A Comparison of the Receptor Stereochemistry in $[Pt(bipy)(NH_3)_2{\cdot}Dinaphtho\text{-}30\text{-}crown\text{-}10][PF_6]_2$ and $[Diquat{\cdot}Dinaphtho\text{-}30\text{-}crown\text{-}10][PF_6]_2$ (bipy = 2,2′-bipyridine)

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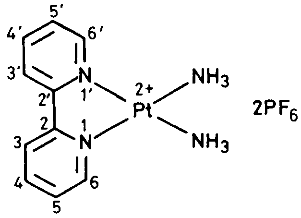
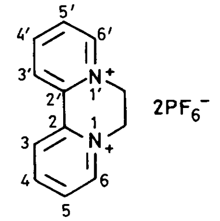
X-Ray crystallography and ^1H n.m.r. spectroscopy have revealed dramatic differences in the binding of $[Pt(bipy)(NH_3)_2]^{2+}$ and $[Diquat]^{2+}$ dications by dinaphtho-30-crown-10 (DN30C10) with the platinum complex adopting a slewed position, apparently in order to maximise overlap between the π-arene systems in the receptor and in the complex, whereas the Diquat dication adopts a symmetrical position more consistent with maximisation of Coulombic interactions.

The *X*-ray structure of the second-sphere co-ordination adduct formed between dibenzo-30-crown-10 (DB30C10) and $[Pt(bipy)(NH_3)_2][PF_6]_2$ (**1**) revealed,[1] for the first time, the ability of macrocyclic polyethers incorporating catechol units to enter into charge transfer interactions with dications containing a 2,2′-bipyridine (bipy) residue. This result led[2—4] to the discovery of a range of 1:1 complexes between the bipyridinium herbicide, Diquat, as its bis(hexafluorophosphate) salt (**2**), and molecular receptors based on the DB30C10 constitution. In addition to π–π charge-transfer interactions, the forces involved in this type of adduct and complex formation also include hydrogen bonding [N–H · · O, C–H · · O], Coulombic attraction [$N^{\delta+}$ · · $O^{\delta-}$, $C^{\delta+}$ · · $O^{\delta-}$], and dispersion forces.[5] The geometry of binding should therefore be sensitive to variations in the relative importance of these various stabilising interactions. We now present crystallographic† and spectroscopic‡ evidence demonstrating that (**1**) and (**2**), which adopt rather similar orientations in adducts with DB30C10, indeed differ markedly in their geometries of binding to dinaphtho-30-crown-10 (DN30C10), a receptor having a significantly more extended π-system.



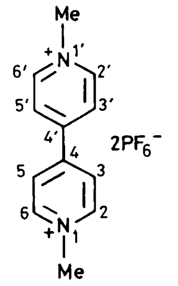
$[Pt(bipy)(NH_3)_2][PF_6]_2$

(**1**)



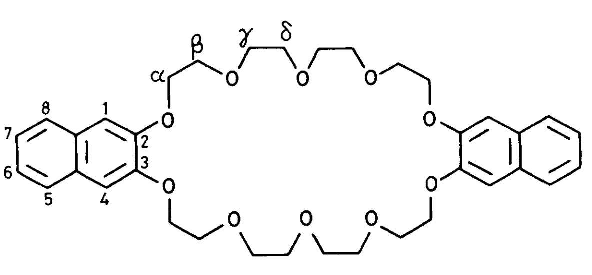
$[Diquat][PF_6]_2$

(**2**)



$[Paraquat][PF_6]_2$

(**3**)



DN30C10

In both instances (Figures 1 and 2), the DN30C10 receptor adopts a horseshoe-shaped conformation as does DB30C10 in the analogous supramolecular systems.[2—4] The $[Pt(bipy)(NH_3)_2]^{2+}$ and $[Diquat]^{2+}$ dications insert deeply into the clefts thus provided. In (**1**)·DN30C10,‡ however, the metal complex is slewed markedly, relative to its position in (**1**)·DB30C10, apparently in order to achieve better overlap between the extended π-electron rich naphtho rings and the π-electron deficient bipyridyl ligand. The two ammine ligands straddle (*cf.* refs. 1 and 6) one of the polyether chains of DN30C10 so that N(1) and N(2) come within hydrogen bond distances (3.0—3.3 Å) of O(4), O(7), and O(10). There is a nearly collinear relationship between the carbon atom C(47)

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† *Crystal data for* [(**1**)·DN30C10]·2H_2O: $PtC_{10}H_{14}N_4{\cdot}C_{36}H_{44}O_{10}{\cdot}P_2F_{12}{\cdot}H_4O_2$, M = 1348.0, monoclinic, space group $P2_1/a$, a = 22.473(8), b = 11.112(6), c = 22.560(7) Å, β = 108.81(2)°, U = 5333 Å^3, Z = 4, D_c = 1.69 g cm^{-3}, μ = 64.7 cm^{-1}. A total of 5774 independent reflections were measured (θ ≤ 50°) using the ω-scan measuring routine. Of these, 4530 had $|F_o| > 3\sigma(|F_o|)$ and were considered observed. No absorption correction was applied. The structure was solved by the heavy atom method and refined anisotropically to $R = R_w$ = 0.164. The crystals were severely twinned. Together with two-fold disorder in the $[Pt(bipy)(NH_3)_2]^{2+}$ dication and disorder in one PF_6^- anion, this twinning accounts for the high R factor. Two discrete positions for Pt were observed. They were refined with occupancies of 85 and 15%. The disorder in the PF_6^- anion was partially resolved into two orientations of 50% occupancies. Disorder was also present in the DN30C10 receptor. Because of the poor crystal quality, this problem could not be resolved. Hydrogen bonding between (**1**)·DN30C10 and the two H_2O molecules is extensive. There are seven O · · · N and O · · · O distances of less than 3.0 Å.

[(**2**)·DN30C10]·0.5H_2O: $C_{12}H_{12}N_2{\cdot}C_{36}H_{44}O_{10}{\cdot}P_2F_{12}{\cdot}(H_2O)_{0.5}$, M = 1119.9, monoclinic, space group $I2/c$ (body-centred cell chosen because C-face-centred cell gave β = 128.1°), a = 22.353(5), b = 11.005(4), c = 22.423(6) Å, β = 104.00(2)°, U = 5352 Å^3, Z = 4, D_c = 1.39 g cm^{-3}. A total of 3594 independent reflections were measured (θ ≤ 58°) using the ω-scan measuring routine. Of these, 2996 had $|F_o| > 3\sigma(|F_o|)$ and were considered observed. The structure was solved by direct methods and refined anisotropically to R = 0.116, R_w = 0.146. Two discrete positions were observed for C(6) and C(8) which were refined with 60% and 40% occupancies, respectively. There are no close contacts between the H_2O molecule and (**2**)·DN30C10.

In both cases, the data were obtained using Cu-K_α radiation (graphite monochromator) on a Nicolet R3m diffractometer. 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.

‡ The crystalline 1 : 1 complexes, (**1**)·DN30C10, m.p. 206—207 °C and (**2**)·DN30C10, m.p. 185—187 °C were isolated from Me_2CO and CH_2Cl_2 solutions, respectively, containing equimolar quantities of the appropriate components on vapour diffusion (P. G. Jones, *Chem. Br.*, 1981, **17**, 222) with n-pentane–n-heptane. Complexes (**1**)·DN30C10 and (**2**)·DN30C10 crystallised with 2.0 and 0.5 mol. equiv. of H_2O, respectively (see the *crystal data*). Adduct and complex formation by the DN30C10 receptor can be monitored (*cf.* D. Parker, *J. Chem. Soc., Chem. Commun.*, 1985, 1129) by positive-ion fast atom bombardment mass spectrometry (6 kV on a Kratos MS80RF spectrometer) using argon. From a 3-nitrobenzylalcohol matrix, (**1**)·DN30C10 reveals peaks distributed around m/z 1167 for the $[Pt(bipy)(NH_3)_2{\cdot}DN30C10{\cdot}PF_6]^+$ ion with a characteristic Pt isotope pattern, whilst (**2**)·DN30C10 afforded a strong $[Diquat{\cdot}DN30C10{\cdot}PF_6]^+$ ion at m/z 965. Interestingly, both (**1**)·DN30C10 and (**2**)·DN30C10 lose one PF_6^- counterion to give the supramolecular cations. ^{1}H N.m.r. spectra have been recorded on a Bruker AM250 spectrometer in CD_2Cl_2 solutions for (**1**), DN30C10, and (**1**)·DN30C10, and in CD_3COCD_3 solutions for (**2**), DN30C10, and (**2**)·DN30C10. Chemical shift assignments were confirmed by double irradiation experiments and the recording of n.O.e. difference spectra. In listing the δ values, those for (**1**), (**2**), and DN30C10 are quoted first of all, followed by those for either (**1**)·DN30C10 or (**2**)·DN30C10. The chemical shift changes (Δδ values) are indicated along with the assignments in parentheses after the δ values. δ for DN30C10/δ for (**1**)·DN30C10 (Δδ, assignment): 3.67/3.86 (+0.10, δ-OCH_2), 3.77/3.86 (+0.09, γ-OCH_2), 3.92/3.86 (−0.06, β-OCH_2), 4.22/3.86 (−0.36, α-OCH_2), 7.11/7.05 (−0.06, 1-,4-H), 7.31/7.05 (−0.26, 6-,7-H), and 7.65/7.05 (−0.60, 5-,8-H). δ for (**1**)/δ for (**1**)·DN30C10 (Δδ, assignment): 4.77/4.52 (−0.20, NH_3), 7.73/7.43 (−0.30, 5-,5'-H), 8.36/7.64 (−0.72, 4-,4'-H), 8.36/6.60 (−1.76, 3-,3'-H), 8.77/8.10 (−0.67, 6-,6'-H). δ for DN30C10/δ for (**2**)·DN30C10 (Δδ, assignment): 3.66/3.83 (+0.17, δ-OCH_2), 3.75/3.83 (+0.08, γ-OCH_2), 3.90/3.78 (−0.12, β-OCH_2), 4.22/3.66 (−0.56, α-OCH_2), 7.25/6.77 (−0.48, 1-,4-H), 7.27/7.27 (0.00, 6-,7-H), 7.67/7.52 (−0.12, 5-,8-H). δ for (**2**)/δ for (**2**)·DN30C10 (Δδ, assignment): 5.70/5.71 (+0.01, NCH_2), 8.60/8.55 (−0.05, 5-,5'-H), 9.10/8.65 (−0.45, 4-,4'-H), 9.24/8.22 (−1.02, 3-,3'-H), 9.50/9.58 (+0.08, 6-,6'-H). See Figure 3 for a diagrammatic representation of the chemical shift data.

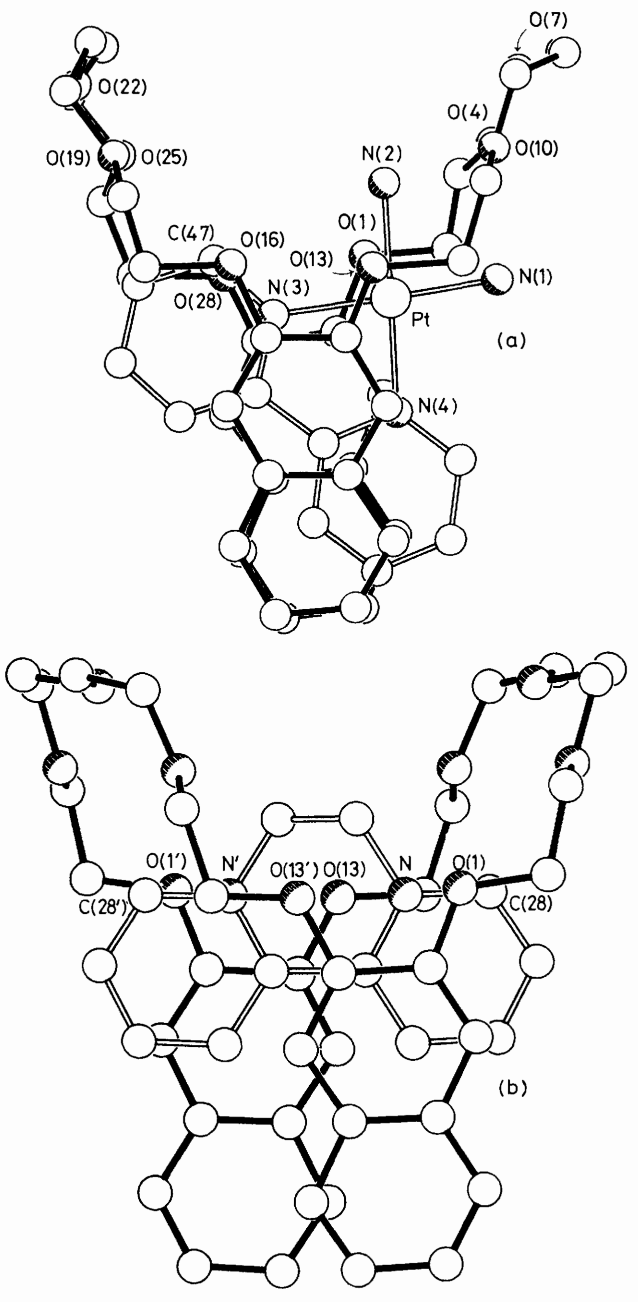

Figure 1. The solid state structures of (a) [Pt(bipy)(NH$_3$)$_2$·DN30C10]$^{2+}$ and (b) [Diquat·DN30C10]$^{2+}$ viewed in parallel projection approximately normal to the mean planes of the bipyridyl and bipyridinium rings, respectively. In order to highlight the DN30C10 receptor, it has been drawn with filled bonds in each case.

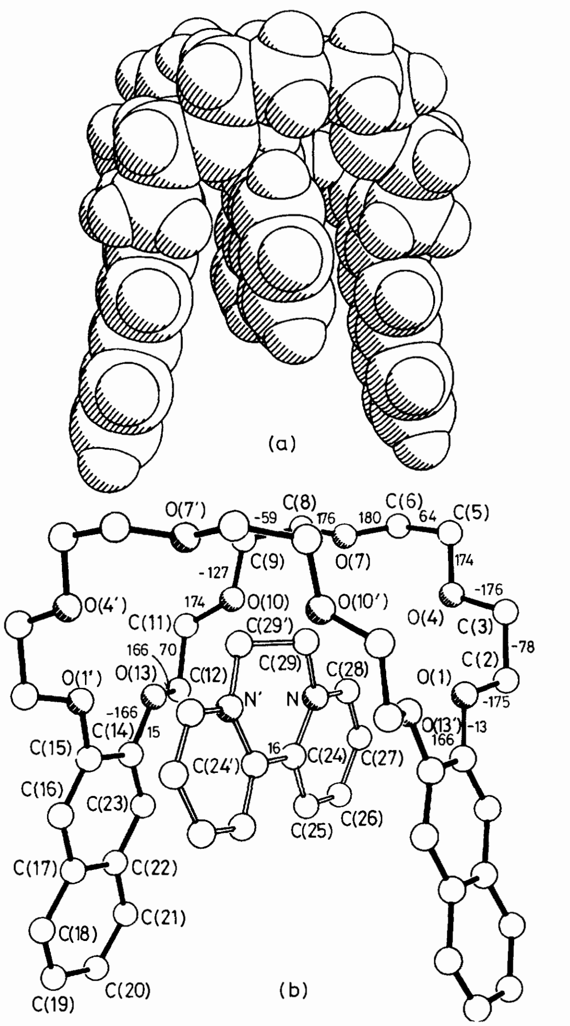

Figure 2. (a) Space-filling and (b) skeletal representations of the *X*-ray structure of [Diquat·DN30C10]$^{2+}$. In order to highlight the DN30C10 receptor, the ball-and-stick diagram has been drawn with filled bonds. Torsional angles (°) (O–C–C–O and C–C–O–C) associated with the 30-membered ring are shown in (b) beside the relevant C–C and C–O bonds. Selected hydrogen bonding contact distances {*R*[C · · · O], *R*[H · · · O] (Å)}, angles (°) between COC planes and HO vectors, C–H · · · O angles (°) at H atoms assuming normal trigonal or tetrahedral geometry: [C(28)–O(4)], 3.08, [H(28)–O(4)], 2.33, 13, 134; [C(29)–O(13)], 3.29, [H(29)–O(13)], 2.45, 33, 145. Twist angle between the pyridinium rings in the [Diquat]$^{2+}$ dication, 16°. Splay angle of the two naphtho rings with respect to each other: 22°.

ortho to the nitrogen atom N(3) of the bipyridyl ligand and the two aryl oxygen atoms O(16) and O(28) in the receptor [distances: O(16) · · · C(47), 3.48; O(28) · · · C(47), 3.47 Å. O(16) · · · C(47) · · · O(28) angle: 171°]. There is also an approximate alignment of the Pt atom with the two aryl oxygen atoms O(1) and O(13) in the receptor [distances: O(1) · · · Pt, 3.58; O(13) · · · Pt, 3.55 Å. O(1) · · · Pt · · · O(13) angle: 156°]. In (**2**)·DN30C10,‡ there is no slewing of the [Diquat]$^{2+}$ dication in the cavity between the two naphtho rings and indeed, the 1 : 1 complex has a crystallographic two-fold axis coincident with the C_2 axis in the dication. Although there is a characteristic alignment§ of the electronegative aryl oxygen atoms of DN30C10 with the formally positive bipyridinium nitrogen atoms [distances: O(1) · · · N, 3.20; O(13) · · · N, 3.62 Å; O(1) · · · N · · · O(13) angle, 178°] current theory[7] suggests that the positive charge on a pyridinium cation is concentrated more in the region of the

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§ The collinear arrangement of O(1) · · · N · · · O(13) and O(1') · · · N' · · · O(13') could be a consequence of the near coincidence in the separation (2.8 Å) between the N and N' atoms in the dication with the distance (2.6 Å) between the two pairs [O(1) and O(13'), and O(1') and O(13)] of aryl oxygen atoms in DN30C10.

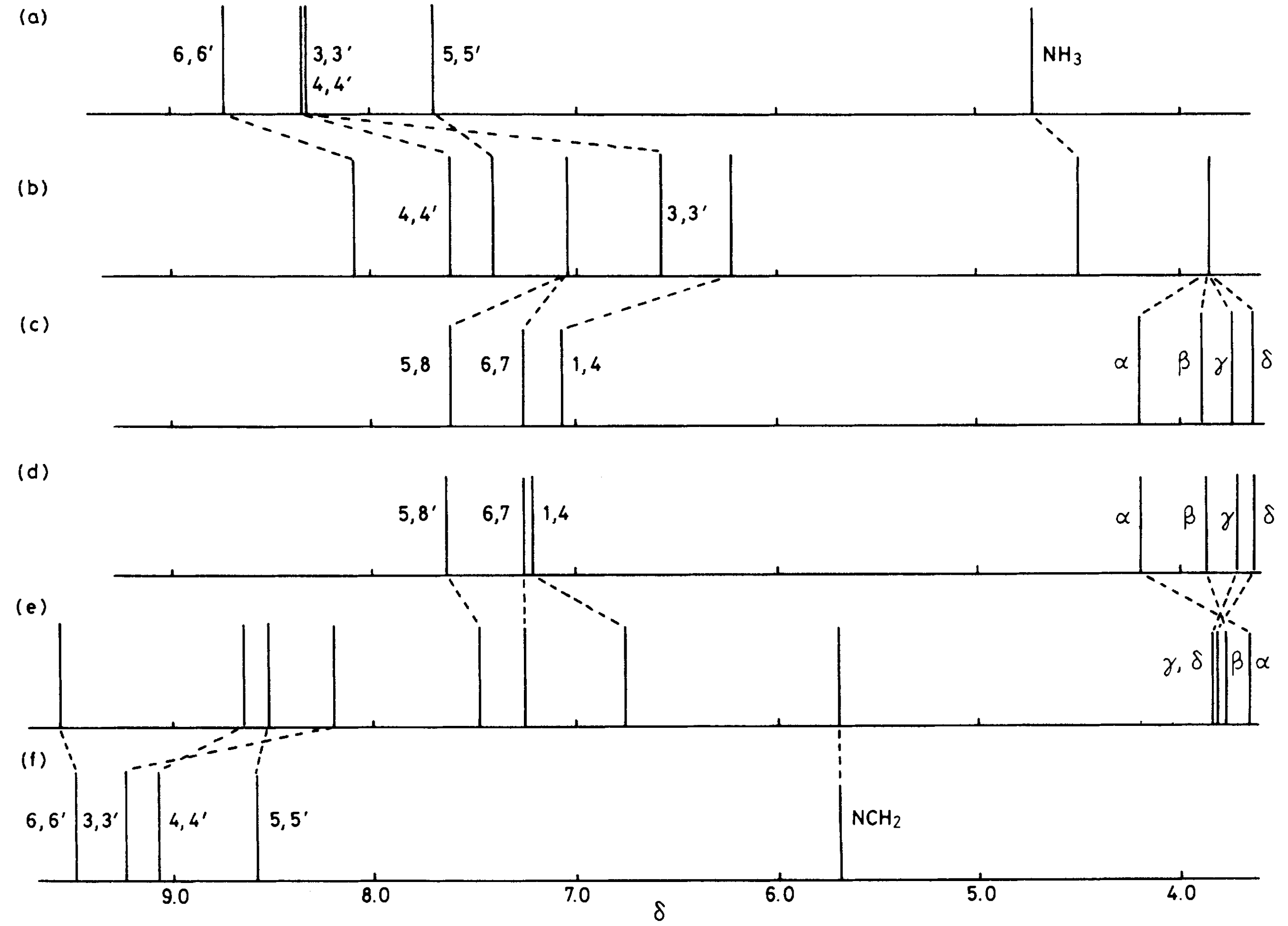

Figure 3. Line diagrams illustrating the ^{1}H n.m.r. chemical shift data for (a) [Pt(bipy)(NH$_3$)$_2$][PF$_6$]$_2$, (**1**), (b) (**1**)·DN30C10, and (c) DN30C10 in CD$_2$Cl$_2$, and (d) DN30C10, (e) (**2**)·DN30C10, and (f) [Diquat][PF$_6$]$_2$, (**2**) in CD$_3$COCD$_3$.

carbon atoms *ortho* to nitrogen than on nitrogen itself.¶ Indeed, we find that there are short non-bonded contacts (3.12 Å) between O(1) · · · C(28), and by symmetry O(1′) · · · C(28′), which are made possible by a shearing of one naphtho ring relative to the other in (**2**)·DN30C10 (Figure 1b). This shearing effect is not observed (Figure 1a) in (**1**)·DN30C10 but is evident in the *X*-ray structure[3] of (**2**)·DB30C10 where there are once again short contacts (3.12, 3.25 Å) between aryl oxygen atoms in DB30C10 and carbon atoms *ortho* to the nitrogen atoms in the [Diquat]$^{2+}$ dication.

There is strong evidence (Figure 3) from ^{1}H n.m.r. spectroscopy‡ that the binding geometries for (**1**)·DN30C10 and (**2**)·DN30C10 observed (Figure 1) crystallographically are also retained in solution. In particular, the ^{1}H n.m.r. signals for 5-,8-H and 6-,7-H on the naphtho rings are virtually unaffected ($\Delta\delta$ −0.12 and 0.00 p.p.m., respectively) by complex formation with the [Diquat]$^{2+}$ dication in keeping with the observed (Figure 1b) solid state structure. Also, as expected, the signals for 5-,5′-H in the [Diquat]$^{2+}$ dication undergo very little change ($\Delta\delta$ −0.05 p.p.m.) in chemical shift on complexation. By contrast, the signals for 5-,5′-H on the bipyridine ligand of the [Pt(bipy)(NH$_3$)$_2$]$^{2+}$ dication undergo a more substantial upfield shift ($\Delta\delta$ −0.30 p.p.m.) on complexation with DN30C10. As a consequence of ring current shielding by the bipyridine ligand, which is now in close proximity to 5-,8-H and 6-,7-H (Figure 1a) on the naphtho rings, very substantial upfield shifts ($\Delta\delta$ −0.60 and −0.27 p.p.m., respectively) are observed for the resonances arising from these protons. Note also that in both (**1**)·DN30C10 and (**2**)·DN30C10, there are significant upfield shifts ($\Delta\delta$ −0.88 and −0.48 p.p.m. respectively) for 1-,4-H on the naphtho rings compatible with their dispositions with respect to the π-arene systems of the substrates.

Whilst the structural variations observed in this investigation are currently the subject of detailed theoretical analysis, they have already had a profound influence[8] on the design and subsequent synthesis of receptor molecules for the related bipyridinium herbicide,[9] Paraquat as its bis(hexafluorophosphate) salt (**3**).

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¶ Charge distributions in the [Diquat]$^{2+}$ dication have been calculated (J. Burdon, M. H. B. Hayes, and M. E. Pick, *J. Environ. Sci. Health, Sect. B*, 1977, **12**, 37) by a CNDO/2 semi-empirical quantum mechanical procedure. The data indicate that the positive charges are concentrated on the *ortho* and *para* positions (*i.e.* 2/2′, 4/4′, and 6/6′) with respect to the nitrogen atoms.

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