

[2]Rotaxane molecular shuttles employing 1,2-bis(pyridinium)ethane binding sites and dibenzo-24-crown-8 ethers†

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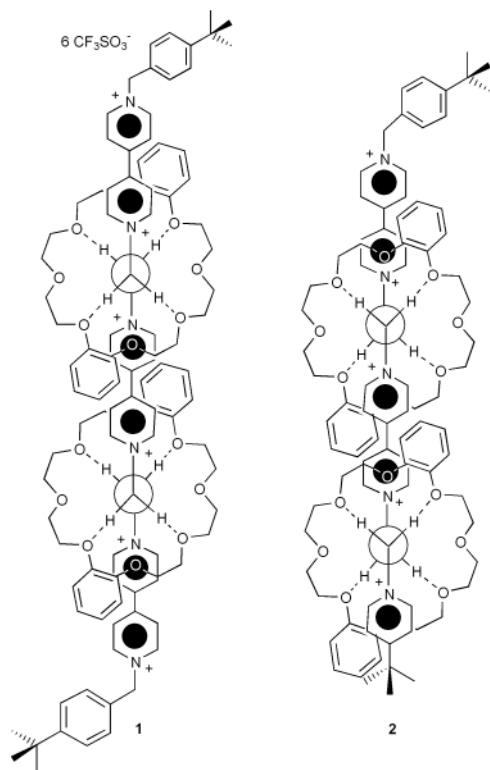
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Symmetrical and unsymmetrical axles containing two binding sites of the 1,2-bis(pyridinium)ethane type are threaded with a single molecule of dibenzo-24-crown-8 ether (DB24C8) resulting in [2]rotaxane molecular shuttles that display translational isomerism.

One of the most intriguing developments in supramolecular chemistry is the ability to construct mechanically linked molecular systems that display switching properties resulting from the relative positioning of the internal components of the supermolecule.¹ An elegant example of this is the [2]rotaxane molecular shuttle pioneered by Stoddart *et al.* in which a single 'wheel' component can occupy either of two binding sites on a dumbbell shaped 'axle'.²

We have recently reported the synthesis of symmetrical and unsymmetrical [3]rotaxanes, **1** and **2**, employing extended axles



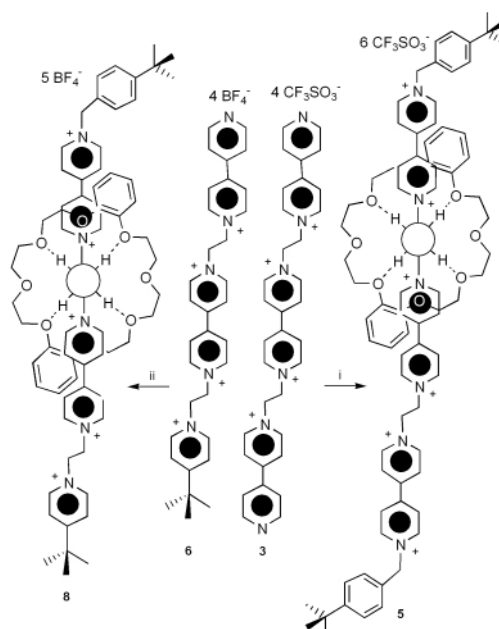
containing two binding sites of the 1,2-bis(pyridinium)ethane type each occupied by a dibenzo-24-crown-8 ether (DB24C8) molecule.³ Although these [3]rotaxanes are saturated and therefore display no translational isomerism, it is possible to prepare [2]rotaxane molecular shuttles with this template and this work is reported herein.

The [2]rotaxanes **5** and **8**† were prepared by mixing **3** and **6** respectively with two equivalents of DB24C8 in MeCN solution

† Electronic supplementary information (ESI) available: ¹H NMR chemical shifts. See <http://www.rsc.org/suppdata/cc/b0/b004784h/>

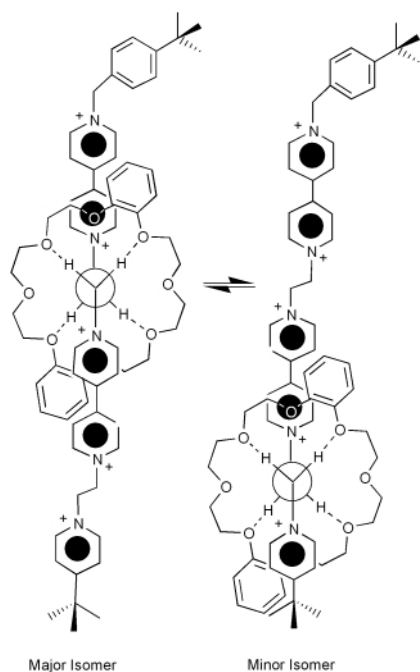
followed by a 2-fold excess of the required equivalents of *tert*-butylbenzyl bromide (Scheme 1).⁴ The mixtures were stirred at room temperature for 2 days, the salts precipitated by the addition of Et₂O and the products isolated as the chloride salts by column chromatography on silica gel (MeOH/MeNO₂/2.0 M NH₄Cl(aq), 3:1:1). Anion exchange with NaCF₃SO₃ and NaBF₄ respectively in aqueous solution produced **5** and **8** in overall yields of 13 and 19% as orange crystalline solids, which were soluble in organic solvents such as MeCN, MeNO₂ and CH₂Cl₂.

Noncovalent interactions between axle and wheel can be inferred by significant chemical shift differences ($\Delta\delta$) in the solution (MeCN-*d*₃) ¹H NMR spectra of **5** and **8** when compared to the respective axles **4** and **7** and free DB24C8.⁵ C–H...O hydrogen bonds from axle protons to crown ether O-atoms are evident from the significant *downfield* shifts for all α -pyridinium and ⁺NCH₂ protons, while π -stacking between the electron-rich catechol and electron-poor pyridinium rings is indicated by *upfield* shifts observed for the β -pyridinium protons and crown aromatic protons. There exists the possibility of two translational isomers; *i.e.* the crown ether can *shuttle* from one binding site to the other. That this dynamic phenomenon occurs is supported by the fact that only one set of resonances is observed at room temperature and there is a slight exchange broadening of the axle protons interacting with the crown oxygen atoms. It was concluded that the crown ether is undergoing fast exchange between the two binding sites and the observed room temperature chemical shifts for **5** and **8** are



Scheme 1 Reagents and conditions: i, 4 equiv. of 4-*tert*-butylbenzyl bromide, 2 equiv. of DB24C8, MeCN, RT, 2 days, SiO₂ (MeOH/MeNO₂/2.0 M NH₄Cl(aq), 3:1:1), *R*_f = 0.35, NaCF₃SO₃(aq), 13%; ii, 2 equiv. of 4-*tert*-butylbenzyl bromide, 2 equiv. of DB24C8, MeCN, RT, 2 days, SiO₂ (MeOH/MeNO₂/2.0 M NH₄Cl(aq), 3:1:1), *R*_f = 0.31, NaBF₄(aq), 19%.

weighted averages of the resonances attributable to the individual occupied and vacant sites.



The ^1H NMR spectrum of **5** coalesced at 293 K yielding a rate of exchange between the equally populated binding sites of 320 Hz with $\Delta G^\ddagger = 57.5 \text{ kJ mol}^{-1}$. Similarly, **8** reached coalescence at 273 K with an exchange rate of 222 Hz and $\Delta G^\ddagger = 54.3 \text{ kJ mol}^{-1}$. For this unsymmetrical [2]rotaxane, the aryl crown ether resonances were used to determine the occupancy of each site. Integration of these signals at 243 K yielded a 2:1 ratio of isomers with the bis(4,4'-bipyridinium)ethane site being favoured. This preference is likely due to two factors: (i) the 4,4'-bipyridinium rings are the most electron-poor resulting in more favourable π -stacking and (ii) there are steric problems caused by the *t*Bu-pyridinium group which disfavour π -stacking.

An X-ray crystal structure determination \S of **8** verified the nature of the interactions observed in solution; a ball-and-stick representation is shown in Fig. 1. The DB24C8 ring is threaded on the unsymmetrical axle such that the S-shaped crown ether ring occupies the more favoured bis(4,4'-pyridinium) moiety. The unoccupied bis(pyridinium)ethane group adopts a *gauche* conformation in the solid state.

It has been demonstrated that the 1,2-bis(pyridinium)ethane/24-crown-8 ether templating motif can be used for the synthesis of symmetrical and unsymmetrical molecular shuttles. Future work will focus on controlling this switching process by external perturbations.

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Notes and references

\ddagger All new compounds were successfully characterized by ^1H NMR spectroscopy (500 MHz, 298 K) and LSI-MS or ESI-MS. NOESY experiments were used to make individual ^1H NMR assignments. Synthetic note: >3 equivalents of DB24C8 produces exclusively [3]rotaxane; 4 <3 equivalents of DB24C8 produces a mixture of [3]rotaxane, [2]rotaxane and thread with the optimum yield of [2]rotaxane produced with 2 equivalents.

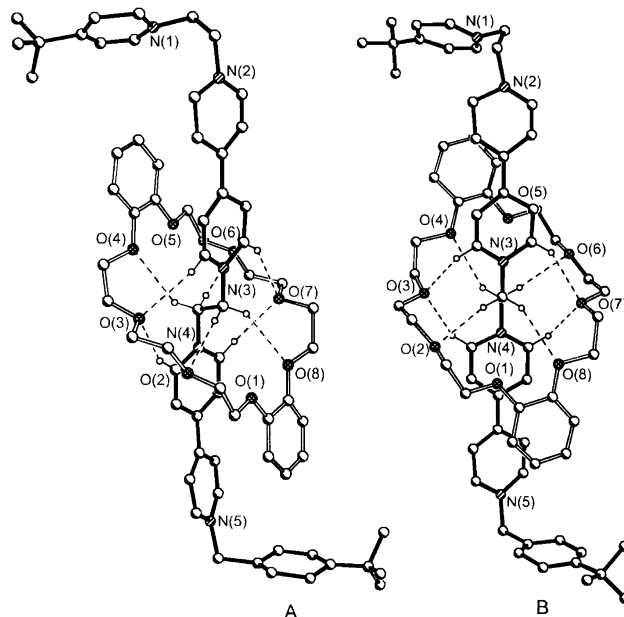


Fig. 1 Ball and stick representations of the X-ray crystal structure of the [2]rotaxane molecular shuttle **8**. (A) showing the basic numbering scheme and (B) a view down the ethane C(22)–C(23) bond. Significant N \cdots O distances (\AA): N(3) \cdots O(4) 3.54, N(3) \cdots O(5) 3.48, N(4) \cdots O(1) 3.56, N(4) \cdots O(8) 3.55. C–H \cdots O distances (\AA) and angles ($^\circ$): H(19A) \cdots O(3) 2.63, C(19)–H(19A) \cdots O(3) 135.0; H(20A) \cdots O(7) 2.47, C(20)–H(20A) \cdots O(7) 151.2; H(22A) \cdots O(2) 2.52, C(22)–H(22A) \cdots O(5) 163.5; H(22B) \cdots O(8) 2.70, C(22)–H(22B) \cdots O(8) 148.7; H(23A) \cdots O(4) 2.65, C(23)–H(23A) \cdots O(4) 147.3; H(23B) \cdots O(6) 2.59, C(23)–H(23B) \cdots O(6) 166.1; H(24A) \cdots O(3) 2.33, C(24)–H(24A) \cdots O(3) 155.3; H(28A) \cdots O(7) 2.57, C(28)–H(28A) \cdots O(2) 138.3.

Selected data for 5: ^1H NMR (CD_3CN): δ 9.22 (m, 8H), 9.00 (d, 4H, $J = 7.63$ Hz), 8.35 (br, 8H), 8.28 (d, 4H), 7.57 (d, 4H, $J = 8.72$ Hz), 7.47 (d, 4H), 6.68 (m, 4H), 6.49 (m, 4H), 5.81 (s, 4H), 5.48 (br, 8H), 4.03 (m, 24H), 1.33 (s, 18H). ESI-MS: m/z 2012.7 ($[\text{M} - \text{OTf}]^+$). **8:** ^1H NMR (CD_3CN): δ 9.28 (br, 4H), 9.12 (br, 2H), 9.01 (d, 2H), 8.83 (br, 2H), 8.28 (br, 8H), 8.06 (br, 2H), 7.59 (d, 2H, $J = 8.29$ Hz), 7.50 (d, 2H), 6.69 (m, 4H), 6.54 (m, 4H), 5.83 (s, 2H), 5.55 (br, 4H), 5.35 (br, 2H), 5.28 (br, 2H), 4.06 (m, 24H), 1.38 (s, 9H), 1.34 (s, 9H). ESI-MS: m/z 1446.6 ($[\text{M} - \text{BF}_4]^+$).

\S *Crystal data for 8:* $\text{C}_{68}\text{H}_{84}\text{B}_5\text{F}_{20}\text{N}_5\text{O}_8$, $M = 1533.45$, monoclinic, $a = 40.78(2)$, $b = 15.808(5)$, $c = 12.336(4)$ \AA , $\beta = 98.48(2)^\circ$, $U = 7866(5)$ \AA^3 , $T = 293(2)$ K, Cc , $Z = 4$, $\mu = 0.115 \text{ mm}^{-1}$, 10068 independent reflections [$R(\text{int}) = 0.0631$], $R1 = 0.0997$, $wR2 = 0.2451$ [$I > 2\sigma(I)$], $R1 = 0.1982$, $wR2 = 0.2999$ [all data], Goodness-of-fit (F^2) = 0.929. Data were collected on a Siemens SMART CCD instrument and solutions performed using the SHELXTL 5.03 Program Library for Structure and Solution and Molecular Graphics, Siemens Analytical Instrument Division, Madison, WI, USA, 1997. CCDC 182/1753. See <http://www.rsc.org/suppdata/cc/b0/b004784h/> for crystallographic files in .cif format.

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