4H), 6.95 (s, 2H), 6.95 (d, $J = 6.9$ Hz, 4H), 7.05 (s, 2H), 7.12 (d, $J = 6.9$ Hz, 4H), 7.30–7.33 (m, 12H), 8.01 (d, $J = 6.9$ Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.66 (q), 14.18 (q), 14.33 (q), 20.94 (t), 22.91 (t), 25.79 (t), 28.07 (t), 29.71 (t), 30.07 (t), 32.11 (t), 36.96 (d), 53.46 (t), 56.54 (t), 79.56 (s), 98.66 (s), 98.67 (t), 113.49 (s), 113.94 (s), 117.60 (d), 119.73 (d), 119.82 (d), 124.42 (s), 124.91 (d), 127.92 (d), 130.17 (d), 133.26 (d), 133.50 (s), 137.64 (d), 138.06 (s), 144.78 (s), 153.55 (s), 155.19 (s), 159.86 (s); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −58.1 ($J_{SiH} = 250$ Hz). Found C, 77.87; H, 7.69; N, 1.41%. Calcd for $C_{110}H_{126}N_2O_{10}Si_2$: C, 78.07; H, 7.50; N, 1.66%.

X-ray Crystallographic Analysis of 1•Hexane. Single crystals of **1**•hexane were obtained by recrystallization from hexane/$CHCl_3$. The intensity data were collected at 120 K on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structures were solved by a direct method and refined by full-matrix least squares on F^2 using SHELXL-97.[7] The non-hydrogen atoms were refined anisotropically except for the minor components of the hexyl group and the solvent molecule. The hydrogen atoms were idealized by using the riding models except for the SiH hydrogens, which were located in the difference Fourier map and refined isotropically. Crystal data of **1**•hexane: $M_r = 1778.53$, monoclinic, space group $C2/c$, $a = 38.695(18)$, $b = 12.832(5)$, $c = 22.567(10)$ Å, $\beta = 116.2376(19)°$, $V = 10051(8)$ Å^3, $Z = 4$, $D_{calcd} = 1.175$ Mg m^{-3}, $T = 120$ K, $R1 = 0.0824$ ($I > 2\sigma(I)$), $wR2 = 0.2267$ (all data). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-292855. Copies of the data can be obtained free of charge via http://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; e-mail: deposit@ccdc.cam.ac.uk).

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