JOC Article

Is [N$^+$−H···O] Hydrogen Bonding the Most Important Noncovalent Interaction in Macrocycle−Dibenzylammonium Ion Complexes?

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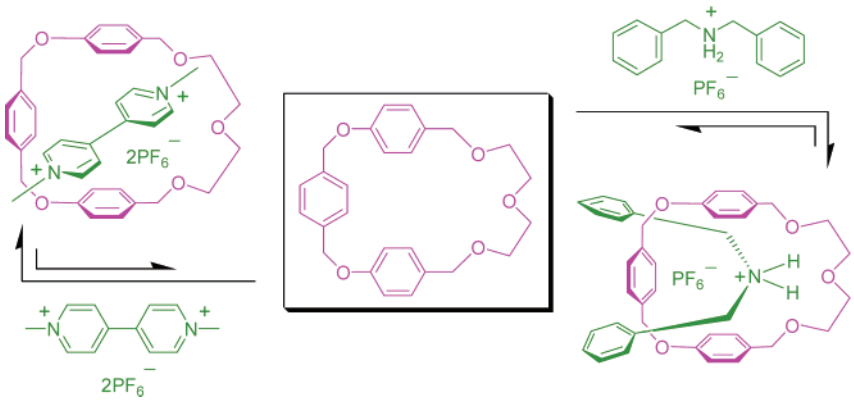

We report a new host molecule in which one diethylene glycol chain (i.e., a loop possessing only three oxygen atoms) incorporated along with two phenolic aromatic rings is linked by a xylene spacer into a macroring. The design of the molecular structure of this macrocycle "amplifies" any potential [cation···π], [N$^+$−H···π], and [N$^+$C−H···π] interactions between the dibenzylammonium (DBA$^+$) ion and the phenolic rings of the macrocycle; as such, these species display a very strong binding affinity in CD_3NO_2 (K_a = 15 000 M^{-1}). The macroring also coordinates to bipyridinium ions in a [2]pseudorotaxane fashion, which makes it the smallest macrocycle (i.e., a 25-membered ring) known to complex both DBA$^+$ and bipyridinium ions in solution. To confirm unambiguously that these pseudorotaxanes exist in solution, we synthesized their corresponding interlocked molecules, namely rotaxanes and catenanes.

Introduction

After their serendipitous discovery by Pedersen,[1] crown ethers have been applied extensively as phase-transfer agents,[2] molecular sensors,[3] and chiral separators[4] because of their ability to form complexes with metal and quarternary ammonium ions.[5] The more-recent finding[6] that crown ethers form pseudorotaxane-like[7] complexes with dialkylammonium ions in solution has been a boon to research efforts aimed at the development of functional interlocked molecular machinery.[8] Many diverse interlocked molecular structures, such as molecular shuttles,[9] molecular switches,[10] and molecular elevators,[11] have been

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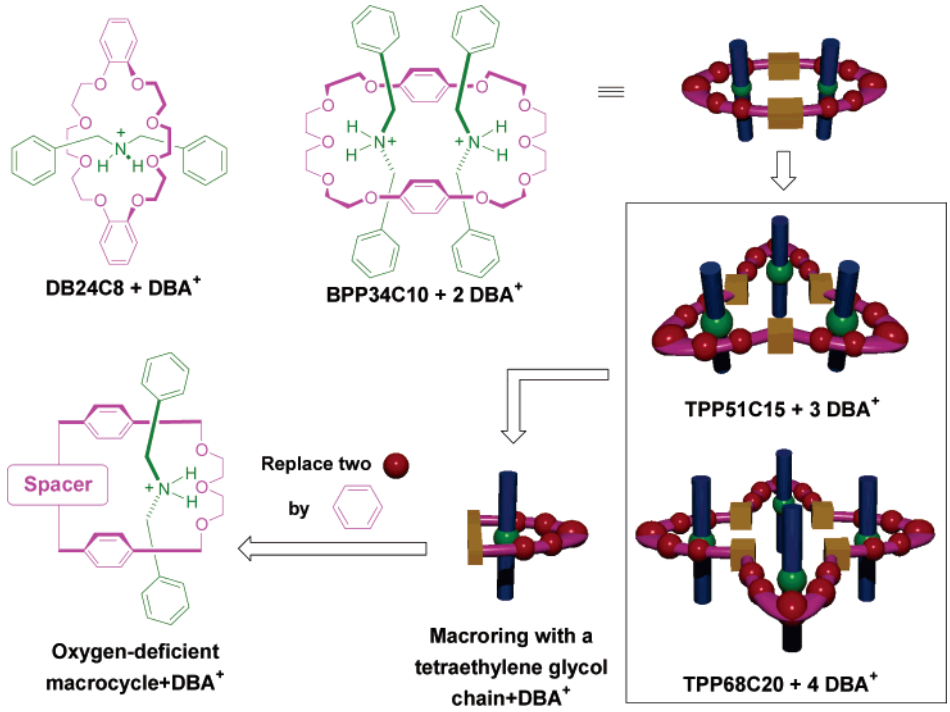

FIGURE 1. Cartoon and structural representations of the concept of deriving the oxygen-deficient macrocycle.

developed on the basis of such crown ether/dibenzylammonium (DBA^+) ion[12] complexation. In this supramolecular system, [N^+−H···O] and [N^+C−H···O] hydrogen bonding between the host and guest units has always been considered to be the most important stabilizing noncovalent interaction.[6,13] For example, the solid-state structure of the [2]pseudorotaxane formed between the DBA^+ ion and dibenzo[24]crown-8 (DB24C8) displays both of these types of interactions.[6a] Indeed, it appears that aliphatic ether oxygen atoms are better hydrogen bond acceptors than are aromatic ether oxygen atoms. For example, consider the decrease in association constants that occurs upon the incorporation of additional benzo units into 24C8 macrocycles: the strength of binding to the DBA^+ ion follows the order [24]crown-8 > benzo[24]crown-8 > dibenzo[24]crown-8 > tribenzo[24]crown-8 > tetrabenzo[24]crown-8.[14] Macrocyclic effects[15] play a role in these systems, too; bis-*m*-phenylene[26]crown-8 is a weaker binder than its isomer DB24C8 because its ring of eight oxygen atoms is not as well preorganized for effective hydrogen bonding to the CH_2-$NH_2^+CH_2$ unit of the DBA^+ ion.[13,16] That is not to say that larger-ring crown ethers are necessarily always poorer binders. Bis-*p*-phenylene[34]crown-10 (BPP34C10), for instance, is capable of binding two DBA^+ ions simultaneously in solution in a 1:2 (host:guest) complex;[17] in this case, the benefits of a five-oxygen-atom oligoether loop (featuring three "good" aliphatic ether oxygen atoms) outweigh the macrocycle's inability to completely encircle the $CH_2NH_2^+CH_2$ center of each ion. Indeed, the even-larger crown ethers tris-*p*-phenylene[51]-crown-15 and tetrakis-*p*-phenylene[68]crown-20 also form complexes with DBA^+ ions (three and four of them, respectively), which suggests that single tetraethylene glycol loops are all that is really required for generating pseudorotaxane-like complexes in solution and in the solid state.[18] This concept suggests that a more diverse set of macrocycles—not just those that technically could be called "crown ethers"—should also bind to DBA^+ ions (Figure 1). Naively, we might consider that as long as we place a suitable number of ether oxygen atoms (say, five of them) into a macrocycle then its remaining structure

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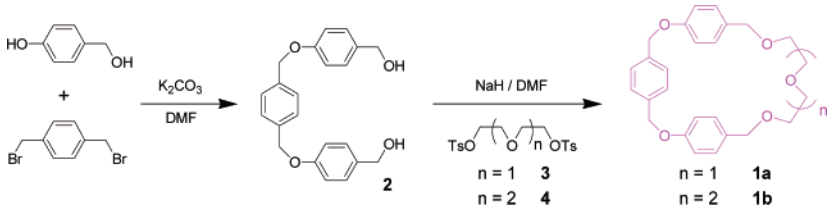
SCHEME 1



would be replaceable—as long as there is enough room, of course, for the threading of the guest ion (i.e., at least 24 ring atoms,[19] or thereabout). In this paper, we demonstrate, however, that this logic is not entirely correct. We have found that a macrocycle containing merely a diethylene glycol loop (i.e., one with just three ether oxygen atoms) is an unusually strong binder toward DBA^+ ions.[20] In fact, it binds more strongly to the DBA^+ ion than does the corresponding macrocycle containing an extra ethylene glycol unit (i.e., a triethylene glycol loop). This enigmatic behavior suggests that there may be other noncovalent interactions that stabilize these complexes. We suggest that, in some cases, the [cation$\cdots\pi$][21] interaction—along with other relatively weak noncovalent interactions, such as [$N^+-H\cdots\pi$][22] and [$N^+C-H\cdots\pi$][22c,d,23] bonding—that exists between the DBA^+ ion and π-electron-rich aromatic rings of the macrocycle can be as stabilizing as the more-traditional [$N^+-H\cdots O$][24] and [$N^+C-H\cdots O$][25] hydrogen bonds.

[Cation$\cdots\pi$] interactions are very important interactions that exist between quarternary ammonium ions and aromatic host macrocycles such as calix[4]arenes[26] and cyclophanes.[27] Although [$N^+-H\cdots\pi$] and [$N^+C-H\cdots\pi$] interactions have not yet been considered as important primary interactions in host−guest systems in solution, they are recognized to play an important role in molecular packing in the solid state.[28] Because we believed that DBA^+ ions should interact favorably with π-electron-rich aromatic rings through [$N^+-H\cdots\pi$], [$N^+C-H\cdots\pi$], and [cation$\cdots\pi$] interactions, it seemed reasonable to consider replacing the two terminal ethylene glycol units in a tetraethylene glycol strand with two π-electron-rich benzyl units such that the [cation$\cdots\pi$] interaction and potential [$N^+-H\cdots\pi$] and [$N^+C-H\cdots\pi$] interactions that may form between the aromatic rings and the $CH_2NH_2^+CH_2$ unit of the DBA^+ ion will compensate for the loss of any [$N^+-H\cdots O$] and [$N^+C-H\cdots O$] hydrogen bonds. To enhance any macrocyclic effect, we closed the loop of this macrocycle by linking the two phenol units through a *p*-xylyl spacer. This macrocycle displays a very strong binding affinity toward the DBA^+ ion in CD_3NO_2 ($K_a = 15\,000\ M^{-1}$) and, remarkably, it binds much more tightly to these ions than do its corresponding symmetrical crown ether (bis-*p*-xylyl-[26]crown-6) and an analogous macrocycle containing a triethylene glycol loop. Relative to normal crown ethers, these macrocycles belong to a new class of "oxygen-deficient" hosts for DBA^+ ions; they feature aromatic rings as crucial structural elements and not just as linkers or synthetically amenable components. Moreover, we have found that these hosts also recognize bipyridinium ions; indeed, they are the smallest macrocycles known to date that form pseudorotaxane-like complexes with both DBA^+ and bipyridinium ions in solution. To confirm unambiguously the existence of these pseudorotaxane-like complexes in solution, we have synthesized and characterized a number of interlocked molecules—rotaxanes and catenanes—incorporating the new macrocycles.

Result and Discussion

Design, Syntheses, and Complexation of the New Macrocycles. Macrocycles **1a** and **1b** (Scheme 1) were both synthesized with use of a simple two-step approach. The reaction

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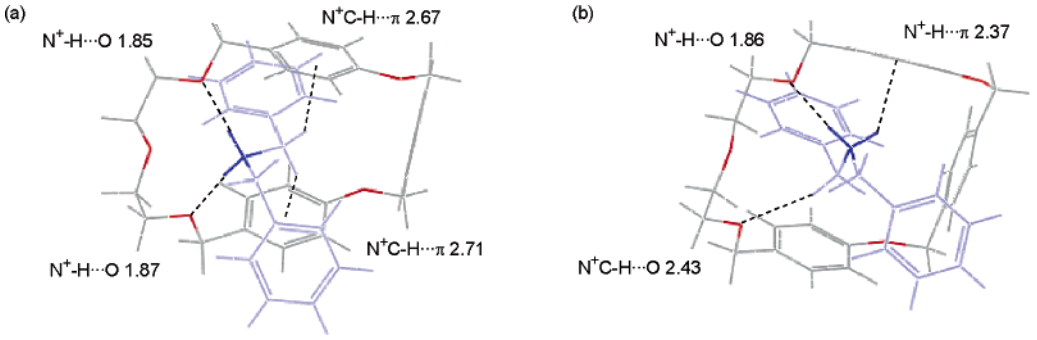

FIGURE 2. (a) Lowest energy structure obtained after optimization of sampled structures obtained from 5000-ps MD of **1a**⊃DBA^+ in a water continuum model. (b) A structure 1.22 kcal/mol above the lowest energy structure displays a different set of binding interactions. All of the H···π contacts are measured relative to the centroid of the relevant phenyl ring; the DBA^+ ion is light blue; its $^+NH_2$ unit is dark blue.

between 4-hydroxybenzyl alcohol and α,α′-dibromo-*p*-xylene under basic conditions afforded the diol **2** in 90% yield and the following [1+1] macrocyclization reactions between diol **2** and the diethylene and triethylene glycol ditosylates (**3** and **4**) gave the desired macrocycles **1a** and **1b**, respectively.[29] The lowest energy structure of **1a**⊃DBA^+ located in the gas phase (see the computational details below) is similar to one found in water (Figure 2a); this finding suggests that macrocycle **1a** presents the oxygen atoms of its diethylene glycol chain and the two π-electron-rich phenolic rings in an appropriate position to provide a good receptor site for [N^+−H···O] and [N^+C−H···π] interactions with the $CH_2NH_2^+CH_2$ center of a threaded DBA^+ ion. Because one local minimum of the same complex, one that displays an [N^+−H···π] interaction between the two components, is located only 1.22 kcal/mol above the lowest energy structure (Figure 2b), it appears that such interactions may also play a role in stabilizing this supramolecular complex.

To test this hypothesis, we examined the ^{1}H NMR spectrum (Figure 3b) of an equimolar mixture (10 mM) of macrocycle **1a** and DBA·PF_6 in $CDCl_3$/CD_3CN (1:1). We observe three sets of resonances, which represent the free macroring **1a** (cf. Figure 3a), free DBA·PF_6 (cf. Figure 3c), and the 1:1 complex formed between **1a** and the DBA^+ ion. This phenomenon implies that the rates of complexation and decomplexation are both slow on the ^{1}H NMR time scale at 400 MHz and 298 K. The splitting of the originally overlapping signals for the protons of the diethylene glycol unit's two methylene groups in macrocycle **1a** into two separate multiplets—one shifted upfield to δ 3.06 and the other downfield to δ 3.59—in the presence of the salt suggests that hydrogen bonding probably takes place between the host and guest, but the most remarkable shift occurs for the methylene protons adjacent to the ammonium center. When uncomplexed, these protons resonate at ca. 4.17 ppm, but this

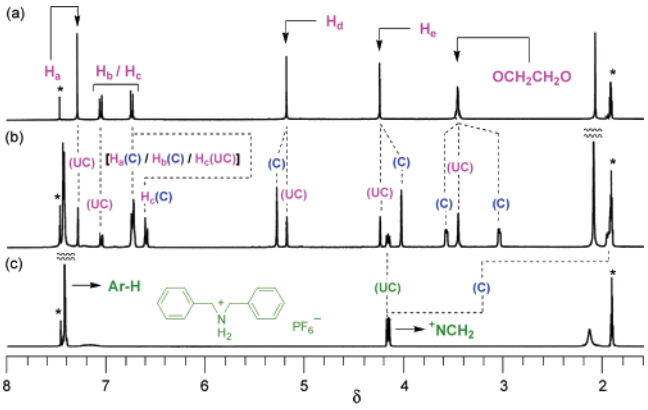

FIGURE 3. Partial ^{1}H NMR spectra [400 MHz, $CDCl_3$/CD_3CN (1:1), 298 K] of (a) macrocycle **1a**, (b) an equimolar mixture of **1a** and DBA·PF_6 (10 mM), and (c) DBA·PF_6. The descriptors (c) and (uc) refer to complexed and uncomplexed states of the components.

signal experiences an upfield shift of >2 ppm (to δ 1.95) upon complexation with **1a**, which suggests that the NH_2^+ center is positioned in the shielding zone between the two phenol units of **1a**, as would be expected for the coexistence of [N^+−H···O] hydrogen bonding with [N^+C−H···π] interactions. Unfortunately, we were not able to detect, possibly because of severe broadening, the signal for the resonance of the NH_2^+ protons, which we expect to also undergo a significant upfield shift. The resonances of the phenolic CH protons shifted upfield to 6.60 and 6.74 ppm from their original positions (δ 6.74 and 7.06, respectively), which suggests the existence of possible aryl−aryl interactions[30] caused by the threading of the DBA^+ ion into the cavity of macroring **1a**. Thus, these shifts suggest that the complex formed between macrocycle **1a** and the DBA^+ ion in solution is likely to have the geometry of a [2]pseudorotaxane [(**1a**⊃DBA)·PF_6] (Scheme 2). Using a single-point method,[31] we determined the association constants (K_a) of this system to be 550 M^{-1} in $CDCl_3$/CD_3CN (1:1) and 15 000 M^{-1} in CD_3NO_2; i.e., the binding strength is comparable to those of crown ether-containing complexes.[32] This result suggests that noncovalent interactions, such as [cation···π], [N^+−H···π], and [N^+C−H···π] interactions between the two phenolic rings and the DBA^+ ion, must contribute significantly toward stabilizing the pseudorotaxane complex because macrocycle **1a** contains only three oxygen atoms that may behave as [N^+−H···O] and [N^+C−H···O] hydrogen bond receptors.

To elucidate the effect that an extra oxygen atom in the oligoethylene glycol motif has on the binding of this category

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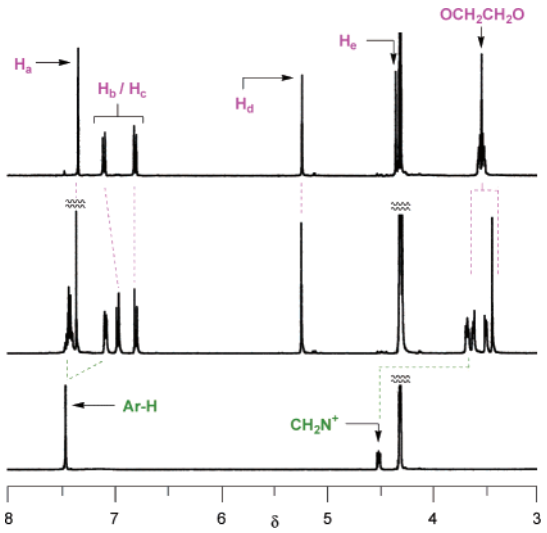


FIGURE 4. Partial ^{1}H NMR spectra (400 MHz, CD_3NO_2, 298 K) of (a) macrocycle **1b**, (b) an equimolar mixture of **1b** and DBA·PF_6 (10 mM), and (c) DBA·PF_6.

of macrocycles to DBA^+ ions, we examined the interaction between DBA·PF_6 and macrocycle **1b**, which contains an extra CH_2CH_2O unit. The ^{1}H NMR spectrum of an equimolar mixture of **1b** and DBA·PF_6 in CD_3NO_2 (10 mM) at room temperature displays significant changes in the chemical shifts of the protons of the complex relative to those of its free components (Figure 4). Unlike the **1a**/DBA^+ ion system, whose rates of complexation and decomplexation are slow at 400 MHz and 298 K, the exchange rates for the complexation of **1b** and the DBA^+ ion are fast under the same conditions so that we observe time-averaged signals in this spectrum.

In the spectrum of the complex, the large upfield shift (from δ 4.50 to 3.64) of the signal for the protons of the benzylic methylene groups adjacent to the NH_2^+ center of the DBA^+ ion suggests that the NH_2^+ center is positioned within the cavity of the macrocycle and is stabilized possibly through [N^+−H···O] and [N^+C−H···π] interactions. This hypothesis is supported by the observation that, upon complexation, the formerly "tight" multiplet (δ 3.48−3.57) for the methylene protons of the OCH_2CH_2O units becomes dispersed over a wider range of chemical shifts (δ 3.39−3.61) and is resolved into three signals (Figure 4b). The shifts in the signals of the aromatic protons suggest the existence of interactions between the electronically complementary aromatic rings of macrocycle **1b** and DBA^+ ion. A Job plot based on the ^{1}H NMR spectroscopic data obtained in CD_3NO_2 provided conclusive evidence for 1:1 complexation (see the Supporting Information). According to these results, a [2]pseudorotaxane-like assembly, [(**1b**⊃DBA)·PF_6] (Scheme 2), seems to be the likely structure of the complex formed between **1b** and DBA^+ ions in CD_3NO_2. From a ^{1}H NMR spectroscopic dilution experiment, we determined the association constant (K_a) for this complex in CD_3NO_2 to be 2200 ± 40 M^{-1}, which is ca. 7-fold weaker than that for the complex formed between **1a** and DBA^+ in the same solvent (K_a = 15 000 M^{-1}). This result suggests that although macrocycle **1b** contains an additional hydrogen bond receptor (i.e., four oxygen atoms, cf. three for **1a**), which, intuitively, should enhance the favorability of [N^+−H···O] and [N^+C−H···O] hydrogen bonding, its larger ring size leads to a structure that is less preorganized to accommodate a more-complete range of noncovalent interactions simultaneously (i.e., a diminished macrocyclic effect). The noncovalent interactions that exist in the lowest energy structure of the complex **1b**⊃DBA^+ in the gas phase are similar to the ones found in **1a**⊃DBA^+ (Figure 2a). The larger size of macrocycle **1b**, however, causes the distance between the proton and the aromatic ring in one of the [N^+C−H···π] interactions to be elongated significantly. Interestingly, the lowest energy structure located for **1b**⊃DBA^+ in water features [N^+−H···O], [N^+C−H···O], [N^+−H···π], and [N^+C−H···π] interactions (Figure 5). Thus, in the complexation of the DBA^+ ion by crown ether-type hosts, our previous assumption that electron-rich aromatic rings can replace some oxygen atoms seems to be supported by both experimental and calculated results, i.e., the loss of [N^+−H···O] and [N^+C−H···O] hydrogen bonds can be compensated for by [N^+−H···π] and [N^+C−H···π] interactions between aromatic rings and the $CH_2NH_2^+CH_2$ unit of the DBA^+ ion.

To estimate the structural importance of the xylene spacer, we synthesized the corresponding symmetrical crown ether **5** from α,α′-dibromo-*p*-xylene and diethylene glycol through a one-step [2+2] macrocyclizaton (Scheme 3). When we mixed equamolar amounts of macrocycle **5** and DBA·PF_6 in CD_3NO_2 at room temperature, we observed a noticeable shifting of signals in the ^{1}H NMR spectrum relative to those of the free species (Figure 6); the rates of the complexation and decomplexation processes were fast on the NMR spectroscopic time scale under these conditions. The upfield shift of the benzylic methylene groups adjacent to the NH_2^+ center of the DBA^+ ion and the dispersal of the methylene protons of the OCH_2CH_2O units into two multiplets over a range of chemical shifts (δ 3.62−3.72) suggest that the NH_2^+ center is stabilized possibly through [N^+−H···O] and [N^+C−H···π] interactions. Again, a Job plot based on the ^{1}H NMR spectroscopic absorption in CD_3NO_2 afforded conclusive evidence for 1:1 complexation (see the Supporting

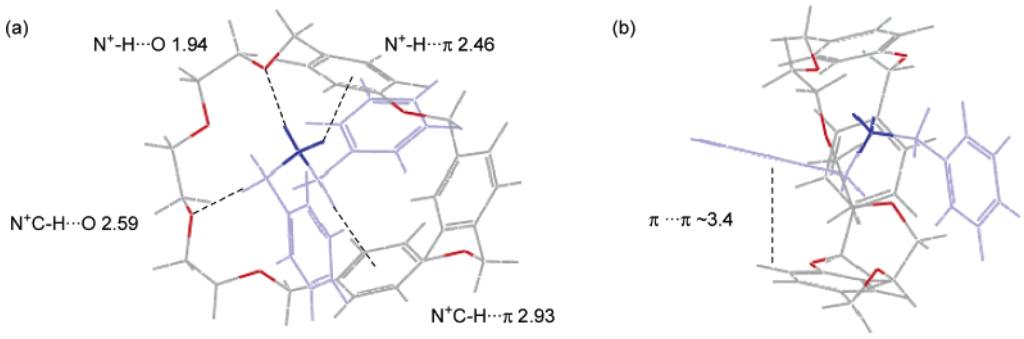
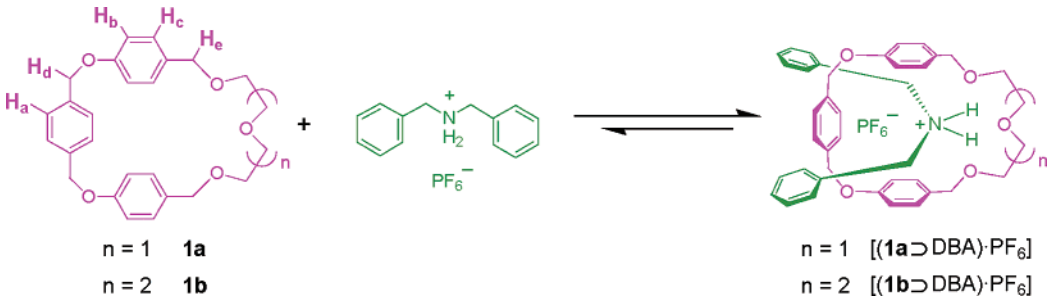
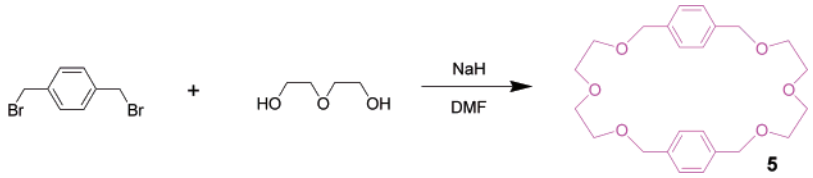


FIGURE 5. (a) Lowest energy structure obtained after optimization of sampled structures obtained from 5000-ps MD of **1b**⊃DBA^+ in a water continuum model; (b) alternative view of the same structure.

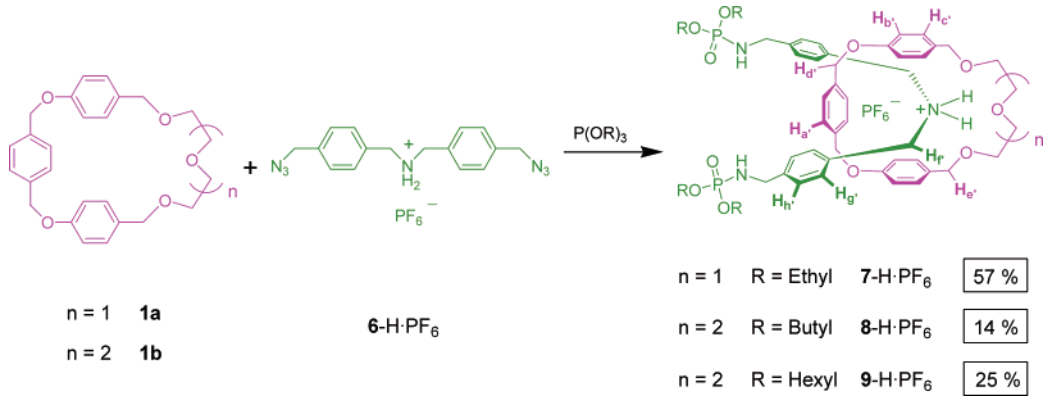
SCHEME 2



SCHEME 3



SCHEME 4



Information). We determined, through a ^{1}H NMR spectroscopic dilution experiment, the association constant for the interaction between macrocycle **5** and the DBA^+ ion in CD_3NO_2 to be 340 ± 40 M^{-1}, which is ca. 50-fold weaker than the one between macrocycle **1a** and the DBA^+ ion. This result suggests—again, counterintuitively—that the presence of a *p*-xylyl unit is more beneficial for the binding of a DBA^+ ion than is a diethylene glycol chain, possibly because of the macrocyclic effect due to (a) its structural rigidity, which places the two phenolic aromatic rings in a better position to take part in the noncovalent interactions between the $CH_2NH_2^+CH_2$ center of the threaded DBA^+ ion, (b) the more-electron-rich aromatic rings, which favor these noncovalent interactions (i.e., a phenolic ring for **1a** vs a xylyl group for **5**), and (c) the slightly smaller size of the macrocycle (25 ring atoms for **1a**, 26 for **5**).

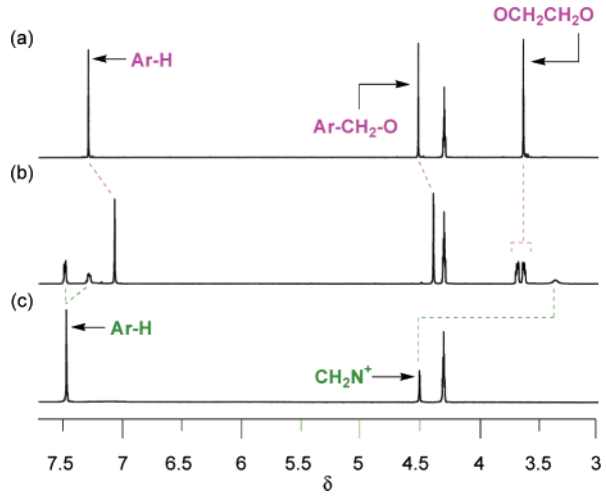


FIGURE 6. Partial ^{1}H NMR spectra (400 MHz, CD_3NO_2, 298 K) of (a) macrocycle **5**, (b) an equimolar mixture of **5** and DBA·PF_6 (20 mM), and (c) DBA·PF_6.

Rotaxanes Formed From "Oxygen-Deficient" Macrocycles and DBA^+ Ions: Synthesis and Thermal Stability. To prove unambiguously that [2]pseudorotaxane complexes form in solution between macrocycles **1a** and **1b** and DBA^+ ions, we chose to stopper such complexes to form their corresponding [2]rotaxanes. From a CPK molecular model, it appeared that because compound **1a** is a 25-membered-ring macrocycle that incorporates three rigid benzene rings, diethyl phosphoramidate groups[33] would serve as suitable stoppers. Thus, we added triethyl phosphite (200 mM) to a solution of benzylic azide **6**-H·PF_6 (100 mM) and macrocycle **1a** (150 mM) in CH_2Cl_2

(30) Chemical double-mutant cycles have been used to measure the strengths of aromatic stacking interactions; the estimated stabilization energies are less than 0.34 kcal/mol, depending on the interacting aromatic system. See: (a) Carver, F. J.; Hunter, C. A.; Jones, P. S.; Livingstone, D. J.; McCabe, J. F.; Seward, E. M.; Tiger, P.; Spey, S. E. *Chem. Eur. J.* **2001**, *7*, 4854−4862. (b) Adams, H.; Hunter, C. A.; Lawson, K. R.; Perkins, J.; Spey, S. E.; Urch, C. J.; Sanderson, J. M. *Chem. Eur. J.* **2001**, *7*, 4863−4878.

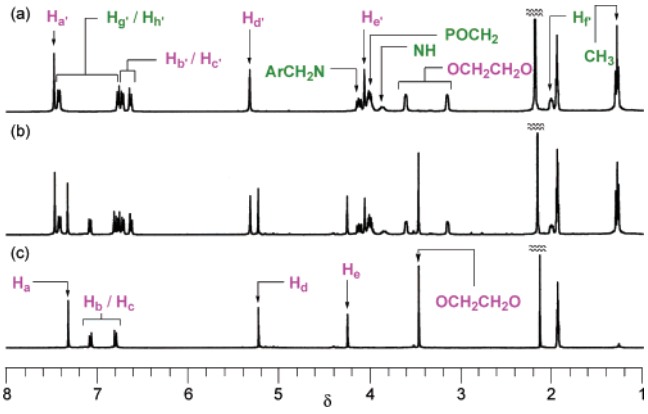


FIGURE 7. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 10 mM, 298 K) of (a) [2]rotaxane **7**-H·PF_6, (b) an equimolar mixture of rotaxane **7**-H·PF_6 and macrocycle **1a**, and (c) macrocycle **1a**.

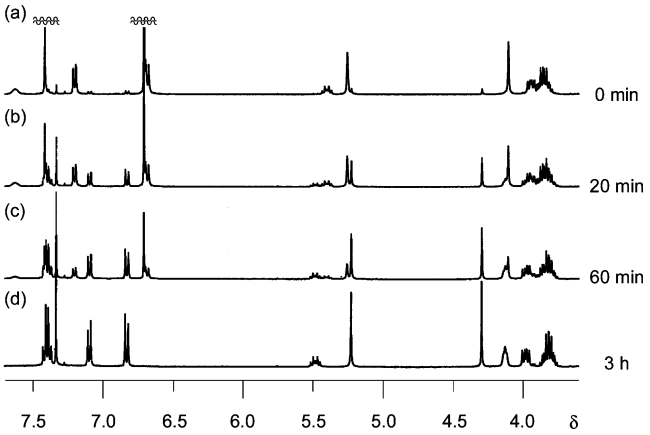


FIGURE 8. Partial ^{1}H NMR (400 MHz, 323 K) spectra displaying the dissociation of [2]rotaxane **8**-H·PF_6 in CD_3SOCD_3 over time: (a) 0 min, (b) 20 min, (c) 60 min, and (d) 3 h.

and isolated the corresponding [2]rotaxane **7**-H·PF_6 in 57% yield after column chromatography over silica gel. The reaction between macrocycle **1b**, benzylic azide **6**-H·PF_6,[33] and triethyl phosphite, however, gave no corresponding [2]rotaxane, probably because macrocycle **1b** contains a 28-membered ring, which it too large to be entrapped by the diethyl phosphoramidate stoppering units. After inspecting CPK molecular models, we believed that the sterically more sizable dibutyl phosphoramidate groups would be more reasonable choices as stoppers. Gratifyingly, when we added tributyl phosphate (200 mM) to an equimolar mixture of the benzyl azide **6**-H·PF_6 and macrocycle **1b** in CH_2Cl_2 (100 mM) we isolated the corresponding [2]rotaxane **8**-H·PF_6 in 14% yield.[34] The ^{1}H NMR spectrum (Figure 7a) of the [2]rotaxane **7**-H·PF_6 recorded in CD_3CN displays upfield shifts in the positions of the signals of the resonances of (a) the methylene protons adjacent to the ammonium center (cf. the corresponding signal for **6**-H·PF_6) and (b) the ethylene protons of the encircled macrocyclic component of **7**-H·PF_6, relative to the positions of these signals in their free components; these shifts confirm that the interactions between these components in the rotaxane are similar to those present in the initial [**1a**⊃DBA]$^+$ complex. The ^{1}H NMR spectrum (Figure 7b) of an equimolar mixture of **7**-H·PF_6 and macrocycle **1a** (10 mM each) in CD_3CN at 298 K corresponds to a superimposition of the two spectra (cf. Figure 7a,c) of the separate components. These spectra establish that no exchange occurs between the macrocycle and dumbbell components in solution and, therefore, proves the constitutional integrity of the [2]rotaxane.[35] We used a similar method to prove the constitutional integrity of [2]rotaxane **8**-H·PF_6 (see the Supporting Information).

To test the thermal stability of the phosphoramidate-stoppered [2]rotaxanes **7**-H·PF_6 and **8**-H·PF_6, we dissolved them individually in CD_3SOCD_3 (5 mM) and heated them to 323 K while monitoring their ^{1}H NMR spectra. The ^{1}H NMR spectrum of [2]rotaxane **7**-H·PF_6, in which macrocycle **1a** is entrapped by diethyl phosphoramidate stoppers, was unchanged after heating for 2 h under these conditions. In contrast, the ^{1}H NMR spectra of the [2]rotaxane **8**-H·PF_6 (Figure 8) indicate that the intensity of the signals of the free macrocycle **1b** increased, and those for **8**-H·PF_6 decreased; i.e., dissociation of the macrocyclic unit of **8**-H·PF_6 occurred in CD_3SOCD_3 at 323 K. Thus, the di-*n*-butyl phosphoramidate terminus/macrocycle **1b** pair does not constitute a true interlocking system, but rather one that is a slippage-amenable rotaxane system. This result led us to prepare the [2]rotaxane **9**-H·PF_6, in which macrocycle **1b** is confined between two slightly larger di-*n*-hexyl phosphoramidate stoppers; this rotaxane is stable as a supramolecular entity in CD_3SOCD_3 at 323 K for at least 2 h.

The fact that it is possible to generate [2]pseudorotaxane complexes in solution from the interaction of DBA^+ ions with macrocycles **1a** and **1b** that contain loops of just three or four oxygen atoms suggests that the cooperative effect of at least five oxygen atoms found in the recognition sites of most of the crown ethers that have been used previously to complex DBA^+ ions is not a necessary prerequisite for efficient binding. Indeed, it appears that [cation···π], [N^+−H···π], and [N^+C−H···π] interactions can be harnessed to play extremely important roles in stabilizing macrocycle/dialkylammonium ion complexes.

Macrocycles 1a and 1b Recognize Bipyridinium Ions. Because the two electron-rich phenol rings linked by an ethylene glycol chain are placed in a distance (ca. 7.0 Å) suitable for π-stacking—based on CPK molecular models and molecular mechanics calculations—we suspected that macrocycles **1a** and **1b** may be able to recognize electron-deficient bipyridinium ions in addition to dialkylammonium ions.[36] When we mixed equimolar amounts (10 mM) of **1b** and methyl viologen bis(hexafluorophosphate) **10**·2PF_6 in CD_3NO_2, the solution turned yellow immediately. The observation of upfield shifts for the signals of aromatic protons of both **1b** and **10**·2PF_6 in ^{1}H NMR spectra, relative to those of the free species, implies that the π-electron-deficient bipyridinium ion may be positioned within the cavity of **1b** such that it stacks with the π-electron-rich

(31) (a) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709−728. (b) Ashton, P. R.; Fyfe, M. C. T.; Hickingbottom, S. K.; Stoddart, J. F.; White, A. J. P.; Williams D. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2117−2124.

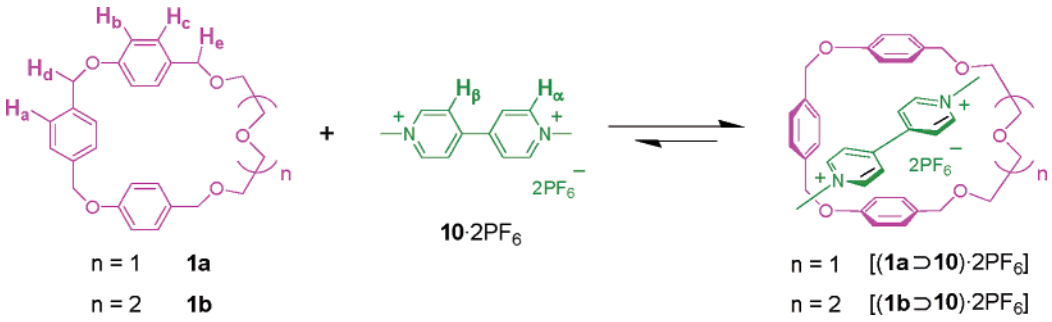
(32) The association constant (K_a) between DB24C8 and DBA^+ ion in CD_3NO_2 has been reported to be 8000 M^{-1}; see: Chiu, S.-H.; Liao, K.-S.; Su, J.-K. *Tetrahedron Lett.* **2004**, *45*, 213−216.

(33) Hung, W.-C.; Liao, K.-S.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Org. Lett.* **2004**, *6*, 4183−4186.

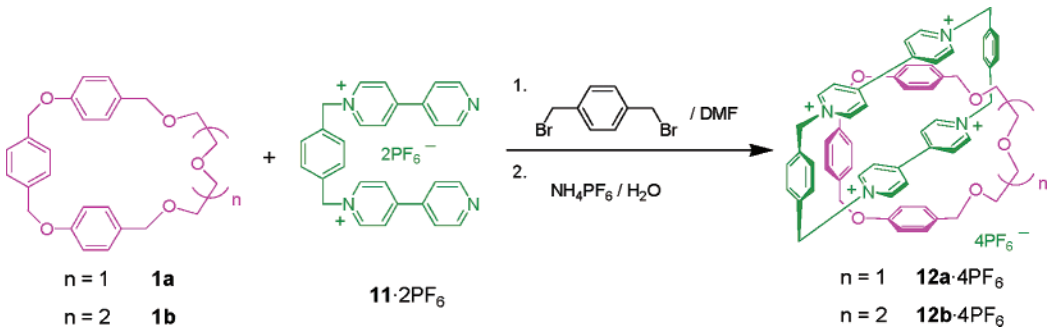
(34) The lower yield of this reaction may be the result of the lower association constant of the interaction between the DBA^+ ion and macrocycle **1b**, relative to that of macrocycle **1a**. Shielding of the ammonium center by the macrocycle has been suggested as an important factor in the success of these stoppering reactions; see ref 33.

(35) A similar method had been applied previously to prove the structural integrity of rotaxanes; see: Chiu, S.-H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 4174−4175.

SCHEME 5



SCHEME 6



phenol rings to form a [2]pseudorotaxane-like complex. The dispersion of the "tight" multiplet (δ 3.48−3.57) for the protons of the OCH_2CH_2O units of uncomplexed **1b** into three distinct signals and the upfield shift of the α-protons on the bipyridinium ion (Figure 9) suggest that weak [C−H···O] hydrogen bonds may exist along with π-stacking interactions in this [2]-pseudorotaxane-like complex [(**1b**⊃**10**)·$2PF_6$] (cf. the similar shifts observed in the NMR spectra of the complex formed between BPP34C10 and **10**·$2PF_6$).[36a,37] From a ^{1}H NMR spectroscopic dilution experiment, we determined the association constant (K_a) for the complexation between **1b** and **10**·$2PF_6$ in CD_3NO_2 to be 130 ± 3 M^{-1}.

We observed similar shifts in the signals of an equimolar mixture of the smaller macrocycle **1a** and **10**·$2PF_6$ under the same conditions (Figure 10); the association constant in this case is 60 ± 7 M^{-1}, i.e., about half that of the interaction between **1b** and **10**·$2PF_6$. This finding implies that even through **1b** is less preorganized for the binding of DBA^+ ions than is **1a**, the extra hydrogen-bond-accepting oxygen atom of its oligoethylene glycol loop and its increased cavity size may be more accommodating for bipyridinium ions such that it may provide simultaneous π-stacking and [C−H···O] hydrogen bonding interactions.

To prove that the complexes that form between **10**·$2PF_6$ and macrocycles **1a** and **1b** have [2]pseudorotaxane-like architectures in solution, we synthesized the corresponding interlocked molecules. We isolated the [2]catenane **12b**·$4PF_6$ (Scheme 6) comprising the macrocycles **1b** and cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) as a yellow solid in 29% yield after reacting **1b**, **11**·$2PF_6$,[37] and α,α′-dibromo-*p*-xylene in DMF at ambient temperature. Reacting macrocycle **1a** under the same conditions gave the corresponding [2]catenane **12a**·$4PF_6$ in 21% yield. Because these syntheses must proceed via pseudorotaxane-like

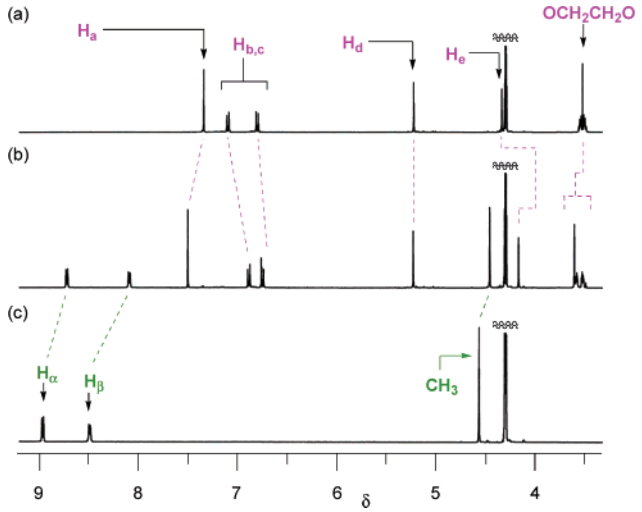


FIGURE 9. Partial ^{1}H NMR spectra (400 MHz, CD_3NO_2, 298 K) of (a) macrocycle **1b**, (b) an equimolar mixture of **1b** and **10**·$2PF_6$ (10 mM), and (c) **10**·$2PF_6$.

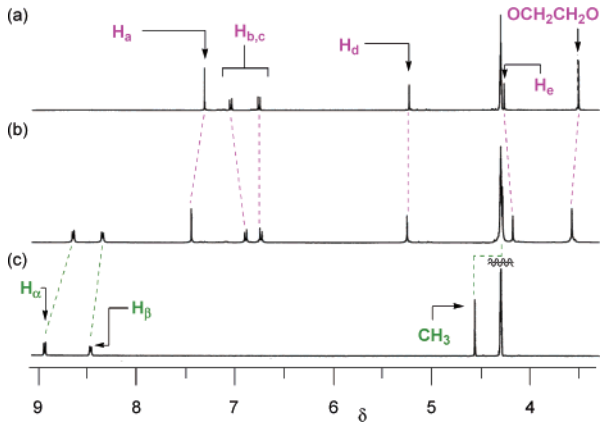


FIGURE 10. Partial ^{1}H NMR spectra (400 MHz, CD_3NO_2, 298 K) of (a) macrocycle **1a**, (b) an equimolar mixture of **1a** and **10**·$2PF_6$ (10 mM), and (c) **10**·$2PF_6$.

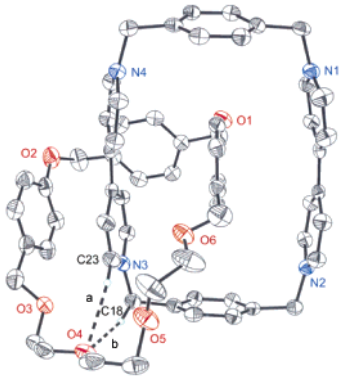


FIGURE 11. Solid-state structure of the [2]catenane **12b**$^{4+}$. Disorder of atoms is observed in the ethylene glycol chain (from O3 to O6). Hydrogen bond geometries (C···O and H···O distances [Å] and C−H···O angles [deg]): (a) 3.321(7), 2.45, 153.0; (b) 3.501(7), 2.59, 153.8.

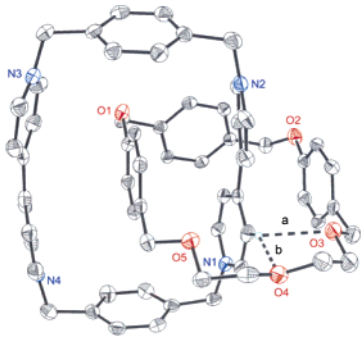


FIGURE 12. Solid-state structure of the [2]catenane **12a**$^{4+}$. Hydrogen bond geometries (C···O and H···O distances [Å] and C−H···O angles [deg]): (a) 2.883(18), 2.39, 112.1; (b) 3.021(18), 2.16, 150.7.

intermediates, we believe that the successful isolation of these two [2]catenanes proves that macrocycles **1a** and **1b** each bind bipyridinium ions in the form of [2]pseudorotaxane complexes.

We used vapor diffusion of isopropyl ether into respective CH_3CN solutions of **12a**·4PF_6 and **12b**·4PF_6 to obtain single crystals, which were suitable for X-ray crystallographic analysis, of both of these [2]catenanes. The solid-state structures (Figures 11 and 12) of these two catenanes reveal the expected π-stacking interactions and [C−H···O] hydrogen bonds between their interlocked macrocycles.

The fact that macrocycles **1a** and **1b** form pseudorotaxane-like complexes with both DBA^+ and bipyridinium ions in solution makes them suitable candidates for the construction of molecular switches. Although large crown ethers, such as BPP34C10 and BMP32C10, can also recognize both of these guests in solution, small crown ethers, such as DB24C8 and BMP26C8, seem to lack this ability.[38] To the best of our knowledge, macrocycle **1a** is the smallest macrocycle (a 25-membered ring) that is capable of complexing both guests in a [2]pseudorotaxane-like fashion in solution. The much smaller ring size of macrocycles **1a** and **1b**, when compared to that of BPP34C10, may make the syntheses of their corresponding functional interlocked molecules much easier because they do not require relatively enormous groups,[36c,39] such as tris(4-*tert*-butylphenyl)methyl units, to serve as effective stopper moieties.

Conclusions

We have synthesized a new category of macrocycles, containing suitably positioned oligoethylene glycol chains and aromatic rings, that form [2]pseudorotaxane-like complexes with both dialkylammonium and bipyridinium ions in solution. The chemical structures of crown ethers that have been reported to bind DBA^+ ions have generally comprised oligoethylene glycol chains that provide a cooperative effect of at least five oxygen atoms; in this paper, however, we demonstrate that such a prerequisite is not a necessary one for efficient binding. With suitable design, the cooperative effects of [N^+C−H···π], [N^+−H···π], and [cation···π] interactions in conjunction with more-traditional hydrogen bonds between the macrocycles and DBA^+ ions can result in extremely stable pseudorotaxane complexes. That is to say, the oxygen atoms of crown ethers can be replaced by phenol units and still retain their effective binding properties toward DBA^+ ions. We are currently trying to identify the major noncovalent interactions that occur between macrocycle **1a** and the DBA^+ ion and stabilize this pseudorotaxane complex. Hopefully, these studies will lead us to a greater understanding and control over less-traditional noncovalent interactions.

Experimental Section

Computational Details. Stochastic molecular dynamics simulations were performed with MacroModel V9.0 in conjunction with the all-atom AMBER* force-field.[40,41] The continuum GB/SA model in MacroModel was used for simulations in water.[42] Constant dielectric treatment was used to estimate the electrostatic interactions. A 200-ps equilibration step with a 1-fs time step was followed

(36) Bipyridinium ions form pseudorotaxane-like complexes with several sizable crown ethers; see: (a) Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1064−1066. (b) Allwood, B. L.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1058−1061. (c) Asakawa, M.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Kocian, O.; Prodi, L.; Raymo, F. M.; Stoddart, J. F.; Venturi M. *J. Am. Chem. Soc.* **1997**, *119*, 302−310. (d) Yamaguchi, N.; Nagvekar, D. S.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2361−2364. (e) Bryant, W. S.; Jones, J. W.; Mason, P. E.; Guzei, I.; Rheingold, A. L.; Fronczek, F. R.; Nagvekar, D. S.; Gibson, H. W. *Org. Lett.* **1999**, *1*, 1001−1004. (f) Huang, F.; Zakharov, L. N.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, *70*, 809−813.

(37) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193-218.

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by a 5000-ps MD run with a 1-fs time step at 300 K. Structures were sampled at regular intervals of 1 ps during the simulations. The sampled structures were then minimized with use of the PR conjugated gradient method to obtain the lowest energy structure in each simulation. A previous study on β-cyclodextrin complexes has shown this method of locating low-energy structures to be superior to using the Monte Carlo multiple minimum (MCMM) search in MacroModel.[43] During the MD simulations, the guest changes orientation and position in the host, but no decomplexation was observed. The lowest energy structures of **1a**⊃DBA^+ and **1b**⊃DBA^+ are stabilized through a combination of [N^+−H···π], [N^+C−H···π], [N^+−H···O], and [N^+C−H···O] contacts between the $CH_2NH_2^+CH_2$ unit of a threaded DBA^+ ion and the oxygen atoms and aromatic rings of the macrocycles. Face-to-face and T-shaped $\pi-\pi$ interactions were also observed between the aromatic rings of both the DBA^+ ion and the macrocycles.

X-ray Diffraction Analyses. The crystals were mounted on a glass fiber. Crystal data were collected on diffractometers installed with monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å at $T = 150$ K. All structures were solved by using the SHELXS-97[44] and refined with SHELXL-97[45] by full matrix least squares on F^2 values with restraints of the disordered motifs. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode. For [2]catenane **12a**·4PF_6, the final indices were $R1 = 0.0599$, $wR2 = 0.1360$ with goodness-of-fit on $F^2 = 0.848$. For [2]catenane **12b**·4PF_6, the final indices were $R1 = 0.0669$, $wR2 = 0.1533$ with goodness-of-fit on $F^2 = 0.987$.

[1,4-Phenylenebis(methyleneoxy-4,1-phenylene)]dimethanol (2). A mixture of 4-hydroxybenzyl alcohol (3.72 g, 30 mmol), α,α′-dibromo-*p*-xylene (2.63 g, 10 mmol), and K_2CO_3 (10 g, 72.4 mmol) in DMF (50 mL) was heated at 50 °C for 2 days. The reaction mixture was cooled to room temperature and the organic solvent was evaporated under reduced pressure. The residue was washed with CH_2Cl_2 (500 mL), H_2O (500 mL), and MeOH (150 mL) to afford the desired product **2** (3.14 g, 90%). Mp 196−198 °C; ^{1}H NMR (400 MHz, CD_3SOCD_3) δ 4.40 (s, 4H), 5.08 (s, 4H), 6.94 (d, $J = 8$ Hz, 4H), 7.21 (d, $J = 8$ Hz, 4H), 7.43 (s, 4H); ^{13}C NMR (100 MHz, CD_3SOCD_3) δ 62.4, 68.7, 113.9, 127.0, 127.3, 134.1, 136.0, 156.2; HR-MS (ES) $C_{22}H_{22}O_4Na$ [M + Na]$^+$ calcd *m*/*z* 373.1416, found *m*/*z* 373.1450. Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33; O, 18.26. Found: C, 75.62; H, 6.27; O, 18.11.

2,9,15,18,21-Pentaoxatetracyclo[21.2.2.2^{4,7}.2^{10,13}]hentriaconta-1(25),4,6,10,12,23,26,28,30-nonaene (1a). Diethylene glycol ditosylate **3** (5.95 g, 14.4 mmol) was added slowly to a solution of diol **2** (5.0 g, 14.4 mmol) and NaH (1.75 g, 42.8 mmol) in DMF (700 mL) and the resulting mixture was stirred at room temperature for 7 days. The reaction was quenched by the addition of MeOH (10 mL) and then the organic solvent was evaporated under reduced pressure. The residue was partitioned between H_2O (500 mL) and CH_2Cl_2 (500 mL); the organic layer was collected, dried ($MgSO_4$), and concentrated to afford a crude product, which was then purified by column chromatography (SiO_2; EtOAc/hexanes, 3:7) to give macrocycle **1a** as a white solid (183 mg, 3%). Mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48−3.52 (m, 4H), 3.58−3.62 (m, 4H), 4.39 (s, 4H), 5.17 (s, 4H), 6.65 (d, $J = 8$ Hz, 4H), 7.06 (d, $J = 8$ Hz, 4H), 7.27 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.1, 69.6, 70.5, 72.6, 115.6, 127.0, 129.0, 130.3, 136.8, 157.0; HR-MS (ES) $C_{26}H_{29}O_5$ [M + H]$^+$ calcd *m*/*z* 421.2015, found *m*/*z* 421.2008. Anal. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71; O, 19.02. Found: C, 74.37; H, 6.78; O, 18.85.

2,9,15,18,21,24-Hexaoxatetracyclo[24.2.2.2^{4,7}.2^{10,13}]tetratriaconta-1(28),4,6,10,12,26,29,31,33-nonaene (1b). Triethylene glycol ditosylate **4** (2.30 g, 5.0 mmol) was added slowly to a solution of diol **2** (1.74 g, 5.0 mmol) and NaH (368 mg, 15.0 mmol) in DMF (500 mL); the resulting mixture was stirred at room temperature for 7 days. The reaction was quenched by the addition of MeOH (5 mL) and the organic solvent was evaporated under reduced pressure. The residue was partitioned between H_2O (300 mL) and CH_2Cl_2 (300 mL); the organic layer was collected, dried ($MgSO_4$), and concentrated to afford a crude product, which was then purified by column chromatography (SiO_2; EtOAc/hexane, 3:7) to give the macrocycle **1b** as a white solid (116 mg, 5%). Mp 78−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50−3.55 (m, 4H), 3.60−3.64 (m, 8H), 4.40 (s, 4H), 5.19 (s, 4H), 6.75 (d, $J = 8$ Hz, 4H), 7.11 (d, $J = 8$ Hz, 4H), 7.26 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.2, 69.5, 70.6, 71.0, 72.9, 115.2, 126.6, 129.0, 130.2, 136.8, 157.3; HR-MS (ES) $C_{28}H_{33}O_6$ [M + H]$^+$ calcd *m*/*z* 465.2272, found *m*/*z* 465.2282. Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94; O, 20.66. Found: C, 72.23; H, 7.02; O, 20.75.

Bis-*p*-xylyl[26]crown-6 (5). α,α′-Dibromo-*p*-xylene (5.0 g, 19 mmol) was added slowly to a solution of diethylene glycol (2.0 g, 19 mmol) and NaH (0.98 g, 40 mmol) in DMF (800 mL); the resulting mixture was stirred at room temperature for 7 days. The reaction was quenched by the addition of MeOH (10 mL) and the organic solvent was removed under reduced pressure. The residue was partitioned between H_2O (500 mL) and CH_2Cl_2 (500 mL); the organic layer was collected, dried ($MgSO_4$), and concentrated to afford a crude product, which was then purified by column chromatography (SiO_2; EtOAc/hexane, 4:6) to give the macrocycle **5** as a white solid (400 mg, 5%). Mp 69−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66−3.72 (m, 16H), 4.59 (s, 8H), 7.31 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.8, 71.2, 73.1, 127.5, 137.5; HR-MS (ES) $C_{24}H_{33}O_6$ [M + H]$^+$ calcd *m*/*z* 417.2277, found *m*/*z* 417.2201. Anal. Calcd for $C_{24}H_{32}O_6$: C, 69.21; H, 7.74; O, 23.05. Found: C, 69.01; H, 7.82; O, 23.17.

[2]Rotaxane 7-H·PF_6. Triethyl phosphite (0.05 mL, 0.28 mmol) was added slowly to a solution of 6-HPF_6 (60 mg, 0.14 mmol) and macrocycle **1a** (90 mg, 0.22 mmol) in CH_2Cl_2 (1.4 mL). After the mixture had been stirred at ambient temperature for 16 h, the solvent was evaporated under reduced pressure. The residue was purified chromatographically (SiO_2: CH_2Cl_2/MeOH, 98:2) and the desired [2]rotaxane **7**-HPF_6 was isolated as a white solid (90 mg, 57%). Mp 85−87 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 1.42 (t, $J = 6.8$ Hz, 12H), 2.14 (t, $J = 6.8$ Hz, 4H), 3.26−3.29 (m, 4H), 3.72−3.74 (m, 4H), 3.97−4.00 (m, 2H), 4.09−4.17 (m, 8H), 4.19 (s, 4H), 4.23−4.27 (m, 4H), 5.44 (s, 4H), 6.76 (d, $J = 10.8$ Hz, 4H), 6.84 (d, $J = 7.6$ Hz, 4H), 6.89 (d, $J = 10.8$ Hz, 4H), 7.54 (d, $J = 7.6$ Hz, 4H), 7.59 (s, 4H); ^{13}C NMR (100 MHz, CH_3CN) δ 17.8 (d, $J_{PC} = 6.9$ Hz), 46.3, 52.2, 63.8 ($J_{PC} = 5.3$ Hz), 69.1, 70.8, 72.1, 75.2, 117.3, 128.7, 128.8, 129.6, 129.7, 130.5, 132.4, 138.6, 142.9 (d, $J_{PC} = 5.3$ Hz), 158.6; HR-MS (ES) $C_{50}H_{68}N_3O_{11}P_2$ [**7**-H]$^+$ calcd *m*/*z* 948.4329, found *m*/*z* 948.4332.

[2]Rotaxane 8-H·PF_6. Tributyl phosphite (0.1 mL, 0.36 mmol) was added slowly to a solution of **6**-H·PF_6 (81 mg, 0.18 mmol) and macrocycle **1b** (83 mg, 0.18 mmol) in CH_2Cl_2 (1.8 mL). After the mixture had been stirred at ambient temperature for 16 h, the solvent was evaporated under reduced pressure. The residue was purified by chromatography (SiO_2: CH_2Cl_2/MeOH, 98:2) and the desired [2]rotaxane **8**-H·PF_6 was isolated as a colorless oil (30 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90−0.94 (t, $J = 7.6$ Hz, 12H), 1.36−1.45 (m, 8H), 1.62−1.69 (m, 8H), 3.08−3.11 (m, 4H), 3.24 (s, 4H), 3.32−3.35 (m, 4H), 3.51−3.54 (m, 4H), 3.97−4.06 (m, 10H), 4.14 (d, $J = 8$ Hz, 4H), 4.19 (s, 4H), 5.18 (s, 4H), 6.73 (d, $J = 8$ Hz, 4 H), 6.79 (d, $J = 8$ Hz, 4 H), 6.89 (d, $J = 8$ Hz, 4 H), 7.28−7.35 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.2, 32.7 (d, $J_{PC} = 7$ Hz), 45.0, 51.2, 66.5, 66.6, 68.3, 70.4 (d, $J_{PC} = 5$ Hz), 74.1, 114.8, 126.8, 127.3, 128.3, 128.5, 128.6, 128.8, 129.6, 136.3, 141.5, 157.2; HR-MS (ES) $C_{60}H_{88}N_3O_{12}P_2$ [**8**-H]$^+$ calcd *m*/*z* 1104.5844, found *m*/*z* 1104.5816.

[2]Rotaxane 9-H·PF_6. Trihexyl phosphite (0.08 mL, 0.22 mmol) was added slowly to a solution of **6**-H·PF_6 (49 mg, 0.11 mmol)

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and macrocycle **1b** (50 mg, 0.11 mmol) in CH_2Cl_2 (0.7 mL). After the mixture had been stirred at ambient temperature for 16 h, the solvent was evaporated under reduced pressure. The residue was purified by chromatography (SiO_2: CH_2Cl_2/MeOH, 98:2) and the desired [2]rotaxane **9**-H·PF_6 was isolated as a colorless oil (37 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 8 Hz, 12 H), 1.25−1.40 (m, 24H), 1.62−1.72 (m, 8H), 3.12 (s, 4H), 3.27 (s, 4H), 3.36 (s, 4H), 3.54 (s, 4H), 4.00−4.04 (m, 10H), 4.15, (d, J = 12 Hz, 4H), 4.20 (s, 4H), 5.20 (s, 4H), 6.74 (d, 4H), 6.79 (d, J = 8 Hz, 4H), 6.89 (d, J = 8 Hz, 4H), 7.31−7.33 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 25.3, 29.8, 30.4, 30.5, 31.4 (d, J_{PC} = 3 Hz), 44.9, 51.1, 66.7, 68.3, 70.3, 70.5, 74.1, 115.0, 127.6, 128.5, 128.7, 129.0, 129.8, 136.5, 141.5, 157.5; HR-MS (ES) $C_{68}H_{104}N_3O_{12}P_2$ [**9**-H]$^+$ calcd m/z 1216.7095, found m/z 1216.7135.

[2]Catenane 12a·4PF$_6$. α,α′-Dibromo-*p*-xylene (32 mg, 0.12 mmol) was added slowly to a solution of **11**·2PF_6 (85 mg, 0.12 mmol) and **1a** (50 mg, 0.12 mmol) in DMF (1 mL); the resulting mixture was stirred at ambient temperature for 24 h. The solvent was evaporated under reduced pressure, the residue was dissolved in MeCN (10 mL), and then saturated aqueous NH_4PF_6 (20 mL) was added. The organic solvent was evaporated and the precipitate was collected and washed with H_2O (5 mL) to afford a yellow solid, which was recrystallized (MeCN/isopropyl ether) to afford the desired [2]catenane **12a**·4PF_6 as a yellow solid (38 mg, 21%). Mp >252 °C dec; ^{1}H NMR (400 MHz, CD_3CN) δ 3.01 (s, 2H), 3.27 (d, J = 8 Hz, 2H), 3.56−3.62 (m, 6H), 3.72−3.74 (m, 4H), 3.78−3.83 (m, 2 H), 5.05 (s, 2H), 5.09−5.11 (m, 2H), 5.32 (s, 2H), 5.58 (d, J = 13 Hz, 2H), 5.70 (d, J = 13 Hz, 2H), 5.74 (s, 4H), 6.08 (d, J = 8 Hz, 2H), 6.40 (d, J = 8 Hz, 2H), 7.74−7.77 (m, 2H), 7.83−7.87 (m, 12H), 7.97 (d, J = 8 Hz, 2H), 8.35 (d, J = 6 Hz, 2H), 8.48−8.54 (m, 2H), 8.72 (d, J = 8 Hz, 2H), 8.85 (d, J = 8 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN) δ 65.0, 65.3, 67.5, 67.7, 70.1, 70.7, 71.7, 73.0, 113.6, 115.3, 125.3, 126.7, 128.0, 128.5, 129.9, 130.0, 130.1, 130.8, 131.1, 137.1, 137.6, 138.9, 139.4, 141.7, 142.2, 144.6, 144.9, 147.0, 154.4, 156.5 (one signal is missing, presumably because of signal overlap); HR-MS (ES) $C_{62}H_{58}N_4O_5$ [**12a**-2H]$^{2+}$ calcd m/z 469.2203, found m/z 469.2198.

[2]Catenane 12b·4PF$_6$. α,α′-Dibromo-*p*-xylene (26.2 mg, 0.1 mmol) was added slowly to a solution of **11** (70.6 mg, 0.1 mmol) and **1b** (46.6 mg, 0.1 mmol) in DMF (1 mL); the resulting mixture was stirred at ambient temperature for 24 h. The organic solvent was evaporated under reduced pressure, the residue was dissolved in MeCN (10 mL), and then saturated aqueous NH_4PF_6 (20 mL) was added. The solvent was evaporated and the precipitate was collected and washed with H_2O (5 mL) to afford a yellow solid, which was recrystallized (MeCN/isopropyl ether) to afford the desired [2]catenane **12b**·4PF_6 (46 mg, 29%). Mp >228 °C dec; ^{1}H NMR (400 MHz, CD_3CN) δ 3.43−3.52 (br, 4H), 3.53−3.55 (m, 4H), 3.67−3.69 (m, 4H), 3.78 (s, 4H), 5.16 (s, 4H), 5.68 (s, 8H), 7.27 (br, 8H), 7.74 (s, 4H), 7.83 (s, 8H), 8.71 (br, 8H) [one signal (8H) is missing, presumably because of severe signal broadening]; ^{13}C NMR (100 MHz, CD_3CN) δ 65.1, 67.7, 70.6, 70.7, 71.2, 71.7, 114.5, 126.6, 128.3, 129.3, 130.8, 137.1, 138.4, 144.2, 146.4, 155.3 (one signal is missing, presumably because of signal overlap); HR-MS (FAB) $C_{64}H_{64}N_4O_6P_3F_{18}$ [**12b**·3PF_6]$^+$ calcd m/z 1419.3751, found m/z 1419.3778.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds and Job plots for the complexation between macrocycles **1a**, **1b**, and **5** and DBA·PF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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