Tetrahedron Vol. 34, pp. 1213 to 1220. Pergamon Press 1978. Printed in Great Britain

THE NMR SPECTRA OF PORPHYRINS—14[1]

SELF-AGGREGATION OF ZINC(II) *MESO*-NITRO AND *MESO*-DINITRO OCTAETHYLPORPHYRINS

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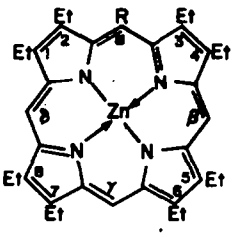
(*Received in the UK 19 July 1977; Accepted for publication, 26 July 1977*)

Abstract—Complex formation in zinc(II) *meso*-nitro-octa-ethylporphyrin (1) and the corresponding α, β-dinitro (2) and α, γ-dinitro (3) zinc(II) chelates has been studied using proton NMR at 220 MHz. This allows complete resolution of all the distinct groups in the proton spectrum, and the large concentration dependence of the spectra of 1 and 2 can be analysed to afford the monomeric and monomer-dimer shifts for all protons in these molecules. In contrast 3 shows no concentration dependence, nor any change upon addition of pyrrolidine, which immediately dissociates the aggregates of 1 and 2. The monomeric ^1H and ^{13}C shifts are reported, together with those of zinc(II) octaethylporphyrin (4), and the complete assignment given allows the substituent shifts of the *meso* nitro groups in the porphyrin to be obtained. Analysis of the monomer-dimer shifts in terms of the ring current model gives the detailed geometries of the dimers, which have an inter-ring separation of *ca* 4.5 Å and a lateral displacement from the vertical of *ca* 1.0 Å. The results also allow the distinction between two different molecular complexes considered previously, and fully confirm our earlier suggestions that binding is due to metal-to-porphyrin, rather than metal-to-substituent, interactions.

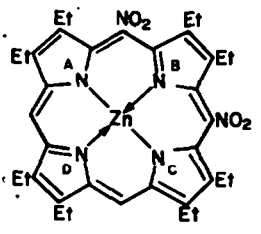
In previous parts of this Series,[2-4] and elsewhere,[5-7] we have identified novel strong aggregation tendencies, in solution, of zinc(II) and other metalloporphyrins. These have been shown to be a characteristic of the metalloporphyrin molecule provided certain conditions are fulfilled; the aggregation increases with increasing polarisation between metal ion and porphyrin ligand, and with increasing substitution with electron-withdrawing substituents on the periphery.[7] Most fascinatingly, this aggregation is not due to metal–ligand side-chain interactions in all but magnesium porphyrins,[6] though the aggregates are immediately dissociated by strong Lewis bases such as amines and alcohols.[8]

One detailed investigation of the thermodynamics and geometry of such complexes has been reported.[2] In zinc(II) *meso*-trifluoroacetoxyoctaethylporphyrin (5), large aggregation shifts in the NMR spectrum were observed which were completely absent in the corresponding metal-free porphyrin (6) and the zinc(II) complex (7) of the *meso*-acetoxyporphyrin. The analysis of these concentration dependent NMR shifts in terms of a monomer-dimer equilibrium provided information on the structure of the dimer. However, although the "tail-to-tail" structure (Fig, 1a) was favoured, the complexity of the spectrum precluded an unambiguous distinction between this and the other (head-to-tail; Fig. 1B) possible structure. Thus, our conclusions with regard to the geometry, and therefore mode of aggregation in these molecules, required further substantiation.

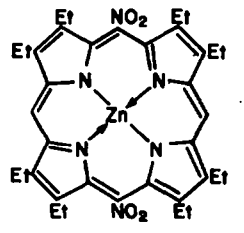
We observed that zinc(II) *meso*-nitro-octaethylporphyrin (1) gave similar concentration dependent NMR spectra to those of 5; however, in this case, high field proton NMR enabled *all* of the separate groups of protons to be resolved. These observations, coupled with similar behaviour of zinc(II) α, β-dinitro-octa-ethylporphyrin (2), but no concentration dependence of the α, γ-isomer (3), suggested that a similar detailed investigation to that of Ref. 2 would be of interest, particularly insofar as it would shed light on the mechanisms of aggregation in metalloporphyrins.[8] We now report the results of this investigation, and show that an unambiguous differentiation between the different proposed structures (Fig. 1a) for 5 can be made.



1 R=NO$_2$
4 R=H
5 R=OCOCF$_3$
7 R=OCOCH$_3$



2



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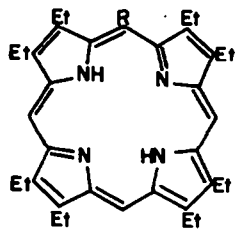

6 R=OCOCF$_3$
8 R=NO$_2$

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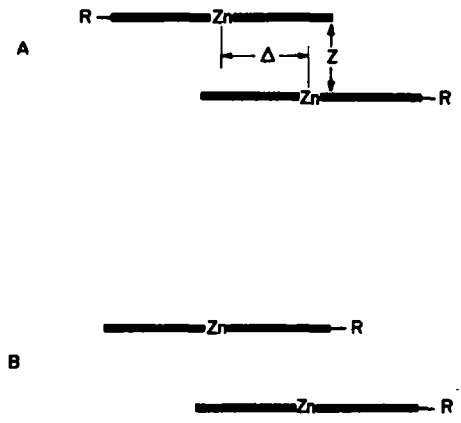

Fig. 1. Elevation views of possible dimers. A = tail-to-tail dimer B = head-to-tail dimer. When (a) R = NO_2, dimers are of compound (1); when (b) R = $OCOCF_3$, dimers are of compound (5).

RESULTS

^{1}H *Spectra.* The experimental proton resonance data are given, in Table 1, for the monomeric species obtained by addition of *ca.* 2 equiv of pyrrolidine[3] to the porphyrin solutions in chloroform. All the spectra are immediately interpretable as overlapping first-order patterns, and there is no sign of any anisochronous methylene protons (unlike the case of 5); Fig. 2 shows the spectra of 1 before (A) and after (B) addition ofpyrrolidine. This simplicity is entirely to be expected since the nitro group (unlike trifluoroacetoxy) is symmetrical about the porphyrin plane in any configuration. Inspection of Table 1 provides a simple rationale for these shifts and the consequent detailed assignment of the peripheral ethyl resonances; the assignments of the *meso* protons are obvious. The *meso* nitro group causes an upfield shift of the immediately adjacent ethyl groups of *ca.* 0.35 ppm (CH_2) and *ca.* 0.23 ppm (CH_3), with very little effect on the remaining substituents. Thus, the ethyls adjacent to the *meso* nitro occur at 3.75, 1.69 (1); 3.67, 1.62 and 3.70, 1.64 (2), and 3.72, 1.68 (3). In the case of 2, which has a pyrrole subunit with a nitro group on either side, the resultant chemical shift of the Et protons on this ring is only slightly upfield of the others, showing the very small influence of the nitro group on the next-but-one substituent. This provides a tentative assignment for the remaining ethyl groups, given in Table 1, some of which were confirmed by the dilution studies (*vide infra*).

The proton chemical shifts of 3 in $CDCl_3$ solution without added pyrrolidine were identical with those in Table 1. However, the shifts of both 1 and 2 in $CDCl_3$ solution alone showed large changes from those of Table 1, and a completely different pattern for the peripheral ethyl resonances was observed (see Fig. 2A for compound 1). The assignments for these spectra were obtained by decoupling experiments relating the various methylene and methyl resonances, and by the dilution experiments (Figs. 3 and 4). Previous results with the *meso*-trifluoro-acetoxyporphyrin[2] and others (Review, Ref. 8) have indicated that addition of methanol (or pyrrolidine) gives essentially infinite dilution shifts, and this is clearly seen in Figs. 2–4, particularly for the *meso* protons, where there is no ambiguity of the assignments at any stage. The plots of the δ values for the CH_2 CH_3 groups at various concentrations versus the δ value of the *meso* protons (Fig. 5) are strictly linear (which is to be expected for a monomer-dimer equilibrium), and

Table 1. Momomeric proton chemical shifts (δ) for zinc(II) *meso*-nitro-octaethylporphyrins[a]

Compound	Proton			
	meso	CH_2	CH_3	
(1)	10.11(β,δ)[b]	3.75	1.69	(2,3)
	10.04(γ)	4.09	1.90	(1,4; 5,8; 6,7)
		4.10	1.91	
(2)	10.07(γ,δ)	3.67	1.62	(2,5)
		3.70	1.64	(3,4)
		4.03	1.89	(7,8)
		4.05	1.89	(1,6)
(3)	10.20(β,δ)	3.72	1.68	(2,3;6,7)
		4.07	1.91	(1,4;5,8)
(4)	10.01	4.11	1.90	

[a] Measured using approx. 0.05 M solutions of the compound in $CDCl_3$ containing approx. 2 equiv of pyrrolidine.

[b] Greek letters and numbers in parentheses are assignments using nomenclature given in structural formulae.

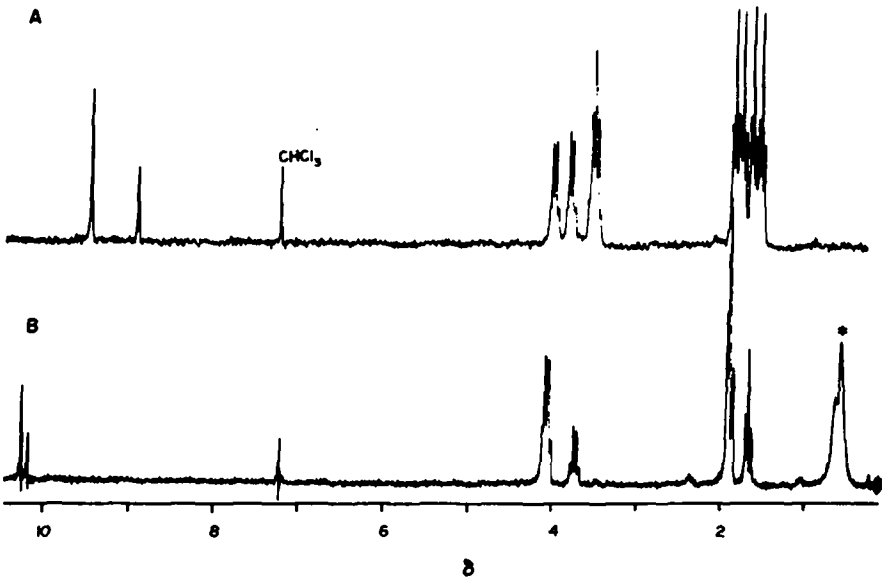

Fig. 2. ^{1}H NMR spectra (220 MHz) of (1) (*ca.* 0.1 M); A, in $CDCl_3$ alone, and B, in $CDCl_3$ containing approx. 2 equiv. added pyrrolidine. The asterisked peak in B is due to pyrrolidine.

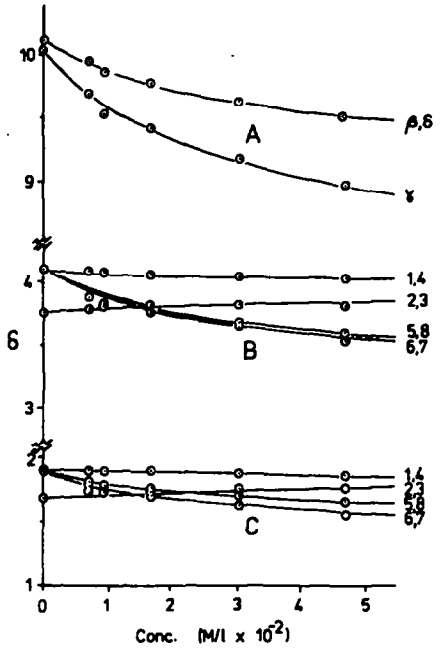

Fig. 3. Observed points (⊙) and calculated plots(—) of ^{1}H NMR spectrum of (1) as a function of concentration in $CDCl_3$. A, *meso*-protons; B, methylene protons; C, methyl protons. Infinite dilution values have been obtained by addition of pyrrolidine (2 equiv.).

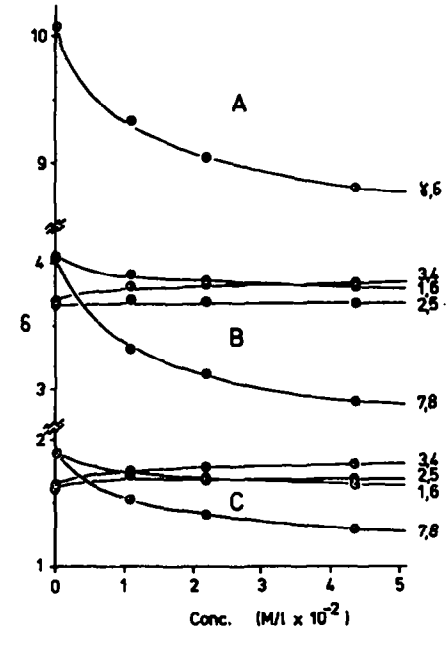

Fig. 4. Observed points (⊙) and calculated plots (—) of ^{1}H NMR spectrum of (2) as a function of concentration in $CDCl_3$. A, *meso*-protons; B, Methylene protons; C, methyl protons. Infinite dilution values have been obtained by addition of pyrrolidine (2 equiv.).

provide a simple and convenient method for assigning the Et group resonances. In the CH_2 and CH_3 curves, the pyrrolidine values are of use in obtaining some of the assignments in the concentrated solutions. For example, in 1, the (2,3) CH_2 and CH_3 resonances are clearly assigned from the infinite dilution values, and give rise to *low* field shifts with increasing concentration. The other three sets of resonances, which are coincident at infinite dilution and move *upfield* with increasing concentration, can only be assigned on the basis of the proposed structure of the complex. In the dinitro compound 2, C(3,4) and C(7,8) may be assigned also from the infinite dilution values, but the distinction between C(1,6) and C(7,8) rests on structural considerations.

In analysing the dilution curves, the accurate linearity of the plots of the *meso* proton shifts versus those of the other protons (Fig. 5, and the corresponding plot for 1 which is not shown) are of considerable utility. The direct proportionality between all proton dilution curves means that only one curve need be analysed completely

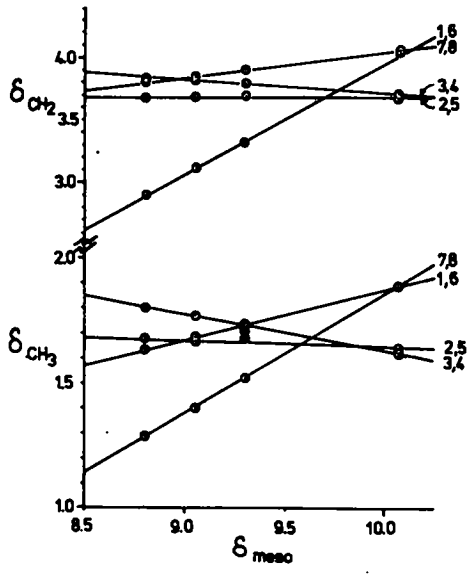

Fig. 5. Plot of δ_{CH_2} and δ_{CH_3} for compound (2) versus $\delta_{meso\text{-}H}$.

for the monomer-dimer equilibrium, since the values for the other protons will be given directly from the slopes of Fig. 5.

The dilution curves for the *γ-meso* proton of 1 and of the *meso* protons of 2 were analysed in terms of a monomer-dimer equilibrium, in which the observed chemical shift (δ_{obs}) at any concentration (a) is given by:[9]

$$\Delta\delta_{obs} = \delta_{obs} - \delta_{mon} = \Delta\delta\{(1+8aK)^{1/2} - 1\}^2/8aK$$

where K is the equilibrium constant and $\Delta\delta$ is $\delta_{dimer} - \delta_{mon}$, the complexation shift. In this analysis the monomeric shifts (δ_{mon}) are those of Table 1. This assumes that pyrrolidine complexation has no intrinsic effect on the proton chemical shifts, and this is supported by the linearity of the plots in Fig. 5 which includes these monomeric shifts. (Any intrinsic effect of the pyrrolidine would differ at the different protons and therefore the monomer shifts would deviate from the line).

Analysis of the dilution curves gave values of K and $\Delta\delta$ of 13 $l.m^{-1}$ and 2.5 ppm respectively for the *γ-meso* proton of 1 and 38 $l.m^{-1}$ and 2.2 ppm for the *meso* protons of 2. The calculated curves are given, together with the observed points for these protons, in Figs. 3 and 4. The error in these parameters are *ca.* 10% for K *and* ±0.2 ppm for $\Delta\delta$, though there is a strong correlation between the parameter errors. The complexation shifts for the other protons were obtained from these as described above, and are given in Table 2.

^{13}C *Studies.* With a view to obtaining more information about the effect of the *meso* nitro on the electron distribution in the porphyrin ring when perturbed with substituents of various types, the ^{13}C spectra of 1, 2 and 3 were obtained in $CDCl_3$ containing excess pyrrolidine[5] to afford the "monomeric" shifts. These are given, together with the previously reported data[4] for zinc(II) octaethylporphyrin, in Table 3.

The separation of the chemically different types of carbon is generally maintained, apart from the ring-carbon resonances. The Et group carbon resonances of 1 are similar to those of the proton spectra in that only one CH_2 and CH_3 resonance is significantly altered from that of zinc(II) octaethylporphyrin (4), and those are immediately assigned to the C(2, 3) ethyl groups. Similar reasoning gives the assignments for 2 and 3, though in 2 there is additional separation of the ethyl groups into a 1:1:2 pattern due to the longer range effects of the two nitro groups.

meso-Carbon assignments follow directly from their relative intensities and comparisons within the series. In 1 the *α meso* carbon was not observed. (The carbon attached to the nitro group was always of very low intensity, presumably due to the absence of neighbouring protons giving less NOE and longer T_1's and also the neighbouring quadrupolar N atom could shorten the carbon T_2.) However, in *meso*-nitro-octaethylporphyrin (8), this signal was observed at 127.7 δ in reasonable agreement with expectations from substituent effects and the effect of metal insertion on the ring carbon chemical shifts.[3]

Table 2. Complexation shifts ($\Delta\delta$) for zinc(II) *meso*-nitro-octaethylporphyrin (1) and zinc(II) *α, β-meso*-dinitro-octaethylporphyrin (2)

Compound	Proton		
	meso	CH_2	CH_3
(1)	2.50(γ)[A]	0.18	0.13 (1,4)
	1.45(β,δ)	-0.20	-0.18 (2,3)
		1.23	0.60 (5,8)
		1.30	0.80 (6,7)
(2)	2.14(γ,δ)	0.42	0.42 (1,6)
		-0.02	-0.04 (2,5)
		-0.22	-0.30 (3,4)
		1.90	1.01 (7,8)

[A] Greek letters and numbers in parentheses are assignments using nomenclature in structural formulae.

Table 3. ^{13}C Chemical shifts[a] (δ_c) for zinc(II) octaethylporphyrin (4) and the *meso*-nitro (1) and the *α,β-meso*-dinitro (2) and *α,γ-meso*-dinitro (3) derivatives

Compound	meso-Carbons	Assignment	C_α	C_β	CH_2	CH_3
(4)[c]	96.2		146.7	141.1	19.8	18.8
(1)	127.7(α)[b]	C(2,3)	138.30	145.36	20.49	18.40
	98.08(β,δ)	C(1,4)	146.40	139.31	19.80	18.67
	97.82(γ)	C(5,8)	148.08[d]	142.63[e]		
		C(6,7)	148.39[d]	142.47[e]		
(2)	130.16(α,β)	C(3,4)	137.66	143.61	20.46	18.04
	99.21(γ,δ)	C(2,5)	139.34	146.43	20.12	18.28
		C(1,6)	147.80	140.53	19.71	18.54
		C(7,8)	149.51	142.71		
(3)	129.27(α,γ)	C(2,3;6,7)	139.50	146.30	20.44	18.26
	99.53(β,δ)	C(1,4;5,8)	147.29	140.55	19.70	18.60

[a] ca. 0.1 M porphyrin in $CDCl_3$ containing ca. 2 equiv pyrrolidine

[b] Estimated from meso-nitro-octaethylporphyrin (8) and substituent shifts, see text.

[c] R. J. Abraham, G. E. Hawkes, and K. M. Smith, J. Chem. Soc., Perkin Trans. II, 627 (1974).

[d,e] These pairs of assignments could be interchanged.

The remaining ring carbon assignments are of interest as detailed comparisons within the series allows the complete assignment of all quaternary ring carbons in the molecules, the first complete assignment for any unsymmetrical porphyrin. The identification of the overlapping C_α and C_β quaternary resonances was initially based on the uniformly lower intensity of the C_α signals, due again presumably to the absence of neighbouring protons decreasing the NOE and increasing T_1, and also possibly to broadening effects (shortening T_2) due to the attached ^{14}N nuclei. The former explanation is supported by the considerably smaller intensities observed for the C_α carbons next to the *meso* nitro group, which is on this basis due to removal of the adjacent *meso* hydrogen. This was of considerable use in assigning these resonances, and the assignments were confirmed in 1 by comparison with the spectrum of *meso*-nitro-octaethylporphyrin (8).† Introduction of zinc(II) into the porphyrin ring produces a pronounced low field shift of the C_α carbons and a much smaller low field shift of the C_β carbons; (in coproporphyrin-I tetramethyl ester the shifts are 4.0 and 0.4 ppm respectively).[3] This general rule was followed by all of the C_α carbons in 1 and all the C_β carbons except C(2,3) which, interestingly, are in a γ orientation to the *meso* nitro group (see later).

The substituent chemical shifts (SCS) of the *meso* nitro group obtained from the complete assignment of 1 and the zinc(II) octaethylporphyrin (4) shifts, were then used, assuming additivity of the substituent shifts, to predict the spectra of 2 and 3. The good agreement found, in which the correct order of all the carbon resonances was obtained, gives both the assignments of the spectra of 2 and 3, and also strongly supports the correctness of the initial assignment of 1. Only in the pyrrole subunits far removed from the *meso* nitro substituent (rings C and D) in which the SCS are virtually constant for all the ring carbons, is there any ambiguity in the assignments. The *meso* nitro SCS are of some interest, and are collected for both the proton and ^{13}C spectra in Table 4. The general pattern is quite similar to the less detailed results for the *meso* acetoxy and *meso* trifluoroacetoxy substituents. For example, the *α*, *β* and *γ* substituent shifts of the *meso* nitro of 31.5, −8.4 and 4.3 ppm respectively compare well with the OAc ($OCOCF_3$) values of 32.1 (30.4), −5.8 (−7.5) and 2.2 (2.7) ppm. Such comparisons suggest that the SCS for at least these carbons are due to electronic (i.e. through bond) effects rather than through space (i.e. electric field) effects, as it is difficult to see why the electric field or magnetic anisotropy of the nitro and $OCOCH_3$ groups should be so similar. This suggestion is reinforced by comparison with the nitro SCS in the benzene ring[11] of 20.0 (C1), −4.8 (ortho) and 0.9 ppm (meta) respectively. These again bear a general resemblance to the values in the porphyrin ring despite the very different electronic state and configuration of the two systems.

The SCS at the Et groups also follow a similar pattern in that the C(2) methylene carbon is deshielded and the corresponding Me carbon shielded by the *meso* substituent, but here the magnitudes of the SCS are quite different (0.69 and −0.40, Table 4 versus 2.3 and −1.8 for $OCOCF_3$).[2] The different signs of the SCS for the methylene carbons and protons are intriguing, and here there is no analogy with the $OCOCF_3$ compound as the spectra in the latter case were too complex for a full assignment. The obvious steric or electrostatic

†It is of interest to note here that the characteristic broadening of the C_α carbons in the free base porphyrins due to NH exchange processes which in some cases precludes detection of these signals,[4] was completely absent for 1, as it is for certain chlorins.[10]

Table 4. ^1H and ^{13}C Substituent Chemical Shifts (SCS) for the *meso*-nitro group

Meso-positions			Other positions							
						CH_2		CH_3		
Assignment	C	H	Assignment	C_α	C_β	C	H	C	H	
α	31.5	-	C(2,3)	-8.4	4.3	0.69	-0.36	-0.40	-0.21	
β,δ	1.88	0.10	C(1,4)	-0.3	-1.8	-0.10	0.0	-0.10	0.0	
γ	1.62	0.03	C(5,6)	1.4	1.5	0.0	0.0	0.0	0.0	
			C(7,8)	1.7	1.4					

mechanism, in which the adjacent electronegative oxygen atoms will remove negative charge from the hydrogens (increasing the polarisation of the C–H bond) gives the reverse of the observed shifts. This mechanism would produce a downfield shift of the protons and an upfield shift of the carbons. The very similar magnitudes of the SCS for the hydrogens and carbons of the ethyl groups suggests that magnetic anisotropy effects may play a considerable role in these SCS. In these, the actual shift (in ppm) is the same for different nuclei at the same position in space, whereas all electronic mechanisms give a factor of *ca.* 20 for ^{13}C compared with ^1H shifts. It is also noticeable that both the ^1H and ^{13}C long-range SCS of the nitro group are larger at the *β, δ-meso* positions than at the *γ-meso* position.

The geometry of the complex. The complexation shifts (Table 2) may now be used to obtain the geometry of the aggregated complex, using similar procedures to those of Ref. 2. Thus, we assume that the porphyrin molecules in the dimer are parallel and that the complexation shifts are solely due to the ring current of the adjacent porphyrin molecule in the complex. These ring current shifts were calculated from the porphyrin ring current model described in Part 13.[1] It is important to differentiate between the absolute values of the complexation shifts and their ratios. The values of the shifts are critically dependent upon the assumptions made in the analysis, i.e. that no higher aggregates are formed, etc., and on the accuracy of the curve fitting procedure. The ratios of the complex shifts, on the other hand, are obtained directly from the experimental data (Fig. 5) and are therefore much more valuable for deduction of the geometry of the complex (see later).

Two dimer structures were consistent with the previous studies[2] of 5, a tail-to-tail dimer (Fig. 1A) in which both porphyrin rings are identical, and a head-to-tail dimer (Fig. 1B) in which the rings are not identical. Although Fig. 1A was favoured, the unresolved spectrum of 5 precluded an unambiguous distinction. The data in Table 2, on the other hand, immediately exclude the head-to-tail dimer (Fig. 1B) for 1. In this structure, due to symmetry of the ring current field about the axis of symmetry of the porphyrin ring, averaging over the two different molecules in the dimer must equalise the complexation shifts for the C(1, 4) and C(5, 8) ethyls and for the C(2, 3) and C(6, 7) ethyl groups. It is clear from Fig. 3 and Table 2 that this is not the case. Indeed, the complexation shifts of the C(2, 3) Et groups, which are unambiguously assigned by the nitro group substituent effect in the monomeric spectrum, are the opposite sign to those of the remaining Et groups in 1. Analogous considerations apply also to 2, thus eliminating Fig. 1B from further consideration.

Fortunately, the structure in Fig. 1A can be shown to be entirely consistent with the observed shifts. The eluçidation of the detailed geometry in the dimer now reduces to the determination of the unknown parameters defining the complex, i.e. Z, the inter-ring separation, and Δ, the lateral displacement. Using only the *meso* proton shifts in 1, which give only one ratio ($\beta, \delta/\gamma$), there is a simple proportionality between the values of Z and Δ which reproduce this ratio. For any value of Z a value of Δ can be found which satisfies this ratio, and increasing Z necessitates increasing Δ. The CH_2 and CH_3 complexation shifts may now be used to better define these parameters; however, the precise conformation of the

ethyl groups is not known in solution. We considered two models: (i) taking the centre of gravity of the CH_2 protons, assuming free rotation of the ethyl groups, and (ii) taking the actual positions of the CH_2 protons with the Et groups perpendicular to the ring plane and pointing away from the adjacent molecule (as in the crystal structure of the thallium(III) chloride complex of octaethylporphyrin[12]). For $Z = 4.5$ Å and $\Delta = 1.0$ Å the calculated dimer shifts are, for model (i) *γ-meso* 1.76, *β, δ-meso* 0.92, CH_2(2, 3) 0.07, CH_2 (1, 4) 0.20, CH_2 (5, 8) 0.45, and CH_2 (6, 7) 0.79 ppm. For model (ii) with the same values of Z and Δ the corresponding methylene shifts are −0.05, 0.08, 0.32 and 0.68 ppm respectively. In the α, β-dinitro compound (2) we consider a dimer structure in which the lateral displacement Δ is along the plane of symmetry of the molecule. For $Z = 4.5$ Å and $\Delta = 1.0$ Å (i.e. a displacement of 1.0 Å along both the *x* and *y* axes) the calculated dimer shifts are for model (i) *γ, δ-meso* 1.70, CH_2 (3, 4) 0.02, CH_2 (2, 5) 0.12, CH_2 (1, 6) 0.50, and CH_2 (7, 8) 1.01 ppm; for model (ii) the corresponding CH_2 shifts are −0.10, −0.03, 0.39 and 0.94 ppm respectively.

DISCUSSION

The results of the preceding Section have demonstrated very clearly that not only is the head-to-tail structure (Fig. 1B) incompatible with the observed complexation shifts, but also more importantly that the tail-to-tail structure (Fig. 1A) is entirely consistent with the observed data, reproducing both the relative magnitudes and signs of the complexation shifts. Thus, the calculated dimer shifts for Fig. 1A are in the correct order for both compounds 1 and 2, and also reproduce the downfield shifts of the 2, 3 methylenes in 1 and of the 3, 4 methylene protons in 2. The calculations are limited largely by our lack of knowledge of the detailed conformation of the Et substituents in solution. We have considered two extreme cases, i.e. free rotation, and a fixed conformation, and it is obvious that in practice an intermediate situation will prevail. (For this reason, the calculations only considered the methylene protons of the Et groups. The rotational envelope of the Me groups is so large as to make calculations for these protons meaningless).

The actual magnitudes of the calculated shifts are all slightly less than the observed complexation shifts, and this is very probably due to the occurrence of higher aggregates in solution, the limiting shifts for a polymeric aggregate being *ca.* 3 times the dimer shifts. It is of interest in this context to compare the complex shifts obtained here with those derived for 5. The complex shifts obtained[2] for 5 are almost twice as large as those for 1; e.g. *meso* H's 4.20 (γ), 2.09(β, δ). However, the shift *ratios* are very similar to those of 1 for all the protons, even to the negative sign for one pair of methylenes, and thus there is no doubt as to the similarity of the complex structures in both molecules. The reason for the much larger shifts obtained for 5 is easily seen when the precise experimental conditions are noted; the concentration range studied here is from 30 mg/ml (0.045 M) to 4 mg/ml (6×10^{-3} M), whereas that in Ref. 2 was from 140 mg/ml (0.20 M) to 23 mg/ml (0.03 M). The lowest concentrations used in Ref. 2 approximate to the highest used here. Thus, if as we suggest higher aggregates are being formed at the higher concentrations used here, there will have been a considerable fraction of higher aggregates in the much more concentrated solutions employed in Ref. 2. The available concentration ranges were dictated by spectrometer sensitivity requirements in Ref. 2 (Varian HA-100) whereas in the present study they were limited by solubility considerations at the upper end. It is clearly of interest to undertake a more detailed analysis in terms of a monomer-dimer-trimer equilibrium in the appropriate case, and this work is in progress in these Laboratories.

This study was, however, concerned with determining the actual geometry of the complex unambiguously, and this is of importance because the structure in Fig. 1A poses many interesting problems as to the nature of the interaction responsible for these aggregates. It is clear that the tentative conclusions reached in Ref. 2 concerning the lack of any substituent-to-metal interaction are fully substantiated. There is no possibility of any nitro-to-metal interaction in Fig. 1A, which is the same generic structure as that proposed for compound 5. Thus, the major interaction clearly involves the metalloporphyrin ring acting directly as a ligand in an intermolecular manner. As As our earlier work has inferred,[6,7] increasing the formal positive charge on the central metal ion has the effect of increasing the strength of the aggregation. This can be brought about by judicious choice of the metal ion (e.g. one having completely filled *d* orbitals) or by varying the peripheral or *meso* substituents. Electron withdrawing substituents place a higher formal positive charge on the metal, making it more attractive to nucleophiles[13] (such as pyridine, piperidine, pyrrolidine, or the π cloud of a neighbouring porphyrin). In general, these metals which are only weakly held in the porphyrin central cavity form the strongest apical ligand-to-metal[14] or intermolecular π–π[7] complexes.

Thus, we can discern certain prerequisites for complexation. The substituent must induce considerable charge polarisation in the macrocycle through electron withdrawal (Hammett relationships indicate[15] that a resonance (not inductive) interaction occurs between the *dπ* metal orbitals and the π orbitals on the porphyrin.) In our series, the *meso* acetoxy group was ineffective, whereas the *meso*-trifluoroacetoxy and *meso*-nitro groups gave strong aggregation. Again, this is in line with the effects of peripheral β substituents[6,7] and the correlation with pK_3 and electrochemical oxidation poten-

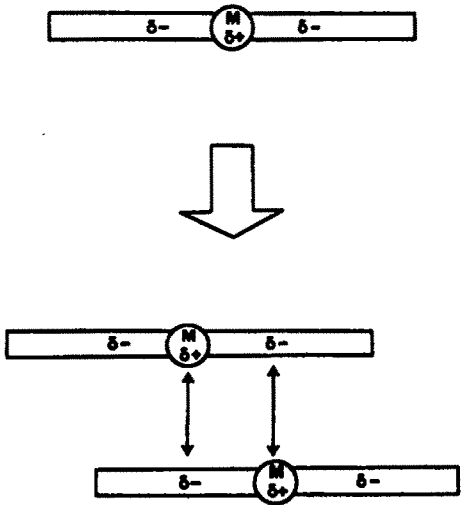

Fig. 6. Schematic diagram of metalloporphyrin dimers.

tials. The other very important point is that a measure of asymmetry is required for the complexation. This is clearly seen in the comparison of the α,β-dinitro compound (2) with the α,γ-isomer (3) (in which no aggregation is apparent.) The symmetrical nature of the α,γ substitution precludes aggregation, possibly because there are no relatively "electron rich" subunits in 3. Recently, a tight dimer in dicyanoferrihaemin has been described[16] in which a donor–acceptor interaction between rings of different electron density occurs; furthermore, a chemical manifestation of different electron densities in porphyrin subunits has recently been described.[17] Our results described herein therefore lend considerable support to our polarisation model of the interaction (Fig. 6) in which increase in intramolecular polarisation (through lack of $d\pi$–$p\pi$ overlap between metal ion and porphyrin ligand) causes an increase in intermolecular interaction of the metal ion with the π system of a neighbouring porphyrin molecule. This model further illustrates an important characteristic of the aggregates, which is that the displacement (Δ) of the porphyrins from the vertically stacked dimer is an essential part of the aggregated structure. However, the theoretical considerations of the precise mechanism of this interaction, in which electrostatic, polarisation, and charge-transfer interactions may all play a part, will be considered in detail elsewhere.

EXPERIMENTAL

NMR spectra. The ^{1}H NMR spectra were obtained using a Perkin-Elmer PE R34 (220 MHz) spectrometer at about 30°. ^{13}CNMR spectra were obtained using a Varian XL-100 instrument, operating in the pulse Fourier transform mode at about 35°, with complete proton noise decoupling, as previously described.[4] The accuracy of the chemical shifts was ±0.01(^{1}H), ±0.05(^{13}C). TMS was employed as internal reference for both ^{1}H and ^{13}C spectra.

Materials. Methods for the preparation of porphyrins 1, 2, and 3 have already been communicated.[18–20] A full paper defining precise experimental details is in preparation.[21]

Acknowledgements—We thank Prof. H. H. Inhoffen for generous gifts of octaethylporphyrin, and the S.R.C. for a studentship (to B.E.) and for grants towards the purchase of the PE-R34 spectrometer.

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