

Porphyrin–Crown Ether Macrotricyclic Co-receptors for Bipyridinium Cations

Maxwell J. Gunter* and Martin R. Johnston

Department of Chemistry, The University of New England, Armidale, NSW 2351, Australia

In order to employ non-covalent interactions to position methyl viologen close to a photoactive centre (in this case a porphyrin) a dibenzo-crown ether, containing *meta*-substituted aromatic rings and tetraethylene glycol ether chains, was strapped across a porphyrin to produce a macrotricyclic host. This host was observed to complex methyl viologen (paraquat) (K_a 50 and 250 dm³ mol⁻¹ and ΔG° -2.3 and -2.9 kcal mol⁻¹ at 298 K and 263 K, respectively) and [Pt(bpy)(NH₃)₂](PF₆)₂ (K_a 1350 dm³ mol⁻¹, ΔG° -4.3 kcal mol⁻¹ at 298 K) by an *induced fit* mechanism, as a result of rotational barriers associated with the diaryl amide linkage. Efforts to improve the complexing ability of these types of hosts involved a shortening of the linking ether chains and reduction of the amide group linking the crown ether and porphyrin moieties. Of these two directions the reduced host was most successful, complexing all the bipyridinium dicationic species examined, although ligand exchange reactions complicated the binding of the platinum complex (for paraquat K_a 480 dm³ mol⁻¹, ΔG° -3.6 kcal mol⁻¹ at 298 K; for diquat K_a 80 dm³ mol⁻¹, ΔG° -2.6 kcal mol⁻¹ at 298 K). In contrast, the host containing shortened ether chains was observed to have similar complexing abilities to its predecessor, as a result of comparable solution conformations (for paraquat K_a 50 dm³ mol⁻¹, ΔG° -2.3 kcal mol⁻¹ at 298 K; for [Pt(bpy)(NH₃)₂](PF₆)₂ K_a 365 dm³ mol⁻¹, ΔG° -2.9 kcal mol⁻¹ at 298 K). However, in this case binding by the platinum complex within the constricted cavity of the host resulted in deformation of the porphyrin and an increased activation barrier to complexation.

The rich photochemistry that can be provided by the porphyrin nucleus has assured its popularity as a component of systems mimicking rapid electron-transfer processes in both photosynthetic model systems and artificial photosynthetic devices. An impressive array of covalently linked porphyrins and electron acceptors or donors has been studied, with suitable variation allowing a detailed investigation of the dependence of electron transfer rates on such factors as donor–acceptor orientation and distance, free energies of reactions and electronic coupling. These factors have been the subject of a recent review.¹ A common impediment to long-lived charge separation confronting each of these systems is that of the non-productive thermal back reaction that follows electron transfer. Attempts to limit this problem have incorporated strategies which include the intramolecular separation of the redox ions formed on electron transfer, well illustrated by the triad and tetrad systems of Gust and Moore,^{2,3} and by the utilisation of the Marcus inverted region by suitable choice of acceptor redox potential.^{1,4} Inherent in these systems is the disadvantage of a lack of intercomponent mobility following electron transfer, and the often complex and lengthy synthetic procedures necessary for their construction.

An alternative approach is provided by the concepts of supramolecular chemistry, in which the donor and acceptor may be positioned by a judicious alignment of non-covalent intermolecular binding factors. Several such systems have included porphyrins as the photoactive component.^{5–17} A variant of the same strategic approach has been the covalent attachment to a porphyrin of a preformed supramolecular host for photoredox active substrates.^{18–21} Although long-lived photoinduced charge separation has been observed in a polymetallic supramolecular system,²² a crucial aspect common to most of these systems which has not been generally addressed in detail is a facility to ensure rapid escape of the redox ion pair after initial electron transfer.

An acceptor that is frequently used in sacrificial artificial photosynthetic systems is methyl viologen (paraquat, 1,1'-dimethyl-4,4'-bipyridinium), its popularity deriving from many factors which have been described,²³ but not the least of which is its redox potential which is suitable for the catalysed

reduction of water. To this end, it has been used in multi-component solution studies in conjunction with porphyrins for the photochemical production of hydrogen from water.

With these principles in mind, we thus set out to devise a supramolecular system which could use the non-covalent principles of molecular recognition to position bipyridinium cations such as methyl viologen in close proximity to a porphyrin, in such a way as to facilitate forward electron transfer, and to retard the back reaction.

Design Strategy

The supramolecular host molecules *par excellence* for the complexation of bipyridinium dicationic species, both methyl viologen (paraquat, PQ²⁺) and diquat (DQ²⁺),† are the dibenzo-crown ethers. The investigations by Stoddart and co-workers of these complexations is exhaustingly extensive. Dibenzo-crown ethers containing a varying number of ethylene units have been synthesised, and combined with various substitution patterns on the crown aromatic rings, including *ortho*-,^{24–28} *meta*-,^{29–30} and *para*-,^{31–34} along with naphthalene-based ethers,^{29,35,36} illustrate the versatility of these hosts. A significant increase in complexation strength was observed on the inclusion of a suitable bridging subunit giving macrobicyclic receptors with increased rigidity and pre-organisation.^{37–40} A common feature of the solid state and solution structures of the complexes observed between the bipyridinium dicationic species and suitably sized dibenzo-crown ethers is the wrapping of the crown ether around the guest in a U-shaped fashion, while maintaining an interplanar distance of 3.4–3.5 Å between the parallel aromatic rings of the host and guest.

From molecular modelling studies, it was apparent that the interphenyl distance of approximately 7 Å between crown ether aromatic rings optimal for bipyridinium complexation could be maintained while strapping the crown ether across the face of a meso-phenyl substituted porphyrin. Attachment of the crown

† Paraquat is 1,1'-dimethyl-4,4'-bipyridinium. Diquat is 6,7-dihydro-dipyrido[1,2-*a*:2',1'-*c*]pyrazidinium.

ether and porphyrin components *via* an amide at the *ortho*-position was most convenient synthetically. However, the use of an amide linking group introduces (i) an electron withdrawing substituent onto the crown aromatic ring, which has been shown to decrease the π -electron donating ability of the ring resulting in a decreased complexation strength,^{26,40} and (ii) an inward tilt of the crown aromatic ring away from the parallel geometry usually observed, which would reduce the extent of charge-transfer interaction. Nevertheless, the possibility of a linear electrostatic interaction between the cationic nitrogen atoms of the bipyridinium guest and the phenolic oxygens of the crown ether (which has been identified as a major force in complex stabilisation^{25,29-32}) would still be retained. This, together with the possibility of charge-transfer interaction with one or both of the two crown aromatic rings^{41,42} held in an essentially pre-organised geometry should facilitate complexation.

Once formed, the crown ether strapped porphyrin should non-covalently position bipyridinium dications in close proximity to the porphyrin with the possibility of efficient photochemical interaction. Photoinduced electron transfer from porphyrin to the bipyridinium acceptor would be followed by electrostatic repulsion of the formed cationic species; subsequent expulsion of the bound guest to spatially separate the redox ions might compete effectively with the thermal back electron-transfer reaction. Such a photochemical system employs the synthetically simpler and more general approach of non-covalently positioning components in a manner analogous to the photoactive components of photosynthesis. However, the challenge of these systems lies in finding a balance between dication complexation strength of the porphyrin host and the electrostatically driven separation of the redox ions. This paper describes the synthesis and complexation behaviour of several systems incorporating these design principles.

meta-Substituted crown ethers have the advantages of symmetry and the versatility to be able to complex both diquat and paraquat with almost equal strength^{29,30} (in contrast to receptors based on *ortho*-substituted aromatic rings which tend to show preferential complexation of the one class of bipyridinium dication²⁵). An ether based on bis-*m*-phenylene-32-crown-10 (BMP32C10) would also contain tetraethylene glycol ether chains which have been identified as being the optimum length to allow maximum π - π electron charge-transfer interaction between both crown aromatic rings and the complexed dication, without impairing the important phenolic oxygen electrostatic interactions.^{25,33}

On the other hand the strapping of a dibenzo-crown ether across the face of a porphyrin effectively fixes the inter-phenyl separation of the crown aromatic rings, in contrast to dibenzo-crown ethers in solution in which the length of the ether chain dictates complexation behaviour.^{25,34} Thus, it was reasoned that a decrease in ether chain length from four ethylene units to three might enhance complexation by creating a smaller, less conformationally mobile, and possibly more suitably sized host cavity. The synthesis of a bis-*m*-phenylene-26-crown-10 (BMP26C10) derivative and its subsequent incorporation into a macrobicyclic host^{43,44} has been described and, although there has been no previous report of the complexation of bipyridinium dications with these crown ethers, modelling studies suggested stabilisation of bipyridinium dications should not be prejudiced by the use of this smaller crown ether component in our porphyrin-based systems.

The porphyrin chosen for strapping by the dibenzo-crown ethers was the α,α -atropisomer of the symmetrical diamino porphyrin **6**, since it provided a simple and well documented^{45,46} synthetic route to the desired *syn*- stereochemistry of suitably reactive functional groups. The crown-ether moieties of the hosts are based on the ethers **5a** and

5b which could be synthesised using Williamson ether methodology.

Synthesis and Solution Conformation

The synthesis of the crown ethers **5a** and **5b** followed the reaction scheme outlined in Scheme 1. Initially, the monobenzylated material **1*** was allowed to react with the appropriate polyethylene glycol bistosylate⁴⁸ **2a** or **2b** to give the protected acyclic polyethers **3a** and **3b**. Removal of the benzylic protection (H_2 , 10% Pd/C) gave the acyclic diphenol polyethers **4a** and **4b**, which after further treatment with bistosylate produced the cyclic crown esters in 13 and 46% yields, respectively. Hydrolysis of the esters produced the dicarboxylic acid derivatives which were converted using thionyl chloride into the acid chlorides **5a** and **5b**. These were then used immediately and without purification in the condensation with the diamino porphyrin **6**^{45,46} under conditions of high dilution⁴⁹ with batch-wise additions of the components to the reaction mixture.⁵⁰ The yields of **7a** and **7b** synthesised in this manner were 62 and 35%, respectively (based on porphyrin consumed).

The application of the usual techniques of NMR spectroscopy allowed complete assignment of the proton and carbon resonances of **7a** and **7b**, and revealed aspects of the solution conformation of the host molecules which could subsequently be used in the interpretation of the complexation of the guest molecules. In the following discussions, a non-systematic numbering system is employed which attempts to make use of the symmetry of the molecule to simplify atom designations. The numbering scheme is outlined in Scheme 1.

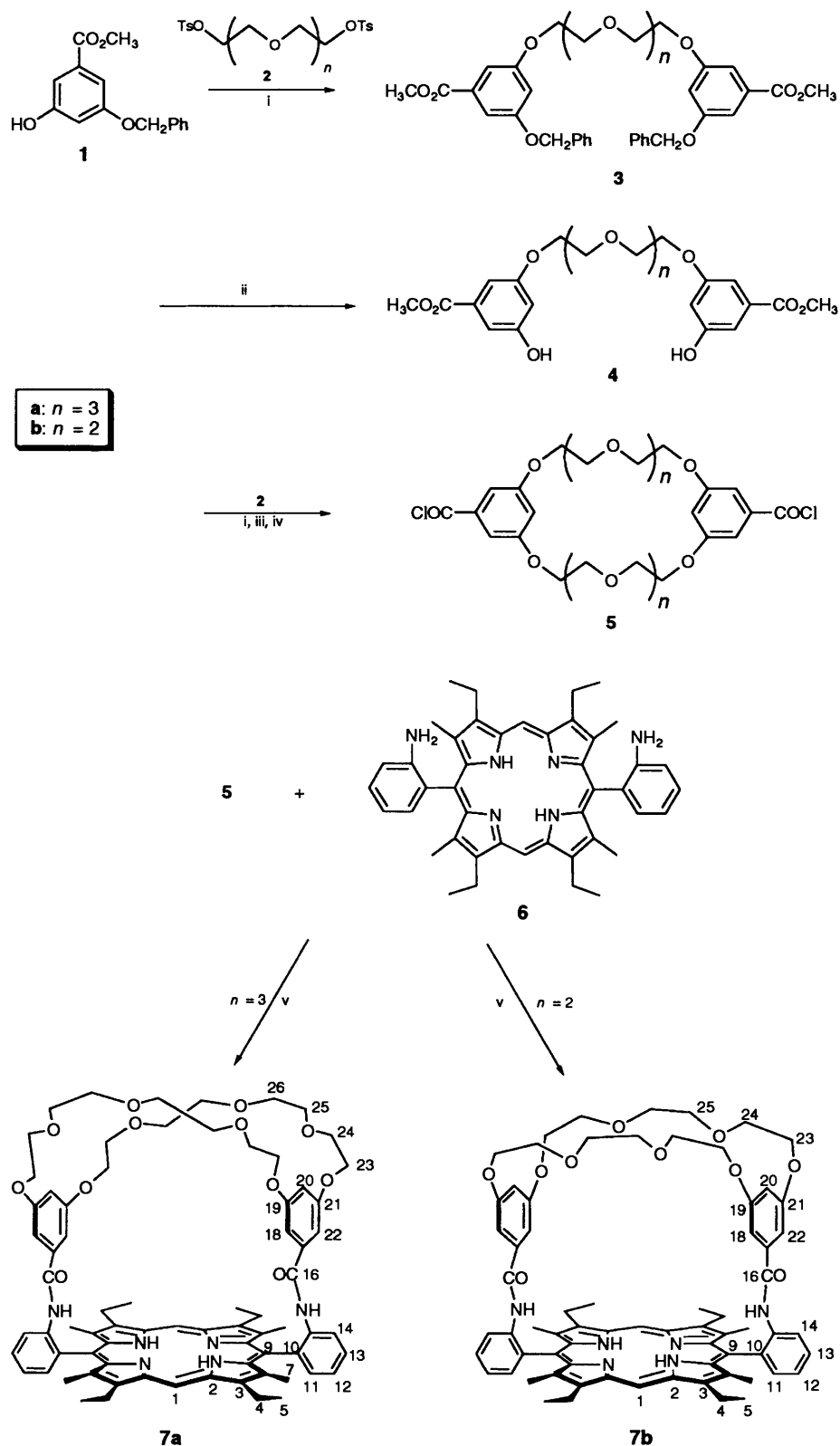
The conformation adopted by **7a** in solution was deduced primarily from an examination of the ¹H NMR resonances of the crown ether moiety. The changes in chemical shifts ($\Delta\delta$) of the methylene protons of the precursor crown ether diester compared to their respective positions in the crowned porphyrin support the structure indicated (Scheme 1) with the ether chains strapping the porphyrin;⁵¹ smaller changes observed for the 25-H and 26-H methylene resonances ($\Delta\delta$ -0.88, -0.68 ppm) compared to those observed for 23-H and 24-H ($\Delta\delta$ -1.59, -1.57 ppm) imply a solution conformation in which the 25-H and 26-H protons are furthest removed from the porphyrin and hence least affected by its ring current. Also, the equivalence observed between 18-H and 22-H suggests a fast exchange between conformations in which the crown aromatic rings are not in conjugation with the amide-*meso*-phenyl system, but rather held at some intermediate angle between 0° (fully conjugated) and 90° (orthogonal) (Fig. 1).†

The resonance for the *meso*-phenyl proton *ortho* to the amide (14-H) is moved considerably downfield due to the deshielding effects of the amide carbonyl; such a shift is consistent with those observed for other amidophenyl porphyrin derivatives.^{52,53} The solution conformations of both **7a** and **7b** were observed to be temperature dependent in [²H₆]acetone.‡

* **1** was readily available by selective extraction from a mixture of the dibenzylated product and diphenolic starting material.^{38,47}

† Although fast exchange between 0° conformations would still result in equivalence between 18-H and 22-H, examination of molecular models indicates that such a conformation leads to considerable steric crowding of the ether chains, and is unlikely to be the predominant conformation in solution. Indeed with the shortened chains of **7b**, such a conformation is virtually proscribed.

‡ The conformations of **7a** and **7b** in solution were examined at various concentrations in the different deuteriated solvents chloroform, acetone, acetonitrile and dichloromethane. In all cases only minor shifts were observed for all resonances, indicating that the conformations of both host molecules may be considered essentially independent of both solvent and dilution. Small chemical shift changes ($\Delta\delta$ +0.03 ppm) were observed on dilution for groups on the porphyrin periphery sensitive to porphyrin aggregation.



Scheme 1 Reagents and conditions: i, NaH/THF; ii, H_2 /Pd/C, $CHCl_3/CH_2Cl_2/EtOH$; iii, NaOH, H_2O , MeOH, then H^+ ; iv, $SOCl_2$; v, CH_2Cl_2 /pyridine, high dilution. The structures also show the numbering scheme employed for the NMR assignments, which although not systematic, is used to simplify the discussion.

Outlined in Fig. 2 is a schematic representation of the resonances of **7a** that undergo significant changes with decreasing temperature (resonances not shown are unaffected). Above 298 K all resonances of **7a** and **7b** remained essentially constant. However, with decreasing temperature the resonances of the ether chains shift downfield indicating movement toward

a conformation in which they are increasingly removed from the shielding effects of the porphyrin and thus into a more expanded configuration. The crown aromatic protons 18-H and 22-H (along with the amide NH) resonances also move downfield with decreasing temperature. These shifts, coupled with the movement of the 14-H resonance upfield may be

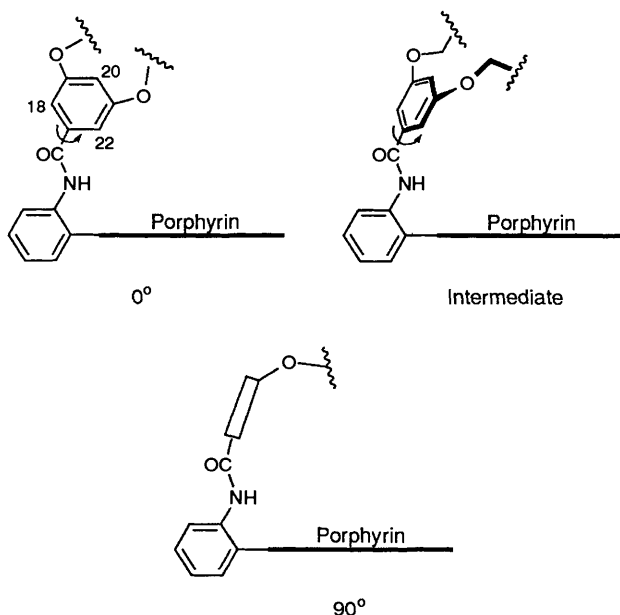


Fig. 1 Possible conformations adopted by **7a** and **7b** in solution, by rotation about the bond indicated. Angles are relative to the *meso*-phenyl plane.

interpreted as the carbonyl group 'transferring' conjugation from the *meso*-phenyl ring to the crown aromatic ring by way of rotation of the C(15)–N, N–C(16) and C(16)–C(17) bonds (Fig. 3). The resonance for protons 18-, 22-H does not split into separate proton resonances at lower temperatures reinforcing the conclusion that the crown aromatic rings are not orientated at 0° relative to the *meso*-phenyl plane. This *face-on* (90° > θ > 0°) conformation of the crown aromatic rings is then predisposed towards substrate stabilisation by both electrostatic and π - π electron charge-transfer interaction.

Complexation Studies

The complexing ability of the porphyrin hosts **7a** and **7b** towards the bipyridinium cations paraquat, diquat, and the platinum complex [Pt(bpy)(NH₃)₂]²⁺ was studied by ¹H NMR spectroscopy.*

Paraquat Hexafluorophosphate.—In the case of paraquat hexafluorophosphate⁵⁴ (PQ²⁺)(PF₆)₂, both the host and guest proton resonances undergo shifts upon mixing of equimolar quantities of each in [²H₆]acetone† (Table 1). These shifts may be interpreted in terms of a 1:1 complex in which the bipyridinium guest is sandwiched between the crown aromatic rings of **7a** or **7b** (Fig. 4) as follows.

On complexation, the proton resonances of paraquat all

* An initial examination was carried out on a solution containing equimolar quantities of host and guest, to detect any complexation-induced alterations in chemical shifts of either molecule. Although this by itself gives no quantitative information on the strength of complexation, it does yield qualitative information about the geometry of any complex that may form. If complexation-induced changes to resonances of either host or guest were observed, an association constant was determined by the method outlined below. Although UV/visible spectroscopy has been used extensively to examine dibenzo-crown ether/bipyridinium complexation by monitoring the charge-transfer band (λ_{\max} ca. 400 nm),^{29,30} in the case of porphyrin-containing hosts the high intensity Soret band (λ_{\max} 400–420 nm) precluded accurate spectroscopic titrations.

† Similar shifts were also observed when complexation was examined in [²H₃]acetonitrile.

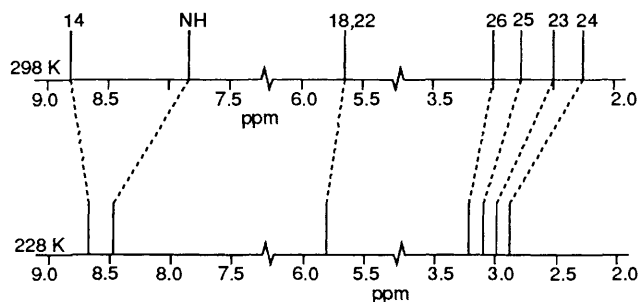


Fig. 2 Schematic representation of selected changes in the ¹H NMR spectrum of **7a** with decreasing temperature in [²H₆]acetone. Labelling is as indicated in Scheme 1.

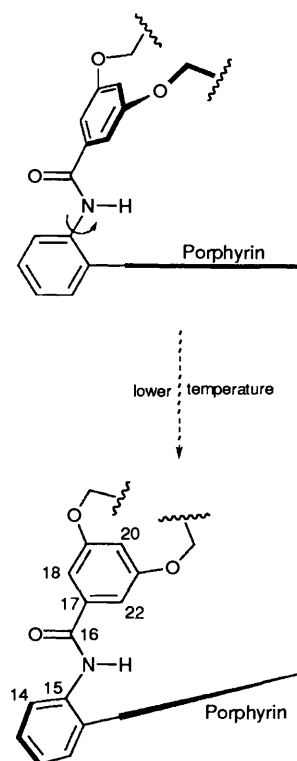


Fig. 3 Conformational changes within **7a** in [²H₆]acetone deduced from variable temperature ¹H NMR measurements

experience negative shifts (Table 1) of a similar magnitude to those for the 1:1 complex between BMP32C10 and paraquat.^{29,30} The shifts are somewhat smaller than might be expected for complexation by a porphyrin-containing host, and may be explained by a weaker complexation of PQ²⁺ by **7a** and **7b** compared to BMP32C10. A possible explanation for this weaker complexation is the inward tilt of the crown aromatics within **7a** and **7b** as a result of the amide linkage preventing exact parallelity with PQ²⁺, thus reducing the effectiveness of π - π electron charge-transfer interaction and resulting in a decreased complexation strength and smaller free energy of complexation. Since the following NMR evidence indicates that the guest inclusion geometry is similar to that encountered previously for dibenzo-crown ethers and bipyridinium dications,^{25,30} identical stabilising forces to those proposed for such systems have been assumed for the porphyrin host complexations here, *viz.*, electrostatic interaction between the phenolic oxygens and the cationic nitrogen atoms of the bipyridinium guests, π - π charge transfer between the π -electron deficient guests and the π -electron rich crown aromatic rings, and hydrogen bonding between acidic hydrogen atoms of the dication and crown ether oxygen atoms.

Table 1 Selected ^1H NMR resonance shifts on binding of various bipyridinium dications by the hosts **7a**, **7b** and **8**, in equimolar solutions of host and guest

HOST: GUEST:	7a [PQ] $^{2+}$ <i>a,b</i>	7b [PQ] $^{2+}$ <i>b,c</i>	7a [Ptbpv(NH $_3$) $_2$] $^{2+}$ <i>b,e</i>	7b [Ptbpv(NH $_3$) $_2$] $^{2+}$ <i>f,g</i>	8 [PQ] $^{2+}$	8 [DQ] $^{2+}$	8 [Ptbpv(NH $_3$) $_2$] $^{2+}$
14-H	8.68 (-0.18)	8.53 (-0.06)	8.50 (-0.35)	7.63 (-0.85)	—	—	—
16-H	—	—	—	—	4.11 (-0.02)	4.07 (-0.05)	3.86 (-0.28)
18-, 22-H	5.47 (-0.04)	5.77 (0.00)	5.50 (+0.08)	5.60 (-0.21)	5.81 (-0.04)	5.81 (-0.04)	5.61 (-0.25)
20-H	5.75 (-0.07)	5.83 (-0.02)	5.87 (+0.12)	6.70 (+0.89)	5.48 (-0.27)	5.57 (-0.17)	5.67 (-0.07)
23-H	2.59 (+0.11)	3.08 (+0.03)	3.04 (+0.70)	<i>d</i>	3.28 (-0.08)	3.30 (-0.06)	3.63 (+0.26)
24-H	2.51 (+0.23)	3.05 (+0.08)	2.95 (+0.85)	<i>d</i>	3.28 (+0.04)	3.30 (+0.07)	3.63 (+0.39)
25-H	2.91 (+0.12)	3.17 (+0.04)	3.24 (+0.58)	<i>d</i>	3.28 (+0.07)	3.30 (+0.10)	3.49 (+0.29)
26-H	3.04 (+0.05)	—	3.32 (+0.41)	<i>d</i>	3.28 (+0.07)	3.30 (+0.10)	3.49 (+0.29)
Amide NH	8.02 (+0.24)	7.87 (+0.10)	<i>d</i>	<i>d</i>	—	—	—
Pyrrole NH	-2.64 (+0.03)	-2.55 (+0.04)	-2.59 (+0.08)	-2.27 (+0.52)	-2.40 (+0.04)	-2.41 (+0.03)	<i>d</i>
2'-, 6'-H (PQ $^{2+}$)	9.07 (-0.28)	9.30 (-0.05)	—	—	8.65 (-0.70)	—	—
3'-, 5'-H (PQ $^{2+}$)	8.30 (-0.52)	8.73 (-0.09)	—	—	7.65 (-1.17)	—	—
^+NMe (PQ $^{2+}$)	4.63 (-0.10)	4.69 (-0.04)	—	—	4.42 (-0.31)	—	—
3',3'' (Pt complex or DQ $^{2+}$)	—	—	4.54 (-3.88)	0.66 (-8.02)	—	8.83 (-0.41)	4.83 (-3.90)
4',4'' (Pt complex or DQ $^{2+}$)	—	—	6.28 (-2.14)	5.31 (-3.24)	—	8.72 (-0.38)	6.77 (-1.83)
5',5'' (Pt complex or DQ $^{2+}$)	—	—	6.85 (-0.95)	6.96 (-0.94)	—	8.40 (-0.20)	7.04 (-0.94)
6',6'' (Pt complex or DQ $^{2+}$)	—	—	7.66 (-0.76)	7.90 (-0.96)	—	9.40 (-0.10)	8.21 (-0.74)
NH $_3$ (Pt complex)	—	—	3.91 (-0.27)	4.18 (-1.21)	—	—	—

^a Spectra recorded at 298 K in [$^2\text{H}_6$]acetone using $\text{CD}_2\text{HCOCD}_2\text{H}$ as reference (δ 2.05). Note that some proton assignments differ from those previously reported.¹⁴ Porphyrin concentration approximately 20 mmol dm^{-3} . ^b Chemical shifts (ppm) of equimolar solutions of the porphyrin host and the guest, recorded under conditions of fast exchange, *i.e.* with only averaged signals of host and guest for bound/unbound equilibria. Values in parentheses ($\Delta\delta$) indicate differences in chemical shift between the uncomplexed and complexed host and guest measured at 1:1 concentration, with a positive sign indicating deshielding and a negative sign indicating shielding. ^c Spectra recorded at 298 K in [$^2\text{H}_6$]acetone/deuteriochloroform (5%) using $\text{CD}_2\text{HCOCD}_2\text{H}$ as reference (δ 2.05 ppm). Porphyrin concentration approximately 9 mmol dm^{-3} . ^d Resonances not unambiguously assigned. ^e Spectra measured at 298 K in [$^2\text{H}_3$]acetonitrile with CD_2HCN as reference (δ 1.95). Porphyrin concentration 9 mmol dm^{-3} . ^f Spectra measured at 278 K in [$^2\text{H}_6$]acetone, under slow exchange conditions. Shifts are for bound substrate. Porphyrin concentration 11 mmol dm^{-3} . ^g Additional $\Delta\delta$ values: 1-H, +0.28; 4-H +0.27; 5-H 0.00; 7-H +0.04; 11-H +0.29; 12-H +0.21.

In the ^1H NMR spectrum of the complexes at equimolar concentrations of guest and host, the shifts of the host resonances are not as pronounced as expected at first sight, but may be rationalised by a combined effect of a complexation-induced conformation change within the porphyrin hosts and the shielding/deshielding effects of the paraquat guest. Upon complexation the crown aromatic rings are enforced into an increasingly orthogonal position relative to the *meso*-phenyl substituent rather than the more co-planar arrangement of the crown aromatic and *meso*-aromatic rings assumed for **7a** and **7b** before complexation (such conformational extremes are shown in Fig. 1). This conformation change is evidenced by several indicators. Firstly the crown aromatic protons (18-, 20-, 22-H) resonances experience only small negative or zero shifts on complexation, yet these protons would be expected to experience the largest effect from the paraquat ring current. The predicted orientation change with respect to the porphyrin would, however, result in deshielding for these protons, which is compensated by a shielding effect from the paraquat, resulting in nett minor shifts overall. Secondly, the 14-H resonance is shifted upfield ($\Delta\delta$ -0.18 ppm for **7a**·PQ $^{2+}$) due to a reduction

in shielding from the carbonyl group as the crown aromatic is rotated with respect to the *meso*-amido-phenyl plane.* Thirdly, the amide NH resonance undergoes a shift ($\Delta\delta$ +0.24 ppm for **7a**·PQ $^{2+}$) which also implies a rotation of the crown aromatic ring.

The flexible nature of the ether chains in solution does not allow an absolute definition of the complexation-induced conformational changes within **7a** or **7b**, but qualitative trends are evident. The deviation of the ether chain shifts from those expected, with all the ether resonances experiencing deshielding,³⁰ may be also explained by the combined effects of several processes. Upon complexation the ether chains must fold outwards in a more expanded conformation (Fig. 4) and are subsequently less shielded by the porphyrin. Inclusion of paraquat then results in shielding of 23-, 24-H which might be expected to have undergone the largest movement on complexation, and results in the small changes observed (Table

* Similar changes to the crown aromatic ring conformation as those observed upon temperature reduction, Fig. 3, are envisaged.

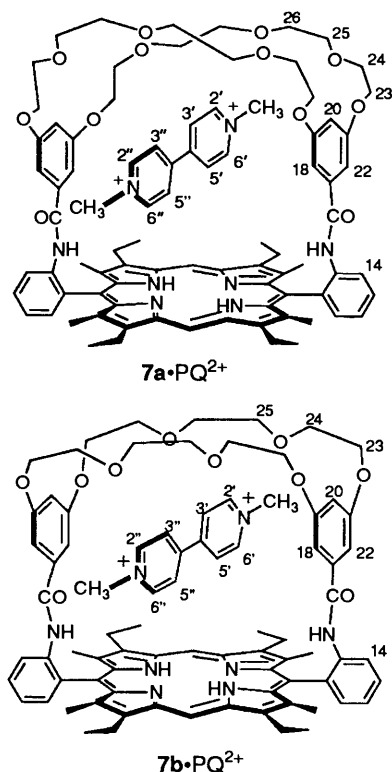


Fig. 4 Inclusion geometry of paraquat dication in the hosts **7a** and **7b**, deduced from NMR measurements. Numbering is used in the discussion of the NMR spectra.

1). The ether protons 25-H and 26-H on the other hand, experience deshielding from both the conformational change and the paraquat ring current.

The porphyrin resonances are little affected by complexation with paraquat, with the exception being the pyrrole NH resonance. Downfield shifts ($\Delta\delta + 0.03$ and $+0.04$ ppm) for these proton resonances are consistent with the orthogonal mode of complexation shown in Fig. 4, since similar shifts have been observed for phenylene chain strapped porphyrins⁵⁵ where the NH protons are deshielded by the orthogonally held aromatic rings.

The association constants for the complexation of paraquat were determined by non-linear least-squares curve fitting of ¹H NMR titration data to be $50 \text{ dm}^3 \text{ mol}^{-1}$ for **7a**·PQ²⁺ and $45 \text{ dm}^3 \text{ mol}^{-1}$ for **7b**·PQ²⁺, with a free energy of complexation $\Delta G^\circ - 2.3 \text{ kcal mol}^{-1}$ * in each case. These complexation strengths are weaker in comparison to BMP32C10/PQ²⁺ (K_2 $760 \text{ dm}^3 \text{ mol}^{-1}$, $\Delta G^\circ - 3.9 \text{ kcal mol}^{-1}$)³⁰ and are a reflection of the conformational rearrangement that must occur within **7a** and **7b** before complexation, together with the inward tilt of crown aromatic rings in the porphyrin hosts compared to the more parallel orientation observed in the BMP32C10/PQ²⁺ complex; this results in a reduction of the contribution from charge transfer toward complex stability in **7a** and **7b**.

The complexation of paraquat by **7a** was found to be both dilution and temperature dependent, with an increase in either dilution or temperature decreasing complexation. As discussed above, **7a** changes conformation with decreasing temperature. Comparing the complexation-induced changes to resonances of **7a** upon complexing paraquat (Table 1), and those that occur with temperature (Fig. 2), it would appear that upon temperature reduction **7a** should adopt a conformation more amenable to complexation; the association constant

increased to $250 \text{ dm}^3 \text{ mol}^{-1}$ ($\Delta G^\circ - 2.9 \text{ kcal mol}^{-1}$) at 263 K.† Cooling of the solution containing equimolar quantities of **7a** or **7b** and paraquat to 230 K failed to separate resonances between bound and unbound paraquat or inequivalence within the paraquat or porphyrin moieties. This indicates a fast equilibrium between bound and unbound paraquat and fast rotation of the guest within the cavities of **7a** and **7b**.

Diquat Hexafluorophosphate.—In the case of diquat hexafluorophosphate^{54,56} (DQ²⁺)(PF₆)₂ little change was observed in the resonances of **7a** or **7b** on guest addition ($\Delta\delta_{av}$ 0.02 ppm) in either deuteriated acetone or acetonitrile. The protons of diquat were, however, shifted minimally upfield ($\Delta\delta_{av} - 0.07$ ppm) which may be interpreted as an overall effect in solution of the magnetic anisotropy of the porphyrin on the dication, rather than specific inclusion complex formation. The selective complexation of paraquat by **7a** or **7b** contrasts the non-porphyrinic *meta*-substituted crown ether BMP32C10 which complexes both paraquat and diquat cations almost equally well.^{29,30}

Complex [Pt(bpy)(NH₃)₂](PF₆)₂.—The paraquat dication and the square planar platinum(II) complex [Pt(bpy)(NH₃)₂](PF₆)₂ are constitutionally similar⁵⁷ and strong complexes have been observed between this salt and dibenzo[3*n*]crown-*n* ethers; the successful isolation of single crystals containing a 1:1 stoichiometry of host and guest have allowed the complex geometry to be thoroughly studied. The complex was found to be stabilised by hydrogen bonding from the ammine ligands to crown ether oxygen atoms, and electrostatic interactions of the dicationic complex with oxygen crown atoms. In addition, the parallel arrangement of the aromatic systems suggested a π - π charge-transfer stabilisation.⁴² Encouraged by the complexation of the PQ²⁺ dication, the second sphere coordination of porphyrin macrocycles **7** with [Pt(bpy)(NH₃)₂](PF₆)₂ was examined. Collected in Table 1 are selected ¹H NMR shifts from an equimolar solution of [Pt(bpy)(NH₃)₂](PF₆)₂⁵⁸ and **7a** and **7b** in [²H₃]acetonitrile, with significant changes to the chemical shifts of both host and guest clearly evident.

The crown ether moiety of **7a** once again undergoes a complexation-induced conformational change, resulting in shifts different from those expected.⁴² As outlined previously for the paraquat complexes, upon complexation the crown aromatic rings must undergo a rotation so as to maximise both electrostatic and π - π electron charge-transfer interaction with the aromatic guest. This is evidenced by a change in the resonance of 14-H ($\Delta\delta - 0.35$ ppm) which is particularly sensitive to the orientation of the amide carbonyl group. Such a rotation results in a deshielding of the crown aromatic protons which, when combined with the shielding from the bipyridyl ligand, produces only minimal net changes in the chemical shifts of resonances for 20-H and 18-, 22-H (Table 1). The ether chains experience considerable deshielding upon complexation implying movement away from the porphyrin nucleus, augmented by the effects of the bipyridyl ring current.

The resonances for groups on the porphyrin periphery all shift downfield from their unbound positions ($\Delta\delta_{av} + 0.06$ ppm). This direction of shift, in combination with the pyrrolic NH

† Since the conformation of **7a** continues to change with decreasing temperature, the temperature dependence of the enthalpy and entropy terms of the conformational change and the binding need to be evaluated before the full significance of these values can be rationalised. However, due to the experimental difficulties in determining association constants at low temperatures, experiments at more than one low temperature were not carried out. Also, although the conformation of **7b** was also observed to be temperature dependent, no association constants for this host were determined below 298 K.

* 1 kcal = 4.184 kJ.

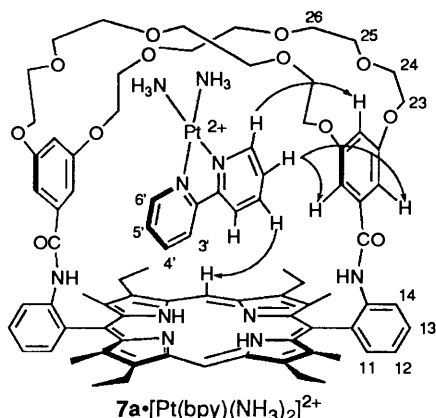


Fig. 5 Inclusion geometry deduced from NMR studies of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2]^{2+}$ within **7a**. Arrows indicate detected NOE interactions observed at 298 K between host and guest.

resonance shift of $\Delta\delta +0.08$ ppm, is consistent with an orthogonal orientation of the bipyridyl ligand relative to the porphyrin.

The resonances of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2]^{2+}$ all experience significant upfield shifts in equimolar solution with **7a** (Table 1). The changes are considerably larger than those reported for dibenzo-crown ether complexation, and are obviously enhanced by the large porphyrin magnetic anisotropy. The inclusion geometry shown in Fig. 5 is supported by (i) the ammine ligand resonance experiencing the smallest change ($\Delta\delta -0.27$ ppm) upon complexation, with progressively larger resonance shifts observed for protons closer to the porphyrin (3'-, 3''-H $\Delta\delta -3.88$ ppm), and (ii) the observation of several NOE interactions between protons on host and guest, represented by arrows in Fig. 5. Presumably, the complex between **7a** and $[\text{Pt}(\text{bpy})(\text{NH}_3)_2]^{2+}$ is stabilised by similar forces to those previously observed with dibenzo complexes,^{42,59,60} viz hydrogen bonding between the ammine ligands and the crown ether, phenolic oxygen electrostatic interaction with the nitrogen cationic atoms, and π - π electron charge transfer between crown aromatic and bipyridyl rings.

* At higher $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ concentrations, the titration plots were observed to deviate from the curve fitted for a 1:1 complex, and which was interpreted as being due to the formation of complexes with stoichiometry other than 1:1. Such data points were however excluded from association constant determination. Additionally, although the conformation of **7a** is temperature dependent, no studies of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ complexation were undertaken below ambient temperature.

† As described above, the examination of the complexation of **7b** with $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ under conditions of slow exchange necessarily implies the cooling of the solution to 273 K or below. However, since the conformation of **7b** was found to be temperature dependent, this has been taken into account for the complexation-induced shifts recorded in Table 1 by comparing the complexed chemical shifts of the equimolar solution with the resonances of uncomplexed **7b** at 253 K recorded in the absence of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$.

‡ An investigation of NOE interactions using parameters optimised for this system, revealed only intramolecular interactions within the host and guest molecules. Both positive and negative NOE signals were observable at 253 K. The positive peaks originated from uncomplexed guest and reflect its fast tumbling in solution. In comparison, complexed guest along with both complexed and uncomplexed host gave negative intramolecular NOE peaks due to their slow tumbling in solution as a result of their relatively larger molecular size.⁶¹ Since the ^1H NMR results clearly indicate a close proximity of guest protons to **7b** and yet no intermolecular NOE signals are observable, this suggests several possibilities: (1) that the intermolecular NOE signals may be accidentally nulled at 253 K, or (ii) the existence of alternative relaxation pathways to intramolecular dipole-dipole relaxation for protons within the host/guest complex.

The association constant for the complexation of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ by **7a** was determined by ^1H NMR titration in $[\text{D}_3]_3\text{acetonitrile}$, using non-linear least-squares data treatment, as $1350 \text{ dm}^3 \text{ mol}^{-1}$ with a ΔG° of $-4.3 \text{ kcal mol}^{-1}$ at 298 K.

At 298 K the ^1H NMR spectrum of a solution containing equimolar quantities of **7b** and $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ revealed broad uninterpretable peaks. Spectra recorded at higher temperatures sharpened several of the resonances and when the solution was cooled to 273 K and below, resonances for both complexed and uncomplexed host and guest were observable, indicating that the slow exchange region of complexation had been reached. This was particularly fortuitous because it allowed the ^1H NMR resonances under slow exchange conditions to be assigned using a combination of COSY-45, NOE difference, and saturation transfer spectroscopy, with the results collected in Table 1.† Hence the limiting values of the shifts of the protons for the bound guest could be determined. The complexation-induced shifts strongly support the inclusion geometry of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ within **7b** similar to that depicted in Fig. 5.

On complexation the resonances of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ protons all experience significant upfield shifts consistent with such an inclusion geometry. Most remarkable is the complexation-induced change of the 3',3'' proton resonance of the bound guest, $\Delta\delta -8.02$ ppm, implying an extremely close proximity to, and hence a large influence by the ring current of, the porphyrin.‡

The shifts of the resonances for groups on the porphyrin periphery upon complexation reflect the position of the protons relative to the complexed bipyridyl ligand. The protons 1-H, pyrrole NH, and 4-H all experience larger deshielding effects than 5-H and 7-H (Table 1) reflecting their closer proximity to the bipyridyl ligand and an increased effect of its ring current.

A resonance shift not previously observed in these porphyrin host complexations was that of the *meso*-phenyl protons 11-H and 12-H (Fig. 5) which are deshielded by $\Delta\delta +0.29$, $+0.21$ ppm respectively, suggesting the presence of strain in the porphyrin ring.^{55,62,63} These shifts imply a puckering of the porphyrin macrocycle, with the *meso*-phenyl rings shifting into a position where these protons experience an increase in deshielding from the porphyrin and suggests a tight fit of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2]^{2+}$ within the cavity of **7b**.

A similar complexation-induced conformational change to that observed in **7b**- PQ^{2+} complexation again occurs within the crown ether subunit of **7b** on $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ complexation. The shift of the resonance for 14-H ($\Delta\delta -0.85$ ppm) is indicative of the conformation change, and is in the same direction as that observed for the complexation of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ by **7a** (14-H $\Delta\delta -0.35$ ppm). Such a conformational change, in conjunction with the bipyridyl ring current, results in the apparently opposing direction of shifts observed for 18-H, 22-H and 20-H resonances (Table 1).

The association constant for the complexation of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ by **7b** was determined at 253 K under conditions of slow exchange⁶⁴ to be $150 \text{ dm}^3 \text{ mol}^{-1}$ with a free energy of complexation $\Delta G^\circ -2.5 \text{ kcal mol}^{-1}$. Since the slow exchange region for the complexation **7b**- $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ was attainable at low temperatures, the kinetic stability of the complex could also be determined. The rate of guest complexation was determined using ^1H NMR§ by monitoring the resonances of 1-H in complexed and uncomplexed environ-

§ The rate of exchange was determined by the coalescence method⁶⁵ with frequency separation ($\delta\nu$) being measured in the slow exchange region and extrapolated to the coalescence temperature T_c . Rates of complexation at T_c were then calculated using $k_c = \pi(\delta\nu)/2^{1/2}$. Free energy of activation was determined using the Eyring equation.

ments, since these resonances represented the most accessible kinetic probe. A $\Delta\nu$ of 60 Hz at a T_c of +31 °C, yielded k_c 133 s⁻¹ and ΔG_c^\ddagger 14.8 kcal mol⁻¹. A comparison of the thermodynamic stability (ΔG° -2.5 kcal mol⁻¹) with the kinetic stability (ΔG_a^\ddagger 14.8 kcal mol⁻¹)* at 253 K reveals a ΔG_a^\ddagger of ≤ 12.5 kcal mol⁻¹, implying that the complexation **7b**. [Pt(bpy)(NH₃)₂](PF₆)₂ is not under diffusion control ($\Delta G_a^\ddagger \approx 3$ kcal mol⁻¹).⁴⁰ The data does however, suggest that **7b** must undergo an energy-demanding conformational change ($\Delta G_a^\ddagger \approx 12$ kcal mol⁻¹) before complexation. The complexation-induced shifts observed (Table 1) identify the components involved in the conformational change as: the crown aromatic rings, the ether chains, and the porphyrin nucleus. The ΔG_a^\ddagger

* The conformational change observed within **7b** upon temperature reduction implies that the extrapolation of ΔG_c^\ddagger (determined at 304 K) to represent ΔG_a^\ddagger at 253 K is not entirely accurate. However, since the conformational changes in **7b** with decreasing temperature position the crown ether moiety in a conformation more amenable to complexation, ΔG_a^\ddagger calculated in this way represents the upper limit of kinetic stability at 253 K.

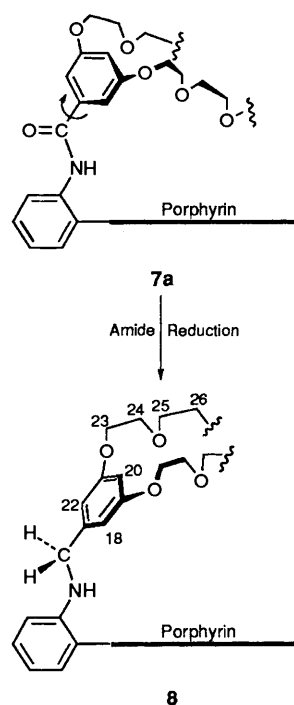


Fig. 6 The conformational change deduced from ¹H NMR measurements, on reduction of the host **7** to form **8**. Numbering is used in the discussion of the NMR spectra.

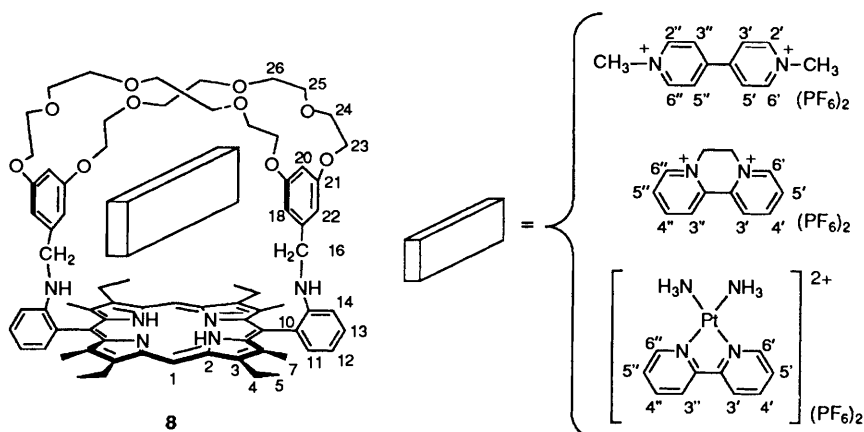


Fig. 7 Geometry of the inclusion complexes formed between **8** and the various bipyridinium dications in [²H₆]acetone, deduced from NMR measurements

value for **7b** is considerably larger than that observed for other dibenzo-crown ether hosts,^{37,39} suggesting that although the crown aromatic rings are attached to either side of a porphyrin in a geometry approximate to that required for complexation, considerable conformational reorganisation is still necessary before complexation.

Improvements to the Host

Since complexation of guests within the cavity of **7** requires a rotation of the crown aromatic ring away from the conformation containing partial conjugation with the amide-*meso*-phenyl system, the removal of this restriction should strengthen the complexation by reducing the extent of reorganisation necessary. To accomplish this, reduction of the amide groups of **7** seemed to us an obvious avenue for investigation. Such a modification has been successfully employed in carbonyl group reduction in other crown ether-containing porphyrin hosts.^{16,17} Furthermore, the replacement of an electron withdrawing amide substituent on the crown aromatic ring with an electron-donating methylene group should enhance the charge-transfer ability of the ring.^{26,40} However, it was recognised that the unfavourable inward tilt of the crown aromatic ring would be increased due to the change in hybridisation of C-16 upon reduction.

Reduction of the amide of **7a** was achieved by insertion of zinc followed by treatment with diborane in tetrahydrofuran. The assignment of the NMR spectrum of the amine derivative **8** was straightforward but, in particular, the resonance of 14-H was dramatically affected, undergoing a 1.89 ppm shift upfield. A comparison of the crown ether subunit resonances of **8** and those of the precursor crown ester revealed an upfield shift for all the proton resonances, indicating that the ether was still strapped across the face of the porphyrin. However, the resonances of **8** have changed considerably in comparison with those of the unreduced host **7a** implying that the crown-ether subunit of **8** has undergone a significant change in conformation upon amide reduction. The most dramatic change was observed for the ether chain resonances which move downfield, suggesting an increased distance from the porphyrin nucleus in an expanded conformation (Fig. 6). The larger change observed for resonances of protons 23-H and 24-H ($\Delta\delta$ +0.93, +1.12 ppm) compared to those for 25-, 26-H ($\Delta\delta$ +0.48, +0.20 ppm) imply a greater movement of the former protons upon reduction, indicating that in the unreduced host **7a** these protons occupy a position somewhat closer to the porphyrin. The crown aromatic protons are also affected by the amide reduction. The smaller shift of 20-H ($\Delta\delta$ -0.06 ppm) compared to that observed for 18-, 22-H ($\Delta\delta$ +0.33 ppm) suggests a

rotation about the bond indicated (Fig. 6), to position the aromatic ring in a more orthogonal conformation relative to the *meso*-phenyl plane, albeit with an increased inwards tilt. The solution conformation of **8** was found to be essentially independent of temperature (to 210 K), in contrast to the considerable temperature variation found in the NMR spectrum of **7a**.

Complexation Studies

Paraquat Hexafluorophosphate.—The complexation of **8** with paraquat was examined by ¹H NMR spectroscopy in [²H₆]acetone. Selected chemical shifts from an equimolar solution of host and guest and a comparison with their uncomplexed positions are collected in Table 1, and suggest an inclusion geometry as shown in Fig. 7. The complexation-induced shifts within the crown moiety of **8** resemble those usually observed for paraquat complexation (BMP32C10/PQ²⁺)^{30,31} being now uncomplicated by the *induced fit* complexation mechanism observed for **7a**.

The protons on paraquat all experience shielding effects upon complexation (Table 1) consistent with an inclusion within the cavity of **8** as outlined in Fig. 7. The large change observed for the resonance of protons 3', 5'-H ($\Delta\delta - 1.17$ ppm) reflects the closer proximity of these protons to the crown aromatic rings.

The changes to resonances within the ether chain of **8** upon complexation are now more easily rationalised. For example, an upfield movement of the 23-H resonance implies a position in which it is inside the zone of shielding of paraquat (*i.e.* in the face of the aromatic ring), whereas 24- and 26-H all experience deshielding effects suggesting a position near the edge of the paraquat molecule. The direction of these shifts is now in agreement with those observed in the literature for dibenzo-crown ethers (BMP32C10)^{30,31} complexations with paraquat, since they are no longer complicated by the conformational change that characterised the complexations of **7** and which produced the apparently anomalous direction of shifts for **7**.PQ²⁺.

The shielding effects of the complexed paraquat ring current also altered the chemical shifts of the crown aromatic proton resonances, along with the secondary amine 16-H resonance (Table 1). Within the crown aromatic ring protons the larger change observed for 20-H compared to 18-, 22-H may be explained by the closer proximity of 20-H to any bound substrate as a result of the larger inward tilt of the crown aromatic rings of **8** compared to **7a**.

The resonances of groups on the porphyrin periphery undergo only small downfield shifts ($\Delta\delta_{av} + 0.02$ ppm) upon complexation, but with the direction of shift being consistent with the inclusion geometry shown (Fig. 7).⁵⁵

The association constant for the complexation of **8** and paraquat was determined by the Higuchi iterative linear graphical method⁶⁶ as K_a 480 dm³ mol⁻¹ with a free energy of complexation $\Delta G^\circ - 3.6$ kcal mol⁻¹. Thus **8** complexes paraquat considerably stronger than its predecessor **7a** (K_a 50 dm³ mol⁻¹, $\Delta G^\circ - 2.3$ kcal mol⁻¹ at 298 K) presumably reflecting the increased preorganisation, and the decreased necessity for reorganisation, of the crown ether moiety within **8**.

Diquat Hexafluorophosphate.—A similar inclusion geometry of diquat within the macrocycle **8** to that observed for paraquat (Fig. 7) may be deduced from the chemical shifts of an equimolar solution of **8** and diquat (Table 1). The protons on

diquat all experience shielding from the porphyrin host **8**, producing an upfield movement of resonances. The geometry of diquat* within the cavity of **8** may be inferred from the relative shifts of the protons within the dication. The methylene (+ NCH₂) resonance experiences only a small shift ($\Delta\delta - 0.10$ ppm) in comparison to the protons 3', 3'' resonance which shifts $\Delta\delta - 0.41$ ppm upon complexation, indicating a closer proximity of the latter to the porphyrin nucleus. Thus the geometry of complexation is similar to that observed for dibenzo-crown ethers.^{25,30,31}

The porphyrin protons of **8** are little affected by the complexation of diquat ($\Delta\delta_{av} + 0.02$ ppm), with the pyrrole NH deshielding ($\Delta\delta + 0.03$ ppm) again indicating an orthogonal mode of complexation.^{55,67} The ether-chain proton resonance shifts upon complexation reflect a transition from the shielding 23-H ($\Delta\delta - 0.06$ ppm) to the deshielding 26-H ($\Delta\delta + 0.10$ ppm) regions of the complexed diquat on progression along the chain, and are consistent with the inclusion geometry depicted in Fig. 7. As was observed with paraquat complexation, the direction of shifts for the ether resonances is in agreement with those in the literature^{30,31} indicating a similar complexation geometry.

The crown aromatic protons are also shielded by the complexed diquat, along with the methylene protons 16-H. The larger complexation-induced shift for 20-H compared to 18-, 22-H again reflect its closer proximity to the guest, due to the crown aryl rings' increased inward tilt as a result of carbonyl reduction.

The association constant for diquat complexation by **8** was determined by a ¹H NMR titration (with the data treated according to Higuchi⁶⁶) as K_a 80 dm³ mol⁻¹ with a ΔG° of -2.6 kcal mol⁻¹. This association constant represents a large improvement from the lack of detectable diquat complexation observed with **7a** and **7b**. However, the complexation is still weak in comparison with BMP32C10 (K_a 390 dm³ mol⁻¹, $\Delta G^\circ - 3.5$ kcal mol⁻¹)³¹ presumably reflecting the inward tilt of the crown aromatic rings within **8**, in contrast to the exact parallel conformation observed and allowed in the BMP32C10/DQ²⁺ complex.

[Pt(bpy)(NH₃)₂](PF₆)₂.—An examination of an equimolar solution of **8** and [Pt(bpy)(NH₃)₂](PF₆)₂ revealed complexation-induced changes, selected values of which are collected in Table 1, for resonances that appeared to be consistent with the formation of an inclusion complex in a manner similar to that depicted in Fig. 7. The guest protons are shifted upfield to varying degrees dependent on the position relative to the porphyrin ring, and the host resonances both for porphyrin and crown ether moieties undergo shifts in the manner expected. However, the determination of an association constant for the inclusion complex proved both troublesome and enlightening. A ¹H NMR titration, following the general method outlined above, produced a complexation isotherm that could not be fitted satisfactorily to equation (1) using a non-linear least-squares curve-fitting procedure. The general shape of the curve, however, indicated that strong complexation was occurring, implying no interference from solution effects or non-ideal behaviour, and indicating the possible presence of multiple equilibria.⁶⁴ Subsequent application of the dilution technique for association constant determination† yielded an approximation for K_a of 6×10^5 dm³ mol⁻¹. Such an association constant is typical for metal-ligand coordination complexes, and combined with the multiple equilibria hinted at by the initial ¹H titration, suggested that the [Pt(bpy)(NH₃)₂]²⁺

* Although there is only one complexation geometry usually observed, there exists two possibilities for the orientation of diquat within **8**; that with the ethylene moiety toward the crown ether or toward the porphyrin.

† In this technique, host and guest concentrations are equal, allowing a linear plot of $\Delta\delta_{obs}$ against $\Delta\delta_{obs}/[conc]$ with successive dilution to determine K_a .

complex was undergoing ligand exchange with the secondary amine groups. Thus, although an inclusion complex between **8** and $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ may well have been forming, the much stronger coordination of platinum to **8** overshadowed inclusion complexation.

Conclusion

Thus, it has been demonstrated that the macrotricyclic host **7a** is a suitable receptor for both paraquat and $[\text{Pt}(\text{bpy})(\text{NH}_3)_2]^{2+}$ dications, and that these are incorporated into the guest in the manner predicted, with the guests sandwiched between the crown aromatic rings and held perpendicularly over the face of the porphyrin. However, the binding of these guests was shown to be restricted by the *induced fit* mechanism, involving a conformational rearrangement of the crown ether moiety as a result of the conjugational preferences of the aryl groups about the amide linkage. The diquat dication was not bound by this receptor. In an attempt to improve the complexing ability of the macrotricyclic porphyrin host, two avenues were pursued, *viz.*, amide reduction and the shortening of the ether chain length. Of these, amide reduction appeared the most successful with the reduced host **8** complexing all three bipyridinium dications. Removal of the restrictions of the induced fit mechanism, and a relaxation in the extent of conformational *reorganisation* in the host led to increased association constants and free energies of complexation, proving that **8** is better able to stabilise the various guest molecules than **7a**. However, ligand-exchange reactions complicated the binding of the platinum complex. The reduction in ether chain length, from tetraethylene glycol units in **7a** to triethylene glycol units in **7b**, on the other hand, was less successful in enhancing the complexation of the various bipyridinium guests, since the resultant host **7b** behaved in a manner directly analogous to **7a** in both solution conformation and complexation behaviour. The shorter chain length considerably reduced the size of the cavity available for guest complexation, and this, although it had no effect on the smaller paraquat molecule, drastically affected the complexation of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2]^{2+}$. In particular, the complexation of $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ by **7b** resulted in a puckering of the porphyrin ring, and the observation of slow exchange in the complexation process, reflecting a tight fit within the cavity of **7b**.

Despite these limitations, these dibenzo-crown ether strapped porphyrins have been successfully employed to position various electron acceptors in close proximity to the porphyrin ring using non-covalent interactions, and creating the opportunity for efficient photochemical interaction. The methodological and design concepts have been established, and improvements and fine tuning of future systems are now possible. Some of these aspects will be the subject of further publications.

Experimental

All solvents were distilled before use, and where necessary dried according to literature procedures. Column chromatography on silica was carried out using Merck Silica Gel 60 (230–400 mesh), and alumina chromatography using Woelm Acid Alumina (activity grade I). Analytical TLC was carried out on Merck Silica Gel 60 G_{254} pre-coated aluminium sheets and preparative plates were produced with Merck Silica Gel 60 PF_{254} containing gypsum.

NMR spectra were acquired using a 300 MHz Bruker AC 300 spectrometer at 298 K, unless otherwise stated. Chemical shifts (δ) are reported in parts per million relative to internal tetramethylsilane. ^{13}C Spectra were referenced against residual

solvent peaks. COSY-45, one bond C-H correlation, and NOESY two-dimensional NMR experiments employed the standard BRUKER parameters unless stated otherwise. Long-range C-H correlation experiments (FLOCK) were parameterised for J_{CH} of 7 or 10 Hz. NOE difference and saturation transfer experiments utilised standard BRUKER pulse programs, with T_1 values generally optimised for the system under investigation. UV spectra were recorded on either a Hitachi U3200, or a Hewlett Packard 8452A diode array spectrophotometer. IR data was collected using a Perkin-Elmer 1725X Fourier transform spectrometer.

FAB-MS were recorded at the University of Adelaide. Microanalyses were performed at the Microanalytical Unit, Research School of Chemistry, Australian National University.

General Method For Association Constant Determination (Non-linear Least Squares).—As an initial screening process to determine whether complexation is occurring or not, a ^1H NMR spectrum was examined for a mixture containing equimolar amounts of host and guest. A quantity of host was weighed out, and a stock solution of guest in non-deuteriated solvent made. An aliquot of guest was added to the host to give equimolar quantities, and the solution stirred for 10–30 min. The solution was then taken to dryness using high vacuum, redissolved in deuteriated solvent, and the ^1H NMR spectrum recorded. Examination of the host and guest resonances for complexation-induced shifts gave an indication as to whether a titration was necessary for association constant determination. This experiment also yielded valuable information regarding the geometry of guest inclusion, based upon the direction and magnitude of chemical shift displacements.

Finally, before a titration was carried out, an estimation of the porphyrin host aggregation concentration was undertaken. This was carried out by recording the ^1H NMR spectra for a series of solutions of the porphyrin host with increasing dilution, starting with a host concentration of $\approx 20 \text{ mmol dm}^{-3}$. A constant chemical shift of the *meso*-protons (1-H), which are sensitive to porphyrin dimerisation, gave an estimate of the maximum concentration necessary to avoid aggregation. Complexation studies were then undertaken below this concentration.

^1H NMR titrations for association constant determination were carried out in a single NMR tube containing a constant volume of solvent, which allowed the host concentration to be maintained constant. An amount of porphyrin host was weighed out, dissolved in non-deuteriated solvent and transferred to the NMR tube and taken to dryness. The desired amount of deuteriated solvent was then added to the residue, the tube marked, and the ^1H spectrum recorded. The desired aliquot of a guest was added from a stock solution (in deuteriated solvent), and the volume reduced to the original level by N_2 -assisted evaporation, with re-addition of solvent if necessary. The concentrations of host and guest, along with the aliquots of guest to be added, were chosen so as to allow a suitably large range of the complexation curve to be measured,^{68,69} as well as enabling up to 15 data points to be recorded.⁷⁰

The chemical shifts for resonances of protons that remained clearly visible during the entire titration were then tabulated against guest concentration. A titration typically involved monitoring the chemical shift of a proton on the host (or guest) as the concentration of guest (or host) was increased. In this case, titrations were carried out using a constant host concentration and increasing guest concentration, since this minimised the wastage of the synthetically hard-won macrocyclic hosts. The change in chemical shift ($\Delta\delta_{\text{obs}}$) thus obtained was fitted to equation (1) (unless otherwise stated) using a

$$\Delta\delta_{\text{obs}} = \frac{\Delta\delta_{\text{m}}}{2[\text{H}]_{\text{t}}} \left\{ \left([\text{H}]_{\text{t}} + [\text{G}]_{\text{t}} + \frac{1}{K_{\text{a}}} \right) - \sqrt{\left([\text{H}]_{\text{t}} + [\text{G}]_{\text{t}} + \frac{1}{K_{\text{a}}} \right)^2 - 4[\text{H}]_{\text{t}}[\text{G}]_{\text{t}}} \right\} \quad (1)$$

non-linear least-squares curve-fitting program⁷¹ to obtain values for the association constant K_{a} and the maximum change in chemical shift, $\Delta\delta_{\text{m}}$. Equation (1) is a solution to the quadratic expression for 1:1 complexation under conditions of fast exchange, and whose derivation is straightforward. The equation relates the observed change in chemical shift ($\Delta\delta_{\text{obs}}$) of a resonance on the host, to the maximum change in chemical shift ($\Delta\delta_{\text{m}}$), total host $[\text{H}]_{\text{t}}$ and guest $[\text{G}]_{\text{t}}$ concentrations along with the association constant K_{a} . Algebraic manipulation of equation (1) allows it to be converted into expressions similar to those previously used.^{72,73}

The K_{a} values reported here are averages calculated from several protons that could be followed during each titration. Such averaging has been employed previously in relation to association constant data⁷⁴ although Dougherty has suggested that a simultaneous fit of each set of proton data to yield a single association constant is an alternative and perhaps a more accurate method.⁷⁵ There have been reported cases where it has been necessary to invoke the formation of higher complexes than 1:1 to obtain satisfactory agreement between experiment and theory.⁷⁶⁻⁷⁸ However, the ability of equation (1) to describe successfully the titration data points was interpreted as an indication that only a 1:1 stoichiometric complex forms under the range of concentrations studied. This conclusion was supported by consistent association constant values from several protons followed during each titration.^{79,80} The errors for individual association constants determined from uncertainty values were typically of the order of 10%. Although errors are not quoted with each association constant, the values should be viewed as containing at least 10% error margins.

Synthetic Procedures.—The nomenclature used is systematic where possible, otherwise terminology described in the literature⁸¹ has been followed.

Methyl 5-benzyloxy-3-hydroxybenzoate 1. Methyl 3,5-dihydroxybenzoate (10 g, 59 mmol) was suspended in DMF (dimethylformamide) with K_2CO_3 (8.15 g, 59 mmol) and the solution stirred at 80 °C for 35 min. Benzyl chloride (6.78 g, 53 mmol) in DMF was added dropwise over 1 h to the solution which was then stirred at 80 °C for 24 h. Upon cooling, the solution was diluted with an equal volume of water, and treated with ice-cold aqueous NaOH (10%). The resulting solution was extracted with Et_2O ($\times 2$) to give the dibenzylated product, followed by ethyl acetate ($\times 2$) to give the monobenzylated material. The organic layers were then washed extensively (H_2O) to remove residual DMF and dried (Na_2SO_4). The monobenzylated product **1** was obtained from the ethyl acetate extract (3.1 g, 20%), m.p. 98–99 °C (from ethyl acetate–hexane) (lit.,⁴⁷ 98 °C); δ_{H} (300 MHz; CDCl_3) 7.36 (5 H, m, ArH), 7.21 (2 H, m, ArH), 6.69 (1 H, t, J 3, ArH), 5.02 (2 H, s, OCH_2) and 3.87 (3 H, s, OCH_3).

1,11-Bis(5'-benzyloxy-3'-methoxycarbonylphenoxy)-3,6,9-trioxaundecane 3a.—The monobenzylated product **1** (12.16 g, 47 mmol) dissolved in dry THF was added dropwise over 30 min to NaH (1.35 g, 56 mmol) suspended in dry THF under a N_2 blanket. The solution was stirred at 50–60 °C for 35 min after which 3,6,9-trioxaundecane-1,11-diyl ditosylate (tetraethylene glycol bistosylate⁴⁸) **2a** (12.06 g, 24 mmol) in dry THF was added dropwise to it over 60 min; the mixture was then refluxed for 15 h. After the mixture had cooled, the solvent was removed by rotary evaporation and the resulting oil

partitioned between CH_2Cl_2 and water. The organic layer was separated, washed (NaOH , H_2O) and dried (Na_2SO_4). Final purification of the residue was carried out by column chromatography (silica) using CH_2Cl_2 – Et_2O (4:1) + 2% EtOH as eluent to yield **3a** as a pale yellow oil (10.07 g, 64%); δ_{H} (300 MHz; CDCl_3) 7.43 (10 H, m, C_6H_5), 7.29 (4 H, s, ArH), 6.84 (2 H, s, ArH), 5.13 (4 H, s, OCH_2), 4.10 (4 H, m, α - OCH_2), 3.96 (6 H, s, CH_3), 3.91 (4 H, m, β - OCH_2) and 3.76 (8 H, m, γ -, δ - OCH_2); m/z 674.2726 (M^+). $\text{C}_{38}\text{H}_{42}\text{O}_{11}$ requires 674.27269 (M^+).

1,11-Bis(5-hydroxy-3'-methoxycarbonylphenoxy)-3,6,9-trioxaundecane 4a. The acyclic polyether **3** (4.77 g, 7.1 mmol) was dissolved in CH_2Cl_2 – MeOH – EtOH (1:1:1) and hydrogenolysed using 10% Pd/C. Upon completion of hydrogen uptake the catalyst was filtered off and the filtrate concentrated to yield the pure reduced acyclic polyether **4a** as a pale yellow oil (2.65 g, 76%); δ_{H} (300 MHz; CDCl_3) 7.16 (2 H, t, J 3, ArH), 7.07 (2 H, t, J 3, ArH), 6.66 (2 H, t, J 3, ArH), 4.08 (4 H, m, α - OCH_2), 3.91 (6 H, s, CH_3) and 3.86–3.72 (12 H, m, β -, γ -, δ - OCH_2); m/z (FABMS) 495.5 ($\text{M} + \text{H}^+$). $\text{C}_{24}\text{H}_{30}\text{O}_{11}$ requires 495.51 ($\text{M} + \text{H}^+$).

Dimethyl 1,4,7,10,13,20,23,26,29,32-Decaoxa[13.13]m-cyclophane-16,35-dicarboxylate; crown-(4) ester. The acyclic polyether **4a** (9.12 g, 18 mmol) dissolved in dry THF (100 cm^3) was added all at once to NaH (1.48 g, 62 mmol) suspended in dry THF (60 cm^3) and under N_2 blanket. The solution was stirred at 50 °C for 5 min after which tetraethylene glycol bistosylate **2a** (10 g, 20 mmol) in dry THF was added dropwise to it with stirring during 10 min; stirring was continued for a further 45 min after which the mixture was refluxed for 16 h. Upon cooling, the solution was quenched with water, acidified with aqueous hydrochloric acid (10 mol dm^{-3}), and extracted with ethyl acetate. The organic layer was then washed with water, and dried (Na_2SO_4). Final purification was carried out using column chromatography with ethyl acetate as eluent to give the crown-(4) ester (1.56 g, 13%), m.p. 106 °C (from ethyl acetate) (Found: C, 58.65; H, 6.8. $\text{C}_{32}\text{H}_{44}\text{O}_{14}$ requires C, 58.89; H, 6.79%); δ_{H} (300 MHz; CDCl_3) 7.12 (4 H, d, J 3, ArH), 6.64 (2 H, t, J 3, ArH), 4.07 (8 H, m, α - OCH_2), 3.85 (6 H, s, CH_3), 3.81 (8 H, m, β - OCH_2) and 3.69–3.64 (16 H, m, γ -, δ - OCH_2).

1,4,7,10,13,20,23,26,29,32-Decaoxa[13.13]m-cyclophane-16,35-dicarboxylic acid; crown-(4) acid. The crown-(4) ester (0.98 g, 1.5 mmol) suspended in methanol was combined with 10% aqueous NaOH and water and refluxed for 1 h. The solution was then acidified with HCl (10 mol dm^{-3}) and extracted with ethyl acetate. The combined extracts were then washed with water, dried (Na_2SO_4) and evaporated to produce a white solid (0.67 g, 71.4%), m.p. 146–148 °C, $\nu(\text{CO})/\text{cm}^{-1}$ 1695; δ_{H} (300 MHz; CDCl_3) 6.96 (4 H, d, J 3, ArH), 6.46 (2 H, t, J 3, ArH), 3.89 (8 H, m, α - OCH_2), 3.63 (8 H, m, β - OCH_2) and 3.51–3.46 (16 H, m, γ -, δ - OCH_2).

1,4,7,10,13,20,23,26,29,32-Decaoxa[13.13]m-cyclophane-16,35-dicarbonyl dichloride 5a. The crown-(4) acid was dissolved in a mixture of dry CH_2Cl_2 and dry C_6H_6 (1:1; 20 cm^3) and thionyl chloride (excess) was added dropwise to it; the solution was then refluxed for 3 h. After this the solution was pumped dry under high vacuum, washed C_6H_6 ($\times 2$), and further pumped to produce a yellow oil, $\nu(\text{CO})/\text{cm}^{-1}$ 1750. Used without further purification.

Crown-(4) Porphyrin 7a. The crown-(4) acid (0.2 g, 0.3 mmol) was converted into its acid chloride **5a** by the method outlined above. The acid chloride dissolved in dry CH_2Cl_2 (150 cm^3) was added all at once to refluxing CH_2Cl_2 (500 cm^3) containing the α,α -diaminoporphyrin **6**^{45,46} (0.14 g, 0.2 mmol) and dry pyridine (3 cm^3). The solution was refluxed for 16 h after which time additional acid chloride and porphyrin were added and refluxing continued. After the final addition of reactants the solution was refluxed for 20 h when the reaction was essentially

complete (TLC). The solution was then concentrated, washed (H₂O, dilute aq. HCl, H₂O, aq. Na₂CO₃, H₂O) and dried (Na₂SO₄). Final purification was carried out using preparative layer chromatography plates and CH₂Cl₂-Et₂O (4:1) + 2% EtOH as eluent. Extraction from silica yielded **7a** (0.5 g, 61.5% based on porphyrin consumed), m.p. (decomp.) > 252 °C (from acetone by slow evaporation) (Found: C, 70.9; H, 6.7; N 6.9. C₇₄H₈₄N₆O₁₂ requires C, 71.13; H, 6.78; N 6.73%); δ_H(300 MHz; CDCl₃)* 10.32 (2 H, s, *meso*-H), 8.99 (2 H, d, *J* 6, ArH), 7.97 (2 H, d, *J* 6, ArH), 7.96 (2 H, t, *J* 6, ArH), 7.65 (2 H, s, NH), 7.62 (2 H, t, *J* 6, ArH), 5.82 (2 H, t, *J* 3, ArH), 5.55 (4 H, t, *J* 3, ArH), 4.05 (8 H, q, *J* 6, CH₂CH₃), 3.15-3.12 (8 H, m, δ-OCH₂), 2.87-2.84 (8 H, m, γ-OCH₂), 2.65 (12 H, s, CH₃), 2.42-2.39 (8 H, m, α-OCH₂), 2.23-2.21 (8 H, m, β-OCH₂), 1.82 (12 H, t, *J* 6, CH₃CH₂) and -2.39 (2 H, br s, NH); δ_C(CDCl₃) 165.16, 159.20, 145.81, 145.11, 141.70, 138.96, 136.22, 136.04, 133.10, 131.02, 130.41, 124.34, 120.34, 111.43, 105.43, 103.79, 97.16, 70.15, 70.06, 67.94, 65.92, 19.89, 17.63 and 13.67.

1,8-Bis(5'-benzyloxy-3'-methoxycarbonylphenoxy)-3,6-dioxaoctane 3b. The monobenzylated material **1** (11.93 g, 46 mmol) dissolved in dry tetrahydrofuran (100 cm³) was added all at once to a suspension of NaH (2.53 g, 0.11 mol) in dry tetrahydrofuran (40 cm³) under N₂, and the solution stirred at 50 °C for 30 min. Triethylene glycol bistosylate⁴⁸ **2b** (9.95 g, 22 mmol) in dry tetrahydrofuran (150 cm³) was then added dropwise over 90 min to the solution which was then refluxed for 40 h. Upon cooling, the solution was acidified, filtered, and concentrated by rotary evaporation. The oily residue was partitioned between water and CH₂Cl₂ and the organic phase was separated, washed with aqueous NaOH (5%) and water and dried (Na₂SO₄). The product was then purified by column chromatography using ethyl acetate-hexane (3:7) as eluent to give **3b** as a colourless oil (9.09 g, 66%); δ_H(300 MHz; CDCl₃) 7.40-7.20 (14 H, m, ArH), 6.74 (2 H, s, ArH), 5.04 (4 H, s, CH₂), 4.13 (4 H, m, α-OCH₂), 3.85 (4 H, m, β-OCH₂), 3.86 (6 H, s, CH₃) and 3.74 (4 H, s, γ-OCH₂); *m/z* 630.2464 (M⁺). C₃₆H₃₈O₁₀ requires 630.24647 (M⁺).

1,8-Bis(5'-hydroxy-3'-methoxycarbonylphenoxy)-3,6-dioxaoctane 4b. The protected acyclic polyether **3b** (3.5 g, 5.6 mmol) was dissolved in CH₂Cl₂-MeOH-EtOH (2:2:1) and hydrogenated using 10% Pd/C. Upon completion, the catalyst was filtered off and the solution concentrated to yield **4b** (2.42 g, 96%), m.p. 132 °C (from CH₂Cl₂-MeOH and hexane) (Found: C, 58.3; H, 5.7. C₂₂H₂₆O₁₀ requires C, 58.66; H, 5.82%); δ_H(300 MHz; CDCl₃) 7.47 (2 H, br s, Ar-OH), 7.09 (2 H, d, *J* 6, Ar-H), 6.98 (2 H, d, *J* 6, ArH), 6.58 (2 H, s, ArH), 4.02 (4 H, m, α-OCH₂), 3.84 (6 H, s, CH₃), 3.80 (4 H, m, β-OCH₂) and 3.73 (4 H, s, γ-OCH₂); *m/z* (FABMS) 451.4 (M + H⁺). C₂₂H₂₆O₁₀ requires 451.45 (M + H⁺).

Dimethyl 1,4,7,10,17,20,23,26-octaoxa[10.10]m-cyclophane-13,29-dicarboxylate; crown-(3) ester. The diphenol acyclic polyether **4b** (2.61 g, 5.8 mmol) in dry tetrahydrofuran (100 cm³) was added all at once to a suspension of NaH (0.48 g, 20 mmol) in dry tetrahydrofuran (50 cm³) under a N₂ blanket, and the mixture stirred at 45 °C for 5 min. Triethylene glycol bistosylate **2b** (3.16 g, 6.9 mmol) in dry tetrahydrofuran was added dropwise over 30 min to the solution which was then refluxed for 50 h. Upon cooling, the solution was acidified (HCl), filtered, and concentrated to an oil by rotary evaporation. The oil was partitioned between water and CHCl₃, and the organic phase separated, washed (aq. NaOH and H₂O) and dried (Na₂SO₄). Final purification was carried out using column chromatography with CH₂Cl₂-Et₂O (4:1) + 2% EtOH as eluent to yield the crown (3) ester as a pale yellow

solid (1.51 g, 46%), m.p. 125 °C (from ethyl acetate) (Found: C, 59.6; H, 6.7. C₂₈H₃₆O₁₂ requires C, 59.57; H 6.43%); δ_H(300 MHz; CDCl₃) 7.16 (4 H, d, *J* 6, ArH), 6.63 (2 H, t, *J* 6, ArH), 4.12 (8 H, m, α-OCH₂), 3.88 (6 H, s, CH₃), 3.86 (8 H, m, β-OCH₂) and 3.74 (8 H, s, OCH₂).

1,4,7,10,17,20,23,26-Octaaxa[10.10]m-cyclophane-13,29-dicarboxylic acid; crown-(3) acid. The crown-(3) ester (0.25 g, 0.4 mmol) was suspended in MeOH (50 cm³) with aqueous NaOH (10%; 20 cm³), water (5 cm³) and refluxed for 2 h. Upon cooling, the solution was acidified to afford a precipitate which was filtered off, washed (H₂O) and pumped dry to yield a white solid (0.22 g, 93%), m.p. 255-256 °C (lit.,⁴³ 257 °C); δ_H(300 MHz; CDCl₃ + CD₃OD) 6.93 (4 H, d, *J* 2, ArH), 6.44 (2 H, t, *J* 2, ArH), 3.87 (8 H, m, α-OCH₂), 3.62 (8 H, m, β-OCH₂) and 3.49 (8 H, s, γ-OCH₂).

1,4,7,10,17,20,23,26-Octaaxa[10.10]m-cyclophane-13,29-dicarbonyl dichloride 5b. The crown-(3) acid was suspended in dry CH₂Cl₂ and stirred with oxalyl chloride (excess) and dry pyridine (2 drops) for 4 h at room temperature. The solution was pumped dry, washed with dry CH₂Cl₂ (× 2), and pumped for a further 10 min to give **5b** as a white solid in quantitative yield, [ν(CO)/cm⁻¹ 1756] which was used without further purification.

Crown-(3) porphyrin 7b. The crown-(3) acid (70 mg, 0.13 mmol) was converted into the acid chloride **5b** as outlined above, and this, dissolved in dry CH₂Cl₂, was added dropwise with stirring over 10 min to a solution of the α,α-diamino porphyrin **6** (54 mg, 0.08 mmol) in dry CH₂Cl₂ (250 cm³) and dry pyridine (2 cm³) under a N₂ atmosphere. The solution was then refluxed overnight. Further acid chloride and porphyrin were added to the refluxing solution and refluxing was continued overnight. After the final addition of reactants the solution was refluxed for an additional 40 h. Upon cooling, the solution was washed [0.05 mol dm⁻³ HCl (× 2), H₂O, aq. Na₂CO₃ and H₂O] and dried (Na₂SO₄). The product was purified by column chromatography (silica) using CH₂Cl₂-Et₂O (4:1) + 2% EtOH as eluent to yield **7b** (70 mg, 35% based on porphyrin consumed), m.p. > 320 °C (from CH₂Cl₂-MeOH) (Found: C, 70.2; H, 6.6; N, 6.8. C₇₀H₇₆N₆O₁₀·2H₂O requires C, 70.21; H, 6.73; N, 7.02%); δ_H(300 MHz; CDCl₃) 10.24 (2 H, s, *meso*-H), 8.71 (2 H, d, *J* 9, ArH), 8.00 (2 H, d, *J* 9, ArH), 7.90 (2 H, t, *J* 9, ArH), 7.59 (2 H, t, *J* 9, ArH), 7.19 (2 H, s, NH), 5.84 (2 H, t, *J* 3, ArH), 5.79 (4 H, d, *J* 3, ArH), 4.02 (8 H, q, *J* 6, CH₂CH₃), 3.15 (8 H, s, γ-OCH₂), 3.01 (8 H, m, α-OCH₂), 2.96 (8 H, m, β-OCH₂), 2.61 (12 H, s, CH₃), 2.24 (4 H, s, 2H₂O), 1.78 (12 H, t, CH₃CH₂) and -2.59 (2 H, br s, NH); δ_C(CDCl₃) 166.38, 159.18, 145.59, 144.99, 141.61, 138.78, 136.73, 135.84, 133.37, 131.62, 130.15, 124.45, 121.34, 111.43, 105.46, 104.63, 97.03, 70.39, 68.67, 66.66, 19.93, 17.86 and 13.75.

Reduced crown-(4) porphyrin 8. The crown-(4) porphyrin **7a** was dissolved in CH₂Cl₂ and the solution heated to reflux; a solution of zinc acetate in MeOH was then added portionwise to it until zinc insertion was complete (TLC); the mixture was then refluxed for a further 5 min. Upon cooling, the solution was washed (H₂O), dried (Na₂SO₄) and concentrated to yield the metallated derivative **7a-Zn**. The complex **7a-Zn** (0.17 g, 0.1 mmol) was dissolved in tetrahydrofuran (dry; 55 cm³) and the solution degassed with N₂ (10 min). Diborane in tetrahydrofuran (prepared according to Brown⁸²) (ca. 2 mol dm⁻³ solution; 13.9 cm³) was added *via* a septum, to the solution which was then refluxed for 1 h under a N₂ atmosphere. After cooling to room temperature, the reaction mixture was quenched with water (2 cm³), and concentrated by rotary evaporation. The residue was taken up in HCl (10 mol dm⁻³; 25 cm³), and the solution refluxed for 7.5 h. Upon cooling, water (30 cm³) was added to the mixture which was then partially neutralised with 10% aqueous NaOH and extracted with CH₂Cl₂ (4 × 50 cm³). The combined extracts were washed [H₂O, aq. Na₂CO₃ (× 2) aq. H₂O] and dried (Na₂SO₄).

* The assignments of the ether chain resonances differ from those previously reported by us.¹⁴

Purification was carried out by column chromatography (silica) using CH_2Cl_2 -Et₂O (4:1) + 2% EtOH as eluent to yield the reduced product **8** (60 mg, 38%), m.p. > 320 °C (from acetone by slow evaporation) (Found: C, 70.2; H, 6.8; N, 6.35. $\text{C}_{74}\text{H}_{88}\text{N}_6\text{O}_{10}\cdot 2\text{H}_2\text{O}$ requires C, 70.62; H, 7.05; N, 6.68%); m/z (FAB-MS) ($\text{M} + \text{H}^+$) 1221; δ_{H} (300 MHz; CDCl_3) 10.18 (2 H, s, meso-H), 7.72 (2 H, t, J 9, ArH), 7.71 (2 H, d, J 9, ArH), 7.21 (2 H, t, J 9, ArH), 7.10 (2 H, d, J 9, ArH), 5.88 (4 H, d, J 2, ArH), 5.76 (2 H, J 2, ArH), 4.14 (4 H, d, J 6, CH_2NH), 4.03 (8 H, q, CH_2CH_3), 3.36–3.32 (32 H, m, OCH_2), 3.19 (2 H, t, J 6, NHCH_2), 2.69 (12 H, CH_3), 2.24 (4 H, s, $2\text{H}_2\text{O}$), 1.79 (12 H, t, J 9, CH_3CH_2) and –2.44 (2 H, br s, pyrrole NH); δ_{C} (CDCl_3) 159.33, 148.52, 145.44, 144.62, 141.75, 140.13, 135.92, 133.46, 130.19, 126.67, 116.02, 113.13, 110.27, 106.42, 100.32, 96.14, 70.54, 69.14, 66.68, 49.24, 19.95, 17.71 and 13.62.

Acknowledgements

Support by the Australian Research Council for part of this work is acknowledged.

References

- M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435.
- D. Gust, T. A. Moore, A. L. Moore, G. Seely, P. Liddell, D. Barrett, L. O. Harding, X. C. Ma, S.-J. Lee and F. Gao, *Tetrahedron*, 1989, **45**, 4867.
- D. Gust, T. A. Moore, A. L. Moore, F. Gao, D. Luttrull, J. M. DeGraziano, X. C. Ma, L. R. Makings, S.-J. Lee, T. T. Trier, E. Bittersmann, G. R. Seely, S. Woodward, R. V. Bensasson, M. Rougée, F. C. De Schryver and M. Van der Auweraer, *J. Am. Chem. Soc.*, 1991, **113**, 3638.
- M. R. Wasielewski, M. P. Niemczyk, W. A. Svec and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 1080.
- T. Hayashi, T. Miyahara, N. Hashizume and H. Ogoshi, *J. Am. Chem. Soc.*, 1993, **115**, 2049.
- Y. Aoyama, M. Asakawa, Y. Matsui and H. Ogoshi, *J. Am. Chem. Soc.*, 1991, **113**, 6233.
- A. Harriman, D. J. Magda and J. L. Sessler, *J. Chem. Soc., Chem. Commun.*, 1991, 345.
- P. Tecilla, R. P. Dixon, G. Slobodkin, D. S. Alavi, D. H. Waldeck and A. D. Hamilton, *J. Am. Chem. Soc.*, 1990, **112**, 9408.
- A. Harriman, Y. Kubo and J. L. Sessler, *J. Am. Chem. Soc.*, 1992, **114**, 388.
- C. Turro, C. K. Chang, G. E. Leroi, R. I. Cukier and D. G. Nocera, *J. Am. Chem. Soc.*, 1992, **114**, 4013.
- J.-P. Collin, V. Heitz and J.-P. Sauvage, *Tetrahedron Lett.*, 1991, **32**, 5977.
- H. L. Anderson, C. A. Hunter and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1989, 226.
- C. A. Hunter, J. K. M. Sanders, G. S. Beddard and S. Evans, *J. Chem. Soc., Chem. Commun.*, 1989, 1765.
- M. J. Gunter and M. R. Johnston, *Tetrahedron Lett.*, 1990, **31**, 4801.
- M. J. Gunter and M. R. Johnston, *Tetrahedron Lett.*, 1992, **33**, 1771.
- A. D. Hamilton, J.-M. Lehn and J. L. Sessler, *J. Chem. Soc., Chem. Commun.*, 1984, 311.
- A. D. Hamilton, J.-M. Lehn and J. L. Sessler, *J. Am. Chem. Soc.*, 1986, **108**, 5158.
- Y. Kuroda, M. Ito, T. Sera and H. Ogoshi, *J. Am. Chem. Soc.*, 1993, **115**, 7003.
- M. C. Gonzalez, A. R. McIntosh, J. R. Bolton and A. C. Weedon, *J. Chem. Soc., Chem. Commun.*, 1984, 1138.
- M. C. Gonzalez and A. C. Weedon, *Can. J. Chem.*, 1985, **63**, 602.
- M. Nango, M. Higuchi, H. Gondo and M. Hara, *J. Phys. Chem.*, 1989, 1550.
- M. Gubelmann, A. Harriman, J.-M. Lehn and J. L. Sessler, *J. Chem. Soc., Chem. Commun.*, 1988, 77.
- F. Vögtle, *Supramolecular Chemistry*, John Wiley and Sons, Chichester, 1992, ch. 2.
- H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, D. J. Williams and J. B. Wolstenholme, *J. Chem. Soc., Chem. Commun.*, 1983, 1140.
- 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.
- F. H. Kohnke, J. F. Stoddart, B. L. Allwood and D. J. Williams, *Tetrahedron Lett.*, 1985, **26**, 1681.
- P. L. Anelli, N. Spencer and J. F. Stoddart, *Tetrahedron Lett.*, 1988, **29**, 1569.
- P. L. Anelli, A. M. Z. Slawin, J. F. Stoddart and D. J. Williams, *Tetrahedron Lett.*, 1988, **29**, 1573.
- 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, *J. Chem. Soc., Chem. Commun.*, 1987, 1054.
- B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1058.
- B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1061.
- P. R. Ashton, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1064.
- P. R. Ashton, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1066.
- A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1070.
- J.-Y. Ortholand, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1394.
- P. R. Ashton, E. J. T. Chrystal, J. P. Mathias, K. P. Parry, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Tetrahedron Lett.*, 1987, **28**, 6367.
- F. H. Kohnke and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1985, 314.
- B. L. Allwood, F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, 311.
- B. L. Allwood, F. H. Kohnke, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 581.
- F. H. Kohnke and J. F. Stoddart, *Tetrahedron Lett.*, 1985, **26**, 1685.
- H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1992, 946.
- H. M. Colquhoun, S. M. Doughty, J. M. Maud, J. F. Stoddart, D. J. Williams and J. B. Wolstenholme, *Isr. J. Chem.*, 1985, **25**, 15.
- N. Wester and F. Vögtle, *Chem. Ber.*, 1979, **112**, 3723.
- N. Wester and F. Vögtle, *Chem. Ber.*, 1980, **113**, 1487.
- M. J. Gunter and L. N. Mander, *J. Org. Chem.*, 1981, **46**, 4792.
- R. Young and C. K. Chang, *J. Am. Chem. Soc.*, 1985, **107**, 898.
- K. Krohn and J. Thiem, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1186.
- J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, 1972, **26**, 1471.
- J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval and F. C. Anson, *J. Am. Chem. Soc.*, 1980, **102**, 6027.
- J. P. Collman, F. C. Anson, C. E. Barnes, C. S. Bencosme, T. Geiger, E. R. Evitt, R. P. Kreh, K. Meier and R. B. Pettman, *J. Am. Chem. Soc.*, 1983, **105**, 2694.
- C. K. Chang, *J. Am. Chem. Soc.*, 1977, **99**, 2819.
- B. Boitrel, E. Camilleri, Y. Fleche, A. Lecas and E. Rose, *Tetrahedron Lett.*, 1989, **30**, 2923.
- S. Licoccia, M. Paci, P. Tagliatesta, R. Paolesse, S. Antonaroli and T. Boschi, *Mag. Res. Chem.*, 1991, **29**, 1084.
- C. M. Elliott and E. J. Hershenhart, *J. Am. Chem. Soc.*, 1982, **104**, 7519.
- M. Momenteau, J. Mispelter, B. Loock and E. Bisagni, *J. Chem. Soc., Perkin Trans. 1*, 1983, 189.
- R. F. Homer and T. E. Tomlinson, *J. Chem. Soc.*, 1960, 2498.
- J. F. Stoddart, *Chem. Br.*, 1991, 714.
- G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1934, 965.
- H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 487–582.
- H. M. Colquhoun, J. F. Stoddart, D. J. Williams, J. B. Wolstenholme and R. Zarzycki, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1051.
- A. E. Derome, *Modern NMR Techniques for Chemistry Research*, Pergamon Press, Oxford, 1987, ch. 6.
- U. Simonis, F. A. Walker, P. Lani Lee, B. J. Hanquet, D. J. Meyerhoff and R. W. Scheidt, *J. Am. Chem. Soc.*, 1987, **109**, 2659.
- D. Reddy and T. K. Chandrashekar, *J. Chem. Soc., Dalton Trans.*, 1992, 619.
- K. A. Connors, *Binding Constants, The Measurement of Molecular Complex Stability*, Wiley, New York, 1987, p. 189.
- J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982, ch. 6.
- M. Nakano, N. I. Nakano and T. Higuchi, *J. Phys. Chem.*, 1967, **71**, 3954.
- N. Nishino, H. Mihara, R. Hasegawa, T. Yanai and T. Fujimoto, *J. Chem. Soc., Chem. Commun.*, 1992, 692.
- W. B. Person, *J. Am. Chem. Soc.*, 1965, **87**, 167.
- D. A. Deranleau, *J. Am. Chem. Soc.*, 1969, **91**, 4044.

- 70 J. Granot, *J. Magn. Reson.*, 1983, **55**, 216.
71 CURVE FIT, K. Raner, 1992, Clayton, Victoria, Australia.
72 K. Saigo, N. Kihara, Y. Hashimoto, R.-J. Lin, H. Fujimura, Y. Suzuki and M. Hasegawa, *J. Am. Chem. Soc.*, 1990, **112**, 1144.
73 C. S. Wilcox and M. D. Cowart, *Tetrahedron Lett.*, 1986, **27**, 5563.
74 F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 362.
75 M. A. Petti, T. J. Sheppodd, J. R. E. Barrans and D. A. Dougherty, *J. Am. Chem. Soc.*, 1988, **110**, 6825.
76 G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, 1965, **87**, 1655.
77 A. A. S. Bright, J. A. Chudek and R. Foster, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1256.
78 R. J. Bailey, J. A. Chudek and R. Foster, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1590.
79 M. D. Cowart, I. Sucholeiki, R. R. Bukownik and C. S. Wilcox, *J. Am. Chem. Soc.*, 1988, **110**, 6204.
80 H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1417.
81 F. Vögtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5847.
82 A. Pelter, K. Smith and H. C. Brown, *Borane Reagents*, Academic Press, New York, 1988, p. 421.

Paper 3/06736J

Received 10th November 1993

Accepted 16th December 1993