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New Bis(benzimidazole) Cations for Threading through Dibenzo-24-crown-8

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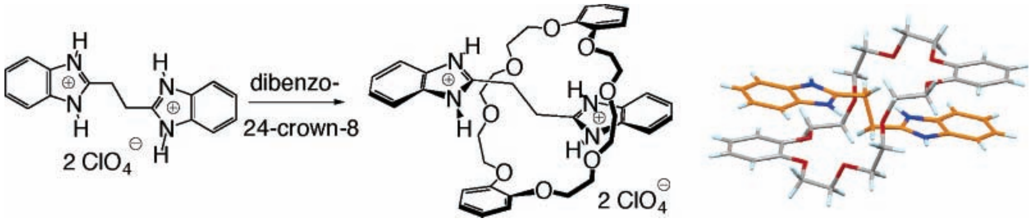
ABSTRACT



We report a simple bis(benzimidazole) dication which can act as new template for threading through dibenzo-24-crown-8. The effect of the solvent and counterion on the magnitude of the binding interaction and on the hydrogen bonding array in the solid state is described.

Rotaxanes[1] are the focus of increasing research interest as they offer the possibility of control in the movement and position of the interlocked components relative to one another in the design of molecular machines and switches.[2] Pseudorotaxanes can also exhibit these properties.[3]

The ongoing search for new motifs[4−6] that template rotaxane formation has furthered our understanding of the requirements in the rotaxane forming process and increased the options available for the development of shuttles, switches, and devices.[7]

The synthesis of rotaxanes from crown ethers either via complexation with a secondary ammonium ion[4] or around quaternerized pyridines[5] has provided a rich source of interlocked structures. Crown ethers themselves have a long pedigree in supramolecular chemistry[8] and still offer many opportunities and new applications[9] even for interlocked architectures.[10]

We sought to develop a new template that would thread through the cavity of dibenzo-24-crown-8 by combining the

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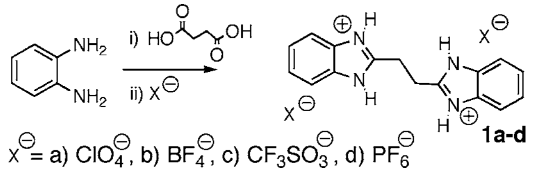
benefits of the π stacking of the electron-deficient pyridinium with the hydrogen bonding ability of the ammonium ions in the form of bis(benzimidazolium) cations. Such advances will further contribute to a supramolecular toolbox for the development of bistable rotaxanes for switching devices.[11]

There are several reports concerned with the interaction of protonated imidazole and benzimidazole cations with crown ethers.[12] The heteroaromatic cations predominantly lie between arrays of crowns in the solid state maximizing their hydrogen bonding and π stacking interactions with neighboring crowns in the crystal lattice but not within the crown cavity. We reasoned that a thread having two such recognition sites joined by a short linker such as the bis(benzimidazolium) cations in threads (**1a**−**d**) could interact with either face of the crown and locate the thread within the crown cavity. These threads were easily accessed from the condensation of 1,2-phenylenediamine and succinic acid catalyzed by hydrochloric acid[13] and ion exchange with a noncoordinating counterion (Scheme 1).

Scheme 1. Synthesis of Bis(benzimidazole) Threads



The ^{1}H NMR spectrum of the bisperchlorate salt (**1a**) with an equivalent of dibenzo-24-crown-8 in d_3-acetonitrile was comprised of signals for free crown and thread (**1a**) and a new set of signals that we assigned to the pseudorotaxane (Figure 1). There are two sets of signals because of the slow exchange on the NMR time scale of the free components and the pseudorotaxane. Both the aromatic protons of the bis(benzimidazole) thread and the crown have moved upfield as they experience a shielding effect from the close proximity of their aromatic systems on pseudorotaxane formation.

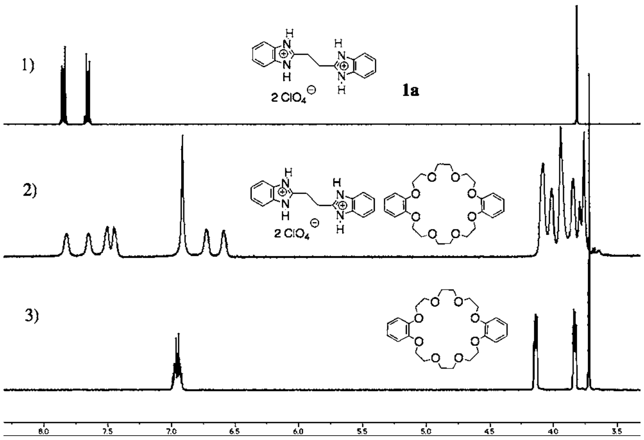


Figure 1. ^{1}H NMR spectra of (1) **1a**, (2) **1a** + dibenzo-24-crown-8, and (3) dibenzo-24-crown-8 in CD_3CN at 2 mM.

The signals associated with the ethoxyethylene chains of the crown and the ethylene of the thread are more complex due to overlapping of bound and unbound signals, and assignment was made using correlation spectroscopy.

From the single-point method,[14] the binding constant[15] was 500 M^{-1}, but this should be considered as an estimate as precipitation of the perchlorate pseudorotaxane began to occur during the acquisition of the NMR spectrum.

The overlapping of key signals in the ^{1}H NMR spectrum hindered the assignment of NOE interactions between the bound thread and crown of the pseudorotaxane, but high-resolution ESI mass spectrometry confirmed the association of the thread and crown (25%) and the thread, crown, and a ClO_4 counterion (4%) as key peaks in the gas phase (see Supporting Information). The low solubility of the perchlorate complex in acetonitrile did fortuitously lead to crystals suitable for single-crystal X-ray analysis with the solid-state structure shown in Figure 2.

The pseudorotaxane **1a**$\subset$dibenzo-24-crown-8 lies on a crystallographic inversion center with the crown ether in a steplike conformation encircling the bis(benzimidazolium) thread which adopts a complementary step but threaded through the center of the crown cavity.

There are several hydrogen bonding interactions responsible for binding the thread within the crown cavity. One NH of each benzimidazolium ion has two charge-assisted hydrogen bonds[16] to aliphatic oxygens of the crown with N···O distances of 2.89 and 3.01 Å and N*H*···O angles of 151° and 128°, respectively. The hydrogens of the ethylene bridge are also involved in CH···O close contacts with crown

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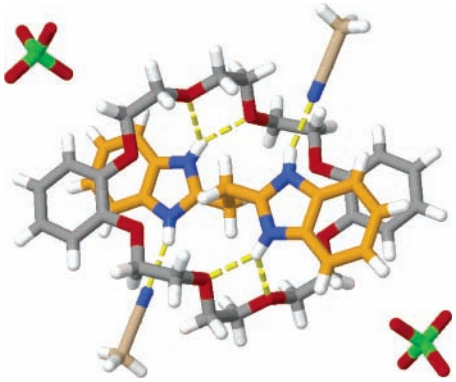

Figure 2. Solid-state structure of **1a**$\subset$dibenzo-24-crown-8 from acetonitrile. Bis(benzimidazolium) thread carbon atoms are orange; crown carbon atoms are gray; and acetonitrile carbon atoms are tan. Hydrogen bonds are represented by yellow dashes.

ether oxygens. The C···O distances vary from 3.35 to 3.52 Å and have C*H*···O angles of 110−157°.

The only two crown oxygens not involved in CH or NH hydrogen bonding lie nearly directly above either imidazolium cation forming charge dipole interactions (O···center of imidazolium ring is 3.28 Å). The axis of the thread lies at a diagonal to the long axis of the crown by 25° to accommodate this and allow an offset π stacking interaction between the electron-rich catechol rings of the crown and the phenyl group of the electron-deficient benzimidazolium rings of the thread.

The other NH of each of the benzimidazolium cations is hydrogen bonded to an acetonitrile solvent molecule with an N···N distance of 2.90 Å and an N*H*···N angle of 156.5° and does not take part in the crown···thread interaction in the solid state.

Confident of the interaction of the bis(benzimidazolium) thread **1a** with the crown in the solid state and solution, we now wanted to investigate the effect of the anion on pseudorotaxane formation and solubility. The bis(benzimidazolium) thread was synthesized with other noncoordinating counterions, tetrafluoroborate (**1b**), trifluoromethanesulfonate (**1c**), and hexafluorophosphate (**1d**). These proved to have far greater solubility than their perchlorate counterpart. In acetonitrile, thread **1d** with hexafluorophosphate exhibited the highest binding interaction with dibenzo-24-crown-8 of the four counterions studied (see Table 1). The binding constants[15] are comparable with the reported values for the interaction of dibenzo-24-crown-8 with quaternary pyridine[17,18] and secondary ammonium ion[4,18] templates in acetonitrile.

The solid-state structures of **1b**$\subset$dibenzo-24-crown-8 and **1d**$\subset$dibenzo-24-crown-8 were also obtained (see Supporting Information) and have an interlocked geometry identical to that described for the perchlorate counterion with one NH of each of the benzimidazolium ions hydrogen bonded to an acetonitrile solvent.

Table 1. K_a (M^{-1}) for Threads **1a−d** and Dibenzo-24-crown-8[a]

thread	acetonitrile	nitromethane
1a (ClO_4^-)	5.0×10^2	18.4×10^2
1b (BF_4^-)	4.7×10^2	14.3×10^2
1c ($TFSA^-$)	3.3×10^2	4.7×10^2
1d (PF_6^-)	6.7×10^2	30.5×10^2

[a] Interactions measured at 25 °C at 2 mM concentration. Errors estimated at 15%. See Supporting Information for experimental details.

As the acetonitrile solvent played a role in the solid-state structure of the rotaxanes, we repeated the measurements in nitromethane. Nitromethane is another solvent capable of dissolving ions but is considered noncoordinating, and we were gratified to observed an increase in binding interaction between the crown and thread (Table 1). This is in line with other studies[19] and reflects the lower donor number[20,21] of nitromethane than acetonitrile. The solid-state structures of each pseudorotaxane with the four different counterions were obtained from nitromethane by the slow infusion of diethyl ether.

The interlocked structure of the perchlorate complex (see Figure 3a) is broadly similar to that from acetonitrile, but all the close contacts and π stacking interactions are slightly shorter (and stronger) highlighting the less-competitive nature of nitromethane in hydrogen bonding and already revealed in the increase in binding interaction.

More pertinent is that the charge-assisted hydrogen bonds of the bis(benzimidazolium) thread to the solvent seen in the solid-state structures from acetonitrile (see Figure 2) have been replaced by an interaction between the thread and the perchlorate counterion. A molecule of nitromethane solvent is still observed in the solid-state structure, but it is sidelined to weak contacts to the crown and outer aromatics of the thread. A similar picture also exists in the solid-state structure of the pseudorotaxanes with the tetrafluoroborate (**1b**) and trifluoromethanesulfonate (**1c**) counterions from nitromethane (see Supporting Information).

In contrast, in the solid-state structure of the hexafluorophosphate pseudorotaxane obtained from crystals grown from

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(21) A referee has suggested that the increase in the observed binding may be due to a higher degree of ion pair dissociation of the thread^{2+} and counterions in nitromethane compared to acetonitrile. As both solvents have similar dielectric constants and polarities, we believe the less-competitive hydrogen bonding accepting nature of nitromethane as expressed by its lower Gutmann donor number is reponsible, though further investigations are underway. See ref 20 for details of solvent parameters.

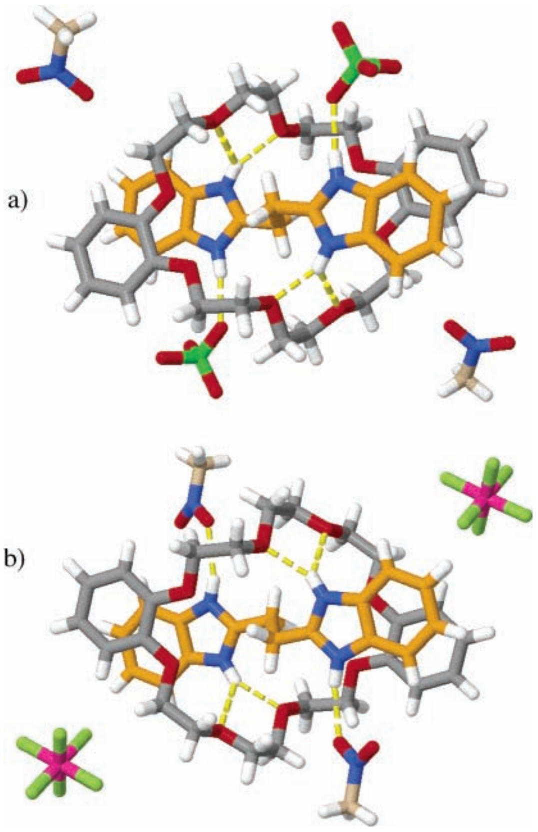

Figure 3. Solid-state structure of (a) **1a**⊂dibenzo-24-crown-8 and (b) **1d**⊂dibenzo-24-crown-8 from nitromethane. The bis(benzimidazolium) thread carbon atoms are orange; crown carbon atoms are gray; and nitromethane carbon atoms are tan. Yellow dashes represent hydrogen bonds.

nitromethane (Figure 3b), the PF_6 is the spectator and it is the weak acceptor nitromethane which takes part in hydrogen bonding to the thread. This highlights the very weak coordinating ability of the PF_6 counterion and why its salts have the highest binding interactions in both acetonitrile and nitromethane. The importance of "noncoordinating" counterions in these types of supramolecular interactions has recently gained more prominence with the realization that they can have more than a spectating role.[22] Recent examples have shown the effect of the counterion on the rate of formation of pseudorotaxanes,[3c,23] the counterion-dependent preorganization of crowns into taco complexes,[10b,24] and the control of translational isomerism in bistable rotaxanes.[25]

In conclusion, we have developed a new template that utilizes charge-assisted hydrogen bonding and charge−dipole interactions to locate a thread within the cavity of dibenzo-24-crown-8. We have explored the effect on the binding constant of both the counterion and solvent and were able to illustrate the enhanced binding in nitromethane with a different hydrogen-bonding pattern and a general shortening of all nonbonding interactions in the solid state. Future work will aim to incorporate this new motif into rotaxanes and shuttles.

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Supporting Information Available: The synthesis and spectroscopic data for compounds **1a**−**d**, their pseudorotaxane complexes with dibenzo-24-crown-8, and the crystallograpic files in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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