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COMPLEXATION OF DIQUAT AND PARAQUAT BY MACROCYCLIC POLYETHERS INCORPORATING TWO DIHYDROXYNAPHTHALENE RESIDUES

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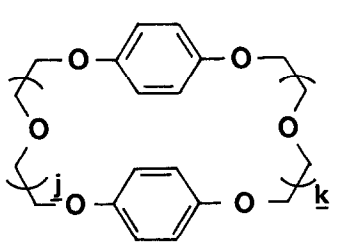
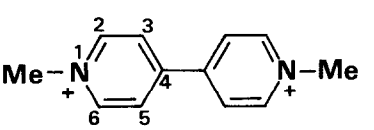
NMR Spectroscopy and FAB mass spectrometry demonstrate that the 38-crown-10 (1/5DN38C10) and 35-crown-9 (1/5DN35C9) ethers incorporating two 1,5-dinaphtho units form 1:1 complexes with the Paraquat [PQT]$^{2+}$ and Diquat [DQT]$^{2+}$ dications in solution. In the solid state, the [PQT.1/5DN38C10]$^{2+}$ complex is stabilised by face-to-face (π/π charge transfer) interactions between the naphtho and bipyridinium rings, whereas the free 1/5DN35C9 receptor features a classic edge-to-face ($H^{\delta+}/\pi$ electrostatic) interaction between its two naphtho rings.

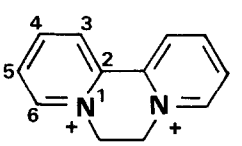
Previously, we have employed[1] UV and NMR spectroscopic measurements, along with FAB mass spectrometry, to assess the series (n = 7-12) of bisparaphenylene-(3n+4)-crown-n ethers [BPP(3n+4)Cn] for their abilities to complex with the bipyridinium dications, Paraquat [PQT]$^{2+}$ and Diquat [DQT]$^{2+}$, in solution. By this simple mapping technique, we found that optimum molecular recognition occurs at n = 9/10 in acetone and succeeded in isolating single crystals of [DQT.BPP31C9][PF_6]$_2$ and [PQT.BPP34C10][PF_6]$_2$ which were characterised[1,2] by X-ray crystallography. Since a not insignificant component of the stabilisation of these 1:1 complexes is the charge transfer interaction between the π-electron rich hydroquinol residues and the π-electron deficient bipyridinium dications, we decided to increase the dimensions of the π-electron donor aromatic rings whilst keeping them planar. Consequently, we have evaluated a range of molecular receptors for [PQT]$^{2+}$ and [DQT]$^{2+}$ incorporating two dihydroxynaphthalene residues with the 1,5-, 2,6-, and 2,7-substitution patterns. Here, we describe (i) the preparation[3] of the two 1,5-dihydroxynaphtho(3n+8)-crown-n ethers (1/5DN35C9 and 1/5DN38C10) where n = 9 and 10, (ii) the



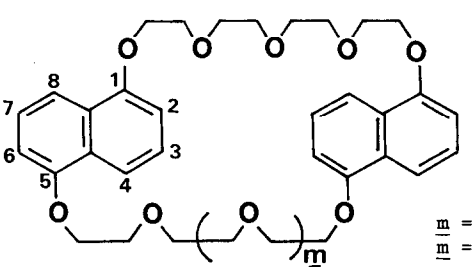
BPP(3n+4)Cn	n	j	k
BPP25C7	7	2	1
BPP28C8	8	2	2
BPP31C9	9	3	2
BPP34C10	10	3	3
BPP37C11	11	4	3
BPP40C12	12	4	4



[PQT]$^{2+}$



[DQT]$^{2+}$



m = 1 1/5DN35C9
m = 2 1/5DN38C10

characterisation of their 1:1 complexes in solution with $[PQT][PF_6]_2$ and $[DQT][PF_6]_2$ by FAB mass spectrometry and NMR spectroscopy, and (iii) the X-ray crystal structures[4] of [PQT.1/5DN38C10]-$[PF_6]_2$ and 1/5DN35C9.

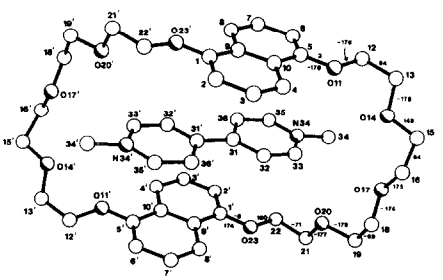


Figure 1. Structure of $[PQT.1/5DN38C10]^{2+}$ in the crystal. There is only one hydrogen bonding distance with C···O less than 3.4 Å: C34···O14 3.28 Å, H34···O14 2.35 Å, C34—H34···O14 163°: in the case of C33···O20 3.13 Å, H33···O20 2.70 Å. Separation between parallel naphtho units in the receptor, 7.1 Å. Other receptor-substrate contact distances [Å], angle [°] of contact vector to $[PQT]^{2+}$ plane: O23···C32, 3.63, 84; O11···N34, 3.67, 78; O11···C33, 3.69, 75.

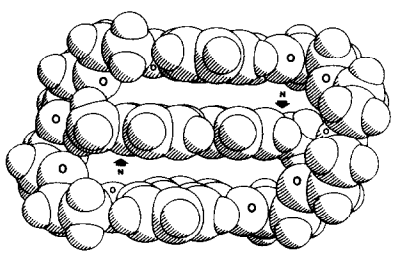


Figure 2. Space-filling representation of $[PQT.1/5DN38C10]^{2+}$

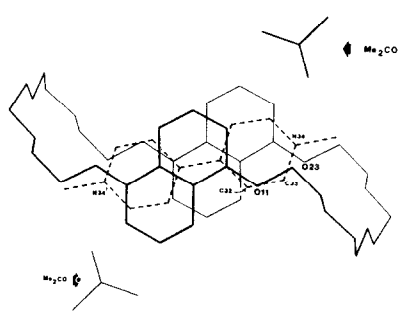


Figure 3. Side-on view (normal to the mean plane of the $[PQT]^{2+}$ dication) of the skele-representation of $[PQT.1/5DN38C10]^{2+}$

The X-ray crystal structure (Figures 1-3) of $[PQT.1/5DN38C10]^{2+}$ possesses a crystallographic centre of symmetry which is coincident for the macrocycle and the planar dication. It is interesting to note that [C—H···O] and van der Waals interactions (Figures 1 and 2) involving the methyl groups and the C-2/6 positions on $[PQT]^{2+}$ and the polyether chains of the receptor appear to be less important in stabilising the 1:1 complex than the charge transfer interactions between the π-electron deficient bipyridinium ring and the two π-electron rich naphtho rings and possibly also the electrostatic interactions between the C-2 and C-3 positions and the N atom in $[PQT]^{2+}$ (C32, C33, and N34 respectively in Figure 3) and the aryl oxygen atoms (O11 and O23 in Figure 3) in the receptor. Increasingly, it would appear from our empirically-based investigations in this area of molecular recognition that a rationalisation of the nature of the noncovalent bonding in these complexes is going to emerge from a theoretical treatment of the interacting molecular orbitals which takes into account their symmetries and charge distribution characteristics.

Comparisons (Table 1) of the ^1H NMR spectra of equimolar proportions of the bipyridinium bis-(hexafluorophosphates) and the 1,5-dinaphtho crown ethers in CD_3COCD_3 solutions with those for free $[PQT][PF_6]_2$, free $[DQT][PF_6]_2$, and the free receptors reveal that there are dramatic upfield shifts (i) for the bipyridinium ring proton resonances in $[PQT]^{2+}$, in particular the H-2,6 doublet, (ii) for all the signals in $[DQT]^{2+}$, in particular the H-3 doublet and (iii) for H-4/H-8 more so and H-3/H-7 less so in the receptors: $[DQT]^{2+}$ induces larger shifts in 1/5DN35C9 while $[PQT]^{2+}$ induces larger shifts in 1/5DN38C10. The sign and magnitudes of the shifts indicate that the central regions of the bipyridinium dications in the 1:1 complexes are oriented with-

Table 1. ^{1}H NMR Chemical shift data [δ values (Δδ values)] in CD_3COCD_3 [a]

Compound/ 1:1 Complex	[PQT]$^{2+}$			[DQT]$^{2+}$					1,5-Dinaphtho-crown		
	H-2,6	H-3,5	$^+$NMe	H-3	H-4	H-5	H-6	$^+$NCH$_2$	H-2/6	H-3/7	H-4/8
[PQT][PF_6]$_2$	9.63	8.83	4.73	-	-	-	-	-	-	-	-
[DQT][PF_6]$_2$	-	-	-	9.23	9.09	8.59	9.49	5.69	-	-	-
1/5DN35C9	-	-	-	-	-	-	-	-	6.46 6.76	7.09 7.15	7.68 7.73
[PQT.1/5DN35C9][PF_6]$_2$	9.06 (-0.30	7.95 -0.88	4.68 -0.05)	-	-	-	-	-	6.57 (+0.11 6.60 (-0.16	6.87 -0.22 7.09 -0.06	7.20 -0.48) 7.34 -0.39)
[DQT.1/5DN35C9][PF_6]$_2$	-	-	-	8.54 (-0.69	8.92 -0.17	8.34 -0.25	9.09 -0.40	5.36 -0.33)	6.48 (+0.02 6.61 (-0.15	7.06 -0.03 7.14 -0.01	7.49 -0.19) 7.52 -0.21)
1/5DN38C10	-	-	-	-	-	-	-	-	6.57	7.22	7.76
[PQT.1/5DN38C10][PF_6]$_2$	8.95 (-0.41	7.87 -0.96	4.70 -0.03)	-	-	-	-	-	6.55 (-0.02	7.09 -0.13	7.37 -0.39)
[DQT.1/5DN38C10][PF_6]$_2$	-	-	-	8.66 (-0.57	8.93 -0.16	8.47 -0.12	9.26 -0.23	5.43 -0.26)	6.59 (+0.02	7.17 -0.05	7.58 -0.18)

[a] The spectra were recorded at ambient temperature on a Bruker AM250 spectrometer using the CD_2HCOCD_2H in the CD_3COCD_3 as reference. The δ values are quoted for 0.013M solutions. The Δδ values in brackets indicate the shifts with respect to the appropriate unbound substrate or free receptor.

in the shielding zones of the naphtho rings: conversely, the naphtho rings experience the mutual influence of the diamagnetic ring currents associated with the bipyridinium rings. These observations not only concur with the solid state geometry (Figures 1-3) of [PQT.1/5DN38C10]$^{2+}$ but they are also supported by ^{13}C NMR spectroscopic data recorded in CD_3COCD_3, *e.g.* in [DQT.1/5DN35C9][PF_6]$_2$ and [DQT.1/5DN38C10][PF_6]$_2$, the resonances for C-2 in [DQT]$^{2+}$ are shifted 2.5 and 1.6 ppm upfield, respectively, while in [PQT.1/5DN35C9][PF_6]$_2$ and [PQT.1/5DN38C10][PF_6]$_2$, the resonances for C-4 in [PQT]$^{2+}$ are shifted 3.2 and 3.3 ppm upfield, respectively.

The X-ray crystal structure (Figures 4 and 5) of 1/5DN35C9 reveals that there is a major conformational difference between the dinaphtho-crown ethers and the related BPP(3n+4)Cn ethers[5] when n = 9/10. Whereas BPP34C10 supports a receptor cavity in the absence of a substrate, 1/5DN35C9 fills (Figure 5) its own cavity as a result of the naphthalene moieties adopting a

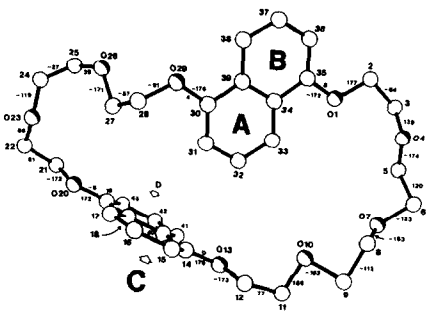


Figure 4. Structure of 1/5DN35C9 in the crystal. The dihedral angle between the mean planes of the naphtho units is 87° and the distance between the centroids of the nearest benzene rings (A and C) is 4.95 Å. Both C31 and C32 on naphtho rings A/B are displaced by 3.59 Å from the plane of naphtho units C/D. The distance of H31 from the centroid of the benzene ring in naphtho unit C/D is 2.81 Å.

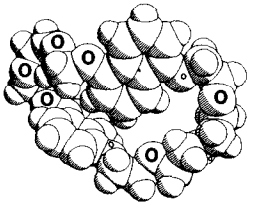


Figure 5. Space-filling representation of 1/5DN35C9

T-geometry where one naphtho ring (A/B) enters into an edge-to-face interaction[6] with the other naphtho ring (C/D). This self-filling of the receptor cavity by virtue of a stabilising electrostatic interaction ($H^{\delta+}/\pi$) probably leads to destabilisation of the 1:1 complexes formed between 1/5DN35C9 and 1/5DN38C10 and the bipyridinium dications. Quantitative measurements of complexation strengths in solution will help to resolve whether crown ethers containing naphthalene rings[7] offer significant advantages over those containing benzene rings[1,2,5,8] for the binding of Diquat and Paraquat.[9]

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2. B.L. Allwood, N. Spencer, H. Shahriari-Zavareh, J.F. Stoddart, and D.J. Williams, *J. Chem. Soc. Chem. Commun.*, 1987, 1064.
3. Experimental: Partial benzylation [K_2CO_3 (1 mol equiv), DMF, rt, 18 h] of 1,5-dihydroxynaphthalene with $PhCH_2Br$ (1 mol equiv) afforded the monobenzyl ether (mp 136-138°C) in 21% yield after chromatography [$SiO_2/CHCl_3$]. Reaction [NaH (0.5 mol equiv), DMF, 70°C, 12 h] of this naphthol with tetraethyleneglycol bistosylate (0.5 mol equiv) gave [$SiO_2/CHCl_3$-Et_2O-MeOH (30:68.5:1.5, v/v)] 1,11-bis-(5'-benzyloxynaphthoxy)-3,6,9-trioxaundecane (81%, mp 106-108°C). Deprotection (H_2, Pd/C, MeOH-$CHCl_3$), followed by separate reactions [NaH (3 mol equiv), THF, 66°C, 72 h] of the derived dinaphthol with 1 mol equiv of tetraethyleneglycol and triethyleneglycol bistosylates afforded [$SiO_2/CHCl_3$-Et_2O-MeOH (30:69:1, v/v)] 1/5DN38C10 (mp 125-127°C) and 1/5DN35C9 (mp 125-128°C), respectively. All new compounds gave satisfactory elemental analysis and spectroscopic data. The ^1H NMR spectroscopic data in CD_3COCD_3 for the aromatic protons in 1/5DN35C9 and 1/5DN38C10 are given in Table 1. Both dinaphtho crown ethers (5 mg) were dissolved in $CHCl_3$ (<1 ml) and equiv amounts of [PQT][PF_6]$_2$ and [DQT][PF_6]$_2$ in Me_2CO (<3 ml) were added. The solvents were blown off with N_2 and the crystalline samples (deep red) were analysed by FAB mass spectrometry (6kV on a Kratos MS80RF spectrometer) using argon. From a 3-nitrobenzylalcohol matrix, the crystals of [PQT.1/5DN38C10][PF_6]$_2$ afforded a strong [PQT.-1/5DN38C10.PF_6]$^+$ ion at *m/z* 967 as a result of the loss of one [PF_6]$^-$ counterion from the 1:1 complex. Similarly, [DQT.1/5DN38C10][PF_6]$_2$, [PQT.1/5DN35C9][PF_6]$_2$, and [DQT.1/5DN35C9][PF_6]$_2$ yielded peaks at *m/z* 965, 923, and 921, respectively. The crystals of the 1:1 complexes were redissolved in CD_3COCD_3 (for NMR spectroscopic investigation) and then subsequently subjected to vapour diffusion with $^iPr_2O$. With 1/5DN35C9, only colourless single crystals of the free receptor were isolated which were suitable for X-ray crystallography (Figures 4 and 5): in the case of 1/5DN38C10, however, single red crystals suitable for X-ray crystallography (Figures 1-3) were isolated of the 1:1 complex with [PQT][PF_6]$_2$.
4. Crystal data: For 1/5DN35C9: triclinic, a = 11.263(3), b = 12.255(3), c = 12.577(3) Å, α = 88.24(2), β = 64.35(2), γ = 82.21(2)°, V = 1550 Å^3, space group $P\bar{1}$, Z = 2, ρ_{calcd} =1.27 g cm^{-3} μCu-Kα = 7.1 cm^{-1}, 2861 independent observed reflections with [$|F_o| \geq 3\sigma(|F_o|)$, $\theta \leq 58°$], R = 0.089, R_w = 0.108. The high R factor is a consequence of disorder around C9 in one of the polyether chains in the molecule. For [PQT.1/5DN38C10][PF_6]$_2$: triclinic, a = 11.071(3), b = 11.523(3), c = 14.137(4) Å, α = 65.54(2), β = 77.75(2), γ = 63.51(2)°, V =1490 Å^3, space group, $P\bar{1}$, Z = 1 (the complex possesses a centre of symmetry), ρ_{calcd} = 1.37 g cm^{-3}, μCu-Kα = 15.1 cm^{-1}, 2764 independent observed reflections with [$|F_o| \geq 3\sigma(|F_o|)$, $\theta \leq 58°$], R = 0.096, R_w = 0.10. Disorder in the PF_6^- ions is responsible for the high R factor. Data were measured on a Nicolet R3m diffractometer, using the ω-scan routine with graphite-monochromated Cu-Kα radiation. Both structures were solved by direct methods and refined anisotropically. Further details of the crystal structure investigations can be obtained from the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. Any request should be accompanied by the full literature citation for this communication.
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6. This edge-to-face stacking of aromatic rings is a well-known phenomenon in the case of benzo ring systems (S.K. Burley and G.A. Petsko, *Science*, 1985, **229**, 23; *J. Amer. Chem. Soc.*, 1986, **108**, 7995) and has been observed (ref 5) in the solid state structure of BPP25C7.
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