Synthesis and Conformation of Macrocyclic Porphyrin Dimers with Potentially Spacious Cavities

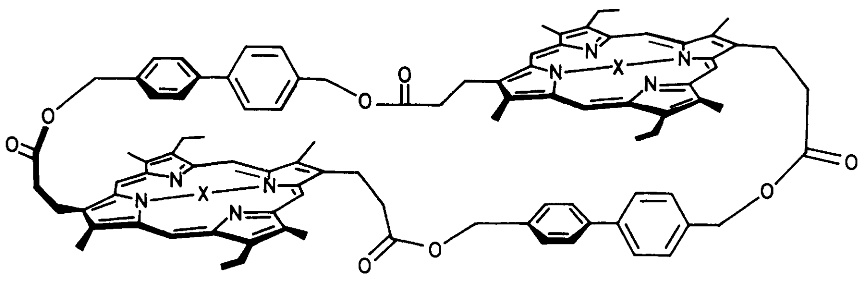
Christopher A. Hunter, M. Nafees Meah, and Jeremy K. M. Sanders*

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

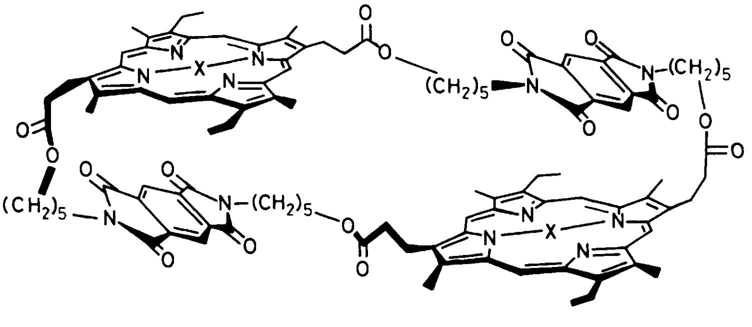
The importance of π–π donor–acceptor interactions is demonstrated in the synthesis and conformation of macrocyclic porphyrin dimers covalently linked by biphenyl or pyromellitimide bridges.

As a first step towards the construction of synthetic enzymes capable of binding, recognition, and catalysis, we have prepared macrocyclic porphyrin dimers containing potentially spacious cavities. These molecules have the potential to bind two ligands within a single cavity. We demonstrate here the importance of π–π donor–acceptor interactions in the synthesis and conformation of the dimers (**1**) and (**2**), while in the following Communication we describe some conformational switching that can be induced by binding appropriate ligands.

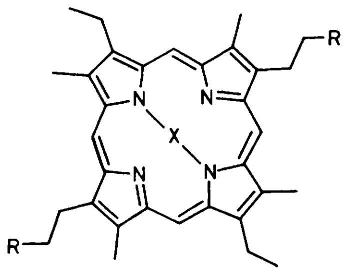
Several cyclic porphyrin dimers have been reported previously but most of these enclose relatively small cavities.[1—3] We envisaged that similar though larger molecules could be generated with more rigid aromatic 'spacers' such as biphenyl. Reaction of mesoporphyrin-II-diol (**3**; $X = H_2$) and biphenyl



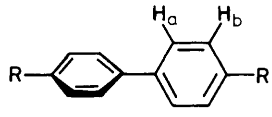
(**1**) $X = H_2$, Zn



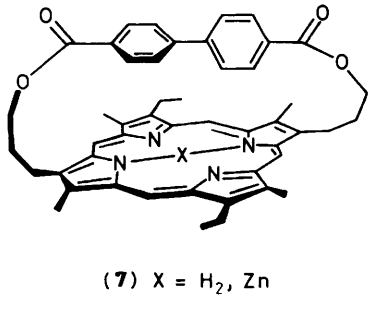
(**2**) $X = H_2$, Zn



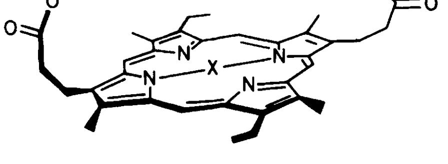
(**3**) $R = CH_2OH$, $X = H_2$, Zn
(**4**) $R = COCl$, $X = H_2$



(**5**) $R = COCl$
(**6**) $R = CH_2OH$



(**7**) $X = H_2$, Zn



(**8**) $X = H_2$, Zn

acid chloride (**5**) in the presence of 4-*N*,*N*-dimethylaminopyridine (DMAP) in dichloromethane under high dilution conditions affords the capped species (**7**; $X = H_2$) in 22% yield as the only cyclic product.† Insertion of zinc into (**3**) prior to the esterification reaction resulted in an improved yield (53%) of the capped species (**7**; X = Zn), but again no dimer was isolated. This remained true even when non-equimolar ratios of alcohol and acyl chloride were used in the initial stages of the reaction.[3]

We believe that the rate determining step is formation of the first ester linkage and that capping is favoured because of the strong π-stacking interaction between the porphyrin and the biphenyl moieties.[4,5] Metallation enhances this interaction,[2b,6] explaining the higher yield. Evidence for π-stacking in this type of system can be clearly seen in the characteristic ring current-induced upfield ^1H n.m.r. shifts of the acceptor in mono-linked porphyrin-acceptor molecules.[5,7]

Although the exact nature of the π–π interaction is still uncertain, it appears to be strongest between a donor and an acceptor. Thus we reasoned that the reaction between mesoporphyrin-II-diacid chloride (**4**) and biphenyl diol (**6**), a poorer acceptor than (**5**), should enable the bimolecular reaction to compete more effectively with cyclisation by reducing the extent of π–π interaction. Indeed, this is observed experimentally and the dimer (**1**; $X = H_2$) is obtained in 13% yield together with the capped species (**8**) (12%). We isolated the similar dimer (**2**) in 12% yield, together with the capped monomer (**10**) (36%), from the reaction of pyromellitimide *N*-diol (**9**) and mesoporphyrin-II-acid chloride (**4**) using more concentrated solutions than previously.[8]

There is a striking similarity between the ^1H n.m.r. spectra of the dimers (**1**) and (**2**) and their corresponding monomeric capped compounds (**8**) and (**10**) (Table 1), the large upfield shifts of the biphenyl and pyromellitimide protons being

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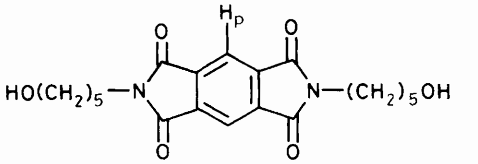
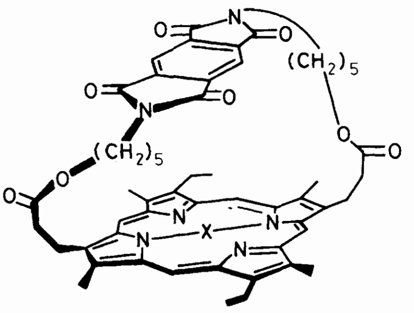
† All new compounds gave satisfactory n.m.r. and fast atom bombardment (FAB) mass spectra.



(9)



(10) X = H_2, Zn

Table 1. Selected ^1H n.m.r. shifts.

Compound	δ/p.p.m.[a]			
	H_a	H_b	H_p	H_{meso}
(**1**) $X = H_2$	3.91	5.49		10.12 9.94
(**1**) X = Zn[b]	4.38	5.60		10.02 9.83
(**2**) $X = H_2$			6.62	10.05 9.79
(**2**) X = Zn			6.05	9.80 9.78
(**7**) $X = H_2$	4.06	6.12		9.89 9.83
(**7**) X = Zn	4.13	6.13		9.80 9.74
(**8**) $X = H_2$	3.83	5.49		10.28 10.08
(**10**) $X = H_2$			7.30	10.12 9.74
(**10**) X = Zn			6.44	10.04 9.88

[a] In $CDCl_3$ solution. [b] In presence of a large excess of 1,4-diazabicyclo[2.2.2]octane (DABCO).

especially remarkable. Clearly, each acceptor group is arranged over a porphyrin ring in the dominant conformer of each dimer, presumably as a result of donor–acceptor interactions. This conclusion is supported by the lack of upfield shifts of the porphyrin *meso* protons, and by the lack of exciton splitting[9] in the electronic absorption spectra of (**1**) and (**2**); the presence of these features is characteristic of strong porphyrin–porphyrin interactions.[2b] The conformations of the free base and zinc derivatives of (**1**), and the free base of (**2**), are essentially identical because there is no possibility of intramolecular metal co-ordination. Metallation of (**2**) brings the pyromellitimide closer to the porphyrin by co-ordination,[8,10] but does not drastically change the overall conformation.

In addition to the ligand-binding properties described in the following Communication, this type of compound can, therefore, be used to probe the relative strengths of donor–acceptor and porphyrin–porphyrin interactions. This knowledge may in turn allow prediction and control of molecular shapes, despite the flexibility and many conformations available to such large rings.

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