[3]Rotaxanes employing multiple 1,2-bis(pyridinium) ethane binding sites and dibenzo-24-crown-8 ethers†

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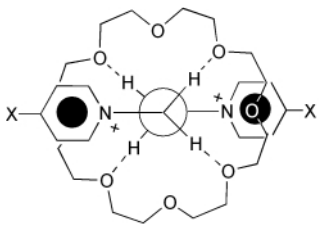
Two binding sites of the 1,2-bis(pyridinium)ethane type are built into an extended axle on to which two molecules of dibenzo-24-crown ether (DB24C8) can thread to produce the first examples of [3]rotaxanes employing this templating motif.

[2]Pseudorotaxanes are commonly used as precursors for the formation of permanently interlocked [2]rotaxanes by addition of 'stopper' components which are bulky enough to prevent unthreading.[1,2] We have recently demonstrated that various 1,2-bis(pyridinium)ethane dications will thread through the 24-membered crown ethers 24C8, B24C8 and DB24C8 to produce a new series of [2]pseudorotaxanes **1a**–**e**.[3]

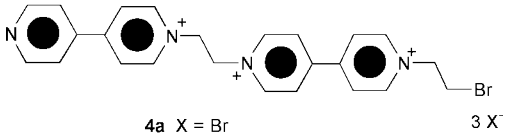


1a X = H
1b X = Me
1c X = Ph
1d X = CO_2Et
1e X = py

For a 1,2-bis(4,4′-bipyridinium)ethane **1e**, (X = py) axle and a DB24C8 wheel, we have shown that the [2]pseudorotaxane is easily converted to a permanently interlocked [2]rotaxane.[4] This was achieved either by alkylation at the terminal pyridine nitrogen atoms with bulky *tert*-butylbenzyl groups, **2**, or stoppering with appropriately large organopalladium fragments, **3**.

Herein, we describe the synthesis of both symmetrical and unsymmetrical [3]rotaxanes by employing extended axles containing two binding sites for a dibenzo-24-crown-8 ether molecule. Although the rotaxanes presented here are saturated and therefore display no translational isomerism, such higher order [*n*]rotaxanes (*n* > 2) are not nearly as prevalent as simpler [2]rotaxanes.[5] The study of these multiple-sited systems is important for the future development of molecular devices such as those based on Stoddart's notion of a molecular shuttle.[6,7]

The key synthetic intermediate in this work is **4b**, which can be used to alkylate a pyridine derivative to create a second bis(pyridinium)ethane binding site.[8] We reacted **4b** with 4-*tert*-butylpyridine, to produce **5** (Scheme 1), since the Bu^t group can act directly as a stopper and with 4,4-bipyridine, to yield **6** (Scheme 2), as this provides a terminal pyridine moiety. Subsequent monoalkylation of **5** and dialkylation of **6** with *tert*-butylbenzyl bromide yields the dumbbell shaped axles **7** and **8**.

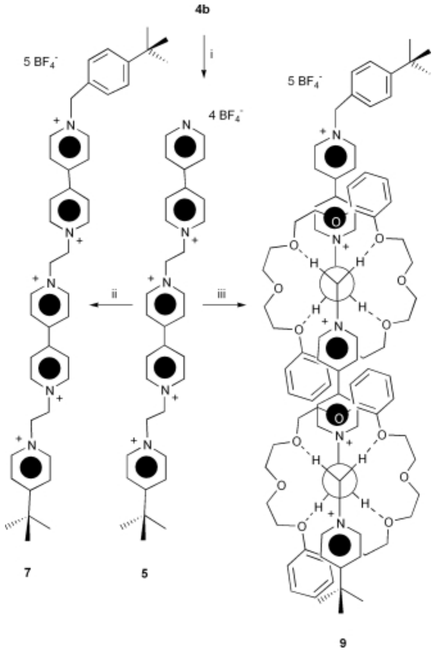


4a X = Br
4b X = BF_4

The [3]rotaxanes **9** and **10** were prepared by mixing **5** and **6**, respectively, with four equivalents of DB24C8 in MeCN solution followed by a two-fold excess of the required equivalents of *tert*-butylbenzyl bromide.‡

Non-covalent interactions between axle and wheel are evident from significant chemical shift differences in the solution (CD_3CN) ^1H NMR spectra of **9** and **10** when compared to **7**, **8** and free DB24C8. A network of *sixteen* C–H···O hydrogen bonds from axle protons to crown ether O-atoms is evident in both **9** and **10** from the significant *downfield* shifts for all α^+-pyridinium (0.30–0.36 ppm) and $^+NCH_2$ protons (0.21–0.42 ppm). In addition, π-stacking between the electron-rich catechol and electron-poor pyridinium rings is indicated for both rotaxanes by *upfield* shifts observed for the β-pyridinium protons (0.25–0.56 ppm) and crown aromatic protons (0.17–0.42 ppm). Also, since the *tert*-butylpyridinium stopper for the asymmetric [3]rotaxane **9**, is one aromatic ring closer to the center of the molecule, we also observe a C–H···π interaction between the *tert*-butylpyridinium methyl protons and the crown aromatic group ($\Delta\delta = -0.24$ ppm). Unfortunately, the different environments of the DB24C8 catechol rings could not be distinguished by low temperature ^1H NMR spectroscopy owing to the facile nature of the interconversion process.

An X-ray crystal structure determination§ of **10** verified the nature of the interactions observed in solution (Fig. 1). The two DB24C8 rings are threaded on to the centrosymmetric tris(bi-



Scheme 1 *Reagents and conditions*: i, 4-*tert*-butylpyridine, MeCN, 60 °C, 3 days, $NaBF_4$(aq), 45%; ii, 4-*tert*-butylbenzyl bromide, MeCN, 60 °C, 3 days, $NaBF_4$(aq), 25%; iii, 4-*tert*-butylbenzyl bromide, DB24C8, MeCN, room temp., 2 days, SiO_2 [MeOH–$MeNO_2$–2.0 M NH_4Cl(aq), 3:1:1], R_f = 0.47, $NaBF_4$(aq), 18%.

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† Dedicated to Professor Christopher J. Willis on the occasions of his retirement and 66th birthday.

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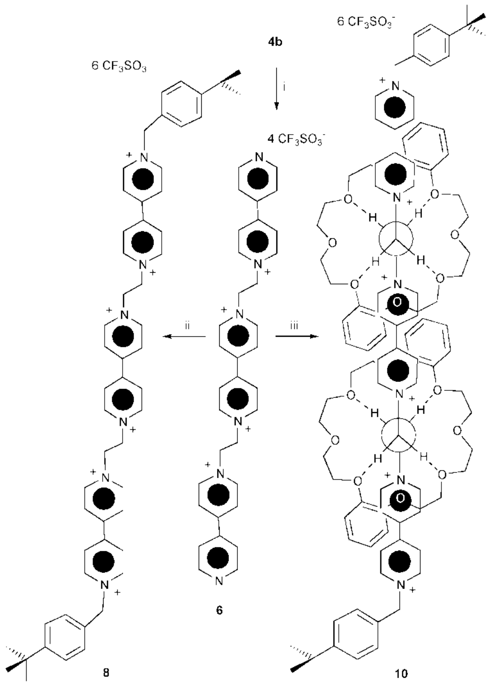

Scheme 2 *Reagents and conditions*: i, 4,4′-bipyridine, $MeNO_2$, 60 °C, 3 days, $NaCF_3SO_3$(aq), 18%; ii, 4-*tert*-butylbenzyl bromide, $MeNO_2$, 60 °C, 24 h, $NaCF_3SO_3$(aq), 22%; iii, 4-*tert*-butylbenzyl bromide, DB24C8, MeCN, room temp., 2 days, SiO_2 [MeOH–$MeNO_2$–2.0 M NH_4Cl(aq), 3 : 1 : 1], R_f = 0.44, $NaCF_3SO_3$(aq), 15%.

pyridinium) axle such that the S-shaped crown ether rings stack stepwise over the three sets of bipyridinium rings. A unique feature of this particular [3]rotaxane design is that the central bipyridinium ring is sandwiched between two aromatic rings from separate crown ether wheels. This has the potential to allow direct communication between the two binding sites through the wheel–axle–wheel overlap. The centrosymmetric [3]rotaxane **10** shows $N^+\cdots O$ interactions ranging from 3.51 to 3.65 Å and *sixteen* C–H···O hydrogen bonds with CH···O distances in the range 2.26–2.77 Å. The orange–red colour of the solid material and the UV absorption data in MeCN solution are consistent with charge transfer interactions between the electron-rich rings of the crown ether and the electron-poor rings of the bipyridinium fragments.

It is clear that the 1,2-bis(pyridinium)ethane/24-crown-8 ether templating motif can be extended to multiply interlocked molecules as demonstrated herein by the synthesis of symmetrical and unsymmetrical [3]rotaxanes.

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Notes and references

‡ All new compounds were successfully characterized by ^1H NMR spectroscopy (500 MHz, 298 K) and LSI-MS or ESI-MS. NOESY experiments were used make individual ^1H NMR assignments.

Selected data: for **9**: $\delta_H(CD_3CN)$: 9.30 (m, 6H), 8.95 (m, 4H), 8.13 (d, 2H, *J* 6.72 Hz), 8.08 (d, 2H, *J* 6.76), 7.95 (m, 4H), 7.75 (d, 2H, *J* 6.85 Hz), 7.59 (d, 2H, *J* 8.44 Hz), 7.48 (d, 2H), 6.74 (m, 8H), 6.68 (m, 4H), 6.51 (m, 4H), 5.82 (s, 2H), 5.61 (m, 6H), 5.45 (m, 2H), 4.04 (m, 48H), 1.34 (s, 9H), 1.18 (s, 9H). UV/VIS (MeCN, CT band): λ_{max} = 406 nm. ESI-MS: *m*/*z* 1894.8 ($[M - BF_4]^+$). For **10**: $\delta_H(CD_3CN)$: 9.33 (d, 4H, *J* 6.84 Hz), 9.30 (d, 4H, *J* 6.84 Hz), 8.95 (d, 4H, *J* 6.84), 8.14 (d, 4H), 8.10 (d, 8H), 7.60 (d, 4H, *J* 7.81 Hz), 7.49 (d, 4H), 6.68 (m, 8H), 6.49 (m, 8H), 5.81 (s, 4H), 5.48 (s, 8H), 4.07 (m, 48H), 1.34 (s, 18H). UV/VIS (MeCN, CT band): λ_{max} = 399 nm. ESI-MS: *m*/*z* 2459.4 ($[M - OTf]^+$).

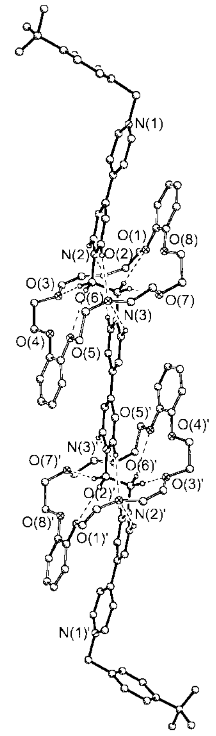

Fig. 1 A ball-and-stick representation of the X-ray crystal structure of the [3]rotaxane **8** showing the basic numbering scheme. $N(2)^+\cdots O$ distances (Å); O(1) 3.65, O(8) 3.61. $N(3)^+\cdots O$ distances (Å) ; O(4) 3.53, O(5) 3.51. C–H···O distances (Å) and angles (°): H(19A)···O(6) 2.52, C(19)–H(19A)···O(6) 149.8; H(20A)···O(2) 2.57, C(20)–H(20A)···O(2) 142.4; H(22A)···O(5) 2.77, C(22)–H(22A)···O(5) 140.9; H(22B)···O(3) 2.35, C(22)–H(22B)···O(3) 169.2; H(23A)···O(7) 2.26, C(23)–H(23A)···O(7) 162.0; H(23B)···O(1) 2.45, C(23)–H(23B)···O(1) 152.6; H(24A)···O(6) 2.53, C(24)–H(24A)···O(6) 140.8; H(28A)···O(2) 2.48, C(28)–H(28A)···O(2) 154.7.

§ *Crystal data* for **10**: $C_{110}H_{126}F_{18}N_6O_{34}S_6$, M = 2610.53, monoclinic, space group $P2_1/n$, a = 16.892(4), b = 14.926(7), c = 25.494(13) Å, β= 107.94(2)°, U = 6115(4) Å^3, T = 293(2) K, Z = 2, μ = 0.219 mm^{-1}, 8401 independent reflections (R_{int} = 0.0583), $R1$ = 0.1368, $wR2$ = 0.3516 ($I > 2\sigma I$), $R1$ = 0.2204, $wR2$ = 0.3959 (all data), Goodness of fit (F^2) = 1.212. 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 182/1593. See http://www.rsc.org/suppdata/cc/b0/b001018i/ for crystallographic files in .cif format.

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