Controlled Conformational Changes in Covalently-linked Dimeric Porphyrins

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We report the preparation of a novel porphyrin dimer which shows a conformational change between parallel and 'clam shell' forms depending on the species at the centre of the porphyrin rings.

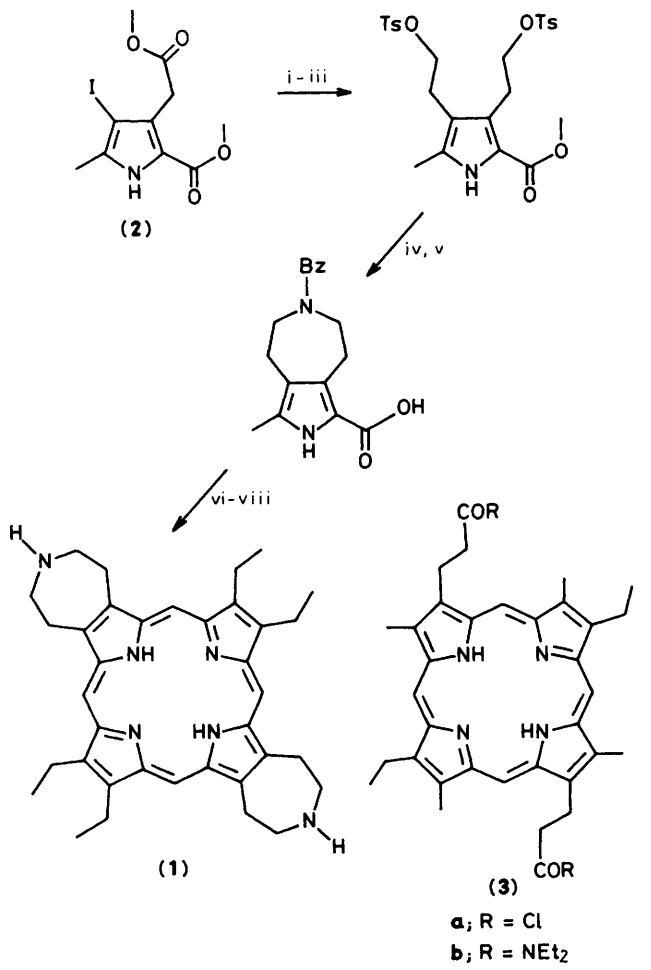
Protein structures containing several interacting hemes or chlorophylls play important roles in certain enzymes (*e.g.* cytochrome c_3, cytochrome-*c*-oxidase) and photosynthetic reaction centres, respectively.[1] In recent years there has been strong interest in preparing structural analogues of these proteins in order to investigate their mechanism of action and also to reproduce their properties in small molecules.[2] For example, cofacial metalloporphyrin dimers linked through the β-positions have been prepared and shown to be effective catalysts for the 4-electron reduction of dioxygen to water.[3] However, little attention has been paid to the control of orientation in dimeric porphyrins or to the construction of higher oligomers.[4]

We report here the synthesis and properties of a novel series of dimeric porphyrins that readily convert between two molecular conformations. Diaminoporphyrin (**1**) was chosen as the basic unit for the dimers because (a) its D_{2h} symmetry should avoid the problem of diastereoisomers that occurs when porphyrins of C_{2h} symmetry are used[3] and which complicates the synthesis of porphyrin oligomers;[4] (b) forming amide bonds to the secondary amines should lead to conformationally restricted dimers.

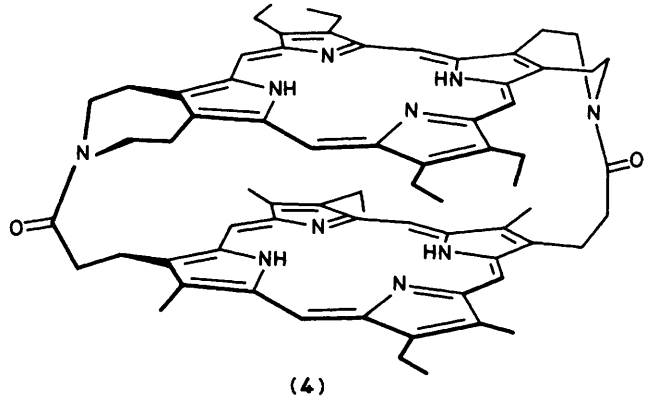
Diamine (**1**)† was prepared from pyrrole (**2**)[5] by the route outlined in Scheme 1. The porphyrin-forming step employed a recent modification of the pyrromethene method.[6,7] High dilution coupling of diamine (**1**) and mesoporphyrin-II diacid chloride (**3a**)[6] gave dimeric porphyrin (**4**)†‡ in 35—40% yield. The ^{1}H n.m.r. spectrum of (**4**) contains four NH signals around δ −8, twelve *meso*-proton signals (see Figure 1a), and a complex region from δ 5.5—1. This is consistent with a closely-spaced dimer (centre–centre distance 4—5 Å)[3a] in two

† All new compounds have been fully characterized spectroscopically and by elemental analysis and/or mass spectroscopy.

‡ Accurate mass observed: 1091·6432, calc. for $C_{70}H_{79}O_2N_{10}$: 1091·6387.



Scheme 1. *Reagents:* i, HO_2CCHO, HI, H_3PO_2; ii, B_2H_6; iii, tosyl chloride, pyridine; iv, $PhCH_2NH_2$; v, KOH, EtOH; vi, 5-formyl-3,4-diethylpyrrole-2-carboxylic acid, HBr; vii, Br_2; viii, HCO_2H, Pd-black.



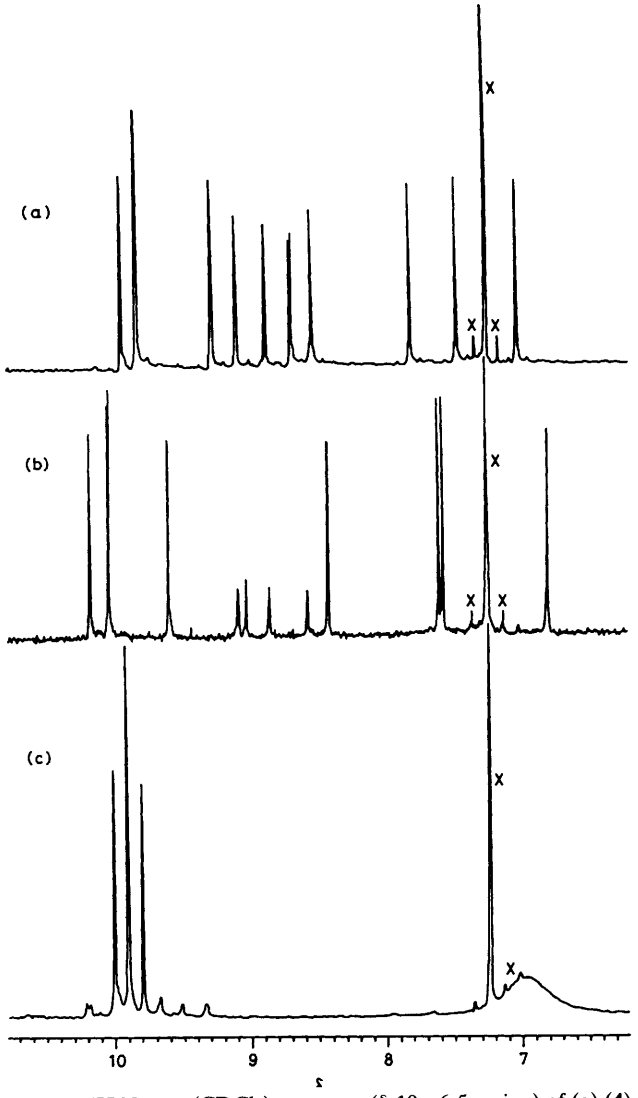


Figure 1. ^1H N.m.r. ($CDCl_3$) spectrum (δ 10—6.5 region) of (a) (**4**), (b) bis-zinc complex of (**4**), and (c), tetraprotonated (**4**). (X denotes solvent or spinning side band.)

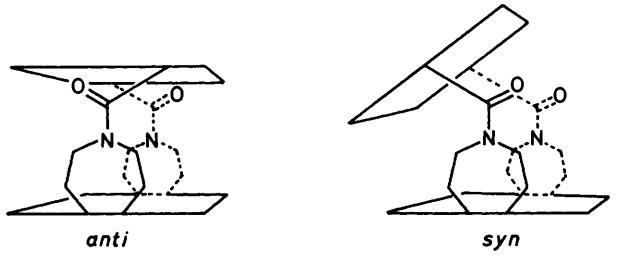


Figure 2. Two conformations of dimeric porphyrin (**4**).

conformational forms. The isomerization occurs owing to the rigidity of the two amide bonds and depends on the relative orientation of the carbonyl groups (Figure 2). In the *anti* form the carbonyls point in opposite directions and the porphyrins are held parallel to each other: the overall two-fold symmetry results in only four *meso*-proton signals around δ 9. In the *syn* form the porphyrin rings are forced into a rigid and unsymmetrical 'clam shell' conformation. Eight *meso*-proton signals are seen in the range δ 10—7 depending on their distance above the partner porphyrin ring. The presence of two separate sets of signals demonstrates a slow interconversion between *syn* and *anti* forms.§

A dramatic conformational switch between the two forms can be induced by changing the species in the centre of the porphyrin rings. In the bis-zinc complex of (**4**)† [formed by treating (**4**) with $Zn(OAc)_2$] four signals at δ *ca.* 9 diminish in

§ The ratio of *syn* to *anti* is estimated to be 2:1.

Table 1. U.v.–visible spectroscopic data (in $CHCl_3$).

Compound	$\lambda_{max.}$ (nm)
(**4**)	381, 504, 540, 572, 626
Zn_2(**4**)	387, 538, 572
Tetra-H^+(**4**)	397, 552, 596
(**3b**)	398, 498, 534, 566, 620
Zn-(**3b**)	400, 532, 568
Di-H^+(**3b**)	404, 550, 592

intensity relative to the other eight *meso* signals (Figure 1b) reflecting a predominance of the *syn* form over the *anti* by 9 : 1. Tetraprotonation of (**4**) (with four equivalents of CF_3CO_2H) causes a shift to the *anti* form (6 : 1 *vs. syn*) with a much simplified *meso*-proton region (Figure 1c).¶ All n.m.r. spectra were run at a concentration of approximately 10^{-3} M; varying the concentration from 2×10^{-2} to 9×10^{-4} M caused no changes in the spectra, discounting aggregation as a source of these effects.

The u.v.–visible spectral data for the three dimer species are collected in Table 1 and compared to free base, zinc, and protonated derivatives of diamide (**3b**). In each dimer there is a significant shift of the Soret band to the blue indicating strong exciton coupling between the porphyrin rings.[3] We are currently preparing other metal complexes of (**4**) and are extending the synthetic approach to higher oligomers.

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¶ As expected these signals are shifted downfield relative to the free-base *anti* form (δ *ca.* 9) owing to protonation.

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