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Synthesis and Conformational Characteristics of Alkyl-Substituted Pillar[5]arenes

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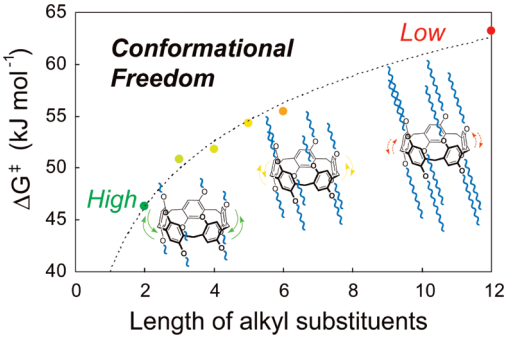

A series of pillar[5]arene derivatives with alkyl groups of different length were synthesized. The new alkyl-substituted pillar[5]arene derivatives 1,4-bis(ethoxy)pillar[5]arene (**C2**), 1,4-bis(propoxy)pillar[5]arene (**C3**), 1,4-bis(butoxy)pillar[5]arene (**C4**), 1,4-bis(pentyloxy)pillar[5]arene (**C5**), 1,4-bis(hexyloxy)pillar[5]arene (**C6**), and 1,4-bis(dodecanoxy)pillar[5]arene (**C12**) were obtained by Lewis acid-catalyzed condensation of dialkoxybenzene monomers with paraformaldehyde. The conformational characteristics of the pillar[5]arene derivatives were investigated by dynamic ^{1}H NMR measurements. When the alkyl substituents were bulkier than methyl groups, the rotation of phenolic units in the pillar[5]arenes was suppressed and their conformation was immobilized. As their length increased, the alkyl substituents packed at the upper and lower rims and thus lowered the conformational freedom of the pillar[5]arenes.

Introduction

Macrocyclic host molecules such as calixarenes,[1] cyclodextrins[2] and cucurbiturils[3] have been the focus of considerable attention due to their interesting conformational, physicochemical, and host−guest properties. Cyclodextrins and cucurbiturils are conformationally fixed, whereas conformational freedom still remains in the calixarene cavity. Calixarenes made from phenolic units have many conformers due to the two possible rotation modes of the phenolic unit: the oxygen-through-the-annulus rotation, and the

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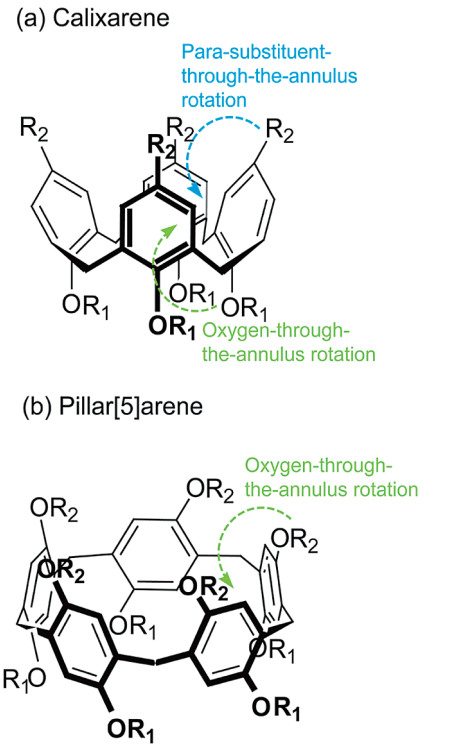

FIGURE 1. Rotation mode for inversion of the phenolic units in (a) calixarene and (b) pillar[5]arene.

para-substituent-through-the-annulus rotation (Figure 1a).[1a−g] The substituent moieties at the lower and upper rim affect the rotation of the phenolic units in calixarenes. For example, *p-tert*-butylcalix[4]arene adopts a cone conformation because hydrogen bonding interactions among the OH groups at the lower rim inhibit the rotation.[1d,e] Modification of the alkyl substituents affects the conformational freedom of the calix[4]arenes. When alkyl substituents bulkier than ethyl groups were introduced into OH groups, the oxygen-through-the-annulus rotation was suppressed and the conformation of the calix[4]arenes was immobilized.[1f] In the members of the *p-tert*-butylcalix[*n*]arene family, the conformational freedom generally trends upward as the size of the calixarene increases.[1g] Clear-cut explication for the rotation of calixarene derivatives has been demonstrated.

We synthesized a new type of macrocyclic host for the first time and named it "pillar[5]arene" (Figure 1b).[4] Pillar[5]arene is a cyclic pentamer that is composed of phenolic units, and has a composition that is analogous to that of typical calixarenes. However, because the repeating units are connected by methylene bridges at the para-position, pillar[5]arene has a unique symmetrical pillar architecture that is quite different from the basket-shaped structure of the meta-bridged calixarenes. Since pillar[5]arene has a symmetrical structure, the only possible rotation mode for the phenolic unit in pillar[5]arene should be the oxygen-through-the-annulus rotation (Figure 1b). We have elucidated the

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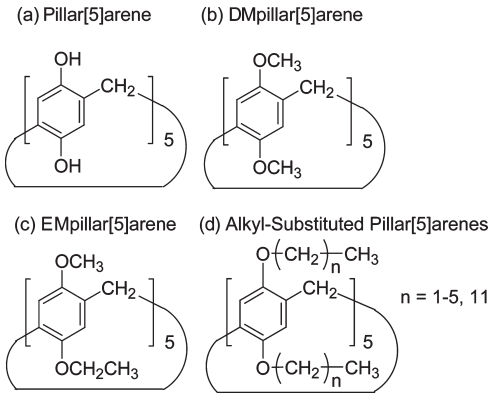

FIGURE 2. Pillar[5]arenes.

conformational flexibility of pillar[5]arene derivatives. As in the study of the conformational characteristics of calixarenes, the conformational flexibility of pillar[5]arenes has been investigated by using dynamic ^{1}H NMR measurements. In the case of unmodified pillar[5]arene (Figure 2a), at −60 °C complex split proton peaks originating from individual conformers were observed, indicating that the oxygen-through-the-annulus rotational motion at that temperature was slow on the NMR time scale. Formation of the *intra*molecular hydrogen bond network stabilized the conformation of pillar[5]arene and slowed the rotational motion. Since dimethoxypillar[5]arene (DMpillar[5]arene, Figure 2b) did not form the *intra*molecular hydrogen bond belt, the rotational motion was fast on the NMR time scale even at −90 °C.[4d] In the nonsymmetric ethoxymethoxypillar[5]arene (EMpillar[5]arene, Figure 2c), the rotational motion was slow on the NMR time scale or did not occur, because of the introduction of the ethoxy and methoxy substituents into pillar[5]arene.[4c] From these results it follows that the substituent moieties at the upper and lower rims are likely to strongly affect the conformational characteristics of pillar[5]arenes. Consequently, in the present study, we prepared a series of pillar[5]arenes with alkyl groups of different length (Figure 2d) to further investigate the conformational characteristics. Using variable-temperature ^{1}H NMR measurements we have elucidated the conformational characteristics of the alkyl-substituted pillar[5]arene derivatives.

Results and Discussion

Synthesis of a Series of Pillar[5]arenes with Different Lengths of Alkyl Moieties. We synthesized a new series of alkyl-substituted pillar[5]arene derivatives, namely 1,4-bis(ethoxy)pillar[5]arene (**C2**), 1,4-bis(propoxy)pillar[5]arene (**C3**), 1,4-bis(butoxy)pillar[5]arene (**C4**), 1,4-bis(pentyloxy)pillar[5]arene (**C5**), 1,4-bis(hexyloxy)pillar[5]arene (**C6**), and 1,4-bis(dodecanoxy)pillar[5]arene (**C12**) (Scheme 1). The corresponding 1,4-dialkoxybenzenes with ethoxy (**M2**), propoxy (**M3**), butoxy (**M4**), pentyloxy (**M5**), hexyloxy (**M6**), and dodecanoxy substituents (**M12**) were used as monomers.[5] Since boron trifluoride diethyl etherate [$BF_3O(C_2H_5)_2$] was an effective Lewis acid for the synthesis of DMpillar[5]arene,[4a] we used $BF_3O(C_2H_5)_2$ for the synthesis of these new

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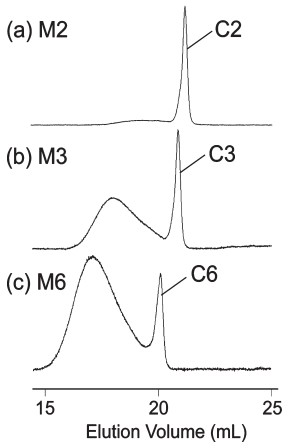
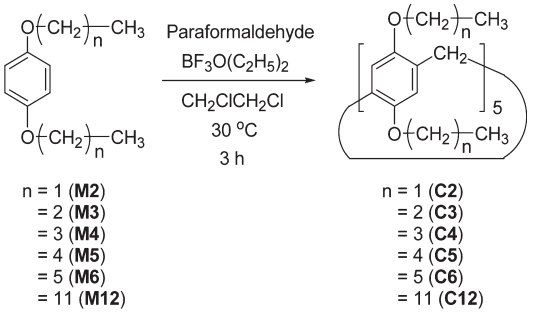


FIGURE 3. SEC traces of the obtained products after washing with methanol, using (a) **M2**, (b) **M3**, and (c) **M6**.

SCHEME 1



pillar[5]arene derivatives. The monomers were reacted with paraformaldehyde in the presence of $BF_3O(C_2H_5)_2$ for 3 h at 30 °C (Scheme 1). The solutions were then poured into methanol and the resulting precipitates were collected by filtration. Figure 3 shows Size-Exclusion Chromatography (SEC) traces of the precipitates. Formation of polymer from **M2** was hardly observed and **C2** was obtained selectively (Figure 3a), as in the synthesis of DMpillar[5]arene. The product from **M3** contained **C3** and polymer (Figure 3b). **M4**−**M6** and **M12** gave mixtures of polymers and small amounts of **C4**−**C6** and **C12**, respectively: Figure 3c shows the SEC trace of the precipitate from **M6**. These observations indicated that long alkyl substituents tended to suppress the cyclization reaction.

We were able to isolate the new pillar[5]arene derivatives **C2**−**C6** and **C12** by recrystallization or silica gel column chromatography, and the structures of **C2**−**C6** and **C12** were confirmed by ^{1}H and ^{13}C NMR, mass, and elemental analysis (Supporting Information). In addition, the structure of **C5** was determined by X-ray crystallography (Figure 4). As for DMpillar[5]arene,[4a] the structure of **C5** was a cyclic pentamer with the constituent units connected by methylene bridges at the para-position. Two acetone molecules were included in the cavity of **C5**. However, unlike DMpillar[5]arene, the structure of **C5** was a distorted pentagon and pillar architecture from the upper and side views, respectively. The introduction of the bulky pentyl substituents should change the symmetrical architecture. The ^{1}H NMR spectrum of **C6** at 30 °C shown in Figure 5 is typical of the entire series: signals at 0.8−1.9 ppm for alkyl moieties (peaks d−g), signals at 3.7 ppm for the methylene adjacent to the

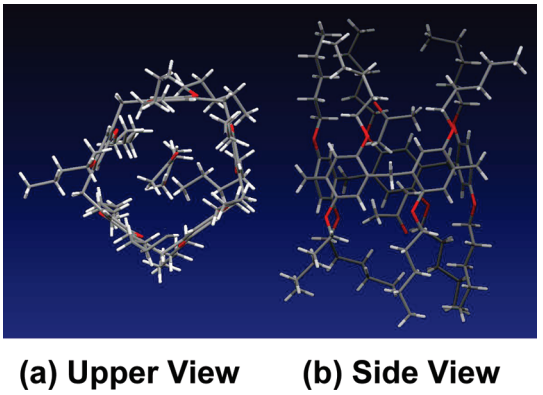


FIGURE 4. Crystal structure of **C5** from the upper (a) and side view (b).

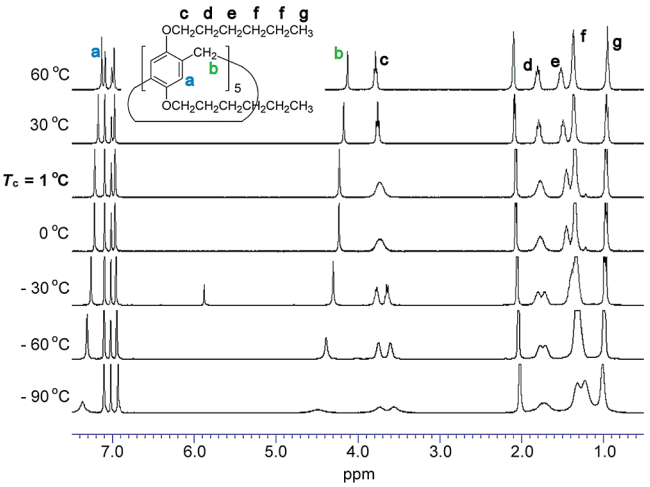


FIGURE 5. Variable-temperature ^{1}H NMR spectra of **C6** (10 mM) in toluene-d_8. The coalescence temperature (T_c) was estimated on the coalescence signal of the methylene protons (peak c).

O atoms (peak c), a singlet at 4.3 ppm for the methylene bridge protons (peak b) and a singlet at 7.2 ppm for the aromatic protons (peak a). Since the peaks of the methylene bridge and aromatic protons were found as equivalent singlet signals, the conformations of all of the pillar[5]arenes were symmetrical. In addition, the mass spectra of all of the pillar[5]arenes showed a strong molecular ion peak at the expected *m*/*e* ratio. Therefore, even for long alkyl chain substituted monomers such as **M6** and **M12**, macrocyclic pentamer preferentially formed. The data indicate that the pentagonal cyclic structure should be the conformationally stable architecture.

Conformational Characteristics of Pillar[5]arenes with Different Length Alkyl Chains. Investigation of the conformational characteristics of the novel alkyl-substituted pillar[5]arene derivatives was carried out with variable-temperature ^{1}H NMR measurements. For **C6** under 1 °C (Figure 5), the proton signal from the methylene moieties adjacent to the O atoms (peak c) was split into two groups of peaks in 1:1 integration ratio. However, the other peaks from **C6** did not change on cooling to −90 °C. If the rotational motion were slow on the NMR time scale, complex proton signals from **C6** should be observed on cooling, which was observed in unmodified pillar[5]arene (Figure 2a).[4d]

It follows that the oxygen-through-the-annulus rotation of the phenolic units was fast on the NMR time scale, or did not occur. Since the proton signal from the methylene moieties near the O atoms in **M6** was not split even at −90 °C (Supporting Information), the split of the methylene protons observed in **C6** under 1 °C resulted from the cyclic structure. By formation of the cyclic structure, the packing of the hexyl chains at the upper and lower rims should be accelerated. Thus mobility of the methylene protons adjacent to the O atoms was suppressed and slow on the NMR time scale at low temperatures. The inside of the cavity is an electron-rich space, thus the methylene protons located in the inner and outer spaces were shielded and deshielded, respectively (Figure 6). Consequently, the methylene proton signal was split in a 1:1 integration ratio. If the oxygen-through-the-annulus rotation of the phenolic units were fast on the NMR time scale, the two methylene protons should be observed as equivalent. Hence the oxygen-through-the-annulus rotation movement of the phenolic units did not occur in **C6**. Since the signal for the hexyl protons adjacent to the O atoms was split and the signals for the other hexyl protons distant from the O atoms were not split under 1 °C, the mobility of the two methylene protons should reflect the conformational freedom around the cavity in **C6**.

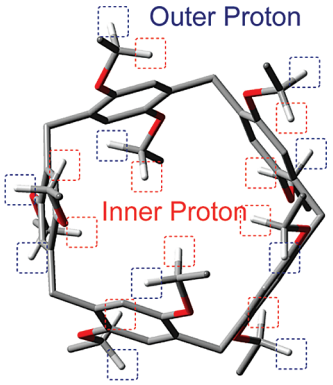


FIGURE 6. Schematic view of the protons located in the inside and outside of the cavity.

Figure 7 shows partial variable-temperature ^{1}H NMR spectra of **C2**−**C5** and **C12**. In all cases, the peak from the methylene moiety (peak c) was split with 1:1 integration ratio

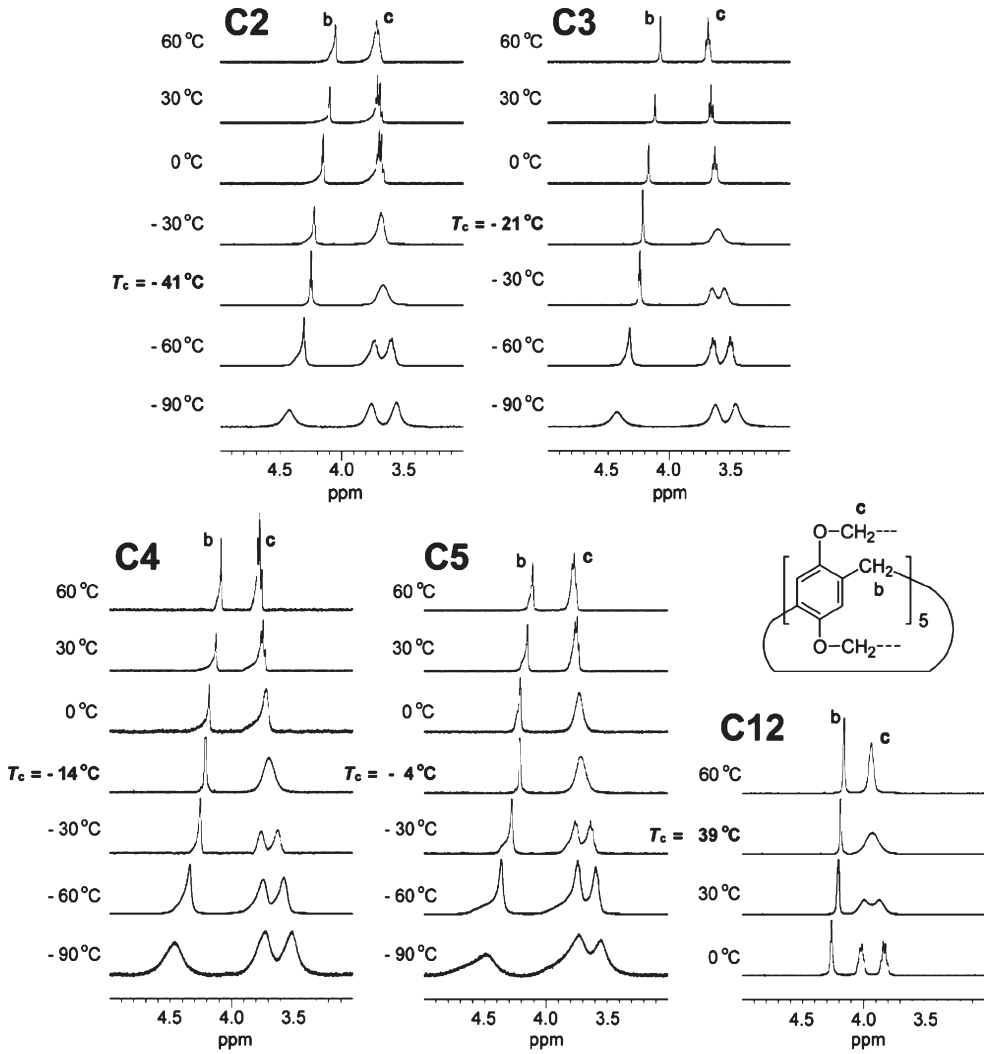


FIGURE 7. Variable-temperature ^{1}H NMR spectra of alkyl-substituted pillar[5]arenes (10 mM) in toluene-d_8. The coalescence temperature (T_c) was estimated on the coalescence signal of the methylene protons (peak c).

TABLE 1. Coalescence Temperatures, ^{1}H NMR Data, and $\Delta G^{\ddagger}$ Values for the Exchange between the Methylene Protons Located in the Inside and Outside of the Cavity

alkyl-substituted pillar[5]arenes	T_c (°C)	$\delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (kJ/mol)
C2	−41	82.0	46.3
C3	−21	66.8	50.9
C4	−14	87.2	51.8
C5	−4	71.6	54.3
C6	1	67.6	55.5
C12	39	76.8	63.2

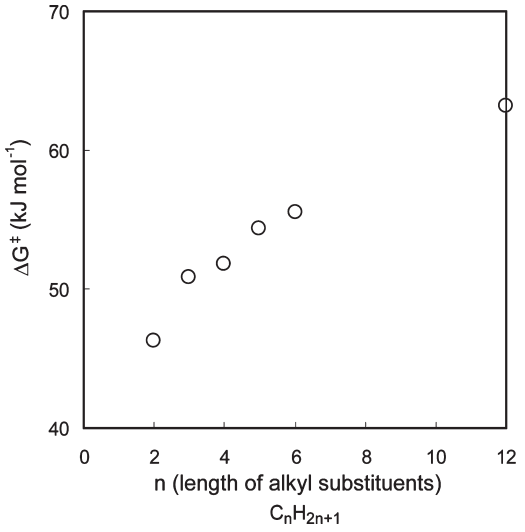


FIGURE 8. Plot of the $\Delta G^{\ddagger}$ values for **C1**−**C6** and **C12** in toluene-d_6 solution.

at low temperatures and coalescence occurred on heating. Therefore, as with **C6**, the oxygen-through-the-annulus rotation of the phenolic units in **C2**−**C5** and **C12** did not occur. From the X-ray crystallographic structure of **C5** (Figure 4), the oxygen-through-the-annulus rotation should be suppressed due to the bulkiness of the pentyloxy moieties, which is consistent with the conformational characteristics of nonsymmetric pillar[5]arene.[4c] The oxygen-through-the-annulus rotation of the phenolic unit in EMpillar[5]arene (Figure 2c), which has short alkyl substituents compared with **C2**−**C5** and **C12**, did not occur or was slow on the NMR time scale even at high temperature. Table 1 shows the coalescence temperatures (T_c) for each of the members of **C2**−**C6** and **C12**. The $\Delta G^{\ddagger}$ values shown in Table 1 were calculated by using the standard equations[6] incorporating the values for $\delta\nu$ and T_c. It is an interesting and little known phenomenon that mobility of the methylene protons around the cavity in **C12** is slow on the NMR time scale and that each methylene proton is able to be observed as a distinguishable split signal even at room temperature. The plot in Figure 8 shows that the barrier to the mobility of the two methylene protons trends upward exponentially as the length of the alkyl substituent increases. As the length of the alkyl substituents increases, the alkyl substituents pack at the upper and lower rims and thus decrease the conformational freedom of the phenolic units of these pillar[5]arenes.

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Conclusions

We successfully synthesized new pillar[5]arene derivatives having different lengths of alkyl chains, and were able to clarify the conformational characteristics of the alkyl-substituted pillar[5]arenes by variable-temperature ^{1}H NMR measurements. The alkyl substituents greatly affect the conformational characteristics of pillar[5]arenes. When the alkyl-substituents were bulkier than methyl groups, the signal from the methylene protons adjacent to the O atoms was split by cooling, indicating that mobility of the methylene protons is slow on the NMR time scale and the methylene protons located in the inner and outer spaces are shielded and deshielded, respectively. However, the signals of the other protons of phenyl and methylene bridges were observed as singlets even at −90 °C. These data indicate that the oxygen-through-the-annulus rotation of phenolic units did not occur and the conformation of the pillar[5]arenes was immobilized. Since the signal for the methylene protons adjacent to the O atoms was split and the signals for the other alkyl protons were not split by cooling, the mobility of the two methylene protons should reflect the conformational freedom around the cavity in pillar[5]arenes. It is interesting that the mobility of the methylene protons in **C12** is slow on the NMR time and the signal of the methylene protons is split even at room temperature. As the length of the alkyl substituents increases, conformational freedom around the cavity in pillar[5]arenes is reduced, because the alkyl substituents pack at the upper and lower rims. The information on the conformational characteristics of pillar[5]arenes that has been obtained in this study is important for revealing the host−guest and self-assembly properties, and may lead to the development of new functional systems based on pillar[5]arenes.

Experimental Section

1,4-Diethoxybenzene (**M2**), 1,4-dipeopoxybenzene (**M3**), 1,4-dibutoxybenzene (**M4**), 1,4-dipentyloxybenzene (**M5**), 1,4-dihexyloxybenzene (**M6**), and 1,4-didodecanoxybenzene (**M12**) were synthesized according to the previous literature.[5]

1,4-Bis(ethoxy)pillar[5]arene (C2). To a solution of 1,4-diethoxybenzene (1.66 g, 10 mmol) in 1,2-dichloroethane (20 mL) was added paraformaldehyde (0.31 g, 10 mmol) under nitrogen atmosphere. Then, boron trifluoride diethyl etherate [$BF_3O(C_2H_5)_2$, 1.25 mL, 10 mmol] was added to the solution and the mixture was stirred at 30 °C for 3 h. The solution was poured into methanol and the resulting precipitate was collected by filtration. The solid was dissolved in $CHCl_3$ and the insoluble part was filtered off. The $CHCl_3$ was removed in vacuo, and the residue was crystallized from acetone (0.413 g, yield 23.2%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, TMS) δ 6.72 (s, 10H, phenyl protons), 3.82 (q, J = 7.1 Hz, 20H, methylene protons), 3.76 (s, 10H, methylene bridges), 1.25 (t, J = 7.1 Hz, 30H, methyl protons). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, TMS) δ 149.8, 128.5, 115.1 (C of phenyl), 63.8 (C of methylene groups), 29.8 (C of methylene bridge), 15.0 (C of methyl groups). Anal. Calcd for $C_{55}H_{70}O_{10}$: C, 74.13; H, 7.92. Found: C, 73.97; H, 7.97. HRMS (FAB) calcd for $C_{55}H_{71}O_{10}$ $[M]^+$ 891.50468, found 891.50438. Melting point (T_m) 157.5 °C.

1,4-Bis(propoxy)pillar[5]arene (C3). This compound was prepared by using the same conditions as those used for the

preparation of **C2** except that 1,4-dipropoxybenzene was used in place of 1,4-diethoxybenzene. Column chromatography (silica gel; CH_2Cl_2:hexane = 1:3 to 1:2) afforded a white solid (0.582 g, yield 28.2%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, TMS) δ 6.80 (s, 10H, phenyl protons), 3.79 (t, J = 6.3 Hz, 20H, $-OCH_2CH_2CH_3$), 3.76 (s, 10H, methylene bridges), 1.71−1.76 (m, 20H, $-OCH_2CH_2CH_3$), 1.00 (t, J = 7.3 Hz, 30H, methyl protons). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, TMS) δ 149.8, 128.2, 115.0 (C of phenyl), 69.8 (C of methylene groups), 29.5 (C of methylene bridge), 23.0 (C of methylene groups), 10.7 (C of methyl groups). Anal. Calcd for $C_{65}H_{90}O_{10}$: C, 75.69; H, 8.80. Found: C, 75.04; H, 8.95. HRMS (FAB) calcd for $C_{65}H_{91}O_{10}$ $[M]^+$ 1031.6612, found 1031.6623. Melting point (T_m) 112.9 °C.

1,4-Bis(butoxy)pillar[5]arene (C4). This compound was prepared by using the same conditions as those used for the preparation of **C2** except that 1,4-dibutoxybenzene was used in place of 1,4-diethoxybenzene. Column chromatography (silica gel; CH_2Cl_2:hexane = 1:2) afforded a white solid (0.191 g, yield 8.2%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, TMS) δ 6.83 (s, 10H, phenyl protons), 3.85 (t, J = 6.6 Hz, 20H, $-OCH_2CH_2-$), 3.75 (s, 10H, methylene bridges), 1.73−1.80 (m, 20H, $-OCH_2CH_2-$), 1.48−1.57 (m, 20H, $-OCH_2CH_2CH_2-$), 0.91 (t, J = 7.3 Hz, 30H, methyl protons). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, TMS) δ 149.8, 128.1, 114.8 (C of phenyl), 67.9, 32.0 (C of methylene groups), 29.4 (C of methylene bridge), 19.5 (C of methylene groups), 14.0 (C of methyl groups). Anal. Calcd for $C_{75}H_{110}O_{10}$: C, 76.88; H, 9.46. Found: C, 76.75; H, 9.77. (FAB) Calcd for $C_{75}H_{111}O_{10}$ $[M]^+$ 1171.8177, found 1171.8181. Melting point (T_m) 131.5 °C.

1,4-Bis(pentyloxy)pillar[5]arene (C5). This compound was prepared by using the same conditions as those used for the preparation of **C2** except that 1,4-dipentyloxybenzene was used in place of 1,4-diethoxybenzene. Column chromatography (silica gel; CH_2Cl_2:hexane = 4:1 to 3:1) afforded a white solid (0.359 g, yield 13.7%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, TMS) δ 6.84 (s, 10H, phenyl protons), 3.85 (t, J = 6.6 Hz, 20H, $-OCH_2CH_2-$), 3.76 (s, 10H, methylene bridges), 1.77−1.84 (m, 20H, $-OCH_2CH_2-$), 1.47−1.54 (m, 20H, $-OCH_2CH_2CH_2-$), 1.35−1.44 (m, 20H, $-OCH_2CH_2CH_2CH_2-$), 0.94 (t, J = 7.3 Hz, 30H, methyl protons). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, TMS) δ 149.9, 128.2, 114.9 (C of phenyl), 68.3, 29.6 (C of methylene groups), 29.4 (C of methylene bridge), 28.5, 22.6 (C of methylene groups), 14.1 (C of methyl groups). Anal. Calcd for $C_{85}H_{130}O_{10}$: C, 77.82; H, 9.99. Found: C, 77.72; H, 10.12. HRMS (FAB) calcd for $C_{85}H_{131}O_{10}$ $[M]^+$ 1311.9742, found 1311.9736. Melting point (T_m) 95.5 °C.

1,4-Bis(hexyloxy)pillar[5]arene (C6). This compound was prepared by using the same conditions as those used for the preparation of **C2** except that 1,4-dihexyloxybenzene was used in place of 1,4-diethoxybenzene. The residue after filtration was crystallized from acetonitrile (0.528 g, yield 18.2%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, TMS) δ 6.83 (s, 10H, phenyl protons), 3.84 (t, J = 6.1 Hz, 20H, $-OCH_2CH_2-$), 3.75 (s, 10H, methylene bridges), 1.76−1.84 (m, 20H, $-OCH_2CH_2-$), 1.48−1.56 (m, 20H, $-OCH_2CH_2CH_2-$), 1.31−1.38 (m, 40H, $-OCH_2CH_2CH_2CH_2CH_2-$), 0.90 (t, J = 7.1 Hz, 30H, methyl protons). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, TMS) δ 149.8, 128.7, 114.8 (C of phenyl), 68.4, 31.8, 29.9 (C of methylene groups), 29.3 (C of methylene bridge), 26,0 22.6 (C of methylene groups), 14.0 (C of methyl groups). Anal. Calcd for $C_{95}H_{150}O_{10}$: C, 78.57; H, 10.41. Found: C, 78.36; H, 10.53. HRMS (FAB) calcd for $C_{95}H_{151}O_{10}$ $[M]^+$ 1452.1307, found 1452.1301. Melting point (T_m) 105.7 °C.

1,4-Bis(dodecanoxy)pillar[5]arene (C12). This compound was prepared by using the same conditions as those used for the preparation of **C2** except that 1,4-didodecanoxybenzene was used in place of 1,4-diethoxybenzene. Column chromatography (silica gel; CH_2Cl_2:hexane = 0:5 to 1:5) afforded a white solid (0.38 g, yield 6.7%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, TMS) δ 6.86 (s, 10H, phenyl protons), 3.86−3.98 (br, 20H, $-OCH_2CH_2-$), 3.74 (s, 10H, methylene bridges), 1.71−1.92 (br, 20H, $-OCH_2CH_2-$), 1.47−1.60 (br, 20H, $-OCH_2CH_2CH_2-$), 1.05−1.39 (m, 160H, $-OCH_2CH_2CH_2CH_2CH_2CH_2-$), 0.85 (t, J = 7.3 Hz, 30H, methyl protons). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, TMS) δ 149.6, 128.0, 114.2 (C of phenyl), 67.9, 32.0, 29.9, 29.7, 29.6 (C of methylene groups), 29.4 (C of methylene bridge), 26.2, 22.7 (C of methylene groups), 14.1 (C of methyl groups). Anal. Calcd for $C_{155}H_{270}O_{10}$: C, 81.16; H, 11.86. Found: C, 81.21; H, 12.18. MS (MALDI-TOF) calcd for $C_{155}H_{270}O_{10}$ $[M + Na]^+$ 2315.05, found 2315. Melting point (T_m) 114.9 °C.

Determination of the Barriers of the Mobility of the Methylene Protons Adjacent to the O Atoms. The $\Delta G^{\ddagger}$ values were estimated by using the coalescence temperatures and the chemical shifts measured in the frozen structures. To determine the coalescence temperatures, the variable-temperature ^{1}H NMR experiments were carried out by the recording of spectra every 1 deg. The chemical shifts ($\delta\nu$) in **C2**−**C6** and **C12** were measured at −90 and 0 °C, respectively. The calculations were carried with eq 1.[6]

$$\Delta G^{\ddagger} = 8.314T_c[22.96 + \log(T_c/\delta\nu)] \quad (1)$$

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Supporting Information Available: Full spectroscopic data for C2−C6 and C12, X-ray crystallographic data of C5 in CIF format, and the variable-temperature ^{1}H NMR spectra of M6. This material is available free of charge via the Internet at http://pubs.acs.org.