Towards a Molecular Abacus

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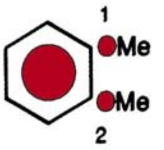
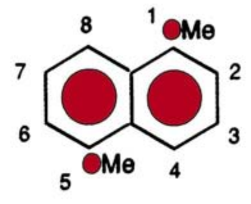
The solid state and solution structures of the 1 : 1 complex formed between the cyclobis(paraquat-*p*-phenylene) tetracationic cyclophane and 1,5-dimethoxynaphthalene has led to the successful design and characterisation by X-ray crystallography of a prototype for the construction of a molecular abacus in the shape of a 2 : 1 complex between the same cyclophane and 1,3-bis(5-hydroxy-1-naphthyloxy) propane.

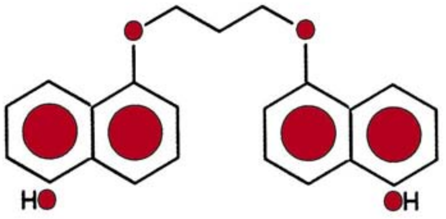
The observation[1] that, in the crystalline phase, 1,2-dimethoxybenzene (1/2DMB) is inserted through the centre of the rigid cavity of the cyclobis(paraquat-*p*-phenylene) tetracation[2] $\mathbf{1}^{4+}$ in a disordered arrangement about the crystallographic symmetry centre producing an apparent structural composition analogous to that of 1,5-dimethoxynaphthalene (1/5DMN) led us to investigate the ability of $\mathbf{1}^{4+}$ to form the structually equivalent 1 : 1 complex with 1/5DMN. Here, we



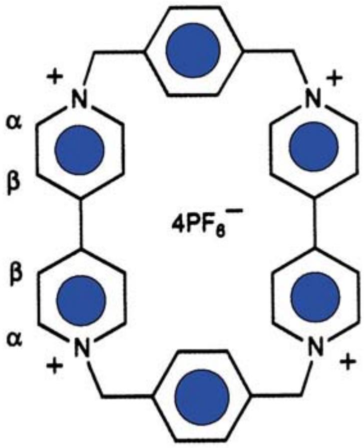
1/2DMB



1/5DMN



BHNP



$\mathbf{1}.4PF_6$

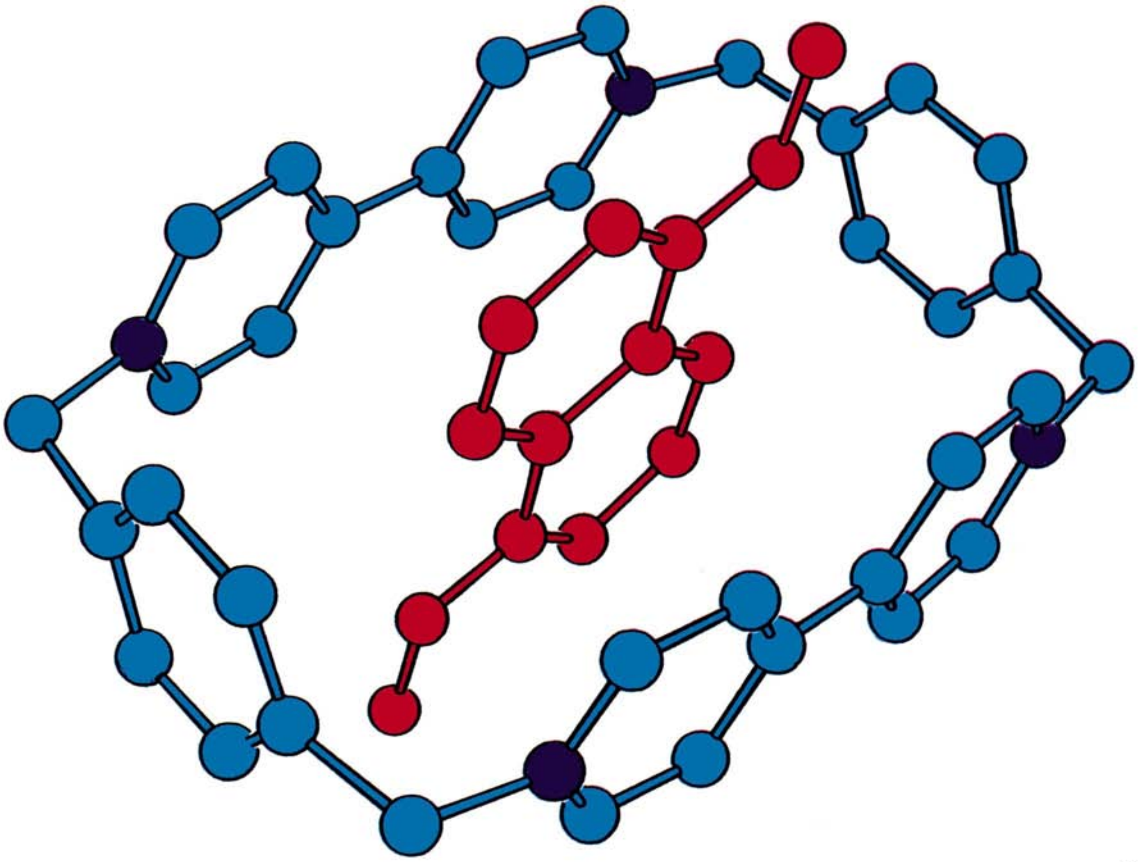


Figure 1

Fig. 1 The structure of **1**·1/5DMN^{4+} in the crystal. The tetracationic macrocycle **1**$^{4+}$ is shaded blue with the N atoms dark blue and 1/5DMN is shaded red with the O atoms dark red.

describe (*a*) the solid state structure† of the tetrakis(hexafluorophosphate) of this 1:1 complex, (*b*) the ^{1}H NMR spectroscopic evidence for its existence in solution, and (*c*) the solid state structure† of the 2:1 complex formed between **1**·4PF$_6$ and 1,3-bis(5-hydroxy-1-naphthyloxy)propane‡ (BHNP).

Single crystals, deep purple in colour, of **1**·1/5DMN·4PF$_6$·2MeCN, suitable for X-ray crystallography, were grown by vapour diffusion of diisopropyl ether into a MeCN solution containing equimolar amounts of **1**·4PF$_6$ and 1/5DMN. The solid state structure reveals (Fig. 1) that 1/5DMN does indeed insert itself through the centre of the tetracationic cyclophane **1**$^{4+}$ in an ordered centrosymmetric manner. The relative orientations of the naphthalene ring and the two OMe groups inside the cavity of **1**$^{4+}$ match almost exactly the image produced[1] by the disordered arrangement of 1/2DMB molecules in **1**·1/2DMB·4PF$_6$·2MeCN. The tetracationic cyclophane adopts a slightly bowed geometry with the macrocyclic ring strain relieved by out-of-plane bending of all six aryl rings.§ In addition to the dispersive and charge transfer interactions associated with the donor–acceptor π-stacking (interplanar separations of 3.41 Å between the π-electron rich and π-electron deficient rings), there are pronounced edge-to-face stabilising interactions[3–5] (H–centroid distance of 2.54 Å) involving H-4, and by symmetry H-8, each of which are directed towards the centres of the paraphenylenedimethyl residues in **1**$^{4+}$ (C–H···centroid angle 159°). The packing within the crystals of the tetracations and their associated PF$_6$$^-$ counterions and also the MeCN

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† *Crystal data* for **1**·1/5DMN·4PF$_6$·2MeCN: $C_{52}H_{50}F_{24}N_6O_2P_4$, M = 1370.9, monoclinic, space group $P2_1/n$, a = 11.218(3), b = 19.756(6), c = 13.980(3) Å, β = 111.23(2)°, U = 2888 Å^3, Z = 2 (the complex is disposed about a centre of symmetry), D_c = 1.58 g cm^{-3}, μ = 24 cm^{-1}.

Crystal data for **1**·0.5BHNP·4PF$_6$·2MeCN: $C_{51.5}H_{48}F_{24}N_6O_2P_4$, M = 1362.9, monoclinic, space group $P2_1/n$, a = 10.881(2), b = 20.043(4), c = 14.066(3) Å, β = 110.09(2)°, U = 2881 Å^3, Z = 2 (the complex is disposed about a centre of symmetry), D_c = 1.57 g cm^{-3}, μ = 24 cm^{-1}.

Data for both structures were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure of **1**·1/5DMN·4PF$_6$·2MeCN was solved by direct methods and refined anisotropically to give R = 0.109, R_w = 0.117 for 2527 independent reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 110°$]. The structure of **1**·0.5BHNP·4PF$_6$·2MeCN, which is virtually isostructural with **1**·1/5DMN·4PF$_6$·2MeCN, was solved using the coordinates of this complex and difference Fourier methods. It was refined anisotropically to give R = 0.084, R_w = 0.095 for 2887 independent reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$].

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Treatment of 1,5-dihydroxynaphthalene with molar equivalents of PhCH$_2$Br and K$_2$CO$_3$ in DMF at room temperature afforded 1-benzyloxy-5-hydroxynaphthalene, m.p. 136–138 °C, in 21% yield after column chromatography [SiO$_2$: CH$_2$Cl$_2$–light petroleum]. Reaction of 2 equiv. of this monobenzylether with 1,3-dibromopropane in DMF in the presence of an excess of K$_2$CO$_3$ at 70 °C gave 1,3-bis(1-benzyloxy-5-naphthoxy)propane, m.p. 156–159 °C , in 45% yield after column chromatography [SiO$_2$: CH$_2$Cl$_2$–CCl$_4$ (1 : 4)]. Catalytic hydrogenolysis (H$_2$, Pd/C) of this dibenzyl ether in CHCl$_3$ afforded BHNP with m.p. 156–158 °C in 45% yield after column chromatography [SiO$_2$: CHCl$_3$–CCl$_4$(1 : 1)]. All new compounds gave satisfactory elemental analyses, mass spectra and ^{1}H NMR spectra.

§ The maximum deviations are associated with the exocyclic C–CH$_2$ bonds emanating from the paraphenylene residues, these bonds subtending an angle of 15° with respect to each other whilst the N$^+$–CH$_2$ bonds associated with the bipyridinium units subtend an angle of 22°.

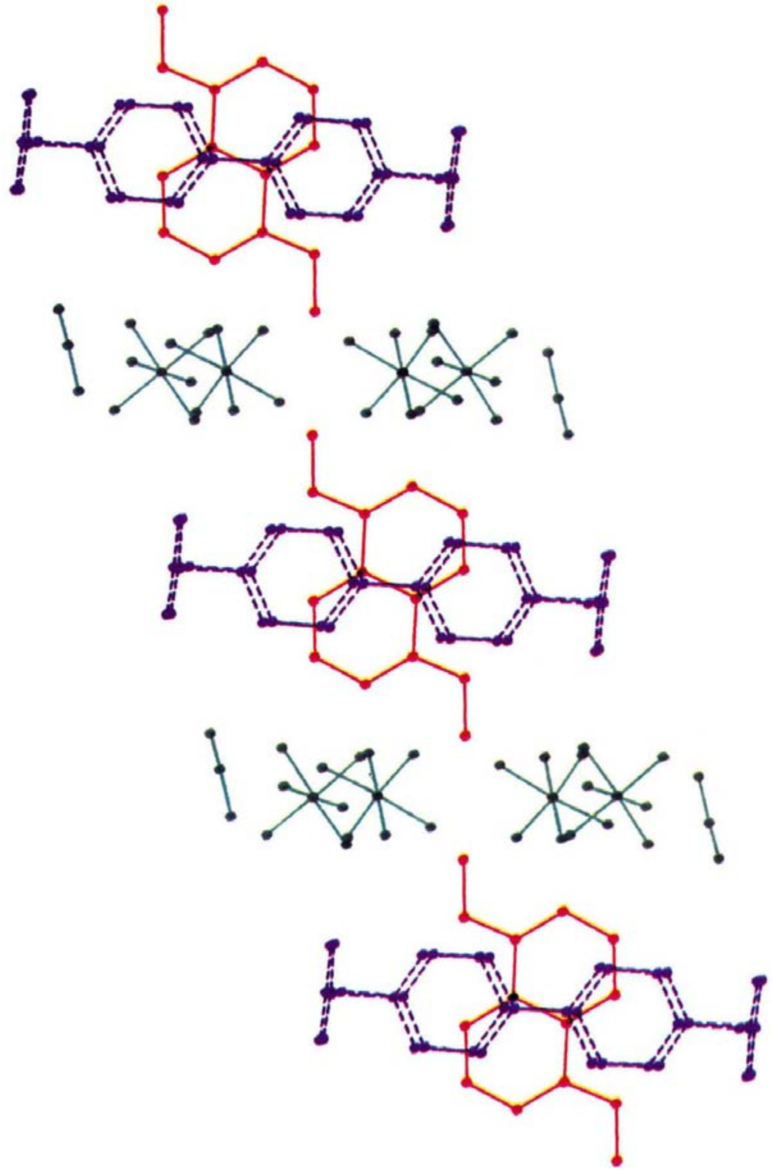

Fig. 2 A skeletal representation of the continuously stacked arrangement of **1**·1/5DMN·4PF_6·2MeCN in the crystal. The tetracationic cyclophane macrocycles $\mathbf{1}^{4+}$ are blue, the 1/5DMN molecules are red, and the PF_6^- counterions and MeCN molecules are green.

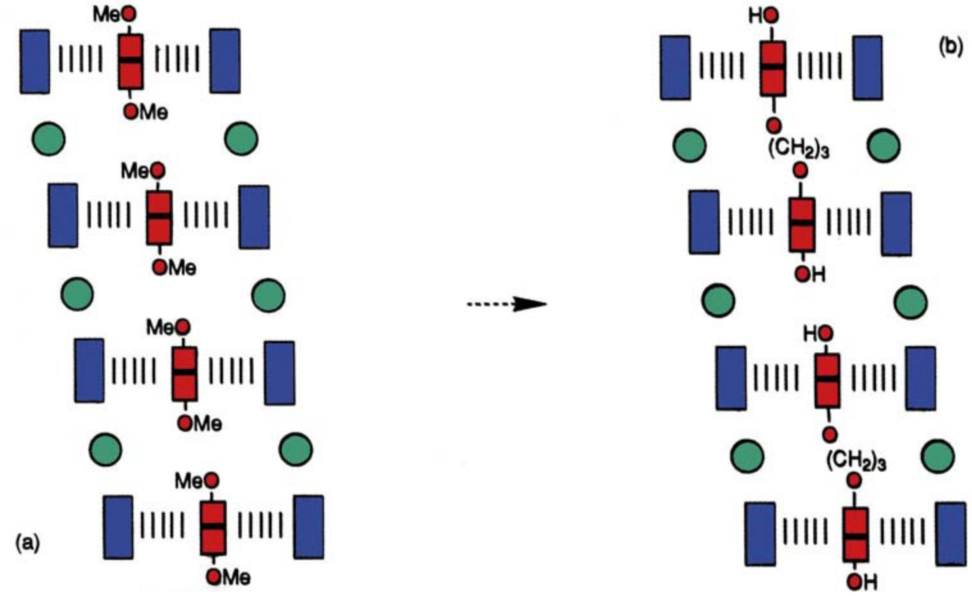

Fig. 3 A diagrammatic representation, employing chemical cartoons, of the relationship between the solid state structure of (*a*) **1**·1/5DMN·4PF_6·2MeCN and (*b*) $(\mathbf{1})_2$BHNP·8PF_6·4MeCN. The tetracationic cyclophane $\mathbf{1}^{4+}$ in cross section ⊟ blue rectangles. The PF_6^- counterions and MeCN solvent molecules ≡ green spheres. 1,5-Dioxynaphthalene rings ⊟ dissected red rectangles.

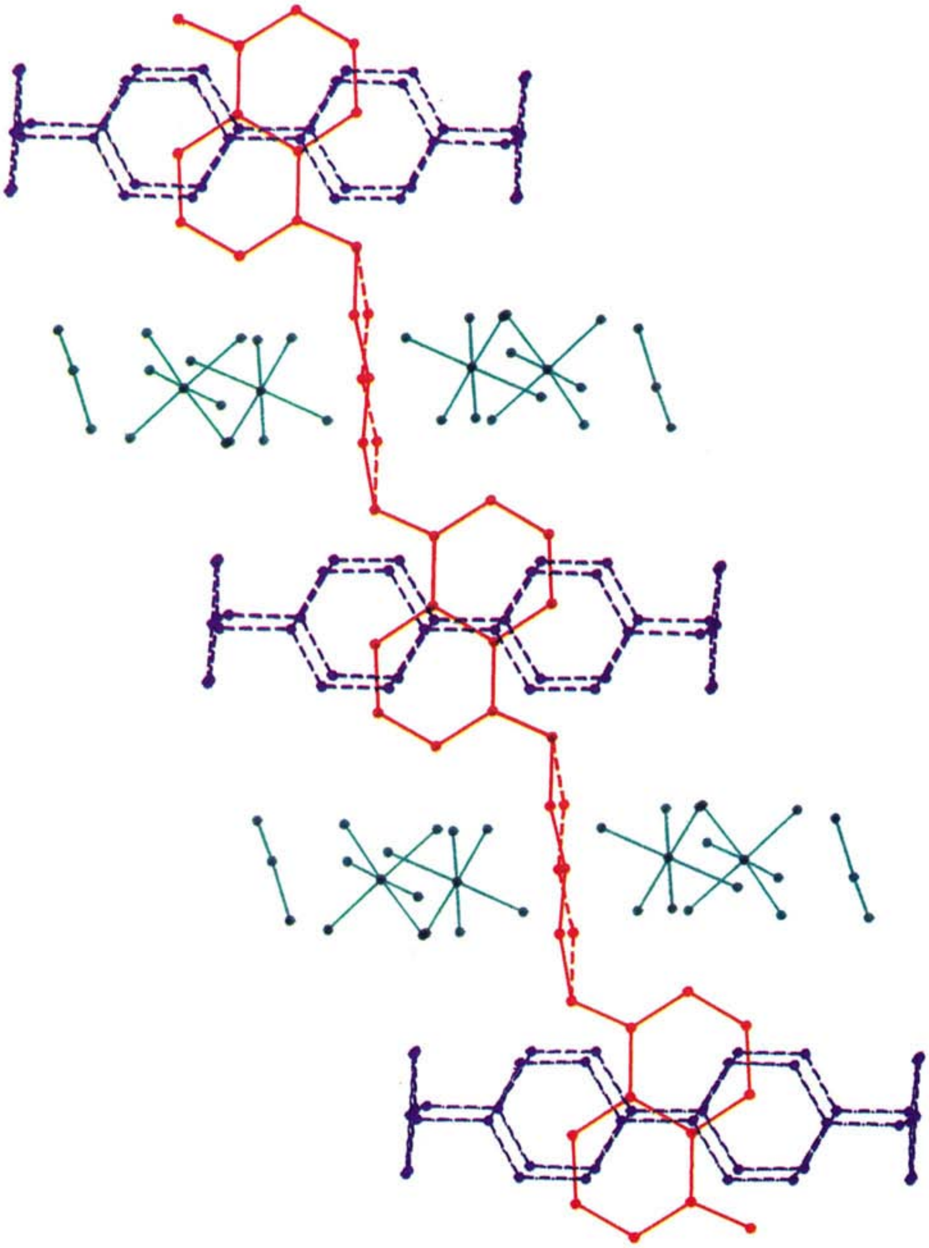

Fig. 4 A skeletal representation of part of the continuously stacked arrangement of **1**·4PF$_6$·2MeCN with the BHNP units inserted through the centre of the stack in a disordered array simulating the threading of a polymeric chain. The tetracationic cyclophane macrocycles **1**$^{4+}$ are blue, the disordered BHNP molecules are red, and the PF$_6$$^-$ counterions and MeCN molecules are green.

solvent molecules, is (Fig. 2) such as to produce a continuous alternately charged stack in the crystalline *a* direction with the 1/5DMN molecules aligned along the free pathway that runs through the centre of the stack.

Quite significant ^{1}H NMR chemical shift changes accompany the formation of a 1 : 1 complex between 1/5DMN and **1**·4PF$_6$ in CD$_3$CN. The $\Delta\delta$ values (where $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free}}$) of −0.54, −0.97 and −4.14 for H-2/6, H-3/7 and H-4/8, respectively, in 1/5DMN are reflected in those of −0.12, −0.64, +0.34 and −0.02, for the H-α, H-β, C$_6$H$_4$ and CH$_2$ protons respectively in **1**$^{4+}$. The most dramatic mutual influences are associated with (*a*) the upfield shift of −4.14 for H-4/8 and (*b*) the downfield shift of +0.34 for the C$_6$H$_4$ protons associated with the edge-to-face related paraphenylene units with the naphthalene ring, indicating that the averaged solution state structure is not unrelated to that observed in the solid state (Fig. 1).

Since the distance between the O atoms of neighbouring 1/5DMN units within the continuous stacks (Fig. 3) of **1**·1/5DMN·4PF$_6$·2MeCN is 5.96 Å, it was concluded that it should be possible to insert a trismethylene bridge between two 1,5-dioxynaphthalene units without seriously perturbing the continuous alternately charged stack. Indeed, MeCN solutions containing **1**·4PF$_6$ and BHNP in the molar ratios 2 : 1 produced, on slow evaporation, single crystals of (**1**)$_2$·BHNP·8PF$_6$·4MeCN, suitable for X-ray crystallographic analysis. The space group is the same and the unit cell is indeed very similar to those of **1**·1/5DMN·4PF$_6$·2MeCN and the solid state structure reveals (Fig. 4) what initially appears to be a 'polymeric' structure with the threaded BHNP units lying across three crystallographic centres of symmetry, two of which are equivalent by lattice translation. Clearly, the BHNP substrate cannot be 'polymeric' and what we are apparently observing is the result of an averaged disordered structure, the dominant feature of which is the familiar channelled arrangement[1,2] of both **1**$^{4+}$ and the 4PF$_6$$^-$ counterions. The chief binding requirement is that the naphtho units lie within the centre of the tetracationic cyclophane **1**$^{4+}$. And clearly they do

(Fig. 4) in $(\mathbf{1})_2\cdot$BHNP$\cdot$8PF$_6\cdot$4MeCN without the relative orientations of the naphtho rings inside $\mathbf{1}^{4+}$, compared to those in $\mathbf{1}\cdot$1/5DMN$\cdot$4PF$_6\cdot$2MeCN, being changed substantially.

The results reported in this Communication suggest that it should thus be possible to elaborate red threads incorporating 1,5-dioxynaphthalene units that can be encircled simultaneously by more than one blue tetracationic bead, so conjuring up the prospect of self-assembling structures with a polyrotaxane-like character.[6] We regard the solid state structure (Fig. 4) of $(\mathbf{1})_2\cdot$BHNP$\cdot$8PF$_6\cdot$4MeCN as the prototype for the construction of a molecular abacus.

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