Bull. Chem. Soc. Jpn. Vol. 80, No. 7, 1377–1382 (2007) 1377

Do Dibenzo[22–30]crown Ethers Bind Secondary Ammonium Ions to Form Pseudorotaxanes?

**Yuji Tokunaga,*[1] Megumi Yoshioka,[1] Tatsuya Nakamura,[1] Tatsuhiro Goda,[1]
Ryuji Nakata,[2] Suzuka Kakuchi,[1] and Youji Shimomura[1]**

[1]Department of Materials Science and Engineering, Faculty of Engineering, University of Fukui, Fukui 910-8507

[2]Natural Science Education Laboratory, Faculty of Education and Regional Studies, University of Fukui,
Fukui 910-8507

Received October 10, 2006; E-mail: tokunaga@matse.fukui-u.ac.jp

In this study, we synthesized dibenzo[22–30]crown ethers and dumbbell-like secondary ammonium salts having stoppers of varying bulk. These crown ethers formed pseudorotaxanes with the ammonium ions in solution and in the gas phase, as evidenced using NMR spectroscopy and MS/MS spectrometry, respectively. The association constants in solution were obtained through regulation of the association and dissociation rates by varying the nature of the stopper groups of the dumbbell-like ammonium ions. The [25]- and [26]crown ether/isopropylphenyl group, the [27]- and [30]crown ether/*tert*-butylphenyl group, and the [22]- and [23]crown ether/furyl group were matched pairs. ^{1}H NMR spectra of mixtures ($CDCl_3/CD_3CN$) of the crown ethers and their matched ammonium salts indicated the presence of three sets of signals in solution: those of the crown ether, the ammonium salt, and their pseudorotaxane. Integration of pertinent signals allowed the association constants of pseudorotaxanes to be determined readily. Among the [22–30]crown ethers, the highest value of the association constant was that for the [24]crown ether/dibenzylammonium ion system; the [25–30]crown ether/ammonium ion systems exhibited moderate values of their association constants [$K_{exp} = 35–114\,M^{-1}$ when using $(ArCH_2)_2NH_2{}^+PF_6{}^-$ as the ammonium salt at 27 °C; $K_{exp} = 21\,M^{-1}$ when using $(ArCH_2)_2NH_2{}^+TsO^-$ at 27 °C]. The [22]- and [23]crown ethers interacted weakly [$K_{exp} = 6–14\,M^{-1}$ when using $(ArCH_2)_2NH_2{}^+TsO^-$ at 27 °C].

Hydrogen bonding was first reported for guiding the self-assembly of [2]pseudorotaxanes from dibenzo[24]crown-8 (DB24C8) and secondary ammonium ions.[1] Since then, these types of pseudorotaxane have garnered much attention because of their unique structures and intriguing properties.[2] Several oligorotaxanes and polyrotaxanes[3] and dendrimers of rotaxanes[4] have been synthesized using DB24C8/ammonium ion systems. In addition, the hydrogen-bonding interactions between secondary ammonium ions and oligo(ethylene glycol) moieties, which are small units of crown ethers have been utilized to prepare a range of attractive supramolecular structures, including a supramolecular cryptant[5] based on a rotaxane, double-stranded rotaxanes,[6] an anion-assisted multi-stranded rotaxane,[7] and a ring–ring pseudorotaxane.[8] Furthermore, reversible-recognition [i.e., threading oligo(ethylene glycol) derivatives through a dicationic cyclophane][9] and pseudorotaxanes formed from modified ammonium ions and crown ethers[10] also have been reported. Despite the well-established hydrogen bonding that occurs between poly(ethylene glycol) units and ammonium ions, fundamental crown ethers that possess small or moderate ring sizes have not been examined sufficiently or systematically for their ability to form such psudorotaxanes,[11,12] possibly because the synthesis of asymmetric crown ethers and the measurement of their association constants are somewhat complex. In contrast, [24]crown-8, which is readily available, has a cavity size that is amenable to passage of phenyl units positioned at the termini of common dumbbell-like compounds, allowing analyses of the stabilities of their pseudorotaxanes when using NMR spectroscopy; i.e., the pseudorotaxane and the uncomplexed species are detectable independently in the NMR spectra of mixtures of the axle- and wheel-like components.[1] The association constants are obtainable readily from integration of the signals of each species, with the chemical shifts of the signals providing information regarding the structure of the complex.[1,12,13]

In this study, we investigated how changing the cavity size of the crown ether, as opposed to the size of the stopper units of the guest, alters the association constants for pseudorotaxane formation. Furthermore, we determined suitable "matched pairs" between the cavity size of the host and the stopper size of the dumbbell-like guest that allowed us to analyze these pseudorotaxanes' thermodynamic stabilities using NMR spectroscopy (Fig. 1).

Results and Discussion

Synthesis of Crown Ethers. The crown ethers chosen for this investigation included DB24C8-*o* **1** as a standard, mono-*meta*-fused DB25C8-*m* **2**,[14] mono-*para*-fused DB26C8-*p* **3**, and DB25C8-*o* **4** and DB26C8-*o* **5**, which possess one and two propylene glycol units, respectively. Two large macrocycles—DB27C9-*o* **6**[14] and DB30C10-*o* **7**,[15] which contain 27- and 30-membered rings, respectively—and three small crown ethers—DB21C7-*o* **8**,[15,16] DB22C7-*o* **9**, and DB23C7-*o* **10**—were also investigated (Fig. 2). The syntheses of crown ethers

Published on the web July 11, 2007; doi:10.1246/bcsj.80.1377

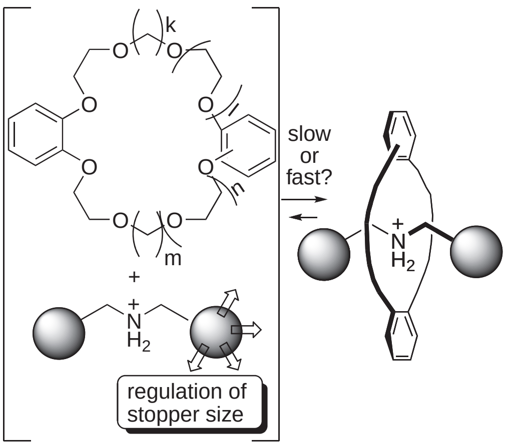


Fig. 1. Illustration of pseudorotaxane formation.

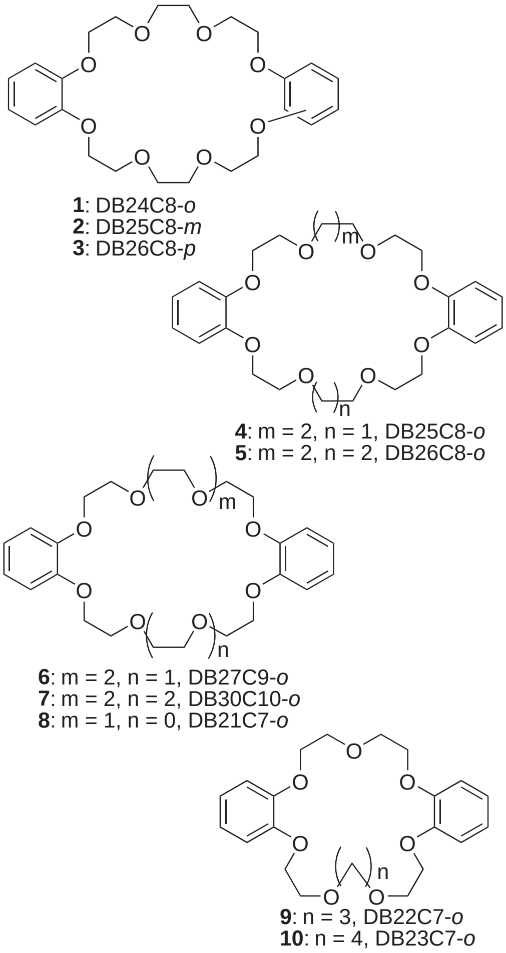
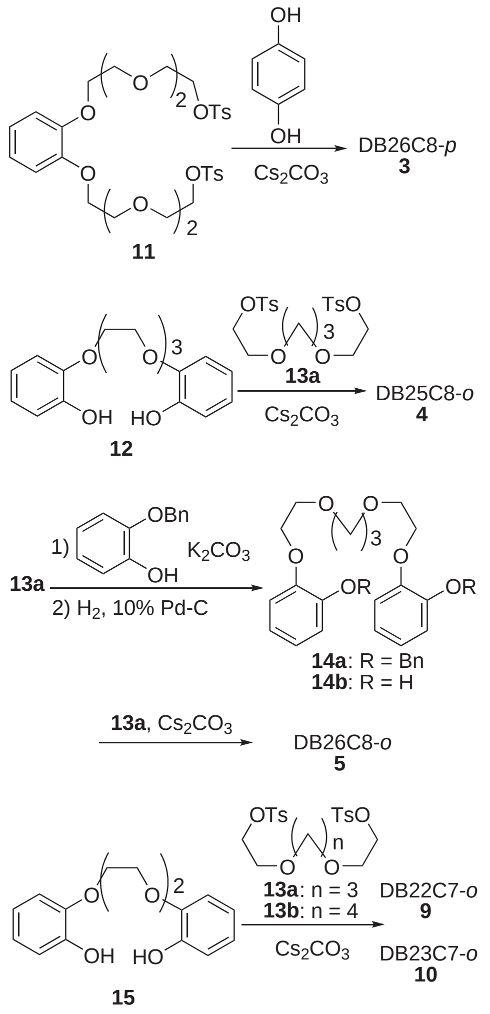


Fig. 2. Crown ether structures.

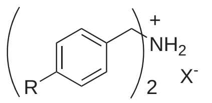
3–5, **9**, and **10** are outlined in Scheme 1. DB26C8-*p* **3** and DB25C8-*o* **4** were synthesized through cyclization reactions of their two components (ditosylate **11** and hydroquinone for DB26C8-*p* **3**; diol **12** and ditosylate **13a** for DB25C8-*o* **4**). A stepwise synthesis were undertaken for the construction of crown ether **5**: the reaction of **13a** with two molar amounts of benzyloxyphenol, followed by deprotection afforded the corresponding bisphenol **14b**, which was then alkylated again with **13a**. The syntheses of small crown ethers **9** and **10** were achieved through cyclization reactions of **15** with the ditosylates **13a** and **13b**, respectively.



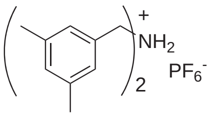
Scheme 1.

Formation of Pseudorotaxanes. As an initial experiment, we performed an NMR spectroscopic titration to monitor the pseudorotaxane formed from DB25C8-*m* **2** and the dibenzylammonium salt **16**PF_6^-. The rates of association and dissociation of the pseudorotaxane were fast on the NMR spectroscopic timescale at room temperature, as reported previously.[17] The ^1H NMR spectrum ($CDCl_3/CD_3CN$, 1:1) of a 1:1 mixture of DB25C8-*m* **2** and **17**PF_6^- (an ammonium salt that possesses isopropylphenyl groups at its termini)[12] provided evidence for pseudorotaxane formation. New signals for the benzylic and aromatic protons of the dumbbell component of the pseudorotaxane **2·17** appeared at 4.37 ppm and at 7.08 and 7.23 ppm, respectively. The six new signals at 3.46, 3.58, 3.65, 3.82, 3.93, and 4.19 ppm correspond to the resonances of the aliphatic protons in the heterocyclic ring of the pseudorotaxane. Such chemical shifting is typical for this type of pseudorotaxane (Fig. 3).[12,17,18] In the same manner, the pseudorotaxanes **3·17** (crown ether: DB26C8-*p*) and **4·17** (crown ether: DB25C8-*o*) were confirmed to exist at room temperature through the use of ^1H NMR spectroscopic titration techniques.[19]

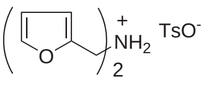
We did not observe any new signals in the ^1H NMR spectrum of a mixture of DB26C8-*o* **5** and **17**PF_6^- at room tempera-



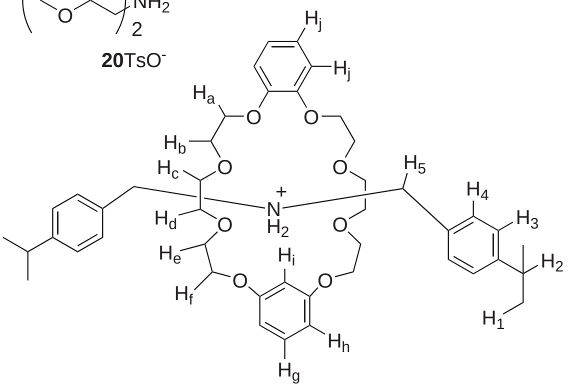
16PF$_6^-$: R = H, X = PF$_6^-$
16TsO$^-$: R = H, X = TsO$^-$
17PF$_6^-$: R = i-Pr, X = PF$_6^-$
18PF$_6^-$: R = t-Bu, X = PF$_6^-$
18TsO$^-$: R = t-Bu, X = TsO$^-$



19PF$_6^-$



20TsO$^-$



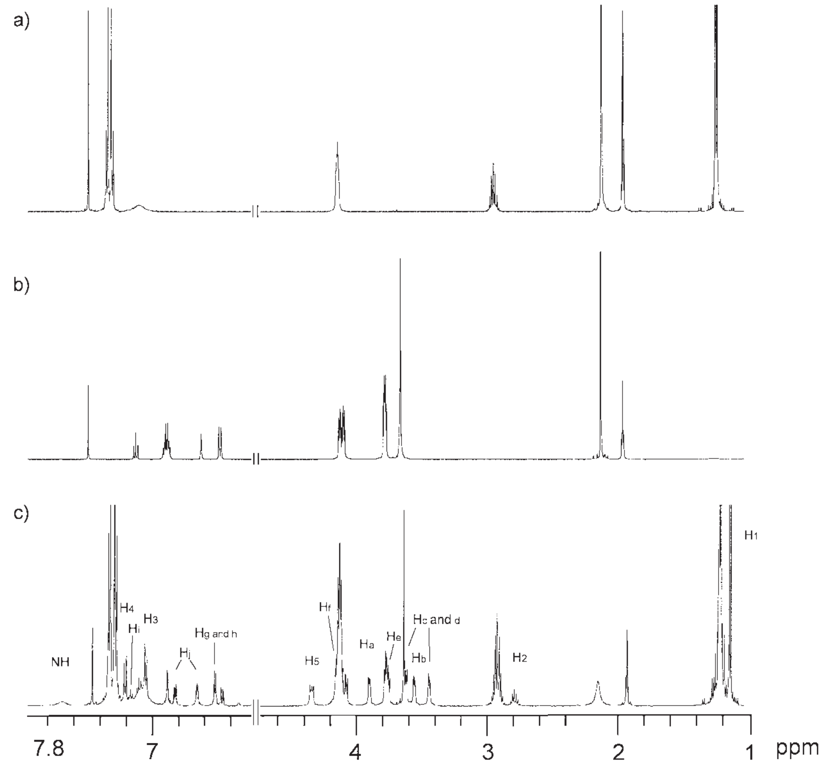


Fig. 3. ^{1}H NMR spectra (500 MHz, CDCl$_3$–CD$_3$CN (1:1)) of a) **17**PF$_6^-$, b) **2**, and c) a 1:1 mixture of **2** (10 mM) and **17**PF$_6^-$ (40 mM).

ture. In contrast, the ammonium salt **19**PF$_6^-$, which is substituted with relatively bulkier 3,5-dimethylphenyl groups, presented one set of pseudorotaxane signals in its ^{1}H NMR spectrum when mixed with the crown ether **5** at room temperature.[19] In the presence of the larger crown ether DB27C9-*o* **6**, the ^{1}H NMR spectrum of **19**PF$_6^-$ displayed time-averaged, broad signals. Finally, we used the ammonium salt **18**PF$_6^-$ as a dumbbell-like component to form the pseudorotaxanes **6**$\cdot$**18** (crown ether: DB27C9-*o*) and **7**$\cdot$**18** (crown ether: DB30C10-*o*).[19] In the ^{1}H NMR spectrum of the mixture of **7** and **18**PF$_6^-$, some of the signals broadened upon increasing the temperature, suggesting that the association and dissociation rates were similar to the NMR timescale at temperatures higher than room temperature.

Our results were surprising. Of the two stopper units of **18** and **19**, the circumference of a *tert*-butyl stopper is smaller than that of a 3,5-dimethylphenyl stopper (Fig. 4). In a simpli-

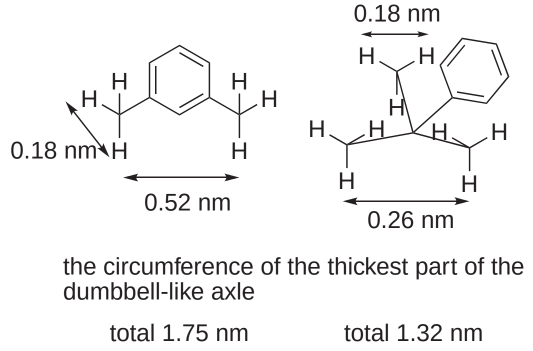
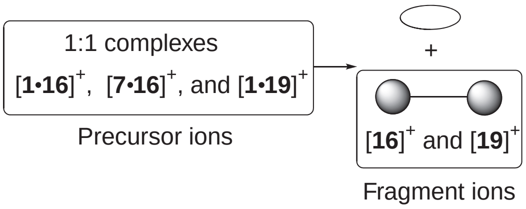


Fig. 4. Structures and sizes of 3,5-dimethylphenyl and *tert*-butylphenyl stoppers. The dimensions given for each stopper are those of measured between the centers of corresponding hydrogen atoms.

fied view, one would expect the association and dissociation processes of the ammonium ion **18** and crown ether **6** to be kinetically faster than those of **19** and **6**. In fact, it has been reported that a 3,5-dimethylphenyl group is bulkier than a *tert*-butylphenyl group for [24]crown ether-based rotaxane systems.[20] We observed, however, that the rates of association and dissociation of **18** and **6** were lower than those of **19** and **6**. Thus, the relative stopper size is not solely responsible for this behavior. In terms of the shapes of the stoppers, the *tert*-butyl group is somewhat spherical and the 3,5-dimethylphenyl group is relatively flat. The crown ether components of pseudorotaxanes formed through hydrogen bonding with ammonium ions are often elliptical. Thus, the relationship between the shapes of the crown ether and the stopper units of the thread-like ion is probably an important factor that regulates the rates of association and dissociation.[21]

Next, we investigated whether the relatively smaller crown ethers DB22C7-*o* **9** and DB23C7-*o* **10** were able to recognize secondary ammonium ions to form pseudorotaxanes. The difurfurylammonium salt **20**TsO$^-$ was used as a dumbbell to determine the appropriate ring size. The crown ethers **9** and **10** both recognized the ammonium ion **20** within their cavities. Consequently, new signals that were attributable to the corresponding pseudorotaxane did not appear in the NMR spectra of a mixture of DB21C7-*o* **8** and **20**TsO$^-$ after 1 h at room temperature. That finding is consistent with the previous report that a minimum of 22 cyclic atoms is required for threading of a polymethylene chain.[22]

All of the crown ethers appeared to form 1:1 complexes with the secondary ammonium ions in the gas phase, as demonstrated using electrospray ionization (ESI) mass spectrometry. In each case, peaks were observed for the crown ether·Na$^+$ adduct, the uncomplexed ammonium ion, and the 1:1 complex formed between the crown ether and the ammonium ion. Furthermore, we performed ESI-MS/MS experiments to compare the collision-induced dissociation (CID) mass spectra of the 1:1 complexes **1·16**, **7·16**, and **1·19**. The complexes **1·19** and **7·16** possessed pseudorotaxane structures in solution, with the formation of the pseudorotaxane **7·16** being kinetically rapid on the NMR timescale. In contrast, **1** and **19** formed a face-to-face complex in solution. The CID mass spectra of the [M − PF$_6^-$]$^+$ ions of the three complexes displayed abundant precursor ions peaks (*m/z* 646 for **1·16**; *m/z* 734 for **7·16**; *m/z* 702 for **1·19**) and small fragment ion peaks corresponding to the [M − PF$_6^-$ − crown ether]$^+$ ions (*m/z* 198 for **16**; *m/z* 254 for **19**) and [M − PF$_6^-$ − crown ether − H]$^+$ ions (*m/z* 253 for **19**).[19] Figure 5 presents a cartoon illustration of the CID process and the branching ratios for dissociation of the 1:1 complexes. These ratios indicate that the gas-phase dissociation of the complex [**1·19**]$^+$ was kinetically faster than those of the [**7·16**]$^+$ and [**1·16**]$^+$ complexes; the results suggest that the kinetic stabilities of the complexes follow the order [**1·16**]$^+$ > [**7·16**]$^+$ > [**1·19**]$^+$.



run	1:1 complexes (Precursor ions)	Branching ratios^a (%)
1	[**1•16**]$^+$ [DB24C8-*o*•(PhCH$_2$)$_2$NH$_2$]$^+$	2.5
2	[**7•16**]$^+$ [DB30C10-*o*•(PhCH$_2$)$_2$NH$_2$]$^+$	4.8
3	[**1•19**]$^+$ [DB24C8-*o*•(Me$_2$C$_6$H$_3$CH$_2$)$_2$NH$_2$]$^+$	13

^{a} [fragment ion]/[precursor ion]

Fig. 5. Branching ratios for 1:1 complexes of ammonium ions and crown ethers.

Table 1. Association Constants between Crown Ethers and Ammonium Ions$^{a)}$

Run	Crown ether	Ammonium salt	$K_{exp}$$^{b)}$ /M^{-1}	ΔG /kJ mol^{-1}
1	DB24C8-*o* **1**	**16** PF$_6^-$	740 ± 70	−16.5 ± 0.3
2	DB24C8-*o* **1**	**16** TsO$^-$	65 ± 2	−10.4 ± 0.1
3	DB25C8-*m* **2**	**17** PF$_6^-$	57 ± 8	−10.1 ± 0.4
4	DB26C8-*p* **3**	**17** PF$_6^-$	35 ± 4	−8.6 ± 0.3
5	DB25C8-*o* **4**	**17** PF$_6^-$	94 ± 8	−11.3 ± 0.2
6	DB26C8-*o* **5**	**19** PF$_6^-$	4 ± 1	−3.4 ± 0.3
7	DB27C9-*o* **6**	**18** PF$_6^-$	98 ± 14	−11.6 ± 0.2
8	DB27C9-*o* **6**	**18** TsO$^-$	21 ± 1	−7.6 ± 0.1
9	DB30C10-*o* **7**	**18** PF$_6^-$	127 ± 33	−12.0 ± 0.8
10	DB22C7-*o* **9**	**20** TsO$^-$	6 ± 0	−4.6 ± 0.2
11	DB23C7-*o* **10**	**20** TsO$^-$	14 ± 1	−6.6 ± 0.2

a) The association constants were obtained by the integrations of pseudorotaxanes and free axles or crowns in the ^{1}H NMR spectra of mixtures of corresponding crowns (10 mM) and ammonium salts (10 mM) at 27 °C. b) K_{exp} = [pseudorotaxane]/[host]$_{uc}$[guest]$_{uc}$.

Next, we calculated the association constants (K_{exp})[23,24] of the pseudorotaxanes through integration of the signals of the three species present in the ^{1}H NMR spectra and from the initial concentrations of the dumbbell- and wheel-shaped components (Table 1), i.e., when the complexed and uncomplexed species were detectable in the NMR spectra. These association constants are not exactly comparable because the counter ions[25] and the dumbbells' termini[26] were not identical; the nature of the counter ion of the ammonium ions has a particularly high influence on the association constant because of ion pairing effects. To provide some meaningful data, all of the NMR spectroscopic titrations were performed at the same concentrations and using the ammonium salts **16** and **18**, which possess two different counter ions (PF$_6^-$ and TsO$^-$), as the dumbbell-shaped components (Runs 1, 2, 7, and 8). The DB24C8/dibenzylammonium ion system provided the highest association constant (Runs 1 and 2). It is likely that the [24]crown ether has a favorable size for hydrogen bonding with the ammonium ion. In comparison, the association constants of [25]crown ethers **2** and **4** were dramatically lower (Runs 3 and 5); their values were similar to (or less than) those of the [27]- and [30]crown ethers **6** and **7** (Runs 7 and 9), the association constants of which were almost identical, although the favorable ring size is 24. Ethylene glycol moieties enhance complex formation, compared with those of propylene and butylene glycol units, because their oxygen atoms are positioned favorably for hydrogen bonding. In contrast, the association constants of **9** and **10** are quite low. It is likely that the [22]- and [23]crown ethers have cavities that are too small to accommodate secondary ammonium ions (Runs 8 and 9).

Summary

Using ^{1}H NMR spectroscopy and ESI-MS/MS techniques, we have demonstrated that [22–30]crown ethers bind secondary ammonium ions both in solution and in the gas phase, respectively. Moreover, the kinetics of pseudorotaxanes formation was modified through regulation of the number of atoms in the crown ether ring, rather then the size of the stoppers of the dumbbell-like secondary ammonium ion. We found that the [25]- and [26]crown ether/isopropylphenyl group, [27]- and [30]crown ether/*tert*-butylphenyl group, and [22]- and [23]crown ether/furyl group were matched pairs. The association constants (K_{exp}) were determined through NMR spectroscopic titration of the matched pairs of the wheels and the axles. The [24]crown ether has the optimal ring size because larger rings lead to decreased association constants and smaller crown ethers lead to face-to-face complexation rather than pseudorotaxane formation. These results will be useful when constructing corresponding rotaxanes.[27,28]

Experimental

General. Infrared spectra were recorded on a Shimadzu FTIR-8600PC. ^{1}H NMR spectra were taken on JEOL EX-400 and LA-500 spectrometers using TMS as an internal standard. Mass spectra were recorded on JMS-700T instrument. All reactions were carried out under a positive atmosphere of dry N_2 unless otherwise indicated. All extracts were dried over $MgSO_4$ and the solvent was removed by rotary evaporation under reduced pressure. Silica gel column chromatography was performed on Silica Gel 60N (Kanto Chemical). Thin-layer chromatography was carried out on a Merk Kieselgel 60PF$_{254}$. The melting points were uncorrected.

DB26C8-*p* (3). A suspension of ditosylate **11** (6.97 g, 10.2 mmol), hydroquinone (1.12 g, 10.2 mmol), and cesium carbonate (19.9 g, 61.2 mmol) in DMF (200 mL) was stirred at 100 °C for 1 d. After evaporation of the solvent under reduced pressure, to the resulting mixture was added AcOEt. The mixture was washed with dilute HCl and H_2O, dried and evaporated. The residue upon evaporation of the mixture was chromatographed (ethyl acetate:toluene = 1:1) to give the crown ether **3** (0.90 g, 20%) as a viscous oil: IR $\nu_{\max}$ ($CHCl_3$) cm^{-1} 3030, 2933, 2894, 1521, 1212. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59–3.68 (m, 8H), 3.73–3.82 (m, 8H), 4.08–4.17 (m, 8H), 6.87 (s, 4H), 6.88–6.94 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 68.80, 68.83, 69.8, 70.2, 70.90, 70.93, 115.4, 116.6, 121.7, 149.1, 153.2. FAB-MS m/z: $C_{24}H_{32}O_8$ 448 [M$^+$]. Found: C, 62.20; H, 7.07%. Calcd for $C_{24}H_{32}O_8\cdot 0.8H_2O$: C, 62.27; H, 7.32%.

DB25C8-*o* (4). According to the above method, the ditosylate **13a** (2.21 g, 4.68 mmol) was transformed into the crown ether **4** (1.00 g, 46%) as a colorless crystal (ethyl acetate:hexane = 1:7): mp 84–85 °C. IR $\nu_{\max}$ (KBr) cm^{-1} 3067, 2932, 2870, 1593, 1223. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90 (quint, $J = 6.3$ Hz, 2H), 3.66–3.70 (m, 4H), 3.80–3.83 (m, 8H), 3.88–3.93 (m, 4H), 4.12–4.18 (m, 8H), 6.87–6.93 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.1, 68.3, 68.8, 69.3, 69.4, 69.8, 71.1, 114.2, 114.4, 121.4, 121.4, 148.9, 149.0. FAB-MS m/z: $C_{25}H_{34}O_8$ 462 [M$^+$]. Found: C, 64.72; H, 7.55%. Calcd for $C_{25}H_{34}O_8$: C, 64.92; H, 7.41%.

1,3-Bis[2-(2-benzyloxyphenoxy)ethoxy]propane (14a). A suspension of 2-benzyloxyphenol (3.47 g, 18.2 mmol), ditosylate **13a** (3.92 g, 8.30 mmol), and potassium carbonate (5.72 g, 41.5 mmol) in DMF (36 mL) was heated at 90 °C for 5 h. After DMF was removed, to the residue was added ethyl acetate. The organic mixture was washed with water and sat. NaCl, dried and evaporated. Chromatography of the residue on silica gel with ethyl acetate–toluene (1:10) as eluent gave the ether **14a** (3.18 g, 72%) as a solid. IR $\nu_{\max}$ (KBr) cm^{-1} 3064, 2943, 2889, 1508, 1220. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.86 (quint, $J = 6.3$ Hz, 2H), 3.58–3.62 (m, 4H), 3.75–3.79 (m, 4H), 4.13–4.17 (m, 4H), 5.11 (s, 4H), 6.85–6.96 (m, 8H), 7.25–7.29 (m, 2H), 7.33–7.36 (m, 4H), 7.43–7.45 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.1, 68.3, 68.9, 69.4, 71.4, 115.0, 115.6, 121.6, 121.8, 127.3, 127.7, 128.4, 137.5, 149.0, 149.4. HR-MS(FAB) m/z: Calct for $C_{33}H_{36}O_6$: 528.2512. Found: 528.2491. Found: C, 73.96; H, 6.85%. Calcd for $C_{33}H_{36}O_6\cdot 0.5H_2O$: C, 73.72; H, 6.94%.

1,3-Bis[2-(2-hydroxyphenoxy)ethoxy]propane (14b). A suspension of the benzyl ether **14a** (2.50 g, 4.73 mmol), 10% Pd–C (0.25 g) in ethanol–$CHCl_3$ (1:1, 40 mL) was stirred under atmosphere of H_2 for 6 h. The reaction mixture was filtered, and the filtrate was concentrated. The residue was purified by silica gel column chromarography (toluene:ethyl acetate = 2:1) to give the diol **14b** (1.48 g, 90%) as a colorless oil: IR $\nu_{\max}$ ($CHCl_3$) cm^{-1} 3684, 3619, 3029, 2895, 1522, 1204. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (quint, $J = 6.1$ Hz, 2H), 3.66–3.71 (m, 4H), 3.73–3.78 (m, 4H), 4.13–4.18 (m, 4H), 6.76–6.84 (m, 4H), 6.90–6.96 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.7, 67.9, 69.2, 70.4, 115.7, 115.8, 120.0, 123.2, 146.0, 147.5. HR-MS(FAB) m/z: Calcd for $C_{19}H_{24}O_6$: 348.1573. Found: 348.1499.

DB26C8-*o* (5). According to the above method, the bisphenol **14b** (1.48 g, 4.25 mmol) was transformed into the crown ether **5** (0.953 g, 47%) as a colorless crystal (hexane:AcOEt = 3:2): mp 103–104 °C. IR $\nu_{\max}$ (KBr) cm^{-1} 3063, 2936, 2878, 1593, 1454, 1261. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92 (quint, $J = 6.3$ Hz, 4H), 3.67–3.71 (m, 8H), 3.81–3.84 (m, 8H), 4.12–4.16 (m, 8H), 6.87–6.92 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 68.7, 68.8, 69.8, 116.6, 121.7, 149.0. FAB-MS m/z: $C_{26}H_{36}O_8$ 476 [M$^+$]. Found: C, 65.29; H, 7.69%. Calcd for $C_{26}H_{36}O_8$: C, 65.53; H, 7.61%.

DB22C7-*o* (9). Colorless crystal (56% yield, hexane:AcOEt = 4:1): mp 85.5–86.5 °C. IR $\nu_{\max}$ (KBr) cm^{-1} 3066, 2963, 2875, 1593, 1224. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88 (quint, $J = 6.3$ Hz, 2H), 3.67–3.72 (m, 4H), 3.79–3.84 (m, 4H), 4.00–4.06 (m, 4H), 4.10–4.20 (m, 8H), 6.85–6.93 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.2, 68.3, 69.0, 69.5, 70.0, 70.4, 114.1, 116.0, 121.3, 122.0, 148.9, 149.6. FAB-MS m/z: $C_{23}H_{30}O_7$ 418 [M$^+$]. Found: C, 65.90; H, 6.99%. Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23%.

DB23C7-*o* (10). Colorless crystal (43% yield, hexane:AcOEt = 7:1): mp 70.5–71.5 °C. IR $\nu_{\max}$ (KBr) cm^{-1} 2928, 2845, 1594, 1516, 1505, 1450, 1222. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66–1.72 (m, 4H), 3.58–3.64 (m, 4H), 3.77–3.82 (m, 4H), 3.97–4.02 (m, 4H), 4.11–4.14 (m, 4H), 4.16–4.22 (m, 4H), 6.85–6.97 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.3, 69.0, 69.1, 70.0, 70.4, 71.2, 113.9, 116.1, 121.3, 122.0, 148.9, 149.6. FAB-MS m/z: $C_{24}H_{32}O_7$ 432 [M$^+$]. Found: C, 66.45; H, 7.26. Calcd for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46%.

ESI-MS and MS/MS Measurements. MS experiments were performed on a four-sector type mass spectrometer (JEOL JMS-700T; JEOL, Tokyo, Japan) connected with an ESI interface. The ion-accelerating voltages were set to 5 kV for MS-1 and 10 kV for MS-2, respectively. Unless stated otherwise, the solution for mass spectrometry contained an equimolar amount (0.5 mM) of a crown ether and ammonium salt in acetonitrile and was sprayed with a flow rate of 2.5 mL h^{-1} by using a syringe pump (Kd ScientificInc., Model 100). ESI-MS was performed at a desolvating temperature of 180 °C and a capillary voltage of 1.8 kV.

The cation of 1:1 complex as a precursor ion selected on MS-1 was collisionally activated by introducing argon into the collision cell located between MS-1 and MS-2 at a pressure sufficient to reduce beam intensity by ca. 10%. By grounding the collision cell, collision energy of 5 kV was chosen. Product-ion spectra were acquired in MS-2 by scanning of magnetic sector.

This work was supported by a Grant-in-Aid for Scientific Research (No. 15750116) from Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Mr. H. Sugawara of this University making spectroscopic measurements.

Supporting Information

^{1}H NMR spectra (500 MHz, $CDCl_3$–CD_3CN (1:1)) of a 1:1 mixture of **3** and **17**PF_6^-, **4** and **17**PF_6^-, **5** and **19**PF_6^-, **6** and **18**PF_6^-, **7** and **18**PF_6^-, **9** and **20**TsO^-, and **10** and **20**TsO^- and ESI-MS/MS spectra of 1:1 complexes **1·16**, **7·16**, and **1·19** are formatted in PDF file.

References

1 P. R. Ashton, P. J. Campbell, P. T. Glink, D. Philp, N. Spencer, J. F. Stoddart, E. J. T. Chrystal, S. Menzer, D. J. Williams, P. A. Tasker, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865.

2 For recent reviews, see: J. P. Sauvage, C. O. Dietrich-Bucheker, *Molecular Catenanes, Rotaxanes and Knots*, VCH-Wiley, Weinheim, **1999**; V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *39*, 3348; R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, M. Venturi, *Acc. Chem. Res.* **2001**, *34*, 445; T. J. Hubin, D. H. Busch, *Coord. Chem. Rev.* **2000**, *200–202*, 5; T. Takata, N. Kihara, *Rev. Heteroat. Chem.* **2000**, *22*, 197.

3 a) N. Yamaguchi, H. W. Gibson, *Angew. Chem., Int. Ed.* **1999**, *38*, 143. b) N. Watanabe, T. Yagi, N. Kihara, T. Takata, *Chem. Commun.* **2002**, 2720. c) S. J. Rowan, J. F. Stoddart, *Polym. Adv. Technol.* **2002**, *13*, 777. d) H. W. Gibson, N. Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.* **2003**, *125*, 3522. e) J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845. f) T. Oku, Y. Furusho, T. Takata, *Angew. Chem., Int. Ed.* **2004**, *43*, 966. g) X.-Z. Zhu, C.-F. Chen, *J. Am. Chem. Soc.* **2005**, *127*, 13158. h) S. J. Cantrill, R. H. Grubbs, D. Lanari, K. C.-F. Leung, A. Nelson, K. G. Poulin-Kerstien, S. P. Smidt, J. F. Stoddart, D. A. Tirrell, *Org. Lett.* **2005**, *7*, 4213.

4 a) H. W. Gibson, N. Yamaguchi, L. Hamilton, J. W. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 4653. b) K. C.-F. Leung, F. Arico, S. J. Cantrill, J. F. Stoddart, *J. Am. Chem. Soc.* **2005**, *127*, 5808.

5 F. Huang, L. N. Zakharov, A. L. Rheingold, J. W. Jones, H. W. Gibson, *Chem. Commun.* **2003**, 2122.

6 W. S. Bryant, I. A. Guzei, A. L. Rheingold, J. S. Merola, H. W. Gibson, *J. Org. Chem.* **1998**, *63*, 7634; P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, J. F. Stoddart, P. A. Tasker, D. J. Williams, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1869.

7 M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2068; P. R. Ashton, A. N. Collins, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 59.

8 S.-H. Chiu, A. R. Pease, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem., Int. Ed.* **2002**, *41*, 270.

9 S.-H. Chiu, J. F. Stoddart, *J. Am. Chem. Soc.* **2002**, *124*, 4174.

10 a) P.-N. Cheng, W.-C. Hung, S.-H. Chiu, *Tetrahedron Lett.* **2005**, *46*, 4239. b) S. J. Loeb, J. Tiburcio, S. J. Vella, *Org. Lett.* **2005**, *7*, 4923.

11 a) For examples, see: W. S. Bryant, I. A. Guzei, A. L. Rheingold, J. S. Merola, H. W. Gibson, *J. Org. Chem.* **1998**, *63*, 7634. b) S.-H. Chiu, A. R. Pease, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem., Int. Ed.* **2002**, *41*, 270.

12 P. A. Ashton, I. Baxter, M. C. T. Fyfe, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 2297.

13 Recently, the rotaxane possessing DB25C8-*m* and secondary ammonium ion was discussed. J. N. Lowe, D. A. Fulton, S.-H. Chiu, A. M. Elizarov, S. J. Cantrill, S. J. Rowan, J. F. Stoddart, *J. Org. Chem.* **2004**, *69*, 4390.

14 R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, J. J. Christensen, *J. Am. Chem. Soc.* **1976**, *98*, 7626.

15 C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017.

16 G. Yapar, C. Erk, *J. Inclusion Phenom. Macrocyclic Chem.* **2002**, *43*, 299.

17 P. R. Ashton, R. A. Bartsch, S. J. Cantrill, R. E. Hanes, Jr., S. K. Hickingbottom, J. N. Lowe, J. A. Preece, J. F. Stoddart, V. S. Talanov, Z.-H. Wang, *Tetrahedron Lett.* **1999**, *40*, 3661.

18 Y. Tachibana, H. Kawasaki, N. Kihara, T. Takata, *J. Org. Chem.* **2006**, *71*, 5093.

19 See Supporting Information.

20 Y. Tachibana, N. Kihara, Y. Furusho, T. Takata, *Org. Lett.* **2004**, *6*, 4507.

21 A. Affeld, G. M. Hübner, C. Seel, C. A. Shalley, *Eur. J. Org. Chem.* **2001**, 2877.

22 I. T. Harrison, *J. Chem. Soc., Chem. Commun.* **1972**, 231. After several days, new signals appeared in the ^{1}H NMR spectrum. The signals might be attributed to corresponding pseudorotaxane, but these were too small to confirm in detail.

23 In the experiments, the association constants are defined;

$$K_{\text{exp}} = [\text{pseudorotaxane}]/[\text{host}]_{\text{uc}}[\text{guest}]_{\text{uc}},$$

where $[\text{host}]_{\text{uc}} = [\text{host}]_0 - [\text{pseudorotaxane}]$ and $[\text{guest}]_{\text{uc}} = [\text{guest}]_0 - [\text{pseudorotaxane}]$. Here, the subscripts "c" and "uc" denote complexed and uncomplexed species, respectively.

24 All mixtures of crowns and ammonium salts were equilibrated at 27 °C within several hours.

25 J. W. Jones, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 7001.

26 M. Horn, J. Ihringer, P. T. Glink, J. F. Stoddart, *Chem. Eur. J.* **2003**, *9*, 4046.

27 P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, N. Spencer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709.

28 Y. Tokunaga, T. Nakamura, M. Yoshioka, Y. Shimomura, *Tetrahedron Lett.* **2006**, *47*, 5901.