

Porphyrin [2]Catenanes—Dynamic Control through Protonation

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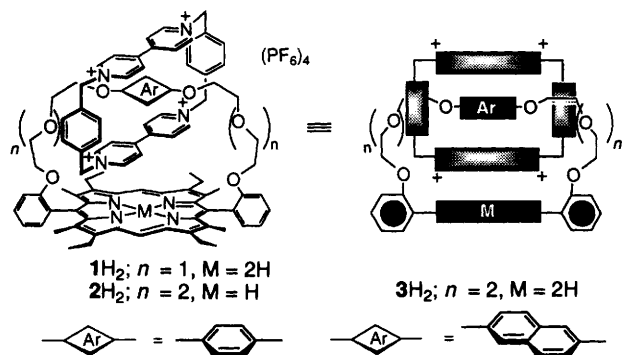
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Protonation of the previously reported porphyrin [2]catenanes in strongly acidic solutions results in electrostatic repulsion of their two components, and conformational reorientations and changes in rotation rates, which are dependent on the structural flexibility of the molecules.

We have recently reported the preparation and properties of porphyrin [2]catenanes.^{1,2} We envisaged that these molecules might have particular applicability as components of photo- or electro-chemically driven molecular scale mechano-electronic devices.^{3,4} The rationale behind their synthesis was that the ability to fine tune the photochemical, electrochemical and chemical properties of the porphyrin by suitable choice of metallation and peripheral substitution might provide a means by which the dynamic behaviour of the catenane could be driven and controlled. For example, we saw the possibility that these porphyrin catenanes may behave as molecular switches, which can be set at either of two different molecular conformations⁵ by using porphyrin protonation as the trigger for conformational change. We now report that simple acid-base chemistry of the metal-free derivatives can indeed control the conformation and dynamic behaviour of the catenanes.

Protonation of the catenanes $1H_2$, $2H_2$, and $3H_2$ ^{1,2} in strongly acidic solutions (acetone or acetonitrile with TFA), or 3 mol dm⁻³ aqueous hydrochloric acid) produces solutions of the porphyrin dications, $1H_4^{2+}$, $2H_4^{2+}$ and $3H_4^{2+}$, respectively, as established by UV-VIS and ¹H NMR spectroscopy. The unprotonated catenanes can be recovered intact by neutralisation of the acidic solutions or by evaporation of the volatile acid. Much stronger acidic conditions than normally required for unhindered porphyrins are necessary to effect protonation, as might be anticipated; the tetrapositively charged macrocycle is held in close proximity to the porphyrin. The result is strong electrostatic repulsion of the tetracation unit from the dispositively charged porphyrin centre.

UV-VIS spectra of the protonated catenanes indicate that the electronic structures of the porphyrin dications are strongly influenced by the proximity and restrictions of the tetracation. This is especially obvious in the 'tight strap' catenane $1H_4^{2+}$; the Soret band appears at 416 nm, compared with 434 nm for the protonated form of its parent hydroquinol strapped porphyrin, and the Q-bands at 544 and 566 nm (cf. 574 and 620 nm for the protonated strapped porphyrin) are also very different and atypical of porphyrin dications.⁶ In the loose strap catenanes $2H_4^{2+}$ and $3H_4^{2+}$, the bands are also shifted, but not to such a large extent (426, 570, 614 nm for $2H_4^{2+}$, and 426, 568, 612 nm for $3H_4^{2+}$, compared with 434, 574, 622 nm for both the protonated strapped porphyrin precursor molecules). This is consistent with increased flexibility in these less constrained molecules allowing movement



of the tetracation without so much conformational distortion or restriction of the porphyrin.[†]

Variable-temperature ¹H NMR measurements in acidic solutions reveal important differences between the tight strap $1H_4^{2+}$ and the loose strap $2H_4^{2+}$ and $3H_4^{2+}$ catenanes both in terms of their conformations and dynamics. In all the unprotonated and zinc porphyrin [2]catenanes examined thus far it was found that there is an electronic interaction that maintains a parallel orientation of the bipyridyl moiety and the porphyrin plane (Fig. 1).² It was envisaged that on protonation of the central nitrogen atoms of the porphyrin, this interaction would be destroyed, and electrostatic repulsion might be accompanied by rotation of the tetracation and the hydroquinol unit in the polyether bridge (to maintain the essential hydroquinol-bipyridinium dication interaction) to maximise the separation of like charges; this would then position the phenylene subunit closest to the porphyrin [Fig. 1(b)].

For $1H_4^{2+}$, under fast exchange conditions (45 °C, [²H₆] acetone-TFA) the pertinent resonances are generally shifted downfield in comparison with those of $1H_2$, reflecting the increased distance between the tetracation and porphyrin moieties as a result of electrostatic repulsion. Slow exchange conditions (-35 °C, [²H₆] acetone-TFA) reveal splitting of the tetracation resonances into equal intensity signals, consistent with the existence of inside and outside environments.[‡] The chemical shift differences indicate that the overall geometry of the tetracation within $1H_4^{2+}$ is similar to that observed in $1H_2$, with the bipyridyl subunits most affected by the porphyrin ring current, albeit at an increased distance.[§] Thus, in terms of the predicted behaviour of the tetracation upon porphyrin protonation, only the repulsion process was observed to occur within $1H_4^{2+}$ [Fig. 1(a)]; it was apparent that 90° rotation [Fig. 1(b)] did not occur, presumably because of the restrictions

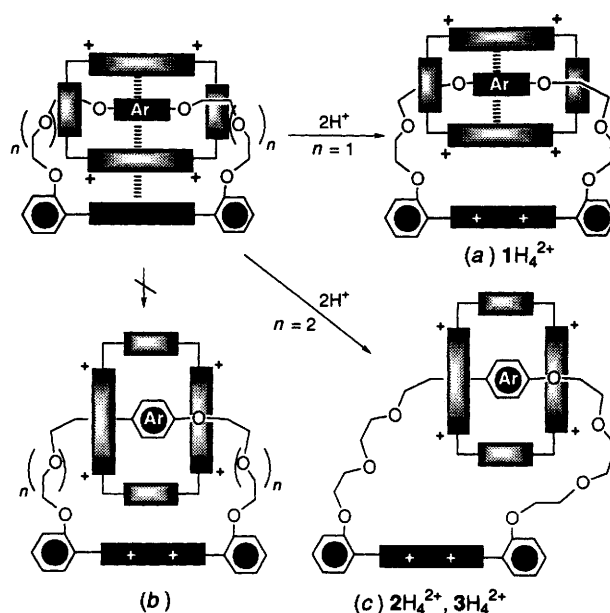


Fig. 1 Possible conformational changes accompanying protonation of the porphyrin [2]catenanes

imposed by the short strap in relation to the rectangularly shaped tetracationic macrocycle.

The tetracation macrocycle rotation rate within 1H_4^{2+} , that is the rate for the interchange of inside and outside positions of the tetracation with respect to the porphyrin, was measured from the ^1H NMR spectrum by the coalescence method. The rate of rotation [1000 s^{-1} , $\Delta_c G^\ddagger$ 12.9 kcal mol $^{-1}$ (1 cal = 4.184 J)] is much faster than that calculated for 1H_2 at the same temperature (80 s^{-1} , $\Delta_c G^\ddagger$ 14.2 kcal mol $^{-1}$), and has a lower energy of activation. The rotation rate and free energy of activation are, however, more comparable with those observed in the non-porphyrinic bis-*p*-phenylene-34-crown-10 based catenane (ΔG^\ddagger 12.2 kcal mol $^{-1}$, 2000 s^{-1}).¹⁰ Thus, a secondary effect of protonation, resulting from removal of the porphyrin-macrocycle electronic interaction and a stretching of the strap away from the porphyrin, is an increased rotation rate of the tetracation around its hydroquinol axis. However, protonation must also introduce an additional, but less restrictive, barrier to rotation *viz.*, that of the close approach of similarly charged regions of the components during the rotation process.

The dynamic ^1H NMR results for 2H_4^{2+} and 3H_4^{2+} , while qualitatively similar to those observed for 1H_4^{2+} , are nevertheless significantly different. Under conditions of slow exchange, the differences in chemical shifts of the protons in the two environments are now smaller for the β -bipyridyl protons ($\Delta\delta$ 0.68 ppm for both 2H_4^{2+} and 3H_4^{2+} , compared with 3.89 and 3.64 ppm respectively for 2H_2 and 3H_2) and larger for the phenylene ($-\text{C}_6\text{H}_4-$) ($\Delta\delta$ 0.39 and 0.50 ppm, compared with 0.10 and 0.15 ppm, respectively, for the unprotonated forms) and methylene ($^+\text{NCH}_2$) ($\Delta\delta$ 1.63 and 1.03 vs. 0.19 and 0.51 ppm, respectively) protons. The larger differences between the α -bipyridyl ($\Delta\delta$ 1.12 and 0.72 ppm) and methylene protons are consistent with a 90° rotation and a diagonal movement of the tetracation away from the porphyrin upon protonation [Fig. 1(c)].[¶] The rectangular shape of the tetracation is then responsible for the estimated greater chemical shift difference between environments in conformation (c) for the phenylene and methylene protons.^{||}

The rotation rate and free energy of activation of the tetracation in 2H_4^{2+} (1500 s^{-1} at 298 K, ΔG^\ddagger 12.6 kcal mol $^{-1}$) are comparable with those of the metal free catenane 2H_2 (1500 s^{-1} at 298 K, ΔG^\ddagger 12.7 kcal mol $^{-1}$) indicating that porphyrin protonation has little effect on the process in this case, and/or there is a balance between the removal of steric influences by the porphyrin on rotation and their subsequent replacement by an electrostatic barrier.

For the naphthoquinol porphyrin catenane 3H_4^{2+} , the twofold symmetry of the naphthalene ring results in eight bipyridyl resonances and several multiplets for phenylene and methylene resonances at low temperatures. The chemical shift differences between various proton environments under slow exchange indicate similar overall behaviour and conformational change to that observed for 2H_4^{2+} ; rates and barriers for rotation of the tetracation were little changed from the unprotonated form ($\Delta_c G^\ddagger$ 16.2 kcal mol $^{-1}$, and five times per second for 3H_4^+ , compared with 15.7 kcal mol $^{-1}$ and 10 times per second for 3H_2). On the other hand, the naphthoquinol catenanes have an additional process which is observable on the NMR timescale.¹¹ The naphthalene ring complexation/decomplexation process (the 'out, turn around, and in again' process) was found to have k_c 165 s $^{-1}$ and $\Delta_c G^\ddagger$ 11.8 kcal mol $^{-1}$ from a $\Delta\nu$ of 74 Hz at T_c -28°C , which is approximately 8000 times per second at 25°C and is faster than that for the unprotonated derivative 3H_2 ($\Delta_c G^\ddagger$ 12.8 kcal mol $^{-1}$, and 1000 times per second). An explanation for this is not immediately obvious; possibly this difference is a result of the smaller influence of the ether chains on

naphthalene ring movements in the expanded conformation adopted by 3H_4^{2+} , in comparison to the more crowded conformation of 3H_2 .

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Footnotes

† The spectral changes upon protonation exhibited by simpler porphyrins can be explained in terms of deformation of the porphyrin macrocycle.⁷⁻⁹

‡ The hydroquinol ring protons resonance in 1H_4^{2+} undergoes broadening upon temperature reduction and, as with 1H_2 and other non-porphyrinic catenanes,¹⁰ may be assigned to 'rocking' of the ring within the tetracation.

§ This was determined, as for 1H_2 ,^{1,2} by the larger separation between the β - ($\Delta\delta$ 3.43 ppm) compared with the α -bipyridyl ($\Delta\delta$ 1.31 ppm) and phenylene ($\Delta\delta$ 0.22 ppm) resonances under slow-exchange conditions.

¶ This conclusion is easily reached by examination of molecular models, taking into account the shielding and deshielding zones of the porphyrin. The various possibilities shown in Fig. 1 assume an orthogonal orientation of the tetracation and the porphyrin accompanying electrostatic repulsion, and although these represent only the two extremes of possible intermediate positions, appear the most likely in minimising unfavourable electrostatic interactions. Nevertheless, any diagonal movement of the tetracation can occur in two possible directions from the porphyrin, both of which result in asymmetry within the porphyrin protons. The lack of observable inequivalence within protons occupying the inside and outside environments within 1H_4^{2+} implies that rapid equilibration between the two possible directions of diagonal shift must be occurring in solution. This would account for the broadening of the porphyrin and crown ether resonances which are observed at low temperatures; however, separation of individual resonances was not possible within the available temperature ranges of the solvents used.

|| The different conformation of the tetracation in conformation (c) would be expected to have differing effects on the porphyrin proton resonances. However, porphyrin protonation alters both porphyrin skeletal structure and ring current making any comparison impossible in the absence of control data.

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