

Quinone-capped Porphyrins: N.M.R. Studies of Static and Dynamic Stereochemistry and Co-ordination Properties

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^1H N.m.r. spectroscopy has been used to investigate the shape, motion, and flexibility of two of the title compounds, and their magnesium derivatives, and to probe the co-ordinative properties of the latter. Coupling constant and n.O.e. results for the porphyrin moiety are analysed in terms of two possible conformations. The cap moiety for simple alkyl-capped porphyrins appears to have a well defined shape. In the title compounds, however, the quinone ring is flipping rapidly and a temperature dependent 'breathing' is observed; the quinone is closer on average to the porphyrin in the compound with additional methylene groups in the cap. At ambient temperature molecular tumbling is severely hindered in these propellor-shaped molecules leading to rapid relaxation and broad lines, but resolution improves substantially on warming. Pyridine titration data for the magnesium derivatives indicate that the metal ion is out-of-plane 5-co-ordinate, bound intramolecularly to a quinone carbonyl, and that it can accept a 6th ligand from the unhindered side of the porphyrin, moving into the plane and pulling the quinone towards the porphyrin. The average orientation of the quinone ring appears to be perpendicular to the porphyrin.

In the preceding paper¹ we described the synthesis and some properties of the quinone-capped porphyrins (1) and (2) and their metallated derivatives (3) and (4). Here we present n.m.r. spectroscopic results which define some of the static and dynamic stereochemistry of this class of molecules, and elucidate some details of the co-ordination chemistry of the central magnesium ion in compounds (3) and (4). An understanding of these properties may be important in the subsequent design of more efficient models for electron-transfer systems: thus the overall aim in this work has been to illuminate and elucidate *chemical* properties rather than to catalogue rigorously spectroscopic properties.

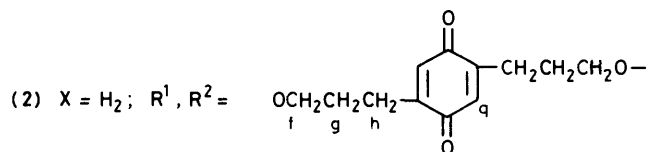
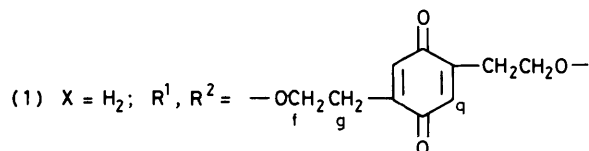
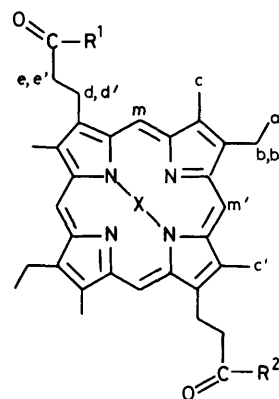
The specific problems we address in connection with compounds (1)–(4) are the effective symmetry of the molecules as a whole, the conformation of the cap, the nature of overall molecular motion and of internal motions, and the co-ordination state of the central metal ion. As an aid to the interpretation of these problems we also include results and analysis for the conceptually simpler capped porphyrins (5) and (6).† We present here only ^1H n.m.r. results. This is (i) because ring-current effects are proportionally so much more important than in ^{13}C n.m.r. spectroscopy, (ii) for sensitivity reasons (our high-field spectra were generally obtained with 0.1–1 mg of porphyrin), and (iii) because proton-proton spin-coupling constants and nuclear Overhauser effects are powerful probes of conformation. It has to be pointed out that the 270 and 400 MHz spectrometers used in this work were essential both for their sensitivity and dispersion. Some of the results described here have been reported in preliminary form.²

RESULTS AND DISCUSSION

Effective Molecular Symmetry.—The 270 MHz spectrum of compound (5) (Figure 1) illustrates many of the features characteristic of capped porphyrins. The meso-protons appear as two singlets (*ca.* δ 10), as do the ring

† We have discussed the radical cations of these compounds elsewhere (J. C. Waterman and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1978, **100**, 1295).

methyl groups (*ca.* δ 3.6), in positions essentially the same as simple porphyrins. The propionate side-chain protons appear in the normal chemical-shift region but as four complex multiplets (each of 2 H) rather than a simple AA'BB' system. In contrast, the cap protons are shifted up-field by up to 4.5 p.p.m. from the usual chemical shift. It is clear that the porphyrin is retaining its chirality on



(3) As (1) but $X = \text{Mg}$

(4) As (2) but $X = \text{Mg}$

(5) $X = \text{Mg}$; $R^1, R^2 = (\text{—OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O—})$

(6) $X = \text{Mg}$; $R^1, R^2 = \text{—O}[\text{CH}_2]_{12}\text{O—}$

the n.m.r. time-scale, *i.e.* racemisation by flipping the cap from above to below the macrocycle takes seconds at least. This motion would render the protons within geminal pairs (d,d' and e,e') equivalent and lead to two simple triplets. That such chiral capped porphyrins are racemic as expected has been demonstrated with an optically active lanthanide shift reagent.³

able to the quinone rule out the strictly parallel conformation; we conclude, therefore, that there is rapid averaging of at least two conformations. Evidence presented below suggests that the carbonyl oxygens are bound intramolecularly to the central metal ion and are exchanging rapidly on the n.m.r. time-scale. This was not the expectation from inspection of C.P.K. molecular models

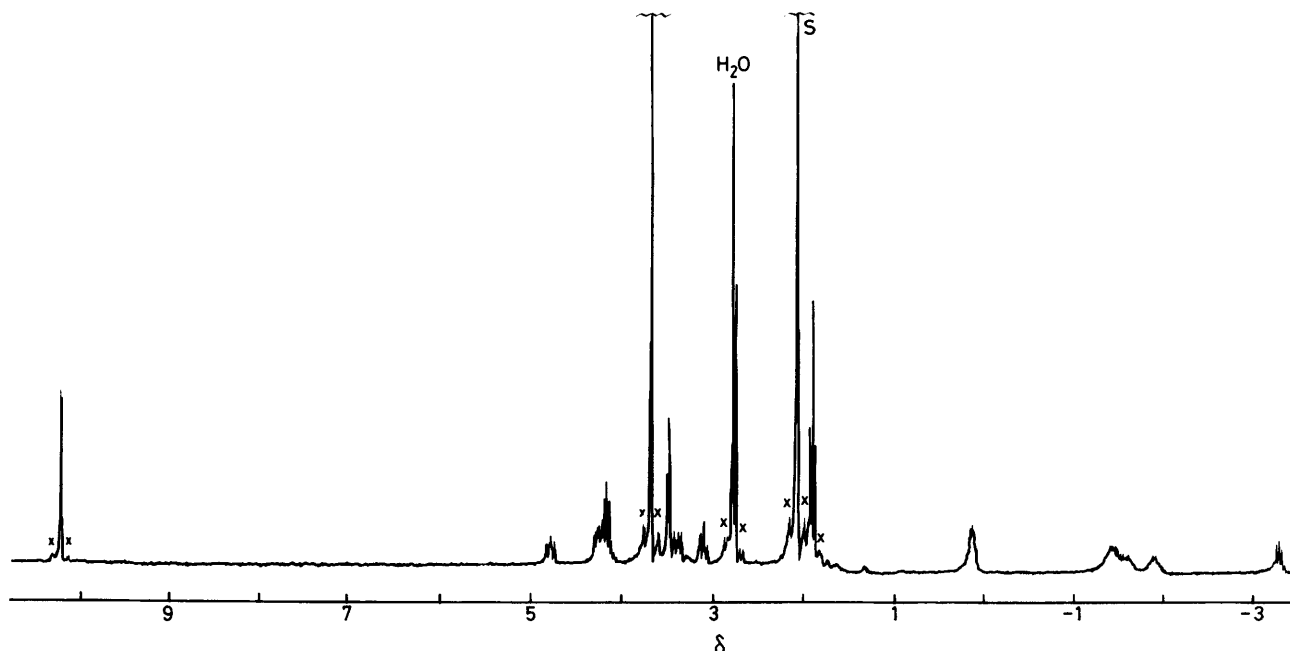


FIGURE 1 270 MHz ^1H N.m.r. spectrum of (5) *ca.* 1 mM in $[^2\text{H}_6]\text{acetone}$. X mark spinning side bands, S marks residual solvent protons

An additional general feature is that capped porphyrin resonances at ambient temperatures are broad: intrinsic line-widths are *ca.* 2 Hz, which is much greater than for simple porphyrins or chlorophylls of comparable molecular weight.⁴ Judicious use of Gaussian resolution enhancement restores most of the lost resolution (Figure 2), but we show below that slow molecular tumbling is responsible for these broad lines and that simple warming may be an alternative and effective measure of resolution control. The spectra of compound (4) (Figure 2) illustrate two further important points: * (a) the two quinone protons, q, are equivalent, appearing as a single peak at *ca.* δ 3 and (b) the spectrum is dramatically dependent on the presence of small quantities of added ligand (pyridine in this case). We return to (b) below, and focus here on the significance of (a).

In principle, the relative orientation of porphyrin and quinone may be parallel or perpendicular (Figure 3), or somewhere in between. Whatever the instantaneous conformation (other than strictly parallel) the molecule contains no symmetry elements at all, so we should see four meso-signals, four ring methyls, eight propionate protons, and a similar doubling of all cap signals. The u.v. spectroscopic properties of compound (4)¹ and lack of specific ring-current shifts at the porphyrin attribut-

which indicated that rotation of the quinone was likely to be difficult if not impossible.

Porphyrin Assignments and Conformation.—Table 1 lists chemical shifts and coupling constants for the porphyrin moieties of compounds (1)–(6), including results in the presence of pyridine for (3) and (4). Gross assignment of signals was straightforward but we used n.O.e. difference spectroscopy both to allow more subtle distinctions and to attempt detailed conformational analysis. The use of the classical nuclear Overhauser experiment for spectroscopic and structural assignments is well established in porphyrins,⁴⁻⁶ but is limited to relatively large effects on well separated signals. In n.O.e. difference spectroscopy⁷ a control spectrum is subtracted from a spectrum containing enhancements: only *changes* in intensity appear. It is relatively simple to measure enhancements as small as 0.2% on broad methyl singlets so spatial connectivities can be established over quite long distances. Figure 4 shows n.O.e. difference spectra for a sample of (4) which is approximately 70% co-ordinated to pyridine. Above the control spectrum is the effect of irradiating the δ 10.1 meso-signal: clearly this is the m proton enhancing H_a and Me_c (δ 3.63). Note the lack of enhancement of H_d . The next spectrum, from irradiation of H_m , enhances H_b and Me_c (δ 3.64). In this way, in combination with decoupling, all

* Also note that the ethyl methylene protons are diastereotopic.

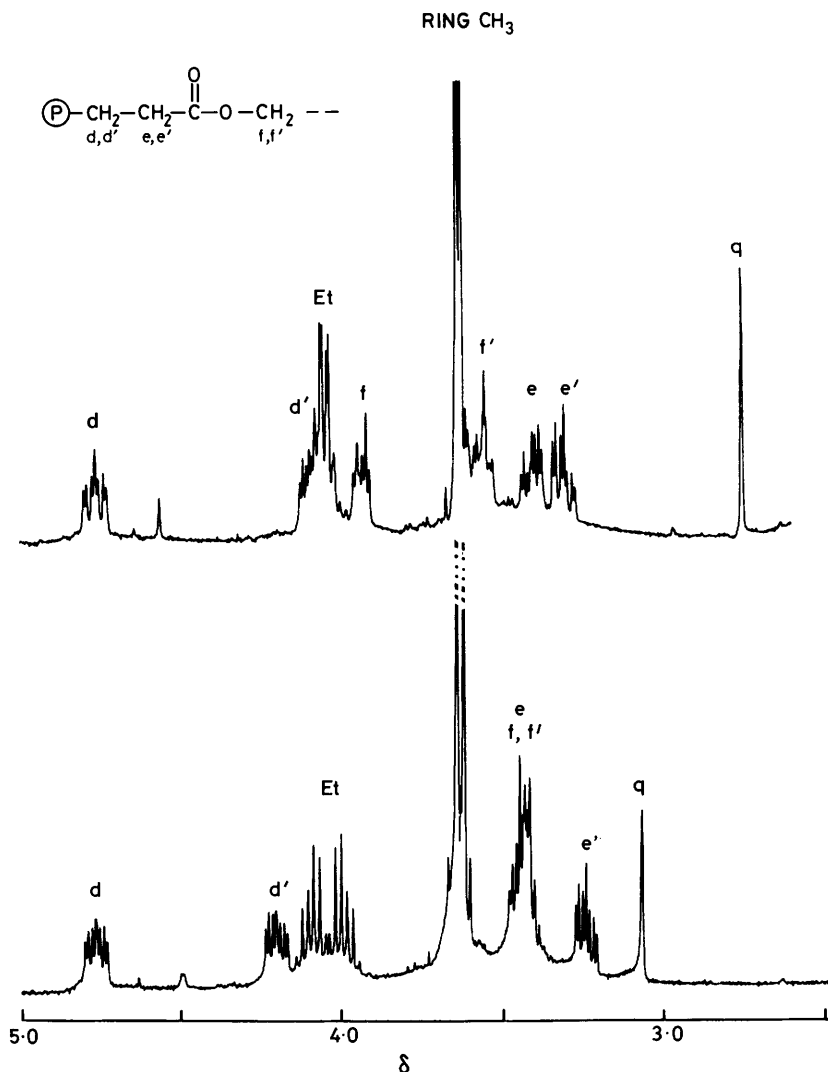


FIGURE 2 Lower trace: partial 400 MHz ^1H n.m.r. spectrum of (4) (1 mg/0.4 ml CDCl_3), resolution enhanced. Upper trace: the same after addition of $\text{C}_6\text{D}_6\text{N}$

the assignments in Table 1 were made. Similar results have recently been reported on other porphyrins.⁹

Conformational information for the propionate chain is, in principle, provided by coupling constants and by detailed analysis of n.o.e. results. The vicinal couplings may be reconciled with the surprising *trans*-relationship of porphyrin and carbonyl group (Figure 5a). This conformation is supported by the observations of n.o.e.'s between H_d and H_e and between $\text{H}_{d'}$ and $\text{H}_{e'}$ and by lack of $\text{H}_{d'}$ - H_e or H_d - $\text{H}_{e'}$ enhancements in (3) (Table 2). Furthermore, the mutual n.o.e.'s between H_m , H_d , and H_e define the average orientation of the chain with respect to the macrocycle as shown (Figure 5a). Finally, the observations of indirect *negative* n.o.e.'s in both directions in the system H_m - H_d - $\text{H}_{d'}$ - H_e suggest its effective linearity.⁹ Our results do not distinguish between a single conformation as shown where the dihedral angle between the C_{de} bond and the pyrrole ring is 90° and a

range of similar geometries with that angle in the range 70 – 110° .*

It is also possible to fit an equilibrium mixture of the two *gauche* conformations (Figure 5b). 3J_g and 3J_t values of ca. 4 and 14 Hz respectively would give, by averaging, the observed values of J_{de} , $J_{de'}$, $J_{d'e}$, and $J_{d'e'}$. The *gauche* conformation is that observed in the crystal structure of two related compounds,¹⁰ but the n.o.e. results detailed above are less easy to accommodate than in the *trans*-geometry. We conclude that it is not easy at present to distinguish these conformations in solution.

Conformation of the Cap.—Table 3 gives the relevant chemical shifts for compounds (1)–(5); the spectrum of the 12-carbon cap of compound (6) is mostly intractable. Compound (5) reveals one interesting feature: the central

* The proximity of H_m and H_e gives the meso-proton detectably (ca. 15%) shorter T_1 than H_m . This effect was first observed in simple porphyrins,⁴ and appears to be diagnostic.⁸

TABLE 1

Proton chemical shifts and coupling constants for the porphyrin moiety of compounds (1)–(6) ^a

	(1)	(2)	(3)	(3) + pyr	(4)	(4) + pyr	(5)	(6)
Chemical shifts (p.p.m. \pm 0.01)								
m	9.95	10.11	9.99	9.92	10.14	10.09	10.21	10.18
m'	9.90	10.02	10.09	9.99	10.06	10.02	10.19	10.14
a	1.87	1.91	1.87	1.90	1.83	1.85	1.94	1.88
b	4.08	4.13	{ 4.12 ^b 4.03	4.09	{ 4.09 ^b 4.02	4.05	4.19	4.13
c	{ 3.63 3.51	3.64	3.62	3.62	3.62	3.63	{ 3.71 3.70	{ 3.67 3.66
c'		3.70	3.70	3.64	3.64	3.64		
d	4.56	4.70	4.77	4.72	4.76	4.76	4.76	4.76
d'	4.22	4.00	4.36	4.27	4.20	4.10	4.23	4.19
e	3.27	{ 3.4	3.20	3.19	3.4 ^c	3.41	3.34	3.41
e'	2.96		3.07	2.98	3.24	3.31	3.06	3.19
Coupling constants (Hz \pm 0.3)								
dd'	13.6	<i>d</i>	14.1	14.0	14.6	14.4	14.2	14.7
de	4.3	<i>d</i>	4.1	4.2	3.8	3.4	3.1	3.9
de'	8.3	<i>d</i>	8.6	9.6	9.0	10.0	9.8	8.3
d'e	8.8	<i>d</i>	8.2	8.2	9.0	8.0	8.9	9.7
d'e'	4.3	<i>d</i>	4.3	4.4	3.8	3.7	3.4	3.9
ee'	12.0	<i>d</i>	12.7	12.4	13.2	13.4	13.2	14.3

^a In CDCl₃ solution for compounds (1)–(4); In [2H₆]acetone for compounds (5) and (6); brackets indicate that assignment within a pair is unknown. ^b $J_{bb'} = 14.6$, $J_{ab} = J_{ab'} = 7.3$ Hz. ^c Approximate shift because of overlap. ^d Not analysed in detail due to overlap.

protons H_j as might be expected are furthest shifted upfield (to $\delta -3.25$), but the adjacent protons H_i ($\delta -1.4$) are less shifted than the next protons H_h ($\delta -1.61$ and -1.89). The most likely explanation is that there is a strongly preferred conformation of the bridge in which H_h and H_{h'} are situated much closer to the ring than the H_i



FIGURE 3 Schematic representation of the two extreme conformations for quinone-capped porphyrins

protons (Figure 6). Although the quintet structure of the H_j resonance (with apparent couplings of 7.7 Hz) suggests no unusual stereochemistry, the two H_i protons have almost the same chemical shift, so this region of the spectrum is very second-order and the coupling constants are probably deceptively simple. Another possibility is that although the porphyrin aromatic ring current has the greatest shielding effect at the centre of the ring, it has local maxima associated with individual pyrroles. This interpretation would be interesting from the theoretical point of view and these compounds could well be useful for refining current porphyrin chemical-shift models.^{11,12}

The situation for the quinone-capped porphyrins is complicated by the fact that their spectra are undoubtedly fast exchange averages of at least two equivalent conformations. Remarkably, the geminal couplings of the methylene protons attached to the quinone moiety are highly characteristic: $J_{gg'}$ in (1) is 18.0 Hz and in (3) is 16.3 Hz. These can arise only from the relationship in Figure 7 being highly preferred for both *g* methylene groups, with θ very close to 60°. Thus the fragment

C–C–quinone–C–C is essentially planar. Vicinal couplings between protons H_f and H_g in compounds (1) and (3) are all in the range 5.5–6.5 Hz reflecting essentially complete rotational averaging. The spectra of compounds (2) and (4) were too strongly coupled for ready analysis (Table 3).

Few useful n.O.e.'s were obtained within the cap except for that illustrated in Figure 4: irradiation of coincident H_g and H_h protons enhanced both H_f and H_q signals in (4).

TABLE 2

N.O.e.'s in (3) ^a + pyridine

Proton irradiated	% Increase in signal ^b					
	H _m	H _d	H _{d'}	H _e	H _{e'}	H _{e''}
H _m		4.1	0	1.6	0	0
H _d	8.1		14.4	2.4	0	-0.3
H _{d'}	-1.4	14.7		0	0	0.6
H _e	1.2	1.9	0		~10 ^c	0
H _{e'}	0	0	1.6	~10 ^c		0

^a 150 μ g in 0.3 ml CDCl₃ undegassed; actual enhancements are shown uncorrected for incomplete (ca. 80%) saturation. ^b Lower limit of detectability is ca. 0.2% for H_{e'}, 0.5% for H_m, and 1.0% for the multiplets. ^c Too close for accurate measurement.

No serious attempt has yet been made to fit the ring-current shifts experienced by the cap to a conformational model. However, it is remarkable that the upfield shift experienced by the quinone proton H_q in the hydroxypropyl compounds (2) and (4) is larger than in the tighter hydroxyethyl derivatives (1) and (3). This could once again reflect local ring-current maxima but is more likely to indicate that *on average* the quinone moiety is actually closer to the porphyrin in the more flexible compounds with longer chains. Similar conclusions have been drawn for Baldwin's 'cap' and 'homo-cap' porphyrins.¹³

Further evidence for such conformational flexibility comes from remarkable temperature-dependent chemical shifts in all the quinone-capped porphyrins and their

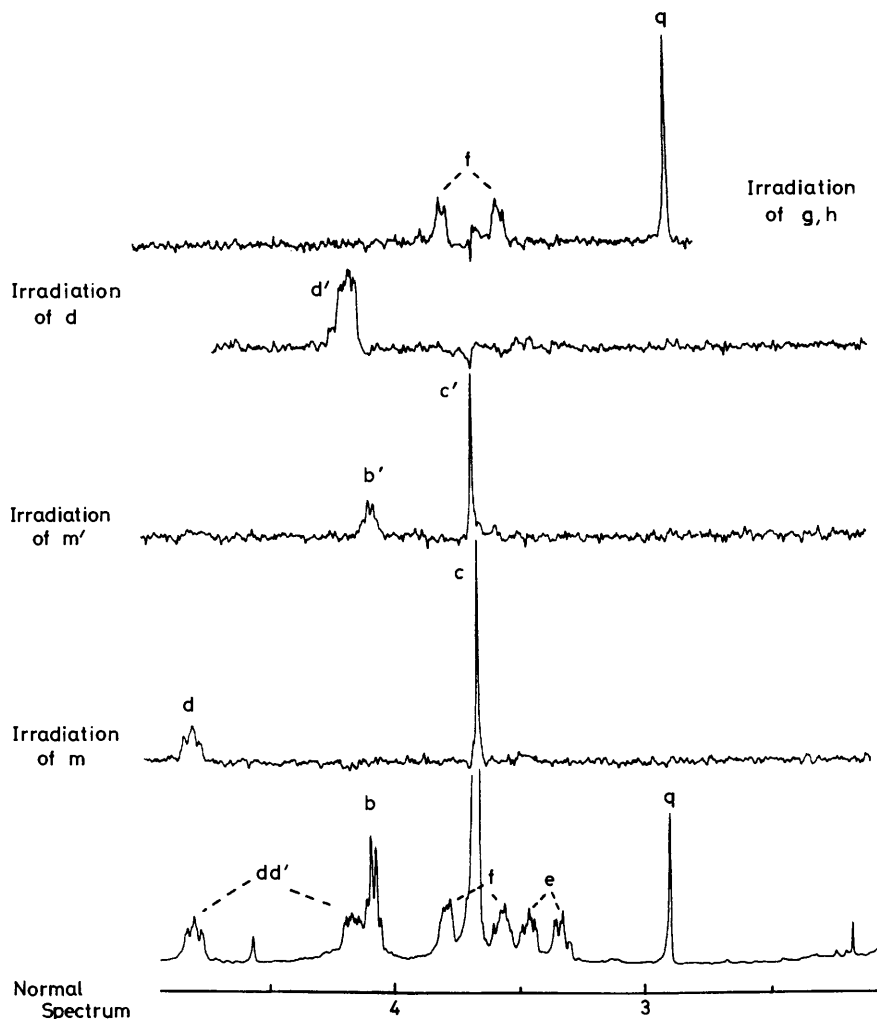
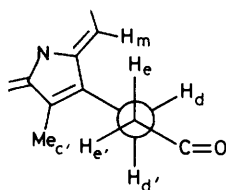
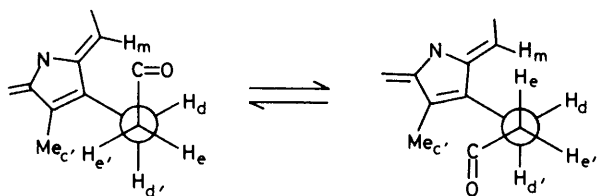


FIGURE 4 400 MHz n.O.e. difference spectra for (4) in the presence of C_5D_5N . Ca. 1 000 transients were acquired for each irradiation. Lowest trace is the control spectrum. Difference spectra are $\times 16$ vertical display gain



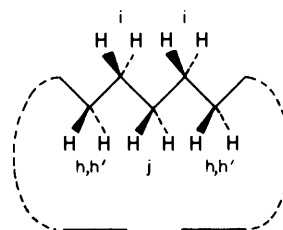
(a) *trans*



(b) *gauche*

FIGURE 5 Conformations of the propionate group

protected hydroquinone precursors. Raising the temperature leaves the spectrum of the porphyrin component essentially unchanged but large downfield shifts are seen in the cap protons, e.g. for (2) in $(CD_3)_2SO$, the linear



(6)

FIGURE 6 Proposed conformation of the cap in (5)

temperature dependence ($\Delta\delta$) of H_h (which resonates at $\delta -0.4$ at ambient temperature) is 5.1×10^{-3} p.p.m./ $^\circ$ and for H_q it is 4.5×10^{-3} p.p.m./ $^\circ$. Thus the room-temperature porphyrin-induced ring-current shift of 3–4 p.p.m. is *reduced* by 0.4 p.p.m. at 110 $^\circ C$ with no sign of a limit being reached. Clearly the average inter-chromo-

TABLE 3
Chemical shifts in the cap ^a

	(1)	(2)	(3)	(3) + py	(4)	(4) + py	(5)
f	3.08	4.27	} 3.08 ^c	3.02	} 3.51 ^c	3.93	} 3.47
f'	2.51	3.51		2.30		3.56	
g	0.16	0.37	1.22	0.35	} 0.45 ^c	} 0.40 ^c	} -0.1 ^c
g'	-0.78	0.22	0.28	-0.35			
h		0.33			0.16	-0.15	-1.61
h'		-0.54					-1.89
i, i'							-1.4 ^c
j							-3.25
q	3.30	2.64	3.57	2.96	3.07	2.76	

^a Conditions as for Table 1. ^b Approx. due to overlap. ^c May be inequivalence within these multiplets.

phore distance increases with temperature and decreases with cooling (Figure 8). This 'breathing' effect can be reproduced in C.P.K. molecular model by simply pulling the chromophores apart, and it results in proton H_t rotating inwards towards the area of ring current (Figure 8). This is reflected experimentally by an *upfield* shift of H_t on warming, $\Delta\delta$ being -2.2×10^{-3} p.p.m./°. The breathing effect appears to be quite different from the specific temperature-dependent conformational changes seen in 'face-to-face' porphyrin dimers.¹⁴

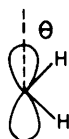


FIGURE 7 Preferred conformation of the cap protons H_g in quinone-capped porphyrins

Molecular Motion.—We mentioned above the broad lines observed in capped porphyrin n.m.r. spectra. These are due to slow molecular tumbling as is clear from comparison of their spin lattice relaxation times with simple porphyrins,⁴ e.g. for compound (4) in CDCl₃ at ambient temperatures representative values (with simple metalloporphyrins in brackets) are meso-protons 0.3 s (0.8), ring methyl groups 0.25 (0.5), and propionate groups 0.15 s (0.25–0.6). Similarly short times are found for the cap protons. Linewidths, given by $1/\pi T_1$, are therefore 1–2 Hz. Relaxation times of comparable protons are independent of the presence of metal or of co-ordinating ligand, ruling out significant aggregation effects.

Why is relaxation so much faster than for porphyrins and chlorophylls of comparable or greater weight? We believe that this is because the motion causing relaxation is a spinning around the fourfold axis like a disk: this motion causes least possible solvent disruption in normal porphyrins (Figure 9). However, in capped porphyrins the same motion is severely hindered as the cap must displace solvent in the same way as a propeller (Figure 9). This model predicts a greater viscosity dependence of T_1 for capped porphyrins than for simple porphyrins and indeed this is observed: when a solution of compound (4) in pyridine is heated from 40 to 80 °C the T_1 values increase by ca. 50%. The corresponding increase for simple porphyrins ca. is 20%. Thus, high-resolution

spectra of capped porphyrins are best obtained at high temperatures, although as we noted in the previous section slightly smaller ring-current shifts are also obtained.

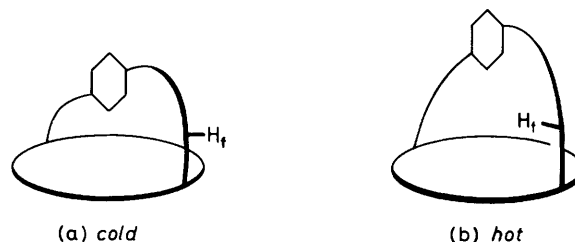


FIGURE 8 Schematic representation of temperature dependent 'breathing'

One interesting by-product of the very rapid room-temperature relaxation of the H_b protons in the cap of compound (4) is that the expected 2 Hz allylic coupling to H_q is missing: this is similar to 'chemical exchange' decoupling seen when paramagnetic ions cause very rapid relaxation, but ours is the first fully diamagnetic example involving only protons of which we are aware.¹⁵

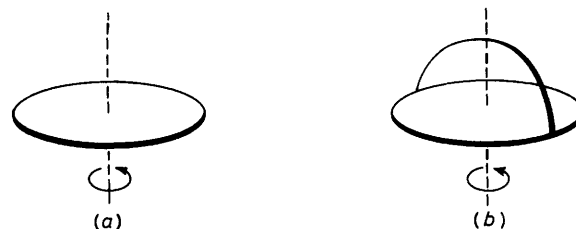


FIGURE 9 The motion of porphyrins and capped porphyrins

Co-ordination Chemistry.—When 1 mol equiv. of pyridine is added to a solution of compound (4) in CDCl₃ large upfield shifts are observed for the pyridine protons and the protons of the cap. On addition of further ligand the pyridine signals shift downfield towards the normal position. Limiting parameters for compounds (3) * and (4) are given in Tables 1 and 3, and spectra are shown in Figure 2. Analysis of the titration data for (4) reveals a 1 : 1 stoichiometry and a binding constant of the order of 25 l mol⁻¹. The pyridine shift ratios $\Delta\beta/\Delta\alpha$ and $\Delta\gamma/\Delta\alpha$ are 0.312 (± 0.005) and 0.26 (± 0.01) respec-

* Paucity of material prevented detailed titration experiments on (3).

tively, essentially identical to similar titrations of pyridine with simple magnesium porphyrins; this observation shows that pyridine is binding to the accessible unhindered side of the porphyrin in the normal way. T_1 Values for compound (4) are unaffected by pyridine binding, ruling out disaggregation phenomena, but those for the bound ligand are dramatically shortened as expected. Shifts in the porphyrin moieties of compounds (3) and (4) on pyridine binding are all less than 0.1 p.p.m.; small but significant changes in couplings within the propionate side-chains are found in both compounds (Table 1).

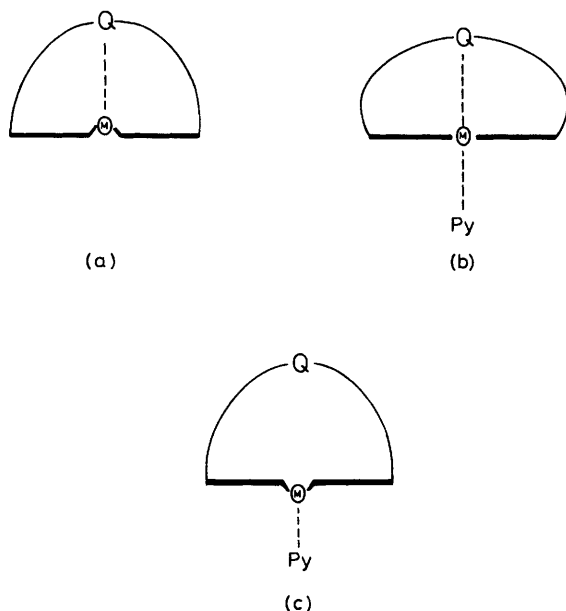


FIGURE 10 Models of co-ordination chemistry for the quinone-capped metalloporphyrins

These results all point strongly towards a picture in which the central magnesium ion in the absence of added external ligand binds a quinone carbonyl as fifth ligand and is displaced out of the porphyrin plane towards the cap (Figure 10a). Addition of pyridine as a sixth ligand pulls the metal into the plane; the metal ion in turn pulls the cap closer to the porphyrin (Figure 10b). The evidence for this interpretation comes from the pyridine binding constant which is only very approximate but which is orders of magnitude weaker than the usual *first* ligand binding to a Mg porphyrin and rather similar to a *second* binding; also induced shift patterns in the cap are the same as those observed in temperature-induced 'breathing.' Further evidence for the maintenance of quinone binding on pyridine addition comes (i) from preliminary electrochemical results, which show no pyridine dependence of E_0 in compound (4) but a very different value from (2), and (ii) from the propionate fragment couplings in (3) and (4) which are slightly pyridine dependent but again are quite different from compound (1). We favour therefore the six-co-ordinate binding in mode in Figure 10(b) rather than the five-co-ordinate

mode in Figure 10(c). The similarity to haemoglobin behaviour has not escaped our notice.

No attempt was made to exclude rigorous traces of moisture in these experiments: just a few μg of water in the n.m.r. solution provide 1 mol equiv. We cannot, therefore, exclude the possibility of water participation either as a bridge between the quinone and Mg ion or as a sixth ligand which is displaced by pyridine.

It is, in any case, clear that *on average* the quinone carbonyls point towards the central metal ion, so that the chromophores are perpendicular rather than parallel. This accounts for the relatively unremarkable photochemical properties of these compounds.¹

EXPERIMENTAL

270 MHz ^1H N.m.r. spectra were obtained at Portsmouth Polytechnic (1976–79) or at the University of British Columbia (1980). 400 MHz Spectra were obtained at U.B.C. (1980) and Cambridge (1981). Digital resolution was generally *ca.* 0.3 Hz/point; for measurement of coupling constants resolution enhancement (generally Gaussian multiplication) was always employed. Spin-lattice relaxation times were measured by inversion-recovery methods. N.O.e. and decoupling difference spectra were acquired with automated sequences described elsewhere.⁷ Deuteriochloroform was purified by passage over alumina before use. Porphyrin solutions were 0.5–5 mM, depending on spectrometer and sample availability. For compound (4) no dependence of chemical shifts or T_1 was observed over this concentration range.

Magnesium 3,13-Dodecamethylenedioxy mesoporphyrinate-II (6). To a solution of magnesium perchlorate (250 mg) in refluxing pyridine (20 ml) was added the corresponding free base porphyrin (*ca.* 10 mg) in pyridine (2 ml). The reaction was complete (u.v.) in 80–150 min. The mixture was poured into ice-cold water (200 ml) containing perchlorate (100 mg) and extracted with ether (3×50 ml). The organic phase was washed and dried, and the solvent was removed. The *product* (50%) was recrystallised from chloroform-petroleum (Found: M^+ , 754.3725. $\text{C}_{46}\text{H}_{58}\text{MgN}_4\text{O}_4$ requires 754.3808), $\lambda_{\text{max.}}$ ($\log_{10} \epsilon$) (Et_2O) 387 (4.75), 408 (5.66), 548 (4.32), and 586 nm (4.26).

Magnesium 3,13-Nonamethylenemesoporphyrinate-II (5).— This compound was prepared by a method analogous to that described above from the free-base porphyrin (Found: M^+ , 712.3294. $\text{C}_{43}\text{H}_{52}\text{MgN}_4\text{O}_4$ requires 712.3338), $\lambda_{\text{max.}}$ 389 (4.79), 409 (5.48), 547 (4.26), and 586 nm (4.15).

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