Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Amabilino, David B. , Ashton, Peter R. and Stoddart, J. Fraser(1995) 'Macrocyclic polyethers incorporating resorcinol residues as templates for cyclobis(paraquat-*p*-phenylene) in the self-assembly of [2]catenanes', Supramolecular Chemistry, 5: 1, 5 — 8
To link to this Article: DOI: 10.1080/10610279508029880
URL: http://dx.doi.org/10.1080/10610279508029880

SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 5–8
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COMMUNICATION

Macrocyclic polyethers incorporating resorcinol residues as templates for cyclobis(paraquat-p-phenylene) in the self-assembly of [2]catenanes†

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†*This communication is dedicated to Professor Donald J. Cram on the occasion of his 75th birthday.*

(Received March 11, 1994)

The self-assembly of [2]catenanes incorporating cyclobis(paraquat-p-phenylene) and either bis(metaphenylene)-32-crown-10 or tris(metaphenylene)-48-crown-15 has been achieved. The dynamic processes associated with the relative motions of the two rings have been studied by variable temperature ^{1}H NMR spectroscopy. Both [2]catenanes display rapid relative movements of the two components, associated with free energies of activation in the region 12–14 kcal mol^{-1} for different processes. The resorcinol residues of the macrocyclic polyethers are bound in the cavity of the cyclophane by π-π stacking, electrostatic interactions, and T-type hydrogen bonding.

An understanding of the relationship between the strength and geometry of binding in host-guest[1–3] complexes, and the ability of such supramolecular systems to undergo self-assembly[4–5] relies, at present, upon an empirical structural and synthetic chemical foundation.[6] The formation of catenanes[7] requires initially the complexation of a linear component threaded through the center of a macrocyclic component. Cyclisation of the linear component then affords a [2]catenane. The solid state 1:1 complex[8–9] formed between bis(paraphenylene)-34-crown-10 **(BPP34C10)** and Paraquat paved the way[7,10] for the template-directed synthesis of [2]- and [3]-catenanes comprised of these building blocks. There is, however, no solid-state structural evidence[11] concerning the geometry of the binding of Paraquat by the crown ether bis(metaphenylene)-32-crown-10 **(BMP32C10)**. One extremely appealing way to test binding geometry is simply to attempt the self-assembly of a [2]catenane incorporating cyclobis(paraquat-*p*-phenylene). Here, we describe the successful self-assembly and the characterization of two new [2]catenanes in which the macrocyclic polyether components contain resorcinol residues.

The macrocyclic polyethers **BMP32C10** and tris(metaphenylene)-48-crown-15 **(TMP48C15)**[12] were prepared (Scheme 1) in 8% and 2% yields, respectively, in a single step (Scheme 1) by the cesium carbonate-promoted reaction[13] of resorcinol (1,3-dihydroxybenzene) with the bistosylate of tetraethylene glycol. The major product of this reaction, in 54% yield, is the crown ether[14] metaphenylene-16-crown-5 **(MP16C5)**. The isolated macrocyclic polyethers **BMP32C10** and **TMP48C15**, which were separated by chromatography, were each reacted under identical conditions (RT) with **1**.2PF_6 and 1,4-bis(bromomethyl)benzene in DMF. After one week, the reaction mixtures were subjected to column chromatography, affording (Scheme 2) the [2]catenanes **2**.4PF_6 and **3**.4PF_6 as yellow solids[15–16] in 17% and 12% yields, respectively. They were characterized by variable temperature ^{1}H NMR spectroscopy and fast atom bombardment mass spectrometry (FABMS).

The FABMS of both catenanes show the characteristic sequential loss of PF_6^- counterions, as well as decatenation in the spectrometer. The highest mass peak for

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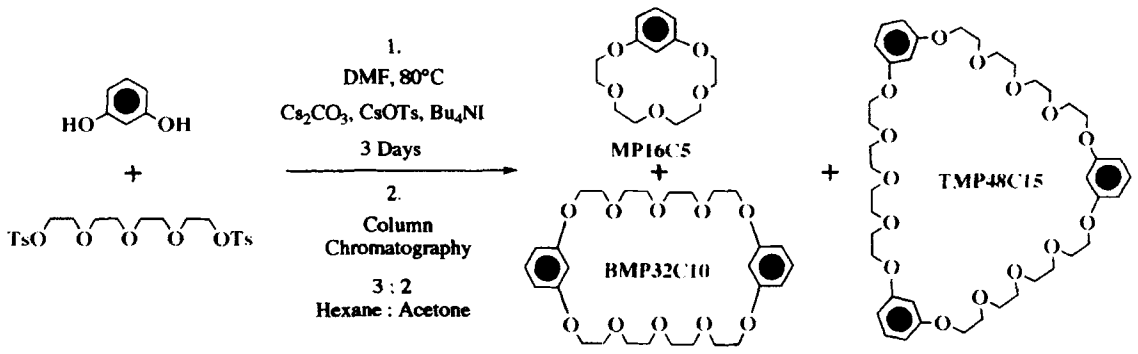


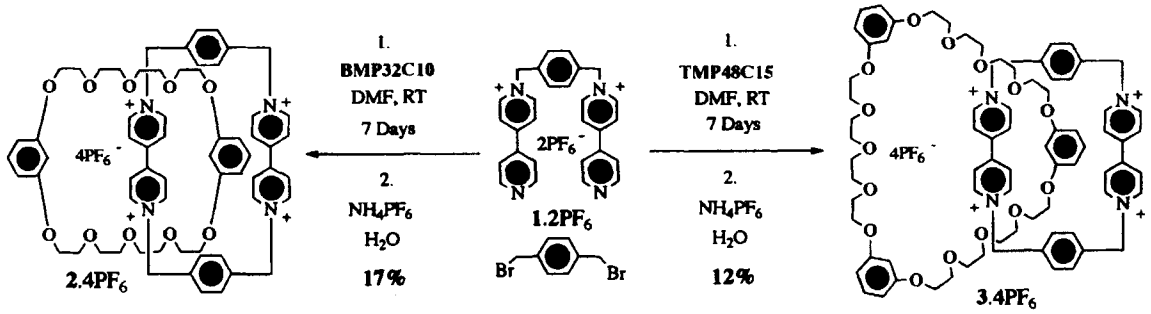
Scheme 1 The synthesis of the macrocyclic polyethers **MP16C5, BMP32C10**, and **TMP48C15** in one step. (See Color Plate I.)

2.4PF_6 was observed at *m/z* 1490, corresponding to [M-PF_6]$^+$, while **3**.4PF_6 gave a peak with *m/z* 1928, which corresponds to the [M+Na]$^+$ ion. Since the [2]catenane **3**.4PF_6 has polyether chains which are not involved in noncovalent bonding interactions with the cyclophane, it presumably binds more readily sodium ions in the metanitrobenzyl alcohol matrix.

The ^{1}H NMR spectra (400 MHz) of both **2**.4PF_6 and **3**.4PF_6 at ambient temperature reveal well-resolved resonances arising from the cyclophane components of the structures, while the resonances for the protons attached to the resorcinol residues are broadened into the baseline of the spectrum on account of an exchange process in which the macrocyclic polyether circumrotates through the cavity of the tetracationic cyclophane (Process I in Figure 1).

When a CD_3COCD_3 solution of **2**.4PF_6 is cooled down to 0°C, the signals, which correspond to the resorcinol residues of the **BMP32C10** component residing 'inside' and 'outside' the tetracationic component of the [2]catenane, become evident in the ^{1}H NMR spectrum. The free energy barrier to the hindered circumrotation of the macrocyclic polyether component through the cavity of the tetracationic cyclophane (Process I in Figure 1) was calculated to be $\Delta G_c^{\ddagger}$ = 13.6 kcal mol^{-1} based on the coalescence[17] at 304 K of the H-4/6 protons attached to the 'inside' and 'outside' resorcinol rings ($\Delta\nu$ = 513 Hz and k_c = 1160 s^{-1}). In the case of **2**.4PF_6, Process II (Figure 1) remains fast on the ^{1}H NMR timescale down to 193 K—below which temperature CD_3COCD_3 freezes. However, an additional process with a free energy barrier $\Delta G_c^{\ddagger}$ = 12.1 kcal mol^{-1} (average value) was calculated from the coalescences at 251 K and 240 K, respectively, of the CH_2 ($\Delta\nu$ = 58 Hz and k_c = 129 s^{-1}) and α-CH ($\Delta\nu$ = 27 Hz and k_c = 60 s^{-1}) proton resonances arising from the tetracationic cyclophane. This process corresponds to the energy required to equilibrate (Process III in Figure 2) the two possible orientations[18] of the resorcinol residue within the π-electron deficient cavity. A resorcinol ring leaves the cavity of the cyclophane and is replaced with one having an orientation where the H-2 and H-5 protons have switched their positions relative to those occupied in the initial structure. The free energy barrier to the analogous process in **3**.4PF_6 in CD_3COCD_3 solution has a similar value of 12.2 kcal mol^{-1} for its $\Delta G_c^{\ddagger}$, calculated from the coalescence temperature of 248 K ($\Delta\nu$ = 38 Hz and k_c = 85 s^{-1}) of the α-CH protons of the cyclophane.[19]

As the solution of **2**.4PF_6 is cooled down, the resonances arising from the protons attached to both the 'inside' and 'outside' resorcinol units shift significantly. In particular, the protons at the 2- and 5-positions of the included ring exhibit resonances which shift (Figure 3)



Scheme 2 The template-directed self-assembly of the [2]catenanes **2**.4PF_6 and **3**.4PF_6. (See Color Plate II.)

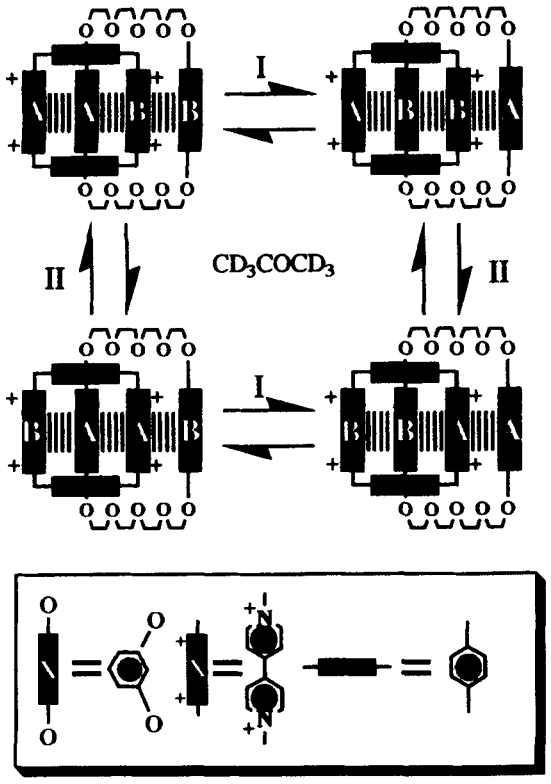


Figure 1 A diagrammatic representation of the two of the dynamic processes (I and II) taking place between the two components of the [2]catenane **2**.4PF_6. (See Color Plate III.)

from δ 1.73 and 3.06 at 253 K, to δ 1.99 and 2.31, respectively, at 193 K. Meanwhile, the resonances of the H-5 and the equivalent H-4 and H-6 protons attached to the 'outside' resorcinol unit shift from δ 6.71 and 6.15 at 253 K, to δ 6.23 and 5.91, respectively, at 213 K, and the chemical shift of the resonance arising from the H-2 proton is essentially invariant with temperature. Interestingly, chemical shift changes with temperature observed for H-2 and H-5 in **3**.4PF_6 are not as dramatic as those observed for the same protons in **2**.4PF_6. The H-2 proton resonance shifts from δ 1.70 at 253K to δ 1.80 at 213 K, while the H-5 proton was revealed at δ 3.85 by

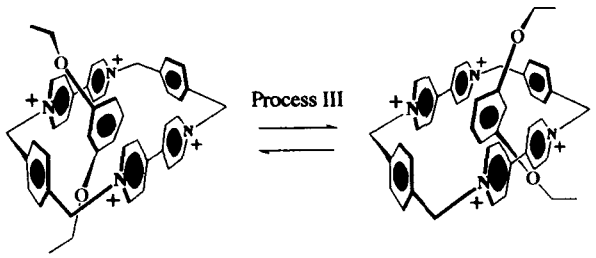


Figure 2 A diagrammatic representation of the equilibration (Process III) of the two possible degenerate orientations of resorcinol units within the cavity of cyclobis(paraquat-*p*-phenylene) in the [2]catenanes. (See Color Plate IV.)

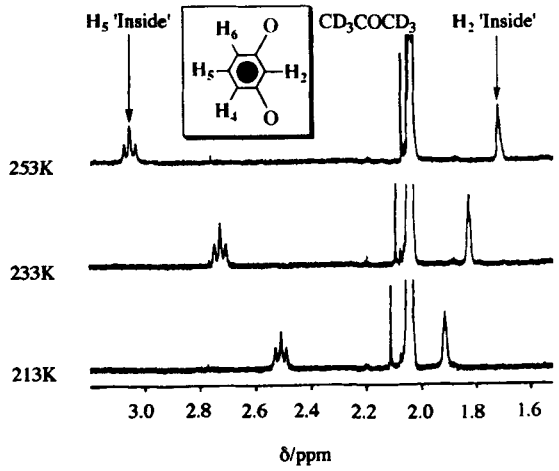


Figure 3 The temperature dependence of the resonances for H-2 and H-5 arising from the 'inside' resorcinol rings in the ^{1}H NMR spectrum of **2**.4PF_6. (See Color Plate V.)

a saturation transfer experiment performed at 265 K. The exact reasons for these chemical shift changes are currently being investigated.

The differences in the free energies of activation for the dynamic processes associated with the relative motions of the components in the two [2]catenanes described here, compared with those observed in isomeric [2]catenanes,[7,19] indicates that the interaction of resorcinol rings in the macrocyclic polyether component with the bipyridinium units in cyclobis(paraquat-*p*-phenylene) is not as significant as the interactions when hydroquinone rings replace the resorcinol rings in the macrocyclic polyether component. In particular, for the isomeric [2]catenane incorporating **BPP34C10**, the free energy barrier[7] to Process I (Figure 1) is 15.6 kcal mol^{-1}, and that to Process II is 12.2 kcal mol^{-1}. In **2**.4PF_6, the activation barrier to Process I is only 13.6 kcal mol^{-1}, and Process II is clearly also associated with a much lower free energy barrier. The relatively poor yields obtained in the catenations also reflect the detrimental influence that constitutional change[20] has upon host-guest interactions[1-3] and associated molecular self-assembly processes. The yield of **2**.4PF_6 is 17%, while the isomeric [2]catenane containing the macrocyclic ether **BPP34C10** was isolated[7] in 70% yield. A detailed understanding of the structural factors that affect the efficiency of self-assembly processes[21] is essential if this approach to synthesis is going to lead to the rapid and precise creation of nanometer scale molecular and supramolecular structures.

ACKNOWLEDGEMENTS

We thank the Science and Engineering Research Council in the UK for the financial support of this research.

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15 **2**.4PF_6 had *m/z* (positive-ion FABMS) 1490, 1345 and 1200, corresponding to, $[M-PF_6]^+$, $[M-2PF_6]^+$, and $[M-3PF_6]^+$; ^{1}H NMR (CD_3COCD_3, 400 MHz, 253K) 1.73 (1H, bt), 3.05 (1H, t), 3.45–3.55 (4H, m), 3.65–3.95 (28H, m), 4.76 (2H, q), 5.61 (1H, bt), 5.95–6.10 (10H, m), 6.71 (1H, t), 8.04 (8H, bd), 8.25–8.40 (8H, m), 9.38 (8H, bd); ^{13}C NMR (CD_3COCD_3, 101 MHz, 233K) 64.9, 65.1, 67.3, 67.4, 69.8 (× 2), 70.1 (×2), 70.5, 71.1, 99.4, 100.5, 105.8, 106.8, 126.1, 127.1, 128.2, 130.9, 131.3, 131.4, 137.9, 138.3, 145.1, 145.6, 146.8, 146.9, 157.7, 160.0.
16 **3**.4PF_6 had *m/z* (positive-ion FABMS) 1928, 1759, 1614 and 1469, corresponding to $[M+Na]^+$, $[M-PF_6]^+$, $[M-2PF_6]^+$, and $[M-3PF_6]^+$; ^{1}H NMR (CD_3COCD_3, 400 MHz, 253K) 1.70 (1H, bt), 3.40–3.50 (4H, m), 3.60–4.00 (45H, m), 4.43 (2H, d), 5.90–6.10 (10H, bm), 6.26 (2H, d), 6.30 (2H, d), 7.04 (2H, t), 8.02 (8H, bd), 8.10–8.30 (8H, bm), 9.36 (8H, bd); ^{13}C NMR (CD_3COCD_3, 101 MHz, 233K) 65.1, 65.2, 67.6 (×2), 69.3, 69.4, 69.5, 69.6 (×2), 69.8, 70.5 (×3), 70.9, 101.2 (×2), 104.5, 106.3, 106.9, 126.4, 127.0, 130.0, 130.9, 131.3 (×2), 137.7, 138.2, 145.1, 145.6, 146.9, 147.2, 157.7, 160.0, 160.2.
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19 A separation of the H-4/6 proton resonances for 'inside' and 'outside' resorcinol residues in **3**.4PF_6 is observed at 308 K in CD_3COCD_3 solution. This temperature dependent process reflects the movement of the tetracationic cyclophane between each of the three resorcinol residues in the **TMP48C15** component. In **3**.4PF_6, the ratio of 'inside' to 'outside' resorcinol residues is 1:2. Since the method described in reference 17 strictly speaking only applies to situations where the exchanging signals have equal intensities, it is not possible to calculate a value of $\Delta G_c^{\ddagger}$ for this process using this treatment.
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