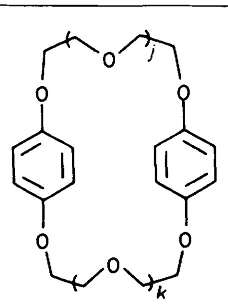
Complex Formation between Bisparaphenylene-(3*n* + 4)-crown-*n* Ethers and the Paraquat and Diquat Dications

Peter R. Ashton,[a] Alexandra M. Z. Slawin,[b] Neil Spencer,[a] J. Fraser Stoddart,[a] and David J. Williams[b]

[a] *Department of Chemistry, The University, Sheffield S3 7HF, U.K.*
[b] *Department of Chemistry, Imperial College, London SW7 2AY, U.K.*

U.v. and n.m.r. spectroscopic investigations in solution have been employed to assess the ability of a series (n = 7—12) of bisparaphenylene-(3n + 4)-crown-n ethers to form stable 1 : 1 complexes with [Diquat]$^{2+}$ and [Paraquat]$^{2+}$ dications; these mappings of molecular recognition are supported by fast atom bombardment mass spectrometry of the 1 : 1 complexes with both [Diquat][PF$_6$]$_2$ and [Paraquat][PF$_6$]$_2$, and a single crystal *X*-ray structure analysis of [Diquat·BPP31C9][PF$_6$]$_2$.

The discovery[1,2] that BPP34C10 has the ability to form stable 1:1 complexes with both the [Diquat]$^{2+}$ and [Paraquat]$^{2+}$ dications[3] poses the question of what is the optimum ring size for most stable complexation within the BPP(3n+4)Cn[4,5] series†‡ towards these dications? Here, we report (i) the



BPP(3n+4)Cn

BPP25C7	$n = 7$	$j = 2$	$k = 1$
BPP28C8	$n = 8$	$j = 2$	$k = 2$
BPP31C9	$n = 9$	$j = 3$	$k = 2$
BPP34C10	$n = 10$	$j = 3$	$k = 3$
BPP37C11	$n = 11$	$j = 4$	$k = 3$
BPP40C12	$n = 12$	$j = 4$	$k = 4$

---

† The structural formulae for [Paraquat][PF$_6$]$_2$ and [Diquat][PF$_6$]$_2$ are illustrated in the first communication (ref. 3) in this series. In the bisparaphenylene-(3n+4)-crown-n derivatives [BPP(3n+4)Cn] and their synthetic precursors the OCH$_2$ groups are designated α, β,γ, *etc.* starting adjacent to the phenylene rings and progressing along the polyether chains. In the case of the unsymmetrical BPP(3n+4)Cn ether receptors, the larger polyether chain is labelled α′,β′,γ′, *etc.* in like manner.

‡ BPP25C7, BPP28C8 (ref. 4), BPP31C9, BPP34C10 (refs. 1 and 2), BPP37C11, and BPP40C12 (ref. 4) were synthesised from the monobenzyl ether (4-BOP), m.p. 120—123 °C, after chromatography (SiO$_2$–CHCl$_3$), of 1,4-dihydroxybenzene and the appropriate (*i.e.* di, tri-, tetra-, and penta-) poly-ethyleneglycol bis(toluene-*p*-sulphonate) (DEGBT, TREGBT, TEGBT, and PEGBT) (J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, 1972, **26**, 1471) by a stepwise procedure (ref. 1).

Reaction (NaH, Me$_2$NCHO, 70 °C, 24 h) of 4-BOP with TREGBT gave 1,8-bis(4′-benzyloxyphenoxy)-3,6-dioxaoctane {74%, m.p. 106—109 °C [CHCl$_3$–light petroleum (b.p. 40—60 °C)], δ (CDCl$_3$, 220 MHz) 3.77 (4H, s, γ-OCH$_2$), 3.85 (4H, t, J 5 Hz, β-OCH$_2$), 4.10 (4H, t, J 5 Hz, α-OCH$_2$), 5.02 (4H, s, 2 × CH_2Ph), 6.89 (8H, m, 2 × C$_6$H$_4$), and 7.38 (10H, m, 2 × Ph)}. Deprotection (H$_2$, Pd/C, MeOH–CHCl$_3$), followed by reaction [NaH, tetrahydrofuran (THF), reflux,

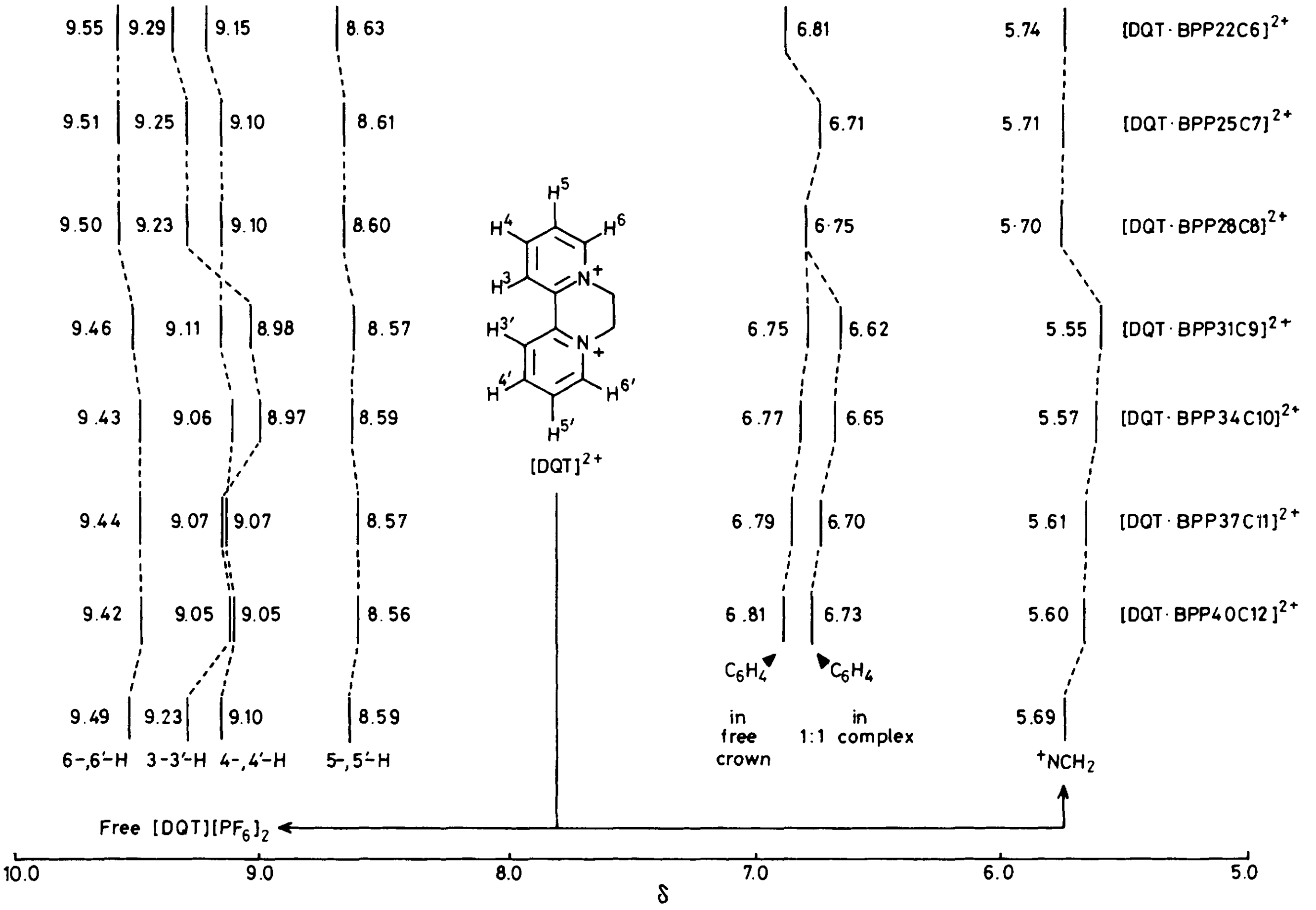


Figure 1. Representation of part of the ^1H n.m.r. spectra of equimolar amounts of $[Diquat][PF_6]_2$ and the BPP($3n$+4)Cn ethers (n = 6—12) in CD_3COCD_3 compared with those of free $[Diquat][PF_6]_2$ and free receptors.

solution spectroscopic evidence which demonstrates that the complexation maxima occur for the $[Diquat]^{2+}$ dication with BPP31C9 and for the $[Paraquat]^{2+}$ dication with BPP34C10, (ii) fast atom bombardment mass spectrometry (f.a.b.m.s.) of $[Diquat \cdot BPP(3n+4)Cn][PF_6]_2$ and $[Paraquat \cdot BPP(3n+4)\text{-}Cn][PF_6]_2$, introduced in a matrix, supporting the trends in molecular recognition observed in solution, and (iii) the X-ray crystal structure§ of $[Diquat \cdot BPP31C9][PF_6]_2$,¶ corresponding to the optimum match observed in solution.

---

48 h] of the derived diphenol with: (a) DEGBT afforded (SiO_2/85% $CHCl_3$–15% Et_2O) the BPP25C7 derivative [16%, m.p. 58—61 °C (Me_2CO–n-C_5H_{12} by vapour diffusion), single crystals suitable for X-ray crystallography, see ref. 5, δ (CD_3COCD_3, 250 MHz) 3.64 (4H, s, γ'-OCH_2), 3.74 (8H, m, β- and β'-OCH_2), 4.02 (8H, m, α- and α'-OCH_2), and 6.71 (8H, s, 2 × C_6H_4)]. (b) TREGBT afforded (SiO_2/Et_2O) the BPP28C8 derivative [16%, m.p. 92—95 °C (MeCN–Pr^i_2O by vapour diffusion), single crystals suitable for X-ray crystallography, lit. (ref. 4) m.p. 96—97 °C, see ref. 5. δ (CD_3COCD_3, 250 MHz) 3.64 (8H, s, γ-OCH_2), 3.75 (8H, m, β-OCH_2), 3.98 (8H, m, α-OCH_2), and 6.75 (8H, s, 2 × C_6H_4)]. (c) TEGBT afforded (SiO_2/15% CH_2Cl_2–85% Et_2O) the BPP31C9 derivative [24%, m.p. 60—62 °C (CH_2Cl_2–Et_2O), δ(CD_3COCD_3, 250 MHz) 3.58—3.70 (12H, m, γ-, γ'-, and δ'-OCH_2), 3.77 (8H, m, β- and β'-OCH_2), 3.97 (8H, m, α- and α'-OCH_2), and 6.75 (8H, 2 × s, 2 × C_6H_4)].

Reaction (NaH, Me_2NCHO, 70 °C, 24 h) of 4-BOP with PEGBT gave 1,14-bis(p-benzyloxyphenoxy)-3,6,9,12-tetraoxatetradecane {80%, m.p. 92—93 °C [CH_2Cl_2–light petroleum (b.p. 40—60 °C)], δ ($CDCl_3$, 220 MHz) 3.72 (12H, m, ε-, δ-, and γ-OCH_2), 3.85 (4H, t, J 5 Hz, β-OCH_2), 4.10 (4H, t, J 5 Hz, α-OCH_2), 5.05 (4H, s, 2 × CH_2Ph), 6.90 (8H, m, 2 × C_6H_4), and 7.40 (10H, m, 2 × Ph)}. Deprotection (H_2, Pd/C, MeOH–$CHCl_3$), followed by reaction (NaH, THF, reflux, 48 h) of the derived diphenol with: (a) TEGBT afforded (SiO_2/66% Et_2O–30% $CHCl_3$–4% MeOH) the BPP37C11 derivative [30%, m.p. 55—57 °C, ($ex.$ CH_2Cl_2–n-C_5H_{12} by vapour diffusion), single crystals suitable for X-ray crystallography, see ref. 5. δ (CD_3COCD_3, 250 MHz) 3.60 (12H, m, ε-, δ, δ'-, γ-, and γ'-OCH_2), 3.77 (8H, m, β- and β'-OCH_2), 3.98 (8H, m, α- and α'-OCH_2), and 6.79 (8H, s, 2 × C_6H_4).] (b) PEGBT afforded (SiO_2/66% Et_2O–30% $CHCl_3$–4% MeOH) the BPP40C12 derivative [23%, m.p. 62—65 °C (Me_2CO–n-C_5H_{12} by vapour diffusion), single crystals suitable for X-ray crystallography, lit. (ref. 4) m.p. 67—69 °C, see ref. 5. δ (CD_3COCD_3, 250 MHz) 3.59 (24H, m, ε-, δ-, and γ-OCH_2), 3.76 (8H, m, β-OCH_2), 4.00 (8H, m, α-OCH_2), and 6.81 (8H, s, 2 × C_6H_4)].

§ *Crystal data* for $[Diquat \cdot BPP31C9][PF_6]_2$: $C_{26}H_{36}O_9 \cdot C_{12}H_{12}N_2 \cdot P_2F_{12}$, M = 968.9, monoclinic, space group $P2_1/c$, a = 13.117(2), b = 19.857(2), c = 16.662(2) Å, β = 97.95(1)°, U = 4298 Å^3, Z = 4, D_c = 1.50 g cm^{-3}, μ(Cu-K_α) = 19 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and refined anisotropically to give R = 0.067, R_w = 0.063 for 3042 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leq 50°$]. There is some disorder in the polyether chain and three principal partial occupancy positions for O(13) were refined. 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.

¶ Red single crystals (m.p. 111—113 °C) suitable for X-ray structural analysis were isolated from Me_2CO solutions containing equimolar quantities of $[Diquat][PF_6]_2$ and BPP31C9 on vapour diffusion with Pr^i_2O.

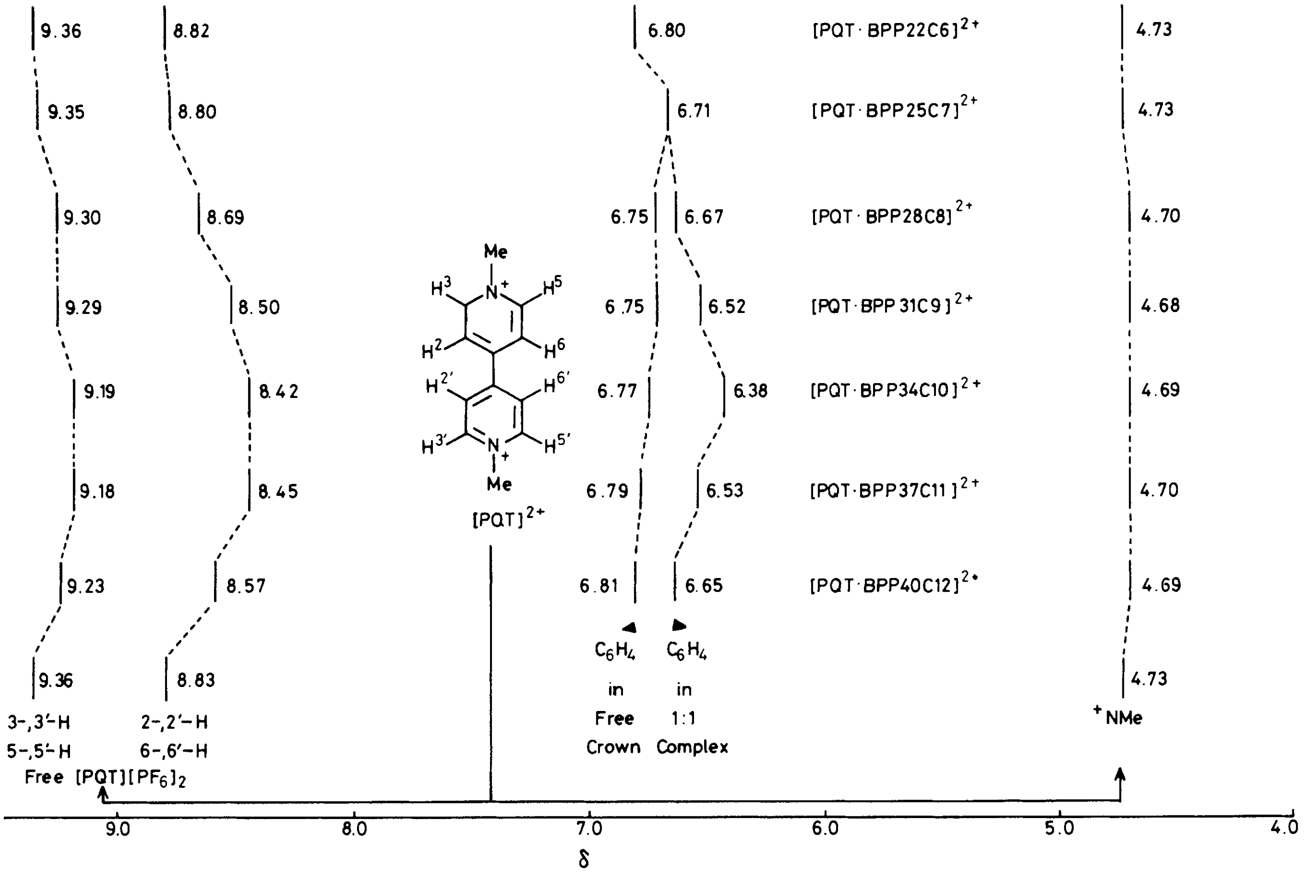


Figure 2. Representation of part of the ^{1}H n.m.r. spectra of equimolar amounts of [Paraquat][PF_6]$_2$ and the BPP(3n+4)Cn ethers (n = 6—12) in CD_3COCD_3 compared with those of free [Paraquat][PF_6]$_2$ and free receptors.

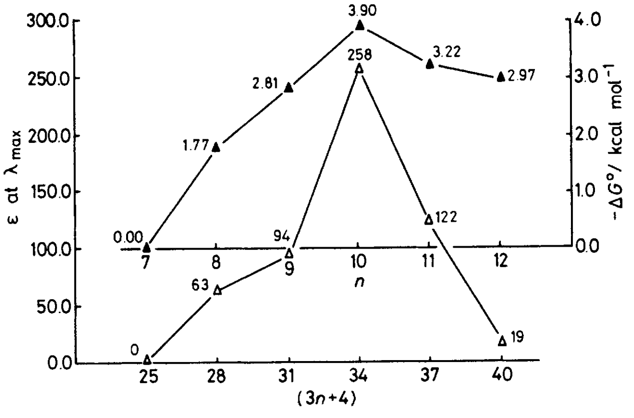


Figure 3. The dependence of ε at $\lambda_{max.}$ for the CT absorption bands of equimolar amounts (4 × 10^{-3} M) of [Paraquat][PF_6]$_2$ and the BPP(3n+4)Cn ethers in acetone upon the ring size (3n+4) of the receptors. Superimposed upon this plot (A) is a plot (B) of $-\Delta G^0$ *vs.* n for the 1 : 1 complexes formed between [Paraquat][PF_6]$_2$ and the BPP(3n+4)Cn ethers (n = 7—12) in acetone.

Comparisons of the ^{1}H n.m.r. spectra of equimolar amounts of the bipyridinium bis(hexafluorophosphates) and BPP-(3n+ 4)Cn (n = 7—12) in CD_3COCD_3 solutions with those for free [Diquat][PF_6]$_2$, free [Paraquat][PF_6]$_2$, and the free macrocycles reveal (Figures 1 and 2) that there are dramatic upfield shifts, in particular, (i) for the 3-,3'-H doublet of the [Diquat]$^{2+}$ dication when n = 9 and 10, (ii) for the 3-,3'-H, 5-, 5'-H doublet of the [Paraquat]$^{2+}$ dication when n = 10 and 11, and (iii) for the aromatic proton resonances of the macrocycles when n = 9—12. The sign and magnitudes of the shifts support the idea that 1 : 1 complexes are formed in solution in which the bipyridinium dications are sandwiched between the two paraphenylene units of the BPP(3n+4)Cn ethers (n = 9—12) such that the 'central regions' of the dications are located within the shielding zones of the hydroquinol rings. This interpretation is supported by comparisons of an analogous nature based on ^{13}C n.m.r. spectra recorded in CD_3COCD_3, *e.g.* in [Diquat·BPP31C9][PF_6]$_2$ and [Paraquat·BPP34C10]-[PF_6]$_2$, the resonances for C-2,-2' and C-4,-4', respectively, in the dications are shifted 1.1 and 2.1 p.p.m. upfield on complexation. In the case of [Paraquat·BPP(3n+4)-Cn][PF_6]$_2$, evidence for the 1 : 1 stoicheiometries of the complexes, at least when n = 8—12, together with estimates of their association constants (K_a) and derived free energies of complexation (ΔG^0) for equilibrium (1) were obtained[6] from a treatment of the concentration dependence of the intensities of the charge transfer (CT) absorption bands ($\lambda_{max.}$ 420—435 nm) in Me_2CO for 1 : 1 mixtures of [Paraquat][PF_6]$_2$ with the BPP(3n+4)Cn ethers. A plot of $-\Delta G^0$ *vs.* n is shown in Figure 3 which also displays the dependence of ε for the CT absorption bands on n: both sets of data point to the conclusion that BPP34C10 is the best receptor for the [Paraquat]$^{2+}$ dication. Significantly, in the case of this dication, [Paraquat·BPP34C10][PF_6]$_2$ is the only crystalline complex to have been isolated in the BPP(3n+4)Cn series of receptors and to have been investigated by *X*-ray crystallography.[1]

$$[\text{Paraquat}][PF_6]_2 + \text{BPP}(3n{+}4)\text{C}n \rightleftharpoons [\text{Paraquat}{\cdot}\text{BPP}(3n{+}4)\text{C}n][PF_6]_2 \quad (1)$$

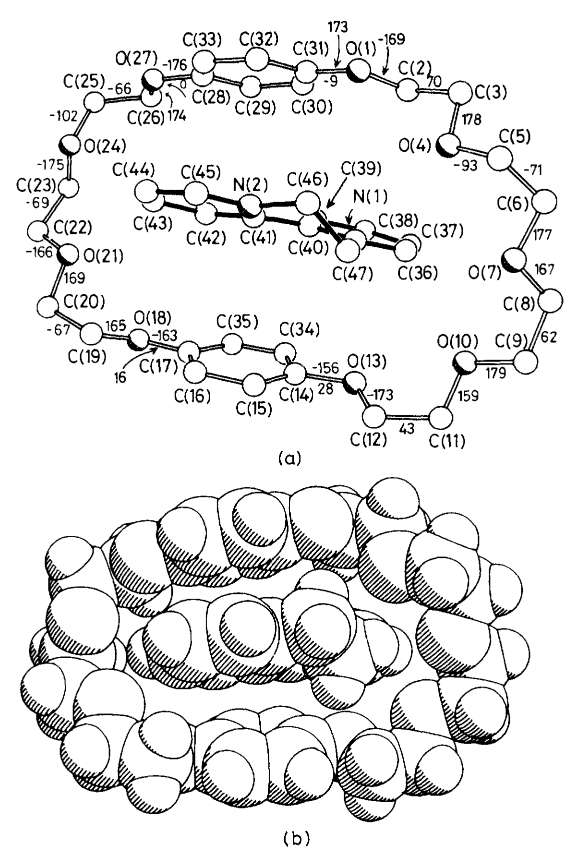


Figure 4. (a) The solid state structure of [Diquat·BPP31C9]$^{2+}$ Torsional angles (°) (O–C–C–O and C–C–O–C) associated with the polyether chains are shown beside the relevant C–C and C–O bonds. Selected host–guest potential hydrogen bonding distances less than 3.4 Å: R[C · · · O], R[H· · · O] (Å), C–H · · · O angles (°) assuming normal trigonal geometries: [C(43)–O(21)], 3.12, [H(43)–O(21)], 2.32, 140; [C(36)–O(10)], 3.18, [H(36)–O(10)], 2.50, 128; [C(36)–O(7)], 3.38, [H(36)–O(7)], 2.49, 155. Other host–guest contact distances (Å): [C(47)–O(4)], 3.24, [C(36)–O(13)], 3.31; [C(43)–O(27)], 3.35; [C(46)–O(4)], 3.37. The distances and angles in the O(1) · · · N(1) · · · O(13) array are [N(1)–O(1)], 4.05; [N(1)–O(13)], 3.33 Å; [O(1)–N(1)–O(13)] angle, 174°. Note that for all quoted distances, angles, and torsional angles, the location of O(13) closest to the plane of its associated paraphenylene ring has been used. (b) Space-filling representation corresponding to (a).

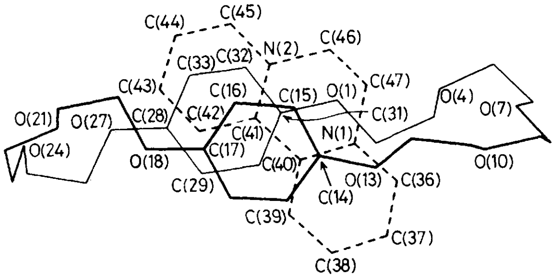


Figure 5. The side-on view of the solid state structure of [Diquat·BPP31C9]$^{2+}$. The [Diquat]$^{2+}$ dication is represented by a dashed line whilst the receptor is represented by a solid line.

In view of the data summarised in Figure 3, it is interesting to note that, from a 3-nitrobenzyl alcohol matrix and using argon, positive ion f.a.b.m.s. (6 kV and Kratos MS80RF spectrometer) has revealed that, whereas BPP25C7 does not afford a [Diquat/Paraquat·BPP25C7·PF$_6$]$^+$ ion, all the other BPP(3n+4)Cn macrocycles give peaks for [Diquat/Paraquat·BPP(3n+4)Cn·PF$_6$]$^+$ ions, *i.e.* at m/z 777, 821, 865, 909, and 953 in the case of [Diquat][PF$_6$]$_2$ and at m/z 779, 823, 867, 911, and 955 in the case of [Paraquat][PF$_6$]$_2$ for n = 8, 9, 10, 11, and 12, respectively. In both cases, the relative intensities of the positive ions with respect to the 'fragment' ions for the parent crown ethers show maxima at n = 9/10.

In the crystal structure§¶ of [Diquat·BPP31C9][PF$_6$]$_2$, we have the first opportunity to examine (Figures 4 and 5) the nature of the binding of the [Diquat]$^{2+}$ dication by a constitutionally-asymmetrical macrocyclic polyether. Whilst the conformations of the two polyether loops deviate slightly from an 'all-*gauche*' geometry,[7] the four phenoxymethylene units remain[1] approximately coplanar with the hydroquinol rings. There are remarkable structural similarities in the positioning of the [Diquat]$^{2+}$ dication within the receptor cavity of BPP31C9 compared with that observed[2] in [Diquat·BPP34C10·H$_2$O]$^{2+}$. In this ternary complex, we considered that the significant tilt of the [Diquat]$^{2+}$ dication with respect to the long axis of the receptor cavity was occasioned by its co-complexation with a water molecule. Here, in the absence of a water molecule, a comparable relative host–guest geometry is displayed. Once again, a dominant feature of the structure of the 1 : 1 complex is the essentially collinear arrangement of O(1) · · · N(1) · · · O(13), the dication pivoting about this axis so as to achieve an alignment and partial overlap of the N(2) pyridinium ring and the C(28)–C(33) hydroquinol ring (Figure 5). In addition, there are characteristic weak C–H · · · O stabilising interactions (see caption to Figure 4).

The qualitative correspondence between solution and solid state structures suggests that a detailed quantitative analysis of ^{1}H and ^{13}C n.m.r. chemical shift data on these and related[1—3,6,8] 1 : 1 complexes could provide the basis for a valuable structural correlation between solid and solution phases in this challenging area of intermolecular conformational analysis.

We acknowledge financial support for this research from A.F.R.C., S.E.R.C., and the Leverhulme Trust.

Received, 11th February 1987; Com. 189

References

1 B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart, and D. J. Williams, preceding communication.

2 B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart, and D. J. Williams, communication preceding the previous one.

3 B. L. Allwood, H. M. Colquhoun, S. M. Doughty, F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, and R. Zarzycki, first communication in this series.

4 R. C. Helgeson, J. M. Timko, and D. J. Cram, *J. Am. Chem. Soc.*, 1974, **96**, 7380; R. C. Helgeson, T. L. Tarnowski, J. M. Timko, and D. J. Cram, *ibid.*, 1977, **99**, 6411.

5 A. M. Z. Slawin, N. Spencer, J. F. Stoddart, and D. J. Williams, following communication.

6 H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, J. B. Wolstenholme, and D. J. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1985, 607.

7 D. A. Laidler and J. F. Stoddart, in 'The Chemistry of Functional Groups. Supplement E. The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues,' ed. S. Patai, Wiley-Interscience, 1980, part 1, p. 1.

8 B. L. Allwood, F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, 311; F. H. Kohnke and J. F. Stoddart, *ibid.*, 1985, 314; F. H. Kohnke, J. F. Stoddart, B. L. Allwood, and D. J. Williams, *Tetrahedron Lett.*, 1985, **26**, 1681; F. H. Kohnke and J. F. Stoddart, *ibid.*, 1985, **26**, 1685; B. L Allwood, F. H. Kohnke, J. F. Stoddart, and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 581.