Complexation of Paraquat by a Bisparaphenylene-34-crown-10 Derivative

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The Paraquat dication forms a 1 : 1 molecular inclusion complex both in acetone solution and in the solid state with the bisparaphenylene-34-crown-10 derivative (BPP34C10) as a result of intra-complex stabilisation from charge transfer interactions as well as from hydrogen and electrostatic bonding.

In the previous communication,[1] ^{1}H n.m.r. spectroscopy in CD_3COCD_3 solution established that BPP34C10† is capable of complexing with $[Paraquat][PF_6]_2$,† as well as with $[Diquat][PF_6]_2$.† In common with BMP32C10,† we noted that free BPP34C10, as revealed by the conformations (I and II) it adopts in the solid state, has a preformed receptor cavity for substrates such as these bipyridinium dications. Not discouraged by our initial failure[2] to isolate a crystalline complex between BMP32C10 and the $[Paraquat]^{2+}$ dication that was suitable for *X*-ray crystallography, we sought (i) structural evidence for the formation of $[Paraquat{\cdot}BPP34C10][PF_6]_2$ and (ii) confirmation by stability constant measurements in acetone solution that a 1 : 1 complex is indeed formed between the $[Paraquat]^{2+}$ dication and BPP34C10. Here, we discuss briefly the positive results we have obtained in these two areas, thus fulfilling one of the main objectives we set[3] ourselves at the beginning of this investigation, namely designing and synthesising receptor molecules for Paraquat.

A charge transfer absorption band is observed ($\lambda_{max.}$ 435 nm) in the u.v. spectrum of $[Paraquat{\cdot}BPP34C10][PF_6]_2$ in

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† The structural formulae for BMP32C10, BPP34C10, $[Paraquat][PF_6]_2$, and $[Diquat][PF_6]_2$ are illustrated in the three preceding communications (refs. 1—3).

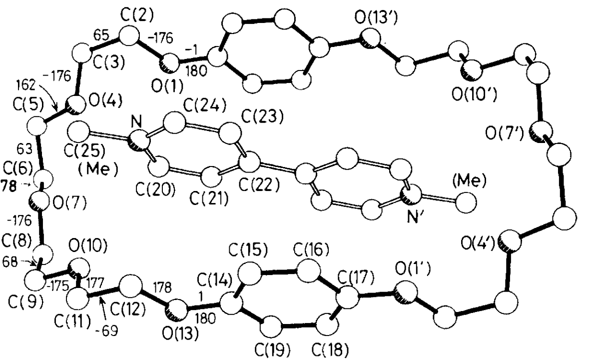

Figure 1. The solid state structure of [Paraquat·BPP34C10]$^{2+}$. Torsional angles (°) (O–C–C–O and C–C–O–C) associated with the polyether chains are shown beside the relevant C–C and C–O bonds. Selected host–guest potential hydrogen bonding distances less than 3.4 Å: R[C · · · O], R[H · · · O] (Å), C–H · · · O angles (°) assuming normal trigonal and tetrahedral geometry: [C(25)–O(4)], 3.25, [H(25)–O(4)] 2.53, 132; [O(7)–C(25)], 3.33, [H(25)–O(7)], 2.51, 144. Other host–guest contact distances (Å): [C(20)–O(10)], 3.28; [C(20)–O(4)], 3.36. Separation between parallel benzo rings in the host, 7.4 Å.

acetone and quantitative analysis[4] of it provided evidence‡ for the 1 : 1 stoicheiometry of the complex in solution together with a value of 730 dm^3 mol^{-1} for its stability constant (K_a), corresponding to a free energy of complexation (ΔG^0) of -3.90 kcal mol^{-1}. Decreasing (n = 6—9) or increasing (n = 11, 12) the macrocyclic ring size leads[5] to an impairment of complexation strengths within the series (n = 6—12) of BPP (3 n + 4) Cn receptors.

The solid state structure§¶ (Figures 1 and 2) of [Paraquat·BPP34C10][PF$_6$]$_2$ reveals (Figure 3) that the conformation of the receptor in the 1 : 1 complex is virtually unchanged on complexation from that (conformation II) observed[3] for the free BPP34C10 macrocycle. The only significant torsional changes (Figure 1) are 21° and 10°, respectively about the O(1)–C(14′) and C(5)–C(6) bonds. In common with the X-ray crystal structure[1] of free BPP34C10 that of the 1 : 1 complex with the [Paraquat]$^{2+}$ dication also possesses a crystallographic centre of symmetry which here is coincident for the macrocycle and the dication: the dication is thus planar. This is comparable with the geometry most commonly observed in X-ray crystal structures[6] of this dication although dihedral angles of 20° and 50° have been reported[7] for some crystalline molecular complexes. The retention‖ of the open conformation adopted by the free BPP34C10 receptor permits (Figures 1 and 2) the insertion of the [Paraquat]$^{2+}$ dication through the centre of the macrocyclic ring with the central axis [C(25) · · · C(25′)] of the dication tilted *ca.* 28° with respect to the O · · · O axes of the hydroquinol units (Figure 4). The binding of the [Paraquat]$^{2+}$ dication can be interpreted as reflecting a balance between (i) charge transfer interactions involving the hydroquinol rings, (ii) electrostatic interactions involving the phenolic oxygen atoms, and (iii) [C–H · · · O] and van der Waals interactions involving the polyether chains of the receptor. Although it is not possible at this stage to say

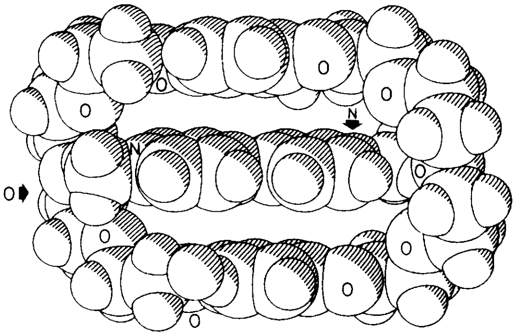

Figure 2. Space-filling representation of [Paraquat·BPP34C10]$^{2+}$.

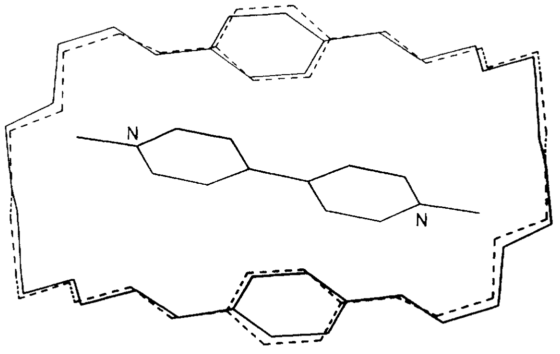

Figure 3. Best least squares fit of the conformation (II) of free BPP34C10 to that of [Paraquat·BPP34C10]$^{2+}$.

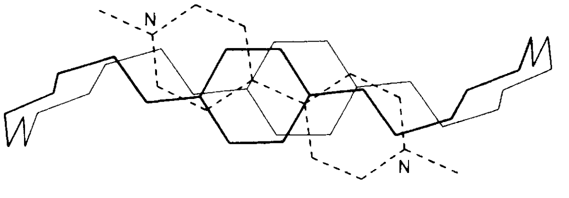

Figure 4. Side-on view (normal to the mean plane of the [Paraquat]$^{2+}$ dication) of the skeletal representation of the solid state structure of [Paraquat·BPP34C10]$^{2+}$.

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‡ A provisional and approximate analysis of the charge transfer absorption band ($\lambda_{max.}$ 436 nm) in the u.v. spectrum of [Diquat·BPP34C10][PF$_6$]$_2$ in acetone indicates that $K_a \simeq 350$ dm^3 mol^{-1} ($\Delta G^0 \simeq -3.5$ kcal mol^{-1}; 1 kcal = 4.184 kJ).

§ Red single crystals (m.p. 265—270 °C), suitable for X-ray structural analysis, were grown from an equimolar mixture of [Paraquat][PF$_6$]$_2$ and BPP34C10 dissolved in acetone and layered with n-pentane. Complex formation with 1 : 1 stoicheiometry was indicated by positive-ion fast atom bombardment mass spectrometry (6 kV on a Kratos MS80RF spectrometer) using argon. From a 3-nitrobenzyl-alcohol matrix, the crystals of [Paraquat·BPP34C10][PF$_6$]$_2$ afforded a strong [Paraquat·BPP34C10·PF$_6$]$^+$ ion at m/z 867 as a result of the loss of one PF$_6^-$ counterion from the 1 : 1 complex.

¶ *Crystal data* for [Paraquat·BPP34C10][PF$_6$]$_2$·2Me$_2$CO: $C_{12}H_{14}N_2 \cdot C_{28}H_{40}O_{10} \cdot P_2F_{12} \cdot C_6H_{12}O_2$, M = 1129, triclinic, space group $P\bar{1}$, a = 10.204(2), b = 11.562(2), c = 13.835(5) Å, α = 105.59(2), β = 98.70(2), γ = 115.47(1)°, U = 1350 Å^3, Z = 1 (the complex possesses a crystallographic centre of symmetry), D_c = 1.39 g cm^{-3}, R = 0.080, R_w = 0.095 for 2369 independent observed reflections [$\theta \leq 50°$, $|F_o| > 3\sigma(|F_o|)$]. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using the ω-scan routine. The structure was solved by direct methods, the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. See Notice to Authors, Issue No. 1.

‖ In common with free BPP34C10 and its 1 : 1 complex with the [Diquat]$^{2+}$ dication, we observe coplanarity of the four phenoxymethylene units with their associated hydroquinol rings (*cf.* ref. 1).

whether the orientation adopted by the [Paraquat]$^{2+}$ dication with respect to two parallel hydroquinol units, which places two symmetry-related oxygen atoms [O(1) and O(1′)] in roughly axial positions relative to C(20) and C(20′) is dictated by (i) and/or (ii) and/or (iii), this alignment concurs with the calculated charge distributions[8] on the free bipyridinium dication. However, a similar charge distribution is claimed[8] to be present in the [Diquat]$^{2+}$ dication, yet in its complexes with a range of diphenol-derived macrocycles, the predominant feature[1—4,9] is the collinearity of two phenolic oxygen atoms with the nitrogen atoms of the bipyridinium dication.

It is clear that a comprehensive theoretical analysis of the nature of the noncovalent bonding in these complexes should take into account the perturbations of the charge distribution which may occur as a consequence of complexation and also satisfy the orbital symmetries of the interacting molecular orbitals.

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