Recl. Trav. Chim. Pays-Bas **112**, 429–430 (1993) 0165–0513/93/06427–02$06.00

A NEW APPROACH TO CONTROLLING CATENATED STRUCTURES

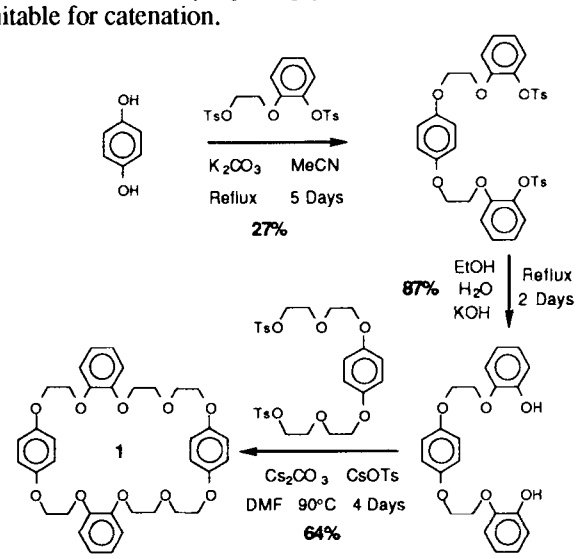
David B. Amabilino and J. Fraser Stoddart*
School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

(Received April 27th, 1993)

Abstract: A [2]catenane comprised of a macrocyclic polyether, analagous to bisparaphenylene 34-crown-10 – but incorporating catechol units in its tetraethyleneglycol chains – and the cyclobis(paraquat-*p*-phenylene) tetracation, has been self-assembled and shown to exist in solution as a non-equimolar mixture of translational isomers.

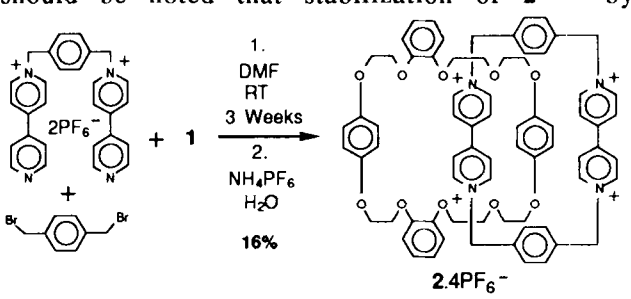
The self-assembly of nanometer-scale molecular and supramolecular structures requires precise and delicate control of structure if they are to have the potential to behave as molecular devices.[1] The template-directed synthesis[2,3] of a [2]catenane comprised of the macrocyclic polyether bisparaphenylene-34-crown-10 (BPP34C10), containing two π-electron rich hydroquinol rings, and the tetracationic macrocycle, cyclobis(paraquat-*p*-phenylene), containing two π-electron deficient bipyridinium units, has led to the realization of a wide range of interlocked molecular compounds with fascinating solid and solution state properties. The same is true of the [2]rotaxanes[3,4] based on dumbbell components where the π-electron rich hydroquinol rings are incorporated within polyether chains suitably stoppered at each end, such that a cyclobis-(paraquat-*p*-phenylene) with its π-electron deficient bipyridinium units can be contained thereon. When such [2]rotaxanes are constructed around two different π-electron rich recognition sites in the dumbbell components, it is possible for them to exhibit translational isomerism.[5] This kind of isomerism is also possible in desymmetrized [2]catenanes, *e.g.* one comprised of 1,5-naphtho-paraphenylene-36-crown-10 and the cyclobis(paraquat-*p*-phenylene) tetracation.[6] It is becoming evident that it is possible to control the relative populations of translational isomers in these molecularly-interlocked systems, so creating the fundamental basis for a new kind of molecular switch. Aside from changing the nature of the π-donating rings themselves in [2]catenanes, it occurred to us that it might be possible to establish some imbalance between the translational isomers of a [2]catenane by desymmetrizing the tetraethyleneglycol chains linking the two hydroquinol rings in BPP34C10. This communication describes (1) the self-assembly of a [2]catenane 2^{4+} incorporating a macrocyclic polyether **1**, analogous to BPP34C10, except that it includes two catechol rings along its tetraethyleneglycol chains and (2) the identification of two translational isomers $\mathbf{2A}^{4+}$ and $\mathbf{2B}^{4+}$ in the ratio 64:36 in both CD_3COCD_3 and CD_3CN solutions at room temperature by ^1H NMR spectroscopy.

The crown ether **1**,[7] required for the self-assembly of the [2]catenane 2^{4+}, was prepared (Scheme 1) in 15% yield overall starting from hydroquinol. In particular, the macrocyclization step was a highly efficient one (64%), probably as a result of the combination of the so-called caesium effect and the presence of four rigid groups. The crown ether is a white solid, which, although soluble in chloroform, is only sparingly soluble in the solvents suitable for catenation.



Scheme 1: Synthesis of the crown ether **1**

The bright red [2]catenane $\mathbf{2}^{8}$ was self-assembled (Scheme 2) from **1**, 1,1'-[1,4-phenylenebis-(methylene)]-bis-4,4'-dipyridinium bis-(hexafluorophosphate), and 1,4-bis(bromomethyl)benzene in DMF in a yield of 16%, following column chromatography ($MeOH/2N\text{-}NH_4Cl/MeNO_2$, 7:2:1) on silica gel and counterion exchange. This low yield compares with the 70% yield obtained[2,3] for the original [2]catenane when the crown ether was the BPP34C10. Although the low solubility of **1** in the reaction mixture might account in part for the lower efficiency of the molecular self-assembly process, it should be noted that stabilization of 2^{4+} by



Scheme 2: Self-assembly of the [2]catenane 2^{4+}

[C-H...O] hydrogen bonding between the αCH-bipyridinium hydrogen atoms and the central oxygen atoms in the polyether chains will be diminished as a result of the catechol units with their less basic oxygen atoms being present in the polyether chain of **1**.

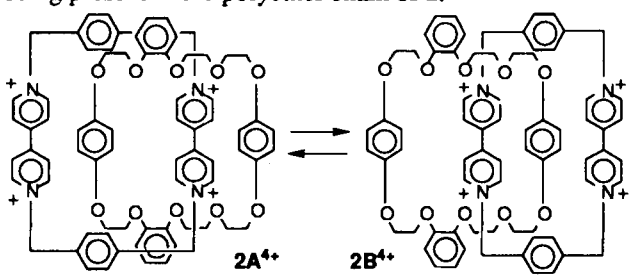


Figure 1: The two translational isomers of **2**

The [2]catenane $\mathbf{2}^{4+}$ exists (Figure 1) as two translational isomers, one ($\mathbf{2A}^{4+}$) in which the catechol residues are closer to the 'inside' hydroquinol ring and the other ($\mathbf{2B}^{4+}$) where they are closer to the 'alongside' hydroquinol ring. ^{1}H NMR spectroscopy indicates that both isomers are present[9] in a CD_3COCD_3 solution of the [2]catenane at +25°C. Integration of the two distinguishable sets of resonances in the ^{1}H NMR spectrum suggests that the ratio of $\mathbf{2A}^{4+}$:$\mathbf{2B}^{4+}$ is 64:36. The resonances for the two isomers were identified by comparison of the ^{1}H chemical shifts for **2**.4PF_6 with those of the original [2]catenane[3] containing BPP34C10. Molecular modelling indicates that in isomer $\mathbf{2A}^{4+}$, where the catechol residues are closer to the 'inside' hydroquinol ring, the catechol π-faces are located in close proximity to the aromatic protons of the paraxylyl spacers in the tetracationic cyclophane, whereas in the isomer $\mathbf{2B}^{4+}$, two of the methylene groups in the tetracationic cyclophane are close to the π-faces of the catechol residues. In isomers $\mathbf{2A}^{4+}$ and $\mathbf{2B}^{4+}$, the signals for the aromatic protons of the paraxylyl spacers resonate at δ 7.84 and δ 8.04, respectively (*cf.* δ 8.04 in the original [2]catenane[3]), whilst those for the methylene groups resonate at δ 6.04 and δ 5.90, respectively (*cf.* δ 6.02 in the original [2]catenane[3]). At 25°C, the circumrotation of the tetracationic cyclophane through the macrocyclic polyether of the [2]catenane $\mathbf{2}^{4+}$ is fast on the ^{1}H NMR timescale. By contrast, the other circumrotation process - that of the macrocyclic polyether passing through the tetracationic cyclophane - is slow. However, upon warming up a CD_3CN solution of **2**.4PF_6, the signals of the αCH and βCH bipyridinium protons, which each resonate as overlapping doublets in the 270 MHz ^{1}H NMR spectrum at room temperature, can be identified as doublets at δ 8.97 and δ 7.77, respectively. The temperature dependence of the ^{1}H NMR spectrum of **2**.4PF_6 will be discussed in more detail in a subsequent full paper.

On the basis of the results reported in this communication, we can advocate a new approach to controlling the structures of certain catenanes with respect to the translational isomerism that they exhibit in solution. Such control is important in the design and synthesis of switchable catenanes and rotaxanes.

References and Footnotes

1. *J.F. Stoddart*, Chemistry in Australia, **59**, 576 (1992); Anales de Quimica, **89**, 51 (1993).
2. *D. Philp* and *J.F. Stoddart*, Synlett, 445 (1991).
3. *P.L. Anelli, P.R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M.T. Gandolfi, T.T. Goodnow, A.E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, C. Vicent* and *D.J. Williams*, J. Am. Chem. Soc., **114**, 193 (1992).
4. *P.L. Anelli, N. Spencer* and *J.F. Stoddart*, J. Am. Chem. Soc., **113**, 5131 (1991).
5. *P.R. Ashton, R.A. Bissell, N. Spencer, J.F. Stoddart* and *M.S. Tolley*, Synlett, 914 (1992); *P.R. Ashton, R.A. Bissell, R. Górski, D. Philp, N. Spencer, J.F. Stoddart* and *M.S. Tolley*, Synlett, 919 (1992); *P.R. Ashton, R.A. Bissell, N. Spencer, J.F. Stoddart* and *M.S. Tolley*, Synlett, 923 (1992).
6. *P.R. Ashton, R. Ballardini, V. Balzani, M. Blower, M. Ciano, M.T. Gandolfi, L. Prodi, C.H. McLean, D. Philp, N. Spencer, J.F. Stoddart* and *M.S. Tolley*, New. J. Chem., In press.
7. The crown ether **1** has: *m/z* (FAB$^+$MS) 671 $[M + K]^+$, 655 $[M + Na]^+$ and 632 $[M]^+$; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 6.93 (m, 8H), 6.75 (s, 4H), 6.69 (s, 4H), 4.33 (t, 4H), 4.19 (m, 4H), 4.13 (t, 4H) and 3.95 (m, 12H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 153.1, 153.1, 149.4, 148.9, 122.1, 121.6, 115.9, 115.6, 115.5, 114.4, 70.1, 69.7, 69.5, 68.5, 68.2 and 67.3.
8. The [2]catenane **2**.4PF_6 has: *m/z* (FAB$^+$MS) 1587 $[M\text{-}PF_6]^+$, 1442 $[M\text{-}2PF_6]^+$ and 1297 $[M\text{-}3PF_6]^+$; ^{1}H NMR (400.14 MHz, CD_3COCD_3) δ 9.45 (d, 5.12H, J = 7 Hz, αCH **A**), 9.39 (d, 2.88H, J = 7 Hz, αCH **B**), 8.32 (d, 5.12H, J = 7 Hz, βCH **A**), 8.27 (d, 2.88H, J = 7 Hz, βCH **B**), 8.04 (s, 2.88H, xylyl aromatic **B**), 7.84 (s, 5.12H, xylyl aromatic **A**), 7.38-7.29 (m, 2.88H, catechol CH), 7.23-7.04 (m, 5.12H, catechol CH), 6.38 (s, 2.56H, 'alongside' hydroquinol **A**), 6.34 (s, 1.44H, 'alongside' hydroquinol **B**), 6.04 (s, 5.12H, CH_2N **A**), 5.90 (s, 2.88H, CH_2N **B**), 4.57 (m, 1.44H, CH_2O **B**), 4.53 (m, 5.12H, CH_2O **A**), 4.30 (m, 1.44H, CH_2O **B**), 4.26 (m, 1.44H, CH_2O **B**), 4.09 (m, 2.56H, CH_2O **A**), 4.01 (m, 2.56H, 'inside' hydroquinol **A**, 2.56H, CH_2O **A**, and 1.44H, CH_2O **B**), 3.87 (m, 1.44H, CH_2O **B**), 3.82 (m, 1.44H, 'inside' hydroquinol **B**, 2.56H, CH_2O **A**, and 1.44H, CH_2O **B**) and 3.53 (m, 2.56H, CH_2O **A**); ^{13}C NMR (100.63 MHz, CD_3COCD_3) δ 153.5, 153.1, 151.3, 151.1, 151.0, 149.3, 149.1, 148.8, 147.3, 145.8, 145.7, 137.7, 131.9, 131.7, 126.6, 126.5, 124.7, 123.0, 122.9, 122.4, 119.5, 116.5, 116.2, 114.9, 114.7, 114.2, 113.1, 73.3, 72.0, 71.7, 71.1, 70.7, 69.4, 68.8, 68.0, 67.6, 66.3, 65.9 and 65.5.
9. There is no evidence in the ^{1}H NMR spectrum of **2**.4PF_6 recorded in CD_3COCD_3 that the catechol residues in the macrocyclic polyether become located 'inside' the tetracationic cyclophane. Since the resonances of their protons (δ 7.04-7.38) are shifted to lower field when compared with those observed (δ 6.89-7.00) in **1**, the catechol residues are clearly located in the deshielding zones of the aromatic units present in the tetracationic cyclophane.

Acknowledgement

We thank the Science and Engineering Research Council in the United Kingdom for providing the financial support to carry out this work.