J. Chem. Soc. Chem. Commun. 1061-64 (1987)

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

Billy L. Allwood,[a] Neil Spencer,[b] Hooshang Shahriari-Zavareh,[b] J. Fraser Stoddart,[b] and David J. Williams[a]

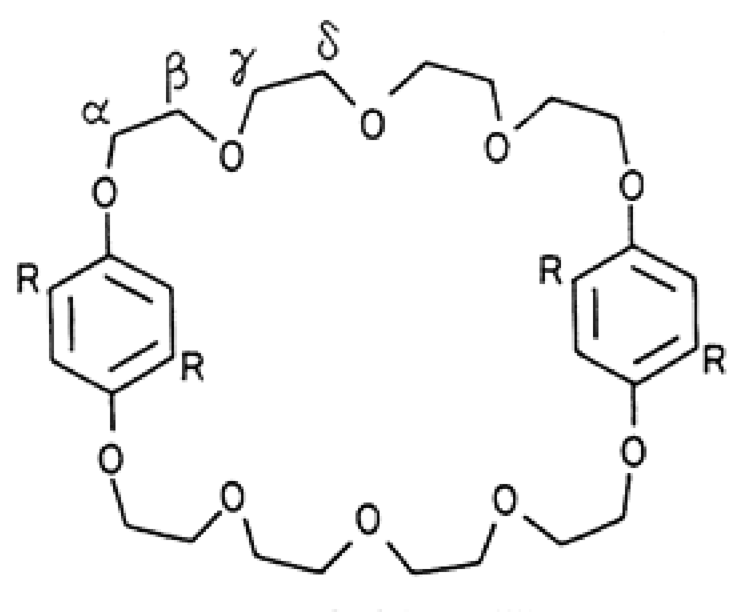
[a] *Department of Chemistry, Imperial College, London SW7 2AY, U.K.*
[b] *Department of Chemistry, The University, Sheffield S3 7HF, U.K.*

X-Ray structural investigations of a bisparaphenylene-34-crown-10 derivative (BPP34C10) and its 1 : 1 : 1 complex with [Diquat][PF_6]$_2$ and H_2O reveal that, of two crystallographically independent conformations (I and II) both supporting large molecular cavities, one (II) retains its gross shape on complexation and interacts with the [Diquat]$^{2+}$ dication by means of hydrogen and electrostatic bonds whilst accommodating weak charge transfer interactions and a hydrogen bonded H_2O molecule within the docking constraints and microcavity, respectively, imposed by the more dominant non-covalent forces.

Greatly encouraged by the observation[1] that BMP32C10† is capable of complexing with [Paraquat][PF_6]$_2$,† as well as with [Diquat][PF_6]$_2$,† by virtue of a combination[2] of electrostatic and charge transfer interactions, we intensified our search for an even better synthetic molecular receptor for the [Paraquat]$^{2+}$ dication. This led to the evaluation of a bisparaphenyl-

---

† The structural formulae for BMP32C10 and for [Paraquat][PF_6]$_2$ and [Diquat][PF_6]$_2$ are illustrated in the two preceding communications (refs. 1 and 2). The structural formula for the bisparaphenylene-34-crown-10 derivative (BPP34C10) is numbered with reference to its systematic name, 1,4,7,10,20,23,26,29,32-decaoxa[13.13]paracyclophane. Note that in BPP34C10 and its precursors, the OCH_2 groups are designated α,β,γ,δ, starting adjacent to the phenylene rings and progressing along the polyether chains. To date, the evidence for the complexation of [Paraquat][PF_6]$_2$ by BMP32C10 comes from experiments in solution only.



BPP34C10 R = H
$(MeO)_4$BPP34C10 R = OMe

ene-34-crown-10 derivative (BPP34C10)[3,4] as a potential complexer of $[Paraquat]^{2+}$ and $[Diquat]^{2+}$ dications. Here, we report on (i) the step-wise synthesis‡ of BPP34C10, (ii) its *X*-ray crystal structure,§ (iii) the *X*-ray crystal structure§ of the 1:1:1 complex formed between BPP34C10, $[Diquat][PF_6]_2$, and H_2O, and (iv) ^1H n.m.r. spectroscopic investigations on the binding of $[Paraquat][PF_6]_2$ and $[Diquat][PF_6]_2$ by BPP34C10 in solution. Although the main reason for evaluating BPP34C10 was to uncover a more efficient receptor[5] for the $[Paraquat]^{2+}$ dication, the evidence obtained[1] from the structural analysis of $[Diquat{\cdot}BMP32C10][PF_6]_2$ suggested that the $[Diquat]^{2+}$ dication should also be bound by BPP34C10 in view of the demonstrated importance of attaining at least one good approximately collinear $[O^{\delta-} \cdots N^{\delta+} \cdots O^{\delta-}]$ electrostatic interaction rather than achieving the expected optimal geometry for charge transfer stabilisation.

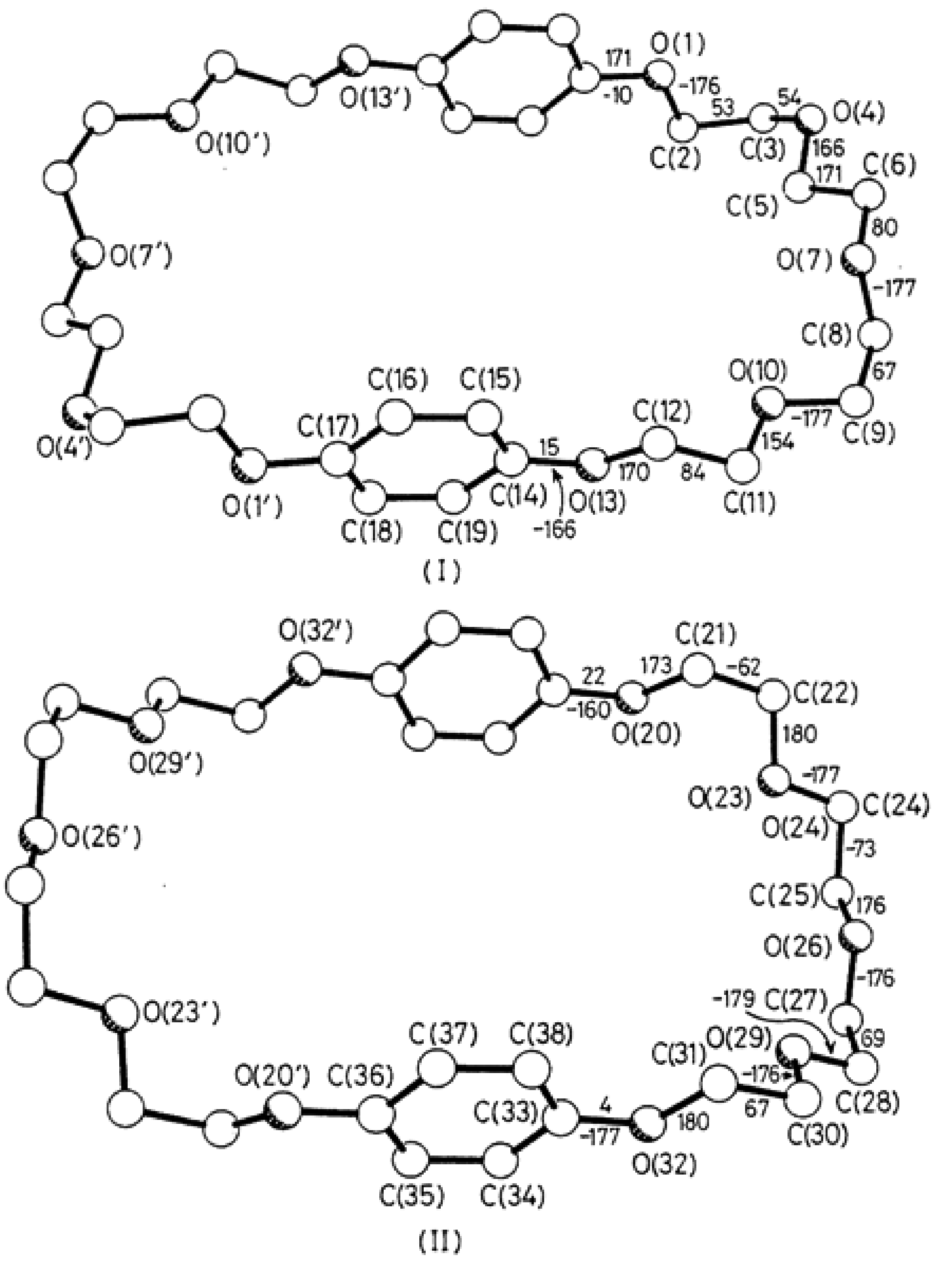


Figure 1. The solid state structure of the two crystallographically independent conformations, (I) and (II), of BPP34C10. Torsional angles (°) (O–C–C–O and C–C–O–C) associated with the two polyether chains are shown beside the relevant C–C and C–O bonds. In both conformations (I) and (II), the aromatic rings are parallel with separations between their mean planes of 7.1 and 7.3 Å, respectively.

In the solid state,‡§ BPP34C10 exists (Figures 1 and 2) in two crystallographically independent conformations, (I) and (II): both possess a crystallographic centre of symmetry and both display unusually open conformations similar to that[1] of BMP32C10. One conformation, namely (II), matches very closely the conformation adopted by the receptor in the solid state structure§¶ (Figure 3) of $[Diquat{\cdot}BPP34C10{\cdot}H_2O][PF_6]_2$. It has (Figure 2) an almost perfectly preformed cavity (approx. free pathway, 10.6 × 4.7 Å) in contrast with the tetramethoxy derivative, $(MeO)_4$BPP34C10, in which the two aromatic rings, although not stacked, are parallel, with one of the methoxy groups on each aromatic ring oriented towards the centre of the receptor cavity.[6] In fact, provided each aromatic ring carries at least one substituent, self-filling of molecular cavities appears to be a general feature of molecular receptors based on an *[n.n]*paracyclophane constitution.

The solid state structure§¶ of $[Diquat{\cdot}BPP34C10{\cdot}H_2O][PF_6]_2$ reveals (Figure 3) an essentially oval-shaped

---

‡ Previously, BPP34C10 has been prepared (ref. 3) in 8% yield by a one-step synthesis from hydroquinol (HQ) and tetraethyleneglycol bis(toluene-*p*-sulphonate) (TEGBT). We preferred to employ a four-step procedure, analogous to that (ref. 1) devised for preparing BMP32C10, because of the opportunities it offers for subsequent constitutional modification. Partial benzylation ($PhCH_2Cl$, K_2CO_3, Me_2NCHO, room temp., 18 h) of HQ afforded (SiO_2–CH_2Cl_2) 4-benzyloxyphenol [63%, oil, δ ($CDCl_3$, 220 MHz) 5.02 (2H, s, CH_2Ph), 6.75 and 6.86 (4H, AB system, J_{AB} 9 Hz, 2-H, 3-H, 5-H, and 6-H), and 7.30—7.50 (6H, m, Ph and OH)]. Reaction (NaH, Me_2NCHO, 80 °C, 24 h) of this phenol with TEGBT gave [SiO_2–CH_2Cl_2–Et_2O (98:2), v/v)] 1,11-bis(4′-benzyloxyphenoxy)-3,6,9-trioxaundecane [68%, oil, δ ($CDCl_3$, 220 MHz) 3.65—3.80 (8H, m, γ- and δ-OCH_2), 3.84 and 4.10 (2 × 4H, 2 × t, *J* 5 Hz, β- and α-OCH_2, respectively), 5.02 (4H, s, 2 × CH_2Ph), 6.86 and 6.92 (8H, AB system, J_{AB} 9 Hz, 2′-H, 3′-H, 5′-H, and 6′-H), and 7.30—7.48 (10H, m, 2 × Ph)]. Deprotection (H_2, Pd/C, MeOH–Et_2O), followed by reaction (NaH, Me_2NCHO, 70 °C, 24 h) of the derived diphenol with TEGBT afforded [SiO_2–CH_2Cl_2–Et_2O (3:7, v/v)] the BPP34C10 derivative [31%, m.p. 87—89 °C (MeOH) single crystals suitable for *X*-ray crystallography, lit. (ref. 3) m.p. 93.5—94 °C, see Figures 1 and 2 for the *X*-ray crystal structure, δ ($CDCl_3$, 220 MHz) 3.82 (16H, br.m, γ- and δ-OCH_2), 3.85 and 4.01 (2 × 8H, 2 × t, *J* 5 Hz, β- and α-OCH_2, respectively), and 6.77 (8H, s, 2 × C_6H_4)].

§ *Crystal data* for BPP34C10: $C_{28}H_{40}O_{10}$, $M = 536.7$, monoclinic, space group $P2_1/c$, $a = 10.890(2)$, $b = 21.450(6)$, $c = 12.361(4)$ Å, $\beta = 106.31(2)°$, $U = 2771$ Å^3, $Z = 4$ (2 independent centrosymmetric molecules in the asymmetric unit), $D_c = 1.29$ g cm^{-3}, $R = 0.052$, $R_w = 0.060$ for 2638 independent observed reflections [$\theta \leqslant 50°$, $|F_o| > 3\sigma(|F_o|)$]. $[Diquat{\cdot}BPP34C10][PF_6]_2{\cdot}H_2O$, $C_{12}H_{12}N_2{\cdot}C_{28}H_{40}O_{10}{\cdot}P_2F_{12}{\cdot}H_2O$, $M = 1029$, triclinic, space group $P\bar{1}$, $a = 10.786(5)$, $b = 11.659(6)$, $c = 20.098(14)$ Å, $\alpha = 96.90(5)$, $\beta = 98.83(5)$, $\gamma = 104.23(4)°$, $U = 2387$ Å^3, $Z = 2$, $D_c = 1.44$ g cm^{-3}, $R = 0.052$, $R_w = 0.060$ for 2638 independent observed reflections [$\theta \leqslant 50°$, $|F_o| > 3\sigma(|F_o|)$]. Data for both structures were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α 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. In $[Diquat{\cdot}BPP34C10][PF_6]_2{\cdot}H_2O$, two discrete positions were observed for C(12): they were refined with 40 and 60% occupancies. 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.

¶ Single red crystals (m.p. 248—252 °C) suitable for *X*-ray structural analysis were grown from an equimolar mixture of $[Diquat][PF_6]_2$ and BPP34C10 dissolved in acetone and layered with n-pentane.

Table 1. ^{1}H N.m.r. chemical shift data [δ values (Δδ values)]^a in CD_3COCD_3.

Compound or complex	[Paraquat]$^{2+}$			[Diquat]$^{2+}$					BPP34C10				
	2-,6-H	3-,5-H	$(\overset{+}{N}Me)_2$	3-,3′-H	4-,4′-H	5-,5′-H	6-,6′-H	$(\overset{+}{N}CH_2)_2$	ArH	α-OCH_2	β-OCH_2	γ-OCH_2	δ-OCH_2
BPP34C10	—	—	—	—	—	—	—	—	6.77	3.96	3.78	3.61	3.61
[Paraquat][PF_6]$_2$	9.36	8.83	4.73	—	—	—	—	—	—	—	—	—	—
[Paraquat·BPP34C10][PF_6]$_2$	9.19	8.42	4.69	—	—	—	—	—	6.38	3.71	3.71	3.71	3.71
	(−0.17)	(−0.41)	(−0.04)						(−0.39)	(−0.25)	(−0.07)	(+0.10)	(+0.10)
[Diquat][PF_6]$_2$	—	—	—	9.23	9.09	8.59	9.49	5.69	—	—	—	—	—
[Diquat·BPP34C10][PF_6]$_2$	—	—	—	8.97	9.06	8.59	9.43	5.57	6.65	3.86	3.75	3.67	3.67
				(−0.26)	(−0.03)	(0.00)	(−0.06)	(−0.12)	(−0.12)	(−0.10)	(−0.03)	(+0.06)	(+0.06)

[a] Spectra were recorded at ambient temperature on a Bruker AM250 spectrometer using CD_2HCOCD_2H as reference. The Δδ 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.

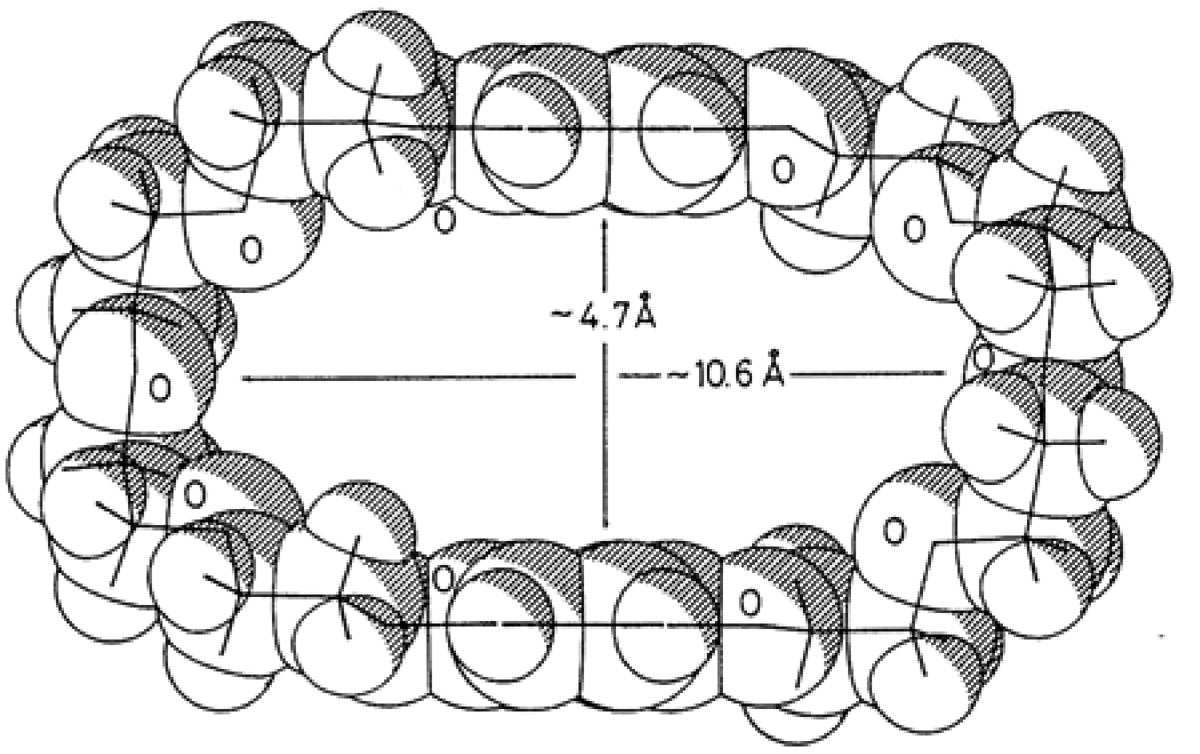


Figure 2. Space-filling representation of conformation (II) of BPP34C10.

receptor cavity with the [Diquat]$^{2+}$ dication passing approximately through the centre of the BPP34C10 which presents one [O(1) to O(13)] of its polyether loops‖ towards acidic hydrogen atoms on carbon atoms [C(39), C(49), and C(50)] α to the nitrogen atoms in the dication. Weak hydrogen bonds with [H ··· O] distances and C–H ··· O angles at the H atoms of 2.55 Å and 129°, 2.47 Å and 149°, and 2.40 Å and 167° have been identified for the contacts [C(39)–O(10)], [C(49)–O(1)], and [C(50)–O(7)], respectively. An almost collinear [O(1) ··· N(1) ··· O(13)] alignment provides additional electrostatic stabilisation and an axis about which the [Diquat]$^{2+}$ dication appears to pivot until it achieves near overlap (Figure 4a) of its C(42)–C(43)–C(44)–C(45) unit with the four-carbon units C(15)–C(14)–C(35)–C(36) and C(38)–C(34)–C(33)–C(32) in the two hydroquinol rings. This observation raises the question of whether this geometry is particularly favourable for efficient charge transfer. The fact that this structural feature is common to the structure (Figure 4b) of the [Diquat·BMP32C10]$^{2+}$ dication suggests that this relative geometrical arrangement of a sandwiched bipyridinium ring system between either two neighbouring resorcinol or two neighbouring hydroquinol rings is particularly favourable. In the [Diquat·BPP34C10·H_2O]$^{2+}$ dication, the above proposal could provide an explanation for the simultaneous entrapment of the H_2O molecule by the second polyether loop bridging O(18) to O(30). The siting of this H_2O molecule is associated with two good hydrogen bonds between O(51) and O(21), and O(51) and O(27) involving H ··· O distances of 1.93 and 2.03 Å, respectively, with corresponding O–H ··· O angles of 178 and 126°. The nearest contact (3.14 Å) of O(51) with the [Diquat]$^{2+}$ dication is to C(46).

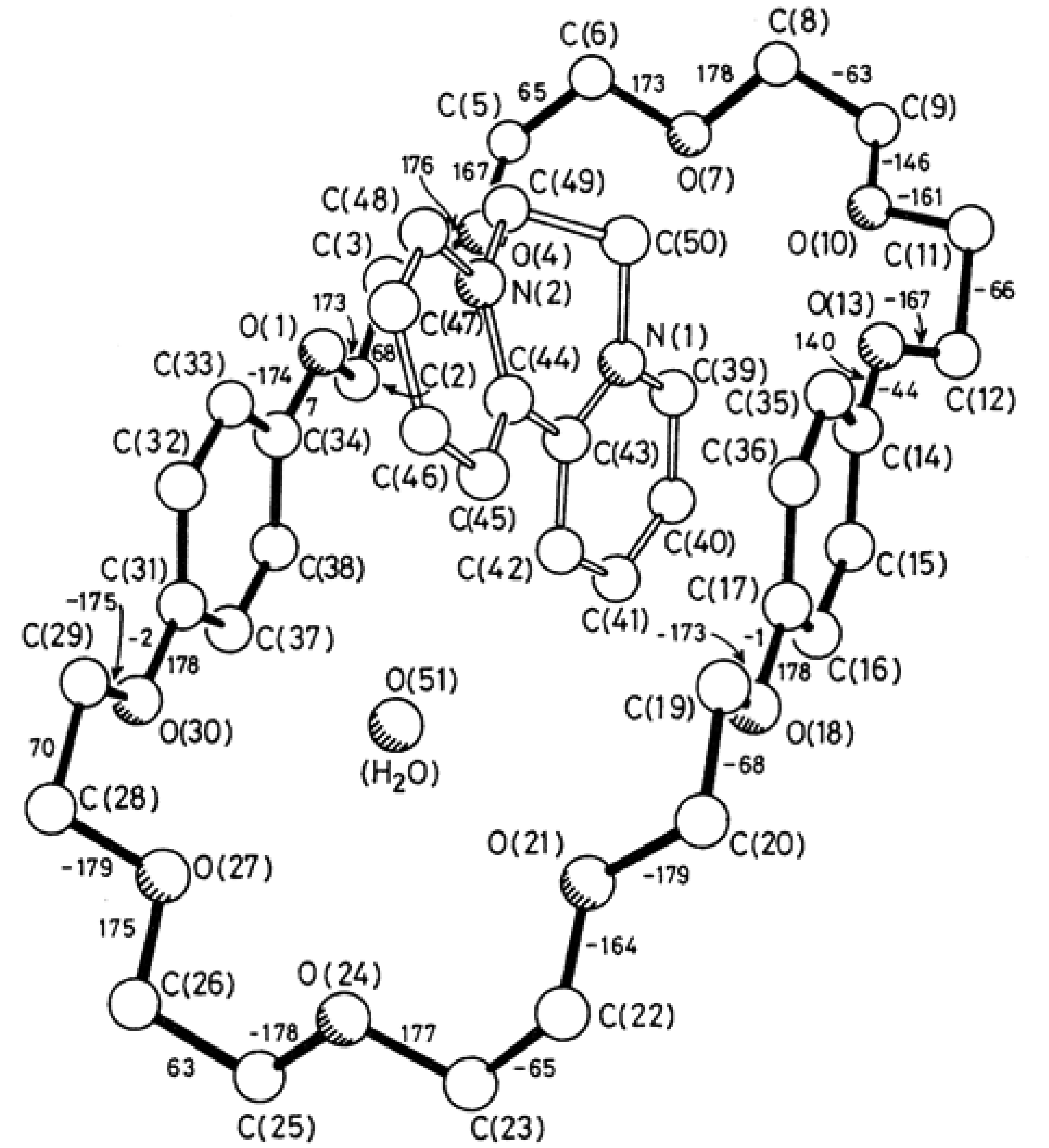


Figure 3. The solid state structure of [Diquat·BPP34C10·H_2O]$^{2+}$. Torsional angles (°) (O–C–C–O and C–C–O–C) associated with the two polyether chains are shown beside the relevant C–C and C–O bonds. Selected host–guest contact distances (Å) less than 3.4 Å: [C(39)–O(10)], 3.25; [C(49)–O(1)], 3.33; [C(50)–O(7)], 3.35; [H_2O–O(21)], 2.89; [H_2O–O(27)], 2.94. Separation (Å) between pyridinium ring N in guest and phenolic O in host: N(1)–O(1), 3.69; N(1)–O(13), 3.20. O(1) ··· N(1) ··· O(13) angle: 170°. Twist angle between pyridinium rings in the guest: 24°. Separation between the benzo rings in the host of 7.0 Å with 3.1° departure from parallel alignment of their mean planes.

Comparison (Table 1) of the ^{1}H n.m.r. spectra of [Paraquat·BPP34C10][PF_6]$_2$ and [Diquat·BPP34C10][PF_6]$_2$ in CD_3COCD_3 with those for the free salts and BPP34C10 reveals that the following probe protons experience substantial upfield shifts: (i) aromatic protons (−0.39 and −0.12 p.p.m., respectively) and α-OCH_2 (−0.25 and −0.10 p.p.m.,

---

‖ The conformation of this polyether loop from O(1) to O(13) is remarkably similar to that of the polyether loop from O(13) to O(1) in the solid state structure (ref. 1) of [Diquat·BMP32C10][PF_6]$_2$.

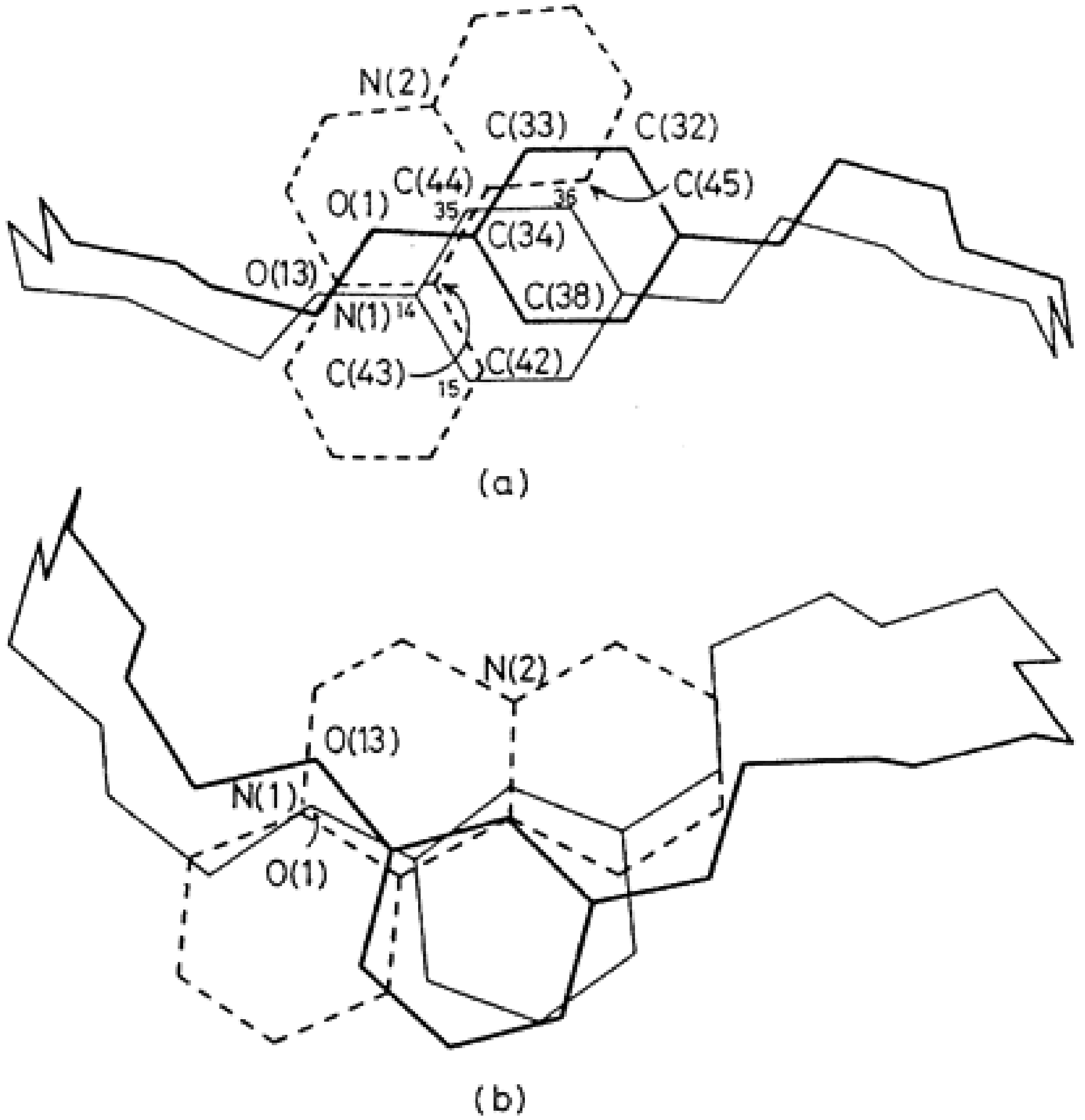


Figure 4. Side-on views of the solid state structures of (a) [Diquat·BPP34C10·H_2O]$^{2+}$ and (b) [Diquat·BMP32C10]$^{2+}$. The [Diquat]$^{2+}$ dication is represented by a dashed line whilst the receptors are represented by solid lines. Note that the H_2O molecule is omitted in the first case.

respectively) in BPP34C10, (ii) 2-,6-H (−0.17 p.p.m.) and 3-,5-H (−0.41 p.p.m.) in [Paraquat]$^{2+}$, and (iii) 3-,3′-H (−0.26 p.p.m.) in [Diquat]$^{2+}$. These observations indicate that, in the 1:1 complexes, both substrates are sandwiched between the hydroquinol rings of BPP34C10. While the upfield shifts highlighted above in (i) and (ii) relate qualitatively to the solid state structure[5] for [Paraquat·BPP34C10][PF_6]$_2$, the selective shift of 3-,3′-H in [Diquat·BPP34C10][PF_6]$_2$ equates rather well with the siting of these protons within the shielding zone of the paraphenylene rings of BPP34C10 in the solid state structure (Figure 4a) of the 1:1 complex.

In both the free and complexed BPP34C10, the phenoxymethylene units are all close to being coplanar[7] with the hydroquinol rings, *cf.* the situation[1] in catechol- and resorcinol-derived receptor molecules. The gross conformation of the receptor in the 1:1:1 complex is very similar to that of conformation (II) in the free BPP34C10. The implication is that complexation of the [Diquat]$^{2+}$ dication by BPP34C10 occurs with little change required in the shape of the molecular receptor.

We thank the A.F.R.C. for their support of this research and the Leverhulme Trust for the award of a Research Fellowship (to J. F. S.).

Received, 11th February 1987; Com. 187

References

1 B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart, and D. J. Williams, preceding communication.
2 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, communication preceding the previous one.
3 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.
4 N. Kawashima, T. Kawashima, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, 1978, 5025.
5 B. L. Allwood, H. Shahriari-Zavareh, N. Spencer, J. F. Stoddart, and D. J. Williams, following communication.
6 J. D. Owen, *Acta Crystallogr., Sect. C.*, 1984, **40**, 951.
7 *Cf.* A. Makriyannis and S. Fesik, *J. Am. Chem. Soc.*, 1982, **104**, 6462; L. I. Kruse and J. K. Cha, *J. Chem. Soc., Chem. Commun.*, 1982, 1329; J. D. Mersh, J. K. M. Saunders, and S. A. Matlin, *ibid.*, 1983, 306.