

Complexation of Paraquat and Diquat by a Bismetaphenylene-32-crown-10 Derivative

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U.v. and ¹H n.m.r. spectroscopic studies in solution on the 1 : 1 complexes both [Paraquat][PF₆]₂ and [Diquat][PF₆]₂ form with the bismetaphenylene-32-crown-10 derivative (BMP32C10), supported by X-ray crystal structures on the free BMP32C10 and [Diquat·BMP32C10][PF₆]₂·Me₂CO, provide further fundamental understanding of the electronic and steric nature of the intermolecular noncovalent interactions that are essential to the successful design and synthesis of a molecular receptor for optimal binding of the [Paraquat]²⁺ dication.

The X-ray structural analyses of [Pt(bipy)(NH₃)₂·DN30C10][PF₆]₂[†] and [Diquat·DN30C10][PF₆]₂[†] revealed¹ the importance of the relative contributions to supramolecular binding of electrostatic and charge transfer interactions. In view of the comparability^{1–3} between the nature and geometry of the binding in [Diquat·DN30C10][PF₆]₂ and [Diquat·DB30C10][PF₆]₂, it was decided to concentrate our initial search for a readily accessible synthetic molecular receptor⁴ for the [Paraquat]²⁺ dication on macrocyclic polyethers incorporating two benzo rings.

CNDO/2 calculations on free [Diquat]²⁺ and free [Paraquat]²⁺ dications indicate⁵ that the positive charge density is concentrated not so much on the nitrogen atoms but on the carbon atoms *ortho* and *para* to them. Nonetheless, all the experimental evidence which has been collected to this point,

demonstrates^{1–3} the propensity for both nitrogen atoms in the [Diquat]²⁺ dication to become involved in parallel and collinear arrangements with the aryl oxygen atoms in DB30C10 and DN30C10. Here, we report on (i) the synthesis[†] of a bismetaphenylene-32-crown-10 derivative (BMP32C10)[‡] incorporating two resorcinol residues,⁶ (ii) the evidence for complexation of both the [Diquat]²⁺ and [Paraquat]²⁺ dications with BMP32C10 in solution, and (iii) the crystal structure

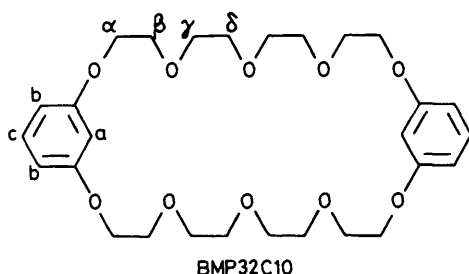
[‡] Partial benzylation (PhCH₂Cl, NaH, Me₂NCHO, room temp., 18 h) of resorcinol afforded (SiO₂-CH₂Cl)₂ 3-benzyloxyphenol [54%, oil, δ (CDCl₃, 220 MHz) 4.96 (2H, s, CH₂Ph), 5.38 (1H, br.s, OH), 6.37–6.47 (2H, m, 2-H and 4-H), 6.53 (1H, d × d, *J* 2.5, 8 Hz, 4-H), 7.09 (1H, t, *J* 8 Hz, 5-H), and 7.24–7.46 (5H, m, Ph)]. Reaction (NaH, Me₂NCHO, 80 °C, 24 h) of this phenol with tetraethyleneglycol bis(toluene-*p*-sulphonate) (TEGBT) gave [SiO₂-CH₂Cl₂-Et₂O (98 : 2, v/v)] 1,11-bis(3'-benzyloxyphenoxy)-3,6,9-trioxaundecane [71%, oil, δ (CDCl₃, 220 MHz) 3.60–3.72 (8H, AA'BB' system, γ- and δ-OCH₂), 3.78 and 4.05 (2 × 4H, 2 × t, *J* 5Hz, β- and α-OCH₂, respectively), 4.98 (4H, s, 2 × CH₂Ph), 6.45–6.63 (6H, m, 2'-H, 4'-H, and 6'-H), 7.12 (2H, t, *J* 8 Hz, 5'-H), and 7.26–7.50 (10H, m, 2 × Ph)]. Deprotection (H₂, Pd/C, MeOH-Et₂O), followed by reaction (NaH, Me₂NCHO, 70 °C, 25 h) of the derived diphenol with TEGBT afforded [SiO₂-CH₂Cl₂-Et₂O (3 : 7, v/v)] the BMP32C10 derivative [39%, m.p. 72–74 °C (*ex.* MeOH), see Figure 2 for the X-ray crystal structure, δ (CDCl₃, 220 MHz) 3.60–3.75 (16H, m, γ- and δ-CH₂), 3.81 and 4.06 (2 × 8H, 2 × t, *J* 5 Hz, β- and α-OCH₂, respectively), 6.44–6.57 (6H, m, H-a, H-b), and 7.10 (2H, t, *J* Hz, H-c).

[†] The structural formulae for the [Pt(bipy)(NH₃)₂]²⁺, [Diquat]²⁺, and [Paraquat]²⁺ dications are illustrated in the previous communication (ref. 1). The descriptors DB30C10 and DN30C10 refer to the constitutionally symmetrical 30-crown-10 derivatives incorporating fused dibenzo and di-(2,3)-naphtho rings. The structural formula for the bismetaphenylene-32-crown-10 derivative (BMP32C10) is numbered with reference to its systematic name, 1,4,7,10,13,20,23,26,29,32-decaoxa[13.13]metabenzophane. Note that in BMP32C10 and its precursors, the OCH₂ groups are designated α,β,γ,δ, starting adjacent to the phenylene rings and progressing along the polyether chains.

Table 1. ^1H N.m.r. chemical shift data [δ values ($\Delta\delta$ values)]^a in CD_3COCD_3 .

Compound or complex	[Paraquat] ²⁺			[Diquat] ²⁺					BMP32C10					
	2-, 6-H	3-, 5-H	(NMe) ₂	3-, 3'-H	4-, 4'-H	5-, 5'-H	6-, 6'-H	(NCH ₂) ₂	H-a	H-b	H-c	α -OCH ₂	β -OCH ₂	γ/δ -OCH ₂
BMP32C10	—	—	—	—	—	—	—	—	6.48	6.48	7.11	4.06	3.78	3.61
[Paraquat][PF ₆] ₂	9.35	8.81	4.72	—	—	—	—	—	—	—	—	—	—	—
[Paraquat·BMP32C10] [PF ₆] ₂	9.12	8.32	4.64	—	—	—	—	—	6.11	6.11	6.92	3.72	3.72	3.72
[Diquat][PF ₆] ₂	—	—	—	9.24	9.10	8.60	9.50	5.70	—	—	—	—	—	—
[Diquat·BMP32C10] [PF ₆] ₂	—	—	—	8.67	8.97	8.56	9.39	5.58	6.05	6.28	7.03	3.78	3.73	3.71
				(-0.57)	(-0.13)	(-0.04)	(-0.11)	(-0.12)	(-0.43)	(-0.20)	(-0.08)	(-0.28)	(-0.05)	(+0.10)

^a Spectra were recorded at ambient temperature on a Bruker AM250 spectrometer using $\text{CD}_2\text{HCOCD}_2\text{H}$ as reference. The $\Delta\delta$ values indicated in parentheses under the respective δ values relate to the chemical shift changes experienced by probe protons in both the substrates and the receptor on 1 : 1 complex formation.



analyses[§] of [Diquat·BMP32C10][PF₆]₂ and the free BMP32C10. The reasons for our choice of BMP32C10 as a receptor are as follows. Since the distance (*ca.* 4.7 Å) between the two aryl oxygen atoms in a resorcinol residue is almost half-way between the separations of *ca.* 2.8 and 7.0 Å for the two nitrogen atoms in the [Diquat]²⁺ and [Paraquat]²⁺ dications, respectively, the opportunity for optimal electrostatic interactions of BMP32C10 with both may be significantly diminished, whilst the potential for charge transfer is retained. The question is raised, with such a self-inflicted detrimental effect possibly being imposed upon one of the two principal intermolecular attractive forces, what structural compromises do the supramolecular complexes seek?

[§] Crystal data for BMP32C10: $\text{C}_{28}\text{H}_{40}\text{O}_{10}$, $M = 536.6$, monoclinic, space group $P2_1/a$, $a = 7.026(2)$, $b = 22.766(5)$, $c = 8.977(3)$ Å, $\beta = 96.04(3)^\circ$, $U = 1428$ Å³, $Z = 2$, $D_c = 1.25$ g cm⁻³, $R = 0.050$, $R_w = 0.068$ for 1425 independent observed reflections [$\theta \leq 50^\circ$, $|F_o| > 3\sigma(|F_o|)$]. [Diquat·BMP32C10][PF₆]₂·Me₂CO, $\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot \text{C}_{28}\text{H}_{40}\text{O}_{10} \cdot \text{C}_3\text{H}_6\text{O}$, $M = 1068.9$, triclinic, space group $P\bar{1}$, $a = 10.431(3)$, $b = 11.261(4)$, $c = 22.279(7)$ Å, $\alpha = 82.05(3)$, $\beta = 82.09(2)$, $\gamma = 74.96(3)^\circ$, $U = 2489$ Å³, $Z = 2$, $D_c = 1.42$ g cm⁻³, $R = 0.094$, $R_w = 0.116$ for 4378 independent observed reflections [$\theta \leq 50^\circ$, $|F_o| > 3\sigma(|F_o|)$].

In both cases, data were measured on a Nicolet R3m diffractometer with graphite monochromated $\text{Cu-K}\alpha$ radiation using the ω -scan routine. The structures were solved by direct methods, the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions. The hydrogen atoms of the included acetone molecule in [Diquat·BMP32C10][PF₆]₂·Me₂CO could not be positioned and so were omitted. In addition, the thermal motion of some of the atoms in this crystal was high, being particularly pronounced for those in the PF₆⁻ anions, in portions of polyether chains, and also, surprisingly, in regions of the [Diquat]²⁺ dication. The shortest acetone-complex contact is 3.16 Å. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

When BMP32C10 is mixed in organic solvents, such as Me₂CO, with equimolar amounts of either [Paraquat][PF₆]₂ or [Diquat][PF₆]₂, yellowish-orange solutions are formed immediately on account of the existence of charge transfer absorption bands with λ_{max} *ca.* 400 nm. Evidence for the 1 : 1 stoichiometries of both these solution complexes, together with measurements of their stability constants (K_a) and derived free energies of complexation (ΔG^0) for the equilibrium (1) were obtained^{2,3} from a treatment of the concentration dependence of the intensities of the absorptions at λ 400 nm in Me₂CO for 1 : 1 mixtures of the bipyridinium bis(hexafluoro)phosphates with BMP32C10. For [Paraquat·BMP32C10][PF₆]₂ and [Diquat·BMP32C10][PF₆]₂, respectively, $K_a = 760$ and 390 dm³ mol⁻¹ corresponding to $\Delta G^0 = -3.9$ and -3.5 kcal mol⁻¹.[¶] Thus, BMP32C10 binds both the [Paraquat]²⁺ and [Diquat]²⁺ dications almost equally well. This is in contrast with DB30C10,^{2,3} which forms a 1 : 1 complex with [Diquat][PF₆]₂ in Me₂CO ($K_a = 17500$ dm³ mol⁻¹; $\Delta G^0 = -5.8$ kcal mol⁻¹) but fails to complex with [Paraquat][PF₆]₂ in Me₂CO. Comparison (Table 1) of the ^1H n.m.r. spectra of [Paraquat·BMP32C10][PF₆]₂ and [Diquat·BMP32C10][PF₆]₂ in CD₃COCD₃ with those for the free salts and BMP32C10 reveals upfield shifts on complexation for most protons, particularly (i) both pyridinium ring protons (2-, 6-H and 3-, 5-H) in [Paraquat]²⁺, (ii) 3-, 3'-H in [Diquat]²⁺, and (iii) H-a, H-b, and α -OCH₂ in BMP32C10. These observations can most easily be interpreted in terms of 1 : 1 complexes in which the bipyridinium unit in the substrates becomes sandwiched between the two resorcinol rings of BMP32C10, such that the anisotropic diamagnetic susceptibility of one aromatic ring reduces the local magnetic field experienced by ^1H nuclei attached to neighbouring stacked aromatic rings. This conclusion is borne out by structural studies on one of the single yellow crystals (m.p. 215–220 °C) of [Diquat·BMP32C10][PF₆]₂, obtained as a Me₂CO solvate on crystallisation of a 1 : 1 mixture of [Diquat][PF₆]₂ and BMP32C10 from this solvent layered with n-pentane. The X-ray crystallographic analysis reveals (Figure 1) the [Diquat]²⁺ dication to be cradled between approximately parallel mirrored resorcinol units in the receptor. There are striking similarities in this complexation by BMP32C10 with the binding of DB30C10^{2,3} and its derivatives^{7–9} towards the [Diquat]²⁺ dication. A combination of [C–H \cdots O] hydrogen bonding, [N⁺ \cdots O] electrostatic interactions, and charge transfer between the π -electron-rich resorcinol rings and the π -electron-deficient

[¶] 1 kcal = 4.184 kJ.

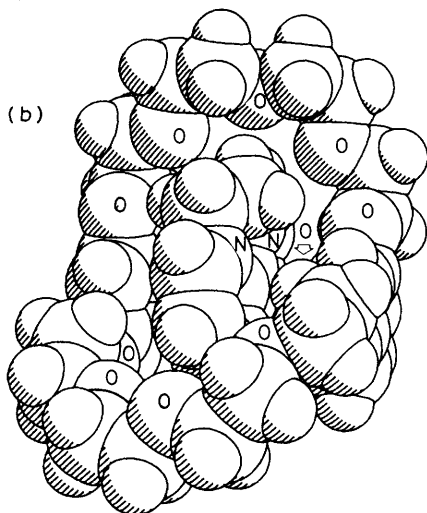
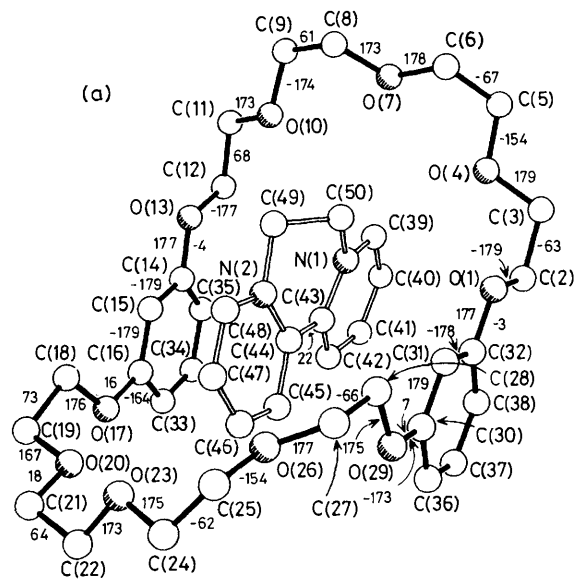


Figure 1. The solid state structure of [Diquat-BMP32C10][PF₆]₂ in both (a) framework and (b) space-filling representations. Torsional angles (°) (O-C-C-O and C-C-O-C) associated with the 32-membered ring are shown beside the relevant C-C and C-O bonds on the framework diagram. Selected C...O contact distances (Å) less than 3.4 Å: [C(39)...O(4)], 3.10; [C(47)...O(26)], 3.17; [C(47)...O(26)], 3.27; [C(59)...O(10)], 3.29; [C(50)...O(4)], 3.27; [C(50)...O(7)], 3.32; [C(46)...O(20)], 3.38; [C(49)...O(10)], 3.39. Separation (Å) between pyridinium ring in guest and phenolic O in host: N(1)...O(1), 3.47; N(1)...O(13), 3.71; O(1)...N(1)...O(13) angle, 168°. Twist angle between the pyridinium rings in the guest, 22°. Separation between the benzo rings in the host of 7.0 Å, with a 3.1° departure from parallel alignment of their mean planes.

bipyridinium dication, clearly stabilise the 1 : 1 complex. As in the case of the catechol-derived receptors,^{2,3,7-11} the phenoxymethylene units in BMP32C10 are all nearly coplanar¹² with the resorcinol rings, thus enhancing their π-donating character. However, there are some important differences; only the more significant ones are highlighted here. (1) Although both linking polyether chains adopt 'all-gauche' conformations, only one chain is looped over the region of the NCH₂ groups of the dication while the other encircles the edge of one of the pyridinium rings. (2) Despite several short [C-H...O] contacts (see caption to Figure 1), there is only one

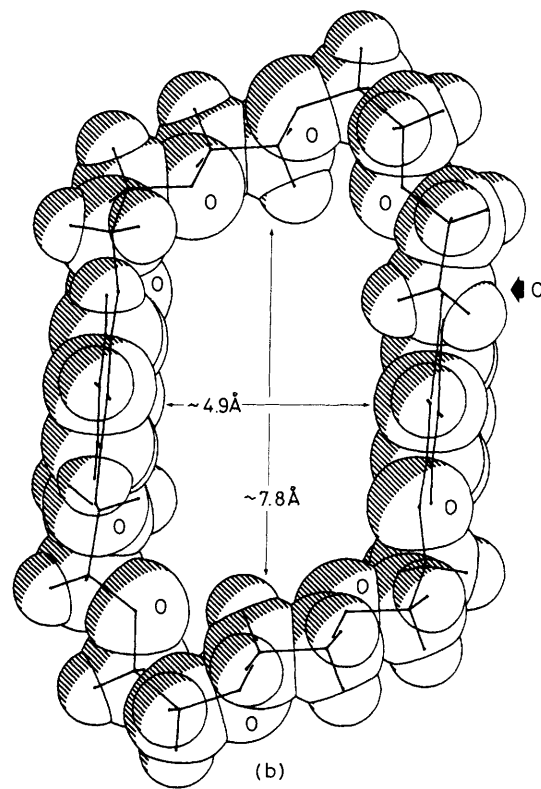
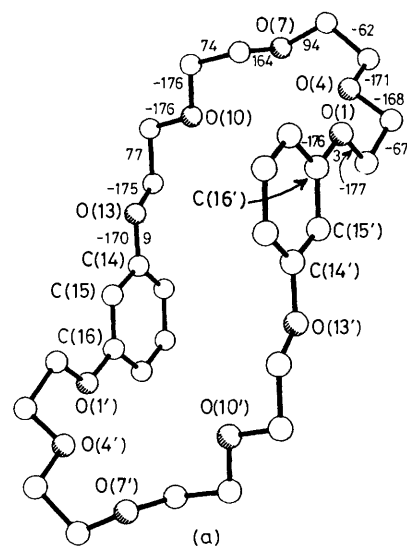
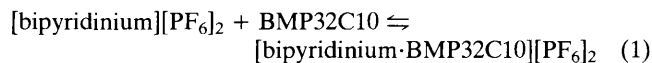


Figure 2. The solid state structure of BMP32C10 in both (a) framework and (b) space-filling representations. Torsional angles (°) (O-C-C-O and C-C-O-C) associated with the symmetry-related polyether chains are shown on the framework representation beside the relevant C-C and C-O bonds in one of the chains. The aromatic rings are parallel with a separation of 7.0 Å between their mean planes. The approximate dimensions of the cavity are shown on the space-filling representation.

acceptable [C-H...O] hydrogen-bonding interaction: [C(50)...O(7)], 3.32 Å, [H(50)...O(7)], 2.38 Å, C-H...O angle, 167°. (3) Because of the distance (4.7 Å) separating the oxygen atoms in resorcinol units, it is not possible to achieve simultaneous alignment of both oxygen atoms on each resorcinol unit with both nitrogen atoms separated by 2.8 Å in

the dication. However, one [N(1)] of the nitrogen atoms is positioned almost collinearly with respect to two [O(1) and O(13)] of the resorcinol oxygen atoms [O(1) ··· N(1) ··· O(13) angle of 168° compared with 106° for O(17) ··· N(2) ··· O(29)], underlining the importance of the contribution from this electrostatic interaction in the binding of the [Diquat]²⁺ dication. (4) There is a 22° in-plane rotation of one resorcinol unit with respect to the other whereas, in the DB30C10 receptors,^{2,3,7-11} the catechol units almost overlap in projection. (5) Normally, large uncomplexed macrocyclic rings, such as DB30C10¹³ and related receptors,⁹ have a tendency to collapse on themselves, *i.e.* they are self-filling. However, the X-ray analysis of the free BMP32C10 reveals (Figure 2) an unusually open conformation for the macrocyclic ring with a large clear passage (approx. free pathway, 7.8 × 4.9 Å) through the centre. There is a crystallographic centre of symmetry in BMP32C10, *cf.* the approximate mirror plane in [Diquat·BMP32C10][PF₆]₂. Comparison of the torsional angles of free and complexed BMP32C10 illustrates the minimal conformational changes required of the flexible molecular receptor to bind the almost rigid substrate. Essentially, rotation about four bonds [O(1)-C(16'), C(13')-C(14'), C(6)-O(7), and C(6')-O(7) in BMP32C10 in Figure 2a] is involved, with the torsional angles about all the other bonds undergoing only very minor changes.



Whilst the opportunity for charge transfer is preserved in [Diquat·BMP32C10][PF₆]₂, the dominant role played by electrostatic bonding, associated mainly with one approximately collinear [O ··· N ··· O] assembly of atoms in the complex, is strongly implied, if not underscored, in all [(1)-(5)] of the supramolecular structure features listed here.

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