Folded Conformation of 5,15-Diarylporphyrins with Anthraquinonyl and Dimethylaminophenyl Groups attached *via* a Sulphonyloxy Group

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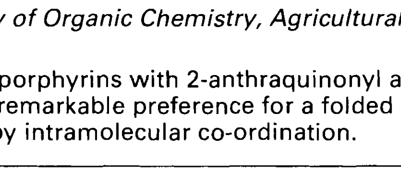
Free base porphyrins with 2-anthraquinonyl and 4-dimethylaminophenyl groups attached through a sulphonyloxy link show remarkable preference for a folded conformation; introduction of zinc causes a conformational change, probably by intramolecular co-ordination.

The interest in triad acceptor–porphyrin–donor sytems as model compounds for the study of the charge separation step in photosynthesis has resulted in numerous publications on quinone-substituted porphyrins in recent years.[1] Model compounds with well defined geometries are especially interesting.

In a recent paper,[2] we reported that in $CDCl_3$ solution the porphyrins (**1a**,**b**) showed preference for a folded conformation in which the tosyl groups are situated in a cofacial position right above and below the porphyrin ring system. We based our conclusion on a large upfield shift of 2—3 p.p.m. for the tosyl protons in the n.m.r. spectra.

The fact that these sulphonyloxy compounds evidently possess rather well defined conformations induced us to prepare a free base porphyrin with two anthraquinone moieties attached through a sulphonyloxy group (**2a**), its zinc complex (**2b**), and in addition a corresponding pair of porphyrins, containing an anthraquinonyl and a dimethylaminophenyl group (**2c**,**d**). In order to increase solubility in organic solvents tetramethyltetraethylporphyrins were prepared instead of the octamethyl derivatives.



(**1**) **a**; R = p-$MeC_6H_4SO_2O$
b; R = p-$MeC_6H_4SO_2O[CH_2]_2O$

Compounds (**2a**,**c**) were obtained by condensation of 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolylmethane (**3**)[3] with aldehyde (**4**) and a 1:1 mixture of (**4**) and (**5**), respectively, under the catalytic influence of p-toluenesulphonic acid, followed by oxidation of the porphyrinogens formed with 2,3-dichloro-5,6-dicyanobenzoquinone (Scheme 1).[4] Isolation of (**2c**) was effected by extraction and chromatography on a silica gel column (gradient elution with chloroform–diethyl ether). Zinc complexes (**2b**,**d**) were prepared by treatment of (**2a**,**c**), with zinc acetate in chloroform–methanol.

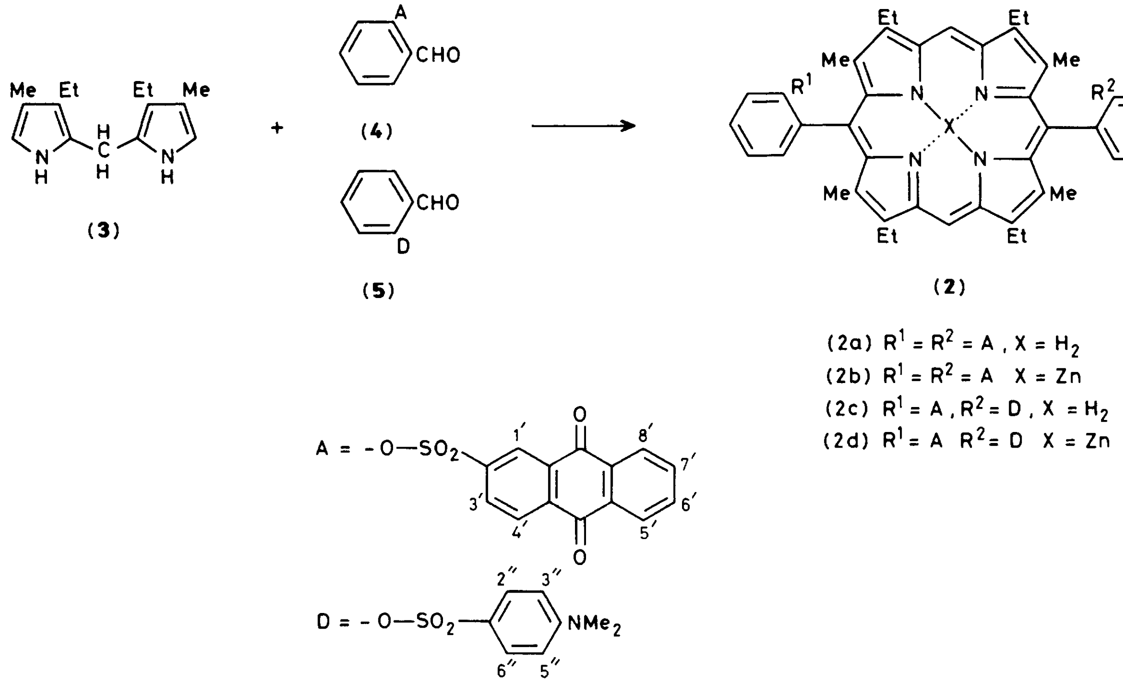
The ^1H n.m.r. spectra of (**2a**—**d**) were measured in $CDCl_3$ solution on a 300 MHz Bruker instrument. In Table 1, the $\Delta\delta$ values are given for the anthraquinonyl and the dimethylaminophenyl protons, $\Delta\delta$ being defined as indicated in Table 1. We cannot exclude the possibility that the assignments of 5′-H and 8′-H (and thus of 6′-H and 7′-H) should be interchanged.

It is interesting that all protons of the anthraquinonyl and dimethylaminophenyl group show upfield shifts which can be explained if we assume that in $CDCl_3$ solution (**2a**—**d**) occur to an important extent in a folded conformation in which the anthraquinone and dimethylaminophenyl moieties are situated above and below the central part of the porphyrin system. Intermolecular aggregation can be ruled out from the n.m.r. spectra by the lack of change in chemical shift with dilution of a solution of (**2d**).

Table 1. ^{1}H N.m.r. $\Delta\delta$ values for (**2a**—**d**) and δ values for (**4**), (**5**) in $CDCl_3$ solution.

		Anthraquinonyl							Dimethylaminophenyl	
		1′-H	3′-H	4′-H	5′-H	6′-H	7′-H	8′-H	2″-H_2, 6″-H	3″-H, 5″-H
$\Delta\delta^a$	(**2a**)	2.48	3.19	4.90	1.44	0.48	0.48	1.07	—	—
	(**2c**)	2.29	2.90	4.60	1.41	0.48	0.48	1.09	2.25	3.30
	(**2b**)	3.30	2.00	2.86	0.90	0.46	0.75	2.83	—	—
	(**2d**)	3.41	1.67	2.58	0.82	0.41	0.68	2.87	2.34	3.69
	(**2d**) + pyridine	2.17	3.39	4.92	1.06	0.37	0.37	1.06	1.24	1.50
δ	(**4**)	8.80	8.25	8.50	8.33	7.89	7.89	8.33	—	—
	(**5**)	—	—	—	—	—	—	—	7.54	6.58

[a] $\Delta\delta$ = δ[ring protons of the anthraquinonyl/dimethylaminophenyl group in the aldehyde (**4**)/(**5**)] − δ[ring protons of the anthraquinonyl/dimethylaminophenyl group in the porphyrin (**2**)]. For numbering of the protons see Scheme 1.



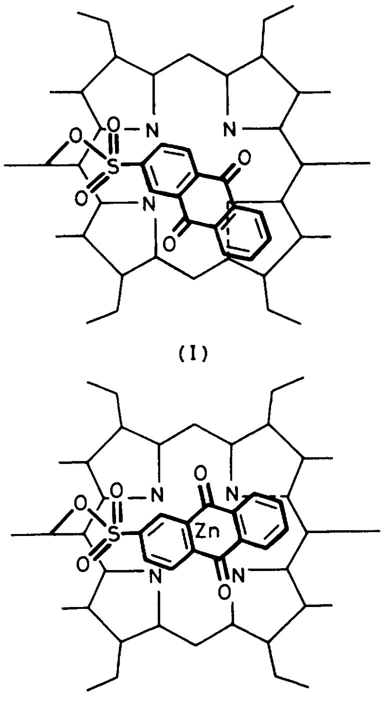
Scheme 1

When trifluoroacetic acid is added to a $CDCl_3$ solution of (**2a**), the upfield shifts disappeared just as found earlier for (**1a**,**b**). We explain this effect by solvation of the porphyrin dication by trifluoroacetate anions. The Coulomb attraction between charged ions will undoubtedly be stronger than the forces responsible for the folding of the molecule.

The chemical shifts measured for the porphyrins are not necessarily those of a single folded conformation but may be the result of time averaging processes between several conformations in equilibrium. However, it seems reasonable to assume that a high percentage of folded conformation(s) is present, as the upfield shifts found for some protons in the anthraquinone part are of the same order of magnitude as those found for zinc(II) *meso*-tetraphenylporphyrin with pyridine as a ligand attached at a distance of 2.5 Å from the porphyrin centre.[5]

Looking more closely at the data of Table 1, we observe different patterns in the $\Delta\delta$ values of 1′-H, 3′-H, 4′-H, and 8′-H for the free bases (**2a**,**c**), and the zinc derivatives (**2b**,**d**). Based on inspection of molecular models two possible folded conformations can be considered: conformation (I) (Scheme 2) with 3′-H and 4′-H nearest to the centre of the porphyrin system and conformation (II) with 1-H and 8-H nearest to the centre (Scheme 2). Conformations (I) and (II) are interconvertible by rotation around the C-2(anthraquinone)–sulphur bond. The free bases (**2a**) and (**2c**) would then preferably be in conformation (I), the zinc derivatives (**2b**) and (**2d**) preferably in conformation (II), in which an intramolecular co-ordination of zinc with the carbonyl oxygen atom is well possible according to the molecular models. Estimating the distances (*r*) of the various atoms to the porphyrin centre with molecular models, we did indeed find a regular decrease in $\Delta\delta$ with increasing *r* on the basis of our assumption that (**2a**) and (**2c**) are in conformation (I), (**2b**) and (**2d**) in conformation (II).

Further evidence for our hypothesis was obtained by studying the influence of pyridine on the n.m.r. spectrum of



(I)

(II)

Scheme 2. Conformations (I) and (II) as seen from above.

the zinc porphyrin (**2d**). Pyridine is a well known ligand for the five-co-ordinate zinc atom[6] and can be expected to compete with the carbonyl group in anthraquinone. Upon addition of deuteriated pyridine to a solution of (**2d**) in $CDCl_3$ we did indeed observe a gradual migration of the signals of conformation (II) in the ^1H n.m.r. spectrum, leading eventually (in an excess of pyridine) to a spectrum very similar to that of the free base [conformation (I)], except that the protons of the dimethylaminophenyl group absorb at lower field. Probably pyridine on co-ordination with zinc approaches from the less crowded dimethylaminophenyl side; in the resulting complex the interaction between Zn and the CO group has been broken and the dimethylaminophenyl part has been pressed aside.

The phenomenon of folded conformations has been described before in the literature, *e.g.* for sulphonyl compounds.[7] The factors causing the preference for folded conformations are not well known. In our compounds an intramolecular π–π interaction may be responsible, together with a repulsion between the lone pairs on the sulphonyl oxygen atoms and the π-electrons of the porphyrin. More detailed investigations, however, are needed to solve this question.

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