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PAPER

Unraveling the molecular recognition of "three methylene spacer" bis(benzimidazolium) moiety by dibenzo-24-crown-8: pseudorotaxanes under study†

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"Three methylene spacer" bis(benzimidazolium) derivatives act as a new template for threading dibenzo-24-crown-8 into [2]pseudorotaxanes. In this Article we sought to unveil the difference in the extent of threading of various "three methylene spacer" bis-benzimidazolium moieties based on differences in aromatic methyl substituent positions and anions through the macrocycle dibenzo-24-crown-8. The temperature of the systems were also varied (low temperatures of 240 K and 253 K), when such interwinding of the thread and crown were not detected at room temperature of 308 K. The presence of such threaded complexes was determined based on ^{1}H-NMR initially and finally corroborated by high resolution mass spectrometry and DFT calculations. 2D-NMR experiments ([1]H–[1]H-NOESY) proved to be a very important tool in elucidating the interaction present between the components of the pseudorotaxanes. The dethreading/rethreading process was studied. DFT optimized structures suggest lower energy H-bonding orientations and compare the effect of methyl substituents on the axle.

Introduction

Molecular recognition is widespread. It lies at the heart of enzyme and receptor specificity, is the source of reagent selectivity in organic synthesis and is a current pursuit of bioorganic chemistry. In this last context, practitioners are concerned with complexing small molecules by larger ones with the ultimate intent of performing chemical operations on the complex. The first step involves the matching of shapes between receptor and substrate and the most readily available receptors have had macrocyclic shapes: cyclodextrins,[1] crown ethers [2,3] and cyclophanes.[4] The advent of supramolecular chemistry has aroused the interest of chemists of many different persuasions in compounds such as catenanes and rotaxanes.[5] The synthetic guidance provided by non-covalent bonds has transformed these interlocked molecular compounds from chemical curiosities into a vibrant area of modern-day research. They are now prime candidates for the construction of artificial molecular machines and the fabrication of molecular electronic devices.[6,7] Much effort has been devoted during the past two decades to trying to understand and control the use of non-covalent interactions in the synthesis of catenanes
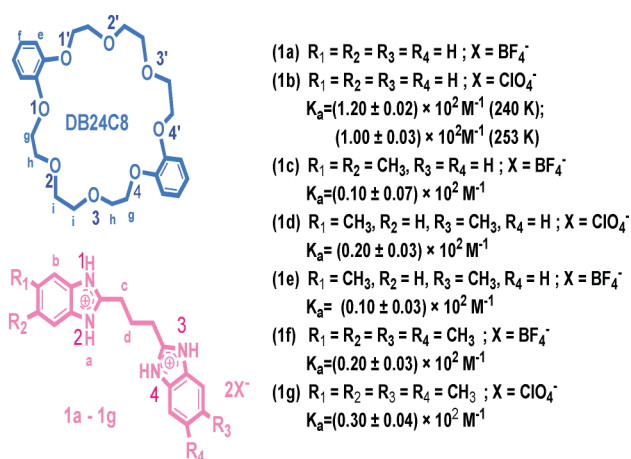
and rotaxanes.[5] Pseudorotaxanes differ from rotaxanes because they lack bulky end groups on the linear unit that prevent dethreading of the cyclic unit.[5] These self-assembly complexes are of special interest to our research because of their unique structural aspects. The term "rotaxane" derives its meaning from the Latin terms for "wheel" and "axle" in which a linear unit is threaded through the cavity of a cyclic unit.[5,8] A [2]rotaxane is a molecule composed of a ring and dumbbell-shaped component. The ring encircles the linear portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers. In contrast, in a [2]pseudorotaxane, at least one of the stoppers on the dumbbell-shaped component is absent with the consequence that dissociation into its two components can occur spontaneously, *i.e.*, it behaves like a 1 : 1 complex. Judicious choice of the constitutions and the sizes of the slippage stoppers and the macrocycle's cavity is essential in order to reach that fine balance between the system being capable of slippage or not.[8] When such a balance is achieved, the macrocyclic component will possess sufficient thermal energy in solution just above room temperature to permit its slow passage over the slippage stopper. In this regard, it has been concluded that a well-defined cut-off between rotaxanes and pseudorotaxanes does not exist.[8]

We sought to develop a new bis-benzimidazole template that would thread through the cavity of dibenzo-24-crown-8 (Scheme 1) by combining the benefits of hydrogen bonding of the bis(benzimidazolium) cations. In our present study we became interested in the "three methylene spacer" bis(benzimidazolium) pseudorotaxane system with dibenzo-24-crown-8, particularly in the differences in association of the different bis-benzimidazole

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(1a) $R_1 = R_2 = R_3 = R_4 = H$; X = BF_4^-

(1b) $R_1 = R_2 = R_3 = R_4 = H$; X = ClO_4^-
$K_a = (1.20 \pm 0.02) \times 10^2$ M^{-1} (240 K);
$(1.00 \pm 0.03) \times 10^2 M^{-1}$ (253 K)

(1c) $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$; X = BF_4^-
$K_a = (0.10 \pm 0.07) \times 10^2$ M^{-1}

(1d) $R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$, $R_4 = H$; X = ClO_4^-
$K_a = (0.20 \pm 0.03) \times 10^2$ M^{-1}

(1e) $R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$, $R_4 = H$; X = BF_4^-
$K_a = (0.10 \pm 0.03) \times 10^2$ M^{-1}

(1f) $R_1 = R_2 = R_3 = R_4 = CH_3$; X = BF_4^-
$K_a = (0.20 \pm 0.03) \times 10^2$ M^{-1}

(1g) $R_1 = R_2 = R_3 = R_4 = CH_3$; X = ClO_4^-
$K_a = (0.30 \pm 0.04) \times 10^2$ M^{-1}

Scheme 1 The "three methylene spacer" axle and DB24C8 wheel. Association constants (K_a) for the pseudorotaxanes are written beside the corresponding thread. The temperatures of the experiment for the pseudorotaxanes formed at temperatures other than room-temperature (308 K) are given within parenthesis.

salts of 2, 2′-(1, 3-propanediyl) bis-1*H*-benzimidazole with the host crown ether.

Results and discussion

Previously published pseudorotaxane formation with two methylene spacer bis(benzimidazolium) system and dibenzo-24-crown-8 exhibited rigorous π-stacking as reported by Clarkson *et al.* as well as Tiburcio *et al.*[9,10] There are no reports of pseudorotaxane formation with "three methylene spacer" bis(benzimidazolium) system and dibenzo-24-crown-8, although there are some reports of such complexations on the imidazolium systems.[6h,11,12] In this work, we have established for the first time, that the "three methylene spacer" bis(benzimidazolium) threads the cavity of dibenzo-24-crown-8 even in the absence of aromatic π-stacking.

Solutions of **1a**$(BF_4)_2$ and DB24C8 and **1b**$(ClO_4)_2$ and DB24C8 (Scheme 1) gave no detectable NMR changes at room temperature (308 K). We proceeded with a low temperature study for one such representative system. Separate peaks for threaded and unthreaded components can be found at lower temperatures for **1b** $\subset$ DB24C8$(ClO_4)_2$ (Fig. 1). Between pseudorotaxanes **1c** $\subset$ DB24C8$(BF_4)_2$ and **1e** $\subset$ DB24C8$(BF_4)_2$ (Scheme 1) with similar anions, similar methylene spacers and equal number of methyl substituents on the thread, the one with an unsymmetrical bis(benzimidazolium) thread gives a higher association constant value. We carried out this complexation study keeping the NMR solvent d^3-acetonitrile constant.

Initially, we also examined the threading possibilities of salts **1e** and **1g** with dibenzo-18-crown-6 and ended up with absolute no pseudorotaxane formation with the salts **1e** and **1g**.[11]

The 1 : 1 stoichiometry of these new [2]pseudorotaxanes was determined from direct integration of the ¹H NMR spectrum. Also, a Job plot of **1g** $\subset$ DB24C8$(ClO_4)_2$ in d^3-acetonitrile based on proton NMR data demonstrated 1 : 1 host–guest complexation (Fig. 2). Another evidence of the 1 : 1 [2] pseudorotaxane structure comes from the ESI mass experiments and HR-ESI mass experiments. For example, in the ESI mass spectrum of an equimolar mixture of **1c** and DB24C8, an intense peak for 1 : 1 complex [{**1c** $\subset$
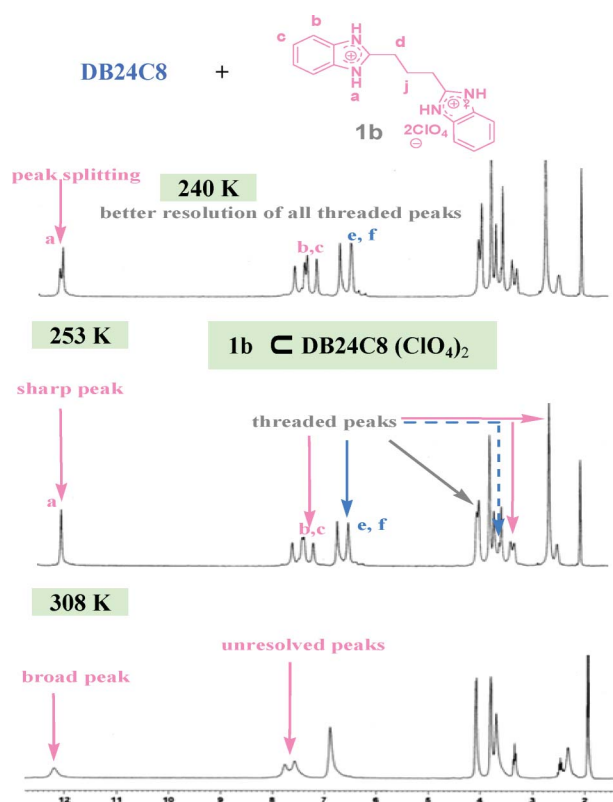

Fig. 1 Stacked ¹H NMR (400 MHz) spectra of the host DB24C8 and guest (**1b**) species that contains a fraction of these compounds in a complexed state **1b** $\subset$ DB24C8$(ClO_4)_2$ (Scheme 1) at temperatures of 308 K, 253 K and 240 K. **1b** and DB24C8 were present in 1 : 1 ratio $(2.0 \times 10^{-2}$ M) in CD_3CN. **¹H NMR (at 240 K)**: δ 12.48–12.42 (br s, 8H, *a* and threaded *a*), 7.76 (br s, 4H, *b*), 7.63–7.52 (m, 8H, *c* and threaded *b*), 7.33 (br s, 4H, threaded *c*), 6.84 (s, 8H, *e* and *f*), 6.62 (br s, threaded *e* and threaded *f*), 4.04–3.98 (m, 16H, *g* and threaded *g*), 3.78 (br s, 16H, *h* and threaded *h*), 3.69 (br s, 8H, *i*), 3.58–3.55 (m, 8H, threaded *i*), 3.36–3.27 (m, 8H, *d* and threaded *d*), 2.67 (m, 2H, *j*) and 2.42 (m, 2H, threaded *j*).
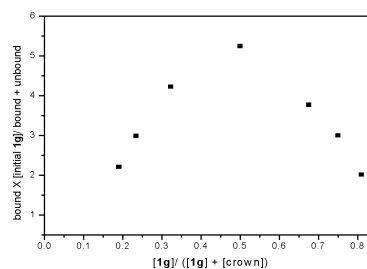

Fig. 2 Job plot showing 1 : 1 stoichiometry of the complex between **1g** and dibenzo-24-crown-8 in d^3-acetonitrile. The sum of the initial concentrations between the host crown and the guest **1g** was kept at 4.0×10^{-2} M.

DB24C8} − H+]+ was found (m/z 753.41). Similarly in the HR-ESI mass spectra of the pseudorotaxane **1g** $\subset$ DB24C8$(ClO_4)_2$, the peak for 1 : 1 host–guest complex [{**1g** $\subset$ DB24C8} − H^+]$^+$ was observed (m/z 781.4167).

Even if the association constants of **1c** $\subset$ DB24C8$(BF_4)_2$, **1d** $\subset$ DB24C8$(ClO_4)_2$, **1e** $\subset$ DB24C8$(BF_4)_2$, **1f** $\subset$ DB24C8 $(BF_4)_2$ and **1g** $\subset$ DB24C8$(ClO_4)_2$ are not as high as the dibenzo-24-crown-8 complexes reported in literature,[9,10] the solubility

of these "three methylene spacer" bis(benzimidazolium) axles are higher than the previously reported recognition units. Recently Noujeim *et al.* demonstrated that in an equimolar solution, the initial concentration and the association constant have the same effect on the ratio of [bound]/[unbound].[12] The association constant of a bis(benzimidazolium)ethane and dibenzo-24-crown-8 is approximately 5×10^2 at 25 °C, almost 10 times higher than those reported by us at 35 °C. The solubility of bis(benzimidazolium)ethane in acetonitrile at 35 °C is almost 15 times lower than our "three methylene spacer" bis(benzimidazolium) compounds (solubility chart, see ESI†). Thus, the ratio of [bound benzimidazolium]/[unbound benzimidazolium] at a saturation concentration is almost equivalent. Moreover, the low association constants reported here are very much in line with previous reports for the bis(imidazolium) salts with dibenzo-24-crown-8. For example 3 and 4 carbon spacers [6h] reported K_a values of 4.3 and 2.2 M^{-1} respectively and K_a values of 56 and 120 M^{-1} for single methylene linked bis(imidazolium) salts with dibenzo-24-crown-8, at room temperature.[11]

^{1}H NMR spectroscopy is a very useful tool for studying translational motion in pseudorotaxanes.[5c,5d,5k,5n,13] The complexes can be observed very easily by ^{1}H NMR. The rate of complexation is slow relative to the NMR time scale and the complexed components can be quantified by integration of the signals in the ^{1}H NMR spectrum. Complex $1g \subset$ DB24C8(ClO$_4$)$_2$ (Scheme 1) gives very distinct and sharp peaks for both the aliphatic and the aromatic region in the ^{1}H NMR spectrum. This system is very unlike that of the previously quoted complexation of two methylene spacer bis(benzimidazolium) system and dibenzo-24-crown-8 [9,10] where there was a very severe overlapping of peaks in the aliphatic region causing difficulty in assignment of ^{1}H NMR signals. Comparing the spectra of the pseudorotaxane $1g \subset$ DB24C8(ClO$_4$)$_2$ (Scheme 1) with both the crown and the free salt (Fig. 3), it is seen that there is an upfield shift in the aromatic
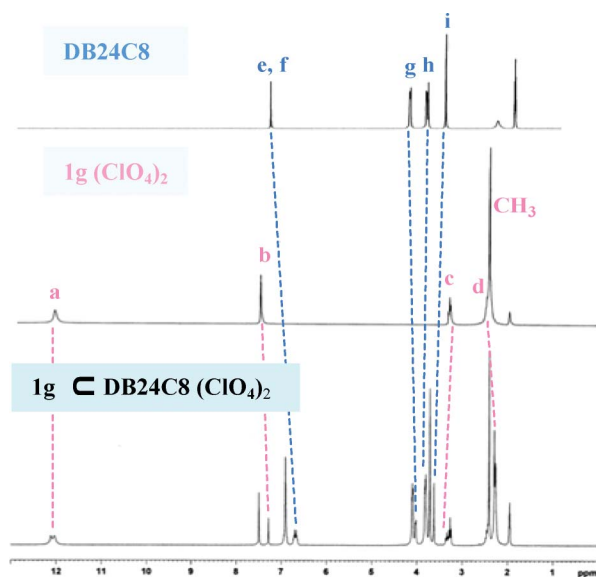
signals of both the crown and the thread due to inclusion induced shielding effects. The resonances due to the aromatic CH of the axle at δ 7.49 shifts to δ 7.28 and for the crown, the multiplet signal at δ 6.94–6.87 shifts upfield as multiplet to δ 6.73–6.64 (spectral data, see ESI†). In all possibilities, the macrocyclic crown adopts an optimum conformation for minimizing repulsive interactions and maximizing H-bonding interactions.

For $1b \subset$ DB24C8(ClO$_4$)$_2$ (Fig. 1), at 308 K, even though extra peaks for threading are not detected, we see substantial broadening of peaks compared to the free axle and crown, suggesting a more rapid rate of association/dissociation. The bulk of at least one methyl group in each aromatic ring of the thread is essential for detection of extra peaks of this [2]pseudorotaxane at room-temperature. Extra peaks for complexation are observed at 253 K and the peaks sharpen considerably as the temperature is lowered to 240 K for both the aromatic as well as the aliphatic region in the ^{1}H NMR spectrum.

The NOESY spectrum of $1f \subset$ DB24C8(**BF$_4$**)$_2$ (Fig. 4) gives correlation between the threaded methylene protons of the crown (H$_g$, H$_h$ and H$_i$) and the threaded aromatic protons of the thread (H$_b$). However, there seems to be no NOE correlation between the aromatic signals of the thread (H$_b$) and the crown (H$_e$ and H$_f$). This implies that the phenyl ring of the thread and phenyl ring of the crown are not parallel to each other and close enough for NOE to occur. In fact the "three methylene spacer" bis(benzimidazolium) axle dives headlong into the cavity of dibenzo-24-crown-8 avoiding the latter's aromatic rings; very much unlike those reported previously for bis(benzimidazolium)ethane pseudorotaxanes with dibenzo-24-crown-8 by Clarkson *et al.* and Tiburcio *et al.* [9,10] Thus, the stabilization present in our studied pseudorotaxanes is mainly H-bonding. Our DFT calculations also reveal a similar picture with no π-stacking between the host and the guest. Distances between the threaded aromatic protons of our "three methylene spacer" bis(benzimidazolium) axles and the methylene protons of dibenzo-24-crown-8 range from 3 Å–5 Å for thread locations where the benzimidazole proton hydrogen bonds to an
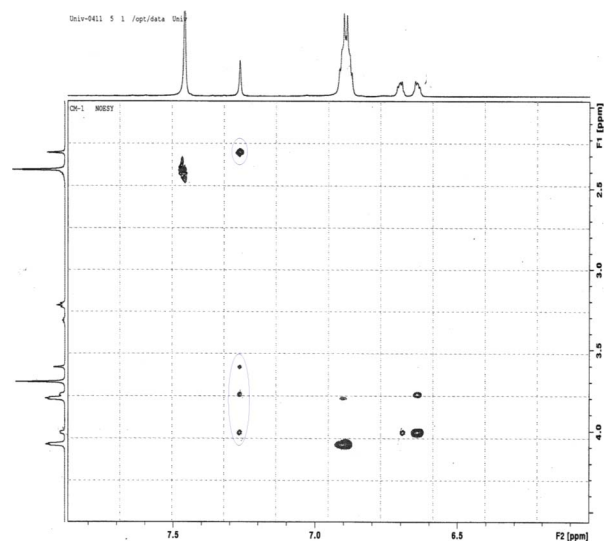

Fig. 3 Stacked ^{1}H NMR spectra (CD$_3$CN) of the host DB24C8, the guest (**1g**) and $1g \subset$ DB24C8(ClO$_4$)$_2$ (Scheme 1). Dotted lines connect the original peaks with their threaded counterparts. **1g** and DB24C8 were mixed in 1:1 ratio (2.0×10^{-2} M) in CD$_3$CN and the ^{1}H NMR taken immediately at room-temperature (308 K).

Fig. 4 NOESY spectrum for $1f \subset$ dibenzo-24-crown-8 (BF$_4$)$_2$ (Table 1). **1f** and dibenzo-24-crown-8 were present in 1:1 ratio (2.0×10^{-2} M each) in CD$_3$CN. NOE correlations between the threaded C*H* of the axle and the threaded methylene of the crown are indicated by the blue circles.

O of the crown. For example, in the DFT optimized structure corresponding to $1f \subset DB24C8$, the minimum distance between an aromatic CH (H_b) and a methylene proton of the crown H_g (O_1–H_g) is 3.175 Å. Along the same side, the distance between H_b and H_h (O_2–H_h) is 4.216 Å and that between H_b and H_i (O_3–H_i) is 3.751 Å. On the opposite end of the thread, there are $H_b \cdots H_g$ distances of 3.949 Å and 3.475 Å near the benzimidazole hydrogen bond bridge (for further details of the DFT calculations, see ESI†).

In order to investigate the dethreading/rethreading process of this new [2]pseudorotaxane system by pH control, we chose an equimolar solution of $1f \subset DB24C8(BF_4)_2$ (Fig. 5) in CD_3CN. Dethreading occurred when ~0.9 equivalents of piperazine ($C_4H_{10}N_2$) was added. We did not add an exactly equivalent amount of base since the resulting free bis-$1H$-benzimidazole was completely insoluble in CD_3CN. Thus the peak that we see at δ 7.44 after addition of the base piperazine is for the salt $1f$ and not the free benzimidazole. Even so, the threaded peaks vanished which is an unambiguous confirmation of the dethreading. This process can be reversed quantitatively by adding ~1.8 equivalents
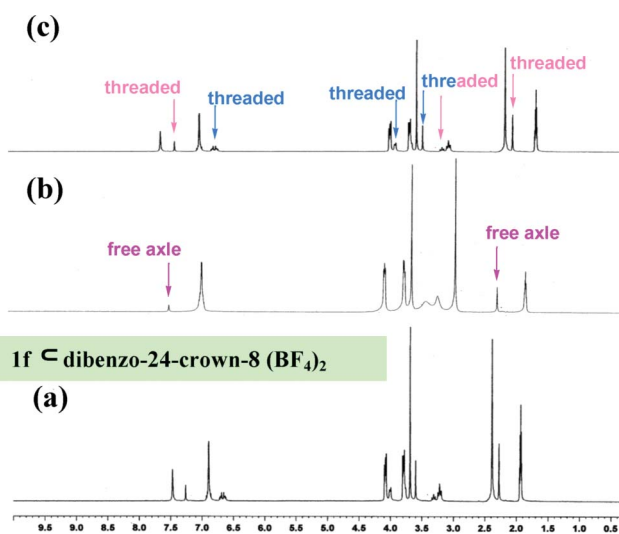

Fig. 5 Stacked ^1H NMR spectra for dethreading/rethreading equilibrium of $1f \subset$ dibenzo-24-crown-8 (BF_4)$_2$. (a) Original threading for $1f \subset$ dibenzo-24-crown-8 (BF_4)$_2$. The concentrations of $1f$ and dibenzo-24-crown-8 were 2.0 ×10^{-2} M each in CD_3CN. (b) $1f$ + dibenzo-24-crown-8 + piperazine, present in 1:1:0.9 ratios. Concentration of piperazine was 1.8×10^{-2} M. (c) $1f$ + dibenzo-24-crown-8 + piperazine + CF_3CO_2H, present in 1:1:0.9:1.8 ratios. Concentration of CF_3CO_2H was 3.6×10^{-2} M.
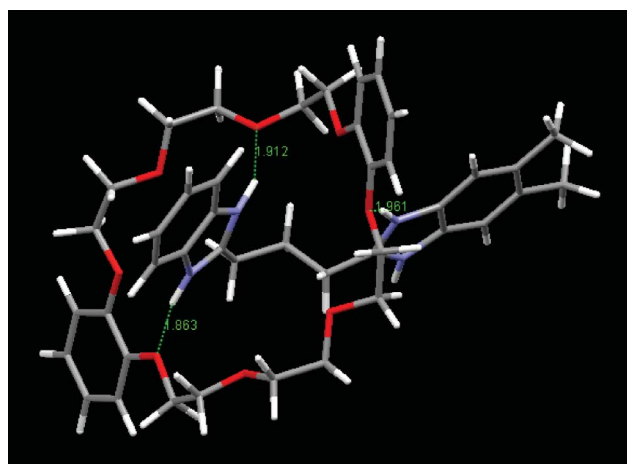
CF_3CO_2H, when the original threaded peaks reappear, indicating the formation of [2]pseudorotaxane once more.

Computational studies

DFT calculations using the hybrid functional B3LYP and a 6-31G**++ basis set were applied to some selected pseudorotaxanes. The 6-31G**++ basis set was chosen because of the need to model hydrogen bonding interactions.[14] Optimized DFT geometries suggest conformations for H-bonding of the bis(benzimidazolium) moieties to O-atoms on the crown ether. Furthermore, relative DFT energies allow a comparison of the stability of isomers where methyl substituents are in different positions. Table 1 summarizes eight optimized DFT structures of the crown and thread structure isolated from anions and solvent. Three H-bonds linking the thread to O-atoms on the crown *via* benzimidazolium protons were present in all cases, irrespective of the number of methyl substituents on the thread. DFT calculations compare two basic modes of binding of the thread to the crown, one in which a hydrogen bonding bridge is directed across the crown ($O_{1'}$ to O_3) and the second with a hydrogen bond bridge along one side (O_1 to O_4). Table 1 shows that the difference in energy between Case **G** (O_1 to O_4) and Case **H** ($O_{1'}$ to O_3), as well as the difference between Case **A** ($O_{1'}$ to O_3) (Fig. 6) and Case **B** (O_1 to O_4) (Fig. 7) are 15.3 kJ, with O_1 to O_4 being energetically preferred. In higher

Fig. 6 Energy minimized structure of DFT Case **A**; a higher energy conformation compared to Case **B** (Table 1) for $1c \subset DB24C8$ (Scheme 1) $O_{1'}$ to O_3 H-bridge is present.

Table 1 DFT optimized structures

$Y \subset DB24C8$	DFT	ΔE (kJ)	R_1	R_2	R_3	$R_4{}^c$	H-bond bridge
1c	**A**	16.16	H	H	CH_3	CH_3	$O_{1'}$ to O_3
1c	**B**	1.08	H	H	CH_3	CH_3	O_1 to O_4
1c	**C**	5.69	CH_3	CH_3	H	H	O_1 to O_4
1d,1e	**D**	1.39	H	CH_3	CH_3	H	O_1 to O_4
1d,1e	**E**^{a}	0.00	H	CH_3	H	CH_3	O_1 to O_4
1f,1g	**F**	—	CH_3	CH_3	CH_3	CH_3	O_1 to O_4
1a,1b	**G**^{b}	0.00	H	H	H	H	O_1 to O_4
1a,1b	**H**	15.31	H	H	H	H	$O_{1'}$ to O_3

^{a} **E** is the lowest conformation of possibilities when there are two H and two CH_3 substituents on the phenyl ring of the thread. ^{b} **G** is the lowest conformation when all substituents on the phenyl ring of the thread are H. ^{c} R_4 side is not H-bonded to the crown.

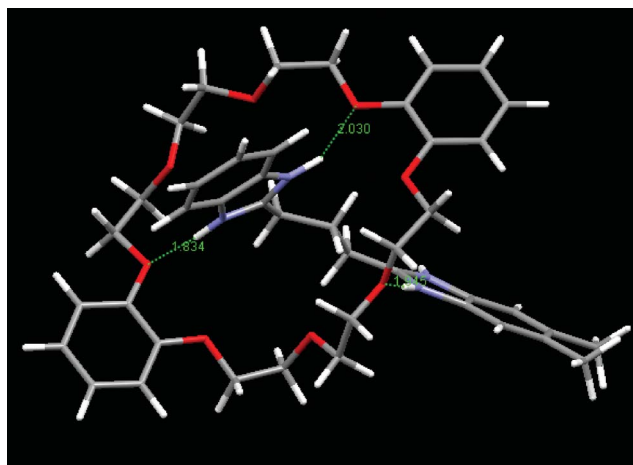This journal is © The Royal Society of Chemistry 2012

Fig. 7 Energy minimized structure of DFT Case **B**; the lowest energy conformation of **1c** ⊂ DB24C8 (Scheme 1) O_1 to O_4 H-bridge stabilizes the system by about 15 kJ compared to Case **A**.

energy conformations ($O_{1'}$ to O_3 bridging), the bridge distance and the $O_2 \cdots O_{2'}$ nonbonded distance across the crown, are smaller by 0.2–0.3 Å (for DFT geometry details, see ESI†).

All isomers with two H and two CH_3 substituents on the phenyl ring of the thread were geometry optimized and their DFT energies compared. There are only small energy differences (about 1 kJ) between Cases **B**, **D** and **E** (Table 1). In Case **C** (Fig. 8), there are two CH_3 substituents on the thread on the same side as the bridging benzimidazolium ring and the energy is 4 to 5 kJ higher than the other three cases. Although the lowest energy isomer, Case **E**, has the shortest H-bond (1.826 Å) the geometries of **B**, **C**, **D** and **E** are not otherwise significantly different (for details see ESI†).
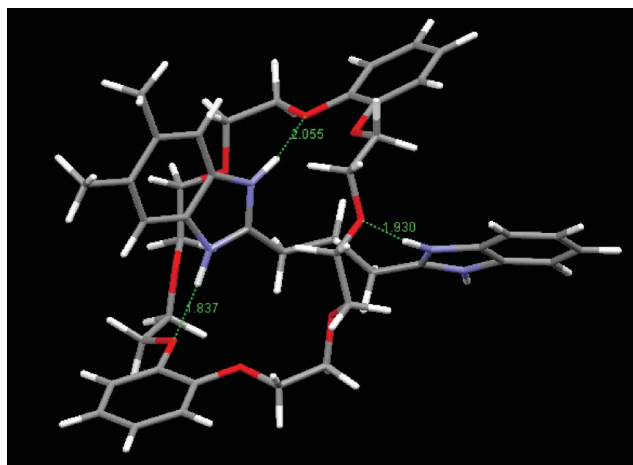

Fig. 8 Energy minimized structure of DFT Case **C**; the highest energy (by 5.69 kJ, Table 1) of all isomers with 2 CH_3 and 2 H substituents on the phenyl ring (thread). Both the CH_3 groups are on the same side as the H-bond benzimidazolium bridge. The lower energy O_1 to O_4 H-bridge is present in this structure.

Conclusion

The DFT structures, association constants and NMR results, support our conclusion that "three methylene spacer"

bis(benzimidazolium) [2]pseudorotaxanes do occur. In addition, DFT calculations indicate that a conformation with one half of the bis(benzimidazolium) axle bridging along one side of the crown are significantly preferred over conformations which span across the crown. Further, the DFT calculations show that there is no π-stacking, and the NOESY experiment suggests the same. Hydrogen-bonding is dominant in the threaded conformations and the calculations suggest that three hydrogen bonds can be formed.

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