The NMR Spectra of the Porphyrins

24†—The NMR Spectra of some Tetraarylchlorins

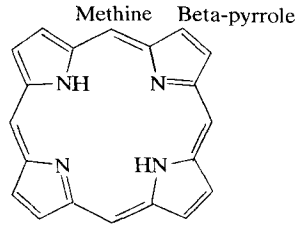
Raymond J. Abraham* **and James E. Plant**
Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK

Geoffrey R. Bedford
ICI Pharmaceuticals Division, Alderley Park, Macclesfield, Cheshire SK10 4TG, UK

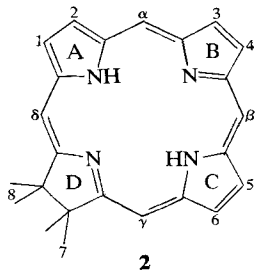
The synthesis and complete assignment of the ^{1}H NMR spectra of 5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (PIVTPP) and its two chiral dihydro adducts 3,4-dihydro-(PIVPTPC-I)- and 7,8-dihydro-(PIVPTPC-II)-porphyrins are reported. The use of the zinc complexes of the chlorins as chiral shift reagents with optically active bases is discussed. Comparison of the observed shift differences between the chlorins and the parent porphyrin with those calculated by a ring current model shows that a decrease in the ring current occurs on chlorin formation, and also specific effects occur at the reduced pyrrole ring, presumably reflecting different steric constraints.

INTRODUCTION

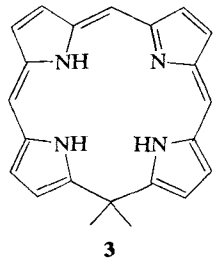
The chlorin (7,8-dihydroporphyrin) ring is found abundantly in nature as the chlorophylls, the pigments of fundamental biological importance responsible for photosynthesis.[1a,2] The saturation in chlorins is traditionally shown in ring D (**2**) and may be compared with the other common dihydroporphyrin, the phlorin system (**3**), in which the conjugation of the macrocycle is interrupted. Under alkaline conditions the equilibrium between the chlorin and phlorin systems has been directly observed.[2a]



1
Porphin



2
Chlorin



3
Phlorin

Chlorins are usually found as the by-products in the synthesis of *meso*-tetraarylporphyrins,[3,4] and may be isolated by fractional crystallization or acid extraction,[5] although chemical methods are available for their removal by selective oxidation to porphyrins.[6] Chlorins are never synthesized directly, owing to the relative ease with which they are oxidized to porphyrins, and are usually obtained by the chemical, photochemical or electrochemical reduction of the respective porphyrin. The best method for the synthesis of tetrarylchlorins is the diimide reduction,[5] which yields about 50% of the crude product.

The NMR spectra of chlorins show characteristic differences from their parent porphyrin structures, and have recently been reviewed by Scheer and Katz.[2] The major differences arise from a reduced ring current due to the removal of one of the peripheral double bonds in the chlorin ring, leading to a downfield shift of the N—H signals and an upfield shift of the peripheral proton signals compared with the parent porphyrin. This is well illustrated by consideration of the porphin and chlorin ^{1}H chemical shifts:[2,7]

	Methine-H[a]	β-pyrrole-H[a]	N-H[a]	Chlorin-H
Porphin (**1**)	10.58	9.74	−3.76	—
Chlorin (**2**)	9.62 (α, β),	9.03 (3, 4),	−2.75,	4.25
	0.96	*0.71*	*−1.01*	
	8.92 (γ, δ),	8.63 (2, 5),		
	1.66	*1.11*		
		8.52 (1, 6),		
		1.22		

[a] *Values in italics* $= \delta_{porphin} - \delta_{chlorin}$

As can be seen, the chlorin methine- and β-pyrrole-H signals all experience an upfield shift compared with porphin, decreasing in magnitude with increasing distance from the reduced ring. The high-field shift of the methine resonances has been explained qualitatively by Woodward's picture of the macrocycle.[2,8,8a] In this model the four pyrrole rings are considered as independent aromatic sub-units which tend to collect electron density from the methine positions. In the 7,8-dihydroporphin ring the aromatic subunit of ring D is essentially removed, increasing the electron density at the neighbouring

* Author to whom correspondence should be addressed.
† For Part 23, see Ref. 1.

CCC-0030-4921/83/0021-0745$06.00

methine positions, causing a high-field shift of the γ and δ protons.

Quantitative studies based on the double dipole approximation have been shown to give a good description of the ring current-induced shifts in the porphyrin and chlorin ring.[9] The approximation has also been used in the application of Zn-TPP as a diamagnetic shift reagent, both in a quantitative sense for determining ligand geometries[10,11] and in a qualitative manner for the dispersion of complex spectra of mono- and multi-functional ligands.[1] Additionally, the model has explained, at least in part, the observed shift differences seen in the atropisomers of *meso*-tetra(2-methoxynaphthyl)porphyrin.[12] More recently, a double dipole model of the macrocyclic ring current in the dihydroporphyrin ring, including a close range approximation,[13] has successfully accounted for the observed shifts in chlorophyll derivatives.[14]

Chiral shift reagents have proved to be of considerable use in structural chemistry,[15] and the preparation of a suitable chiral porphyrin shift reagent would be of general interest. As part of such a project, we report here the synthesis and complete proton spectral assignment of 5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (PIVPTPP) and its two dihydro adducts, 3,4-dihydro-5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (PIVPTPC-I) and 7,8-dihydro-5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (PIVPTPC-II) (Fig. 1). The zinc complexes of each were also prepared, and the observed ^{1}H chemical shifts obtained on reduction of the porphyrin to the chlorin were compared with calculated values using a previously parameterized version of the double dipole model of the macrocyclic ring current.[14]

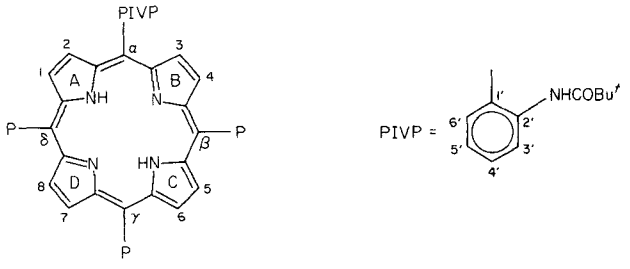


Figure 1. Numbering system used for PIVPTPP and the related chlorins.

RESULTS AND DISCUSSION

Synthesis

PIVPTPP was prepared via a mixed aldehyde condensation of *o*-nitrobenzaldehyde and benzaldehyde with pyrrole, and the resulting mixture of nitroporphyrins reduced with tin(II) chloride in concentrated hydrochloric acid.[16] Treatment of the separated 5-*o*-aminophenyl-10,15,20-triphenylporphyrin with pivaloyl chloride[17] gave PIVPTPP in 4% overall yield from pyrrole. Use of the pivaloyl group restricts the rotation of the aryl-porphyrin C—C bond,[17] thus removing the element of symmetry through the porphyrin plane. This was important for the chiral base studies (see later).

Reduction of PIVPTPP was achieved by the diimide reaction of Whitlock *et al.*[5] The yield was maximized by initially obtaining a chlorin–bacteriochlorin mixture, followed by selective oxidation of the bacteriochlorin with *o*-chloranil. Any unreduced porphyrin was removed by phosphoric acid extraction. Because of the asymmetry of the porphyrin two dihydro adducts were obtained; these were separated by column chromatography to give PIVPTPC-I and PIVPTPC-II in 20.4% and 28.6% yield, respectively, from PIVPTPP.

Zinc insertion was achieved by standard literature methods.[2,18]

^{1}H spectral assignments

The free base and zinc complex proton chemical shifts of PIVPTPP, PIVPTPC-I and PIVPTPC-II are given in Tables 1 and 2, respectively, and the spectra (free base), with assignments, in Figs 2 and 3 (aromatic region).

PIVPTPP. From symmetry arguments we would expect the β protons of PIVPTPP to give two AB systems. As can be seen, only one partially obscured AB system is resolved and can, presumably, be assigned to H-2,3 and H-1,4 [^3J(HH) = 4.78 Hz], as the asymmetry due to the pivaloyl group is likely to be more felt in this part of the porphyrin. The vicinal coupling of the β protons is in good agreement with that obtained for the type III atropisomer of *meso*-tetra(2-methoxynaphthyl)porphyrin.[12] H-2,3 and H-1,4 are assigned provisionally to the upfield and obscured downfield doublets, respectively, because of their positions relative to the amide group. H-5,8 and H-6,7 are thus assigned to the singlet at δ 8.872.

Because of our interest in comparing the chemical shifts of the porphyrin and chlorin species (see later), low-temperature studies of PIVPTPP were carried out at 192 K, which now gave two AB systems and two singlets for the β protons, although some overlapping is evident (Fig. 3a). At this temperature N—H tautomerism[19–21] is slow on the NMR time scale, and further non-equivalence of the pyrrole rings is observed. The downfield broadened singlet and AB systems are assigned to H-5,6 and H-1,2, respectively, in view of the additional coupling observed compared with H-7,8 (singlet) and H-3,4 (AB), which give sharp signals with no further coupling. This additional structure is due to long-range coupling between the nitrogen and β protons, and the value obtained (1.67 Hz) is similar to that seen in low-temperature studies of the dication of TPP.[19] Apart from minor shift differences, the remaining resonances were unchanged at 192 K.

The H-3′ and H-6′ protons of the pivaloyl phenyl ring were assigned provisionally to the doublet of doublets at δ 8.656 and 8.069, respectively. This represents a considerable downfield shift of H-3′ compared with the *meta* protons of the other phenyl rings in the molecule (*ca* 0.89 ppm), and is thought to be due to an anisotropic deshielding effect of the carbonyl group of the amide. This shift was compared with the

Table 1. Proton chemical shifts (δ) of free base PIVPTPP and the related chlorins at 293 and 192 K in CD_2Cl_2

	PIVPTPP		PIVPTPC-I		PIVPTPC-II	
	293 K	192 K	293 K	192 K	293 K	192 K
H-1	8.872	9.088	8.611	8.702	8.226	8.278
H-2	8.794	9.004	8.179	8.245	8.605	8.707
H-3	8.794	8.784	—	—	8.338	8.414
H-4	8.872	8.862	—	—	8.408	8.488
H-5	8.872	9.095	8.213	8.275	8.530	8.620
H-6	8.872	9.095	8.589	8.688	8.215	8.264
H-7	8.872	8.874	8.411	8.504	—	—
H-8	8.872	8.874	8.387	8.475	—	—
H-3′	8.656	8.669	8.642	8.721	8.599	8.636
H-4′	7.818	7.892	7.697	7.765	7.746	7.810
H-5′	7.525	7.605	7.440	7.501	7.457	7.532
H-6′	8.069	8.156	7.760	7.820	7.961	8.031
o-P_β	8.205	8.274	7.896	7.950	8.103	8.155
			7.869		8.051	8.109
o-P_γ	8.205	8.274	8.087	8.145	7.895	7.927
					7.866	7.865
o-P_δ	8.205	8.274	8.087	8.145	7.895	7.927
					7.866	7.865
m,p-$P_{\beta,\gamma,\delta}$	7.771	7.840	7.697	7.765	7.695	7.753
$-CH_2CH_2-$	—	—	4.172	4.240	4.180	4.219
			3.948	3.987		
NHCO	7.162	7.250	7.244	7.358	7.244	7.335
tert-Bu	0.101	0.178	0.321	0.345	0.180	0.229
N—H	−2.760	−2.985	−1.406	−1.571	−1.498	−1.710
			−1.296	−1.470	−1.498	−1.669

corresponding proton of 2-chloropivaloylamidobenzene (**4**) in which the amide moiety, because of hydrogen bonding with the chloro substituent, is approximately coplanar with the ring, and the carbonyl adopts a *cis* conformation with respect to the phenyl ring.[22–25] The shift values compared with chlorobenzene[26] (Δδ) for all the protons of **4** are shown in Table 3, together with the Δδ effects of the amide group of PIVPTPP compared with TPP.[20]

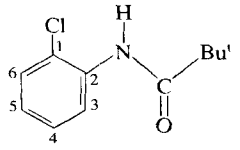


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Table 2. Proton chemical shifts (δ) of zinc PIVPTPP and the related zinc chlorins in $CDCl_3$

	Zn-PIVPTPP	Zn-PIVPTPC-I	Zn-PIVPTPC-II
H-1	8.854	8.405	8.015
H-2	8.776	7.926	8.444
H-3	8.776	—	8.224
H-4	8.854	—	8.284
H-5	8.872	7.972	8.346
H-6	8.872	8.400	7.996
H-7	8.872	8.276	—
H-8	8.872	8.264	—
H-3′	8.754	8.694	8.657
H-4′	7.791	7.632	7.698
H-5′	7.470	7.351	7.382
H-6′	7.996	7.632	7.820
o-P_β	8.215	7.835	8.037
	8.141	7.764	8.004
0-P_γ	8.215	8.031	7.803
o-P_δ	8.215	8.052	7.838
	8.141	7.982	7.792
m,p-$P_{\beta,\gamma,\delta}$	7.739	7.632	7.635
$-CH_2CH_2-$	—	3.974	4.099, 4.104
NHCO	7.342	7.472	7.265
tert-Bu	0.084	0.393	0.227

The agreement in the downfield shift of H-3′ in the porphyrin compared with the chloro compound is sufficient to confirm the assignment, and suggests that the amide group adopts a *cis* conformation with respect to the phenyl ring of the porphyrin. The slightly smaller shift seen for the porphyrin indicates that the amide group is not 'locked' into coplanarity with the ring as in the hydrogen-bonded chloro derivative, but is allowed some degree of rotation about the phenyl nitrogen bond, and a smaller downfield shift is thus observed.

The Δδ values for H-4′ and H-5′ in the porphyrin are in fairly good agreement with those observed in the chloro compound, although a difference is seen for H-6′. This may be due to a conformational difference between the phenyl ring in TPP and PIVPTPP, causing an appreciable ring current effect on the *ortho* proton (see later).

The remaining pivaloyl ring protons were assigned with the aid of decoupling experiments. The broad singlet at δ 7.162 is assigned to the amide proton, and this was confirmed after shaking with D_2O. The porphyrin N—H is a sharp singlet at δ −2.760. The

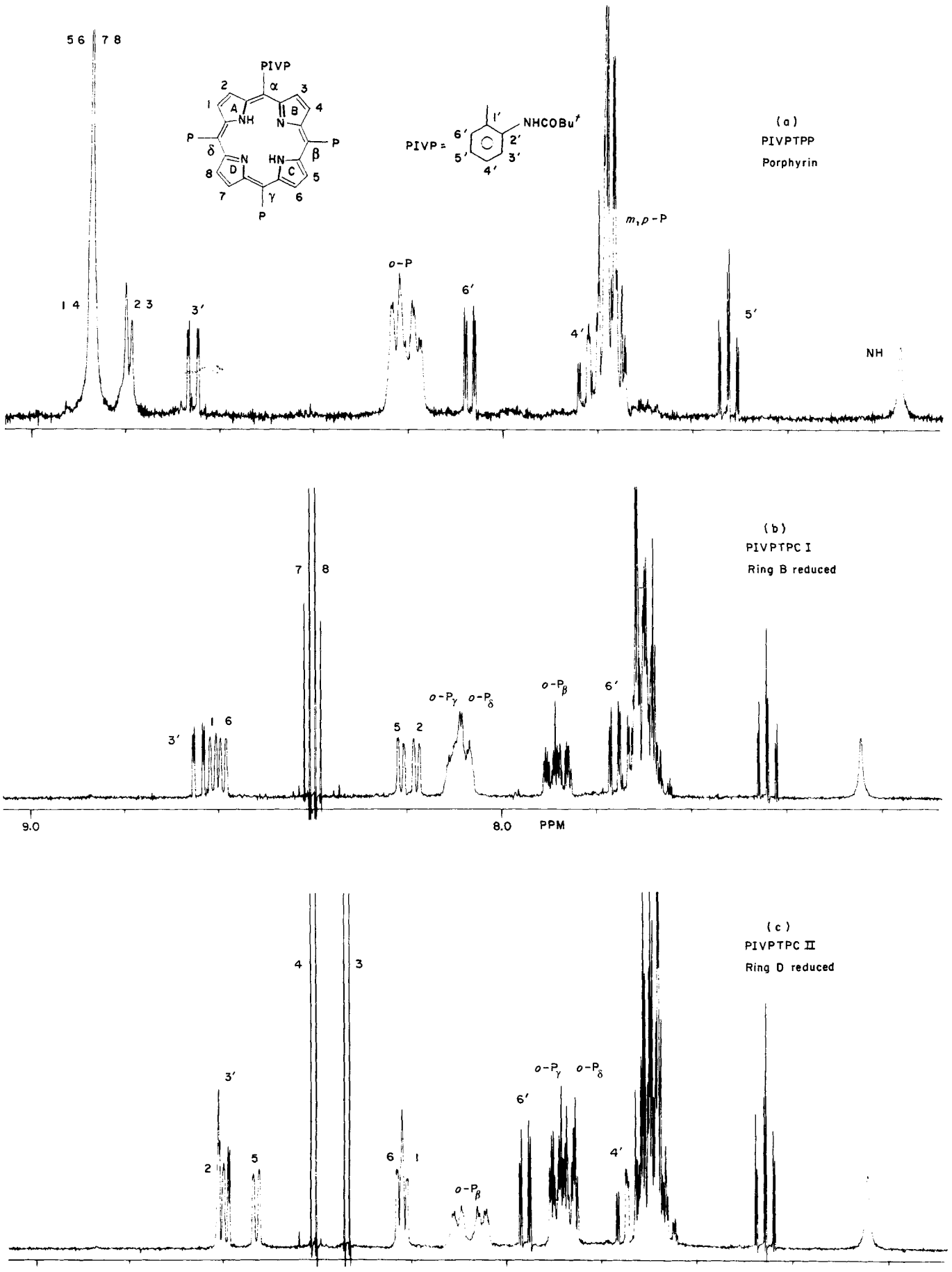


Figure 2. 400 MHz proton spectra at 293 K of free base PIVPTPP (a) and the related chlorins (b and c) in CD_2Cl_2.

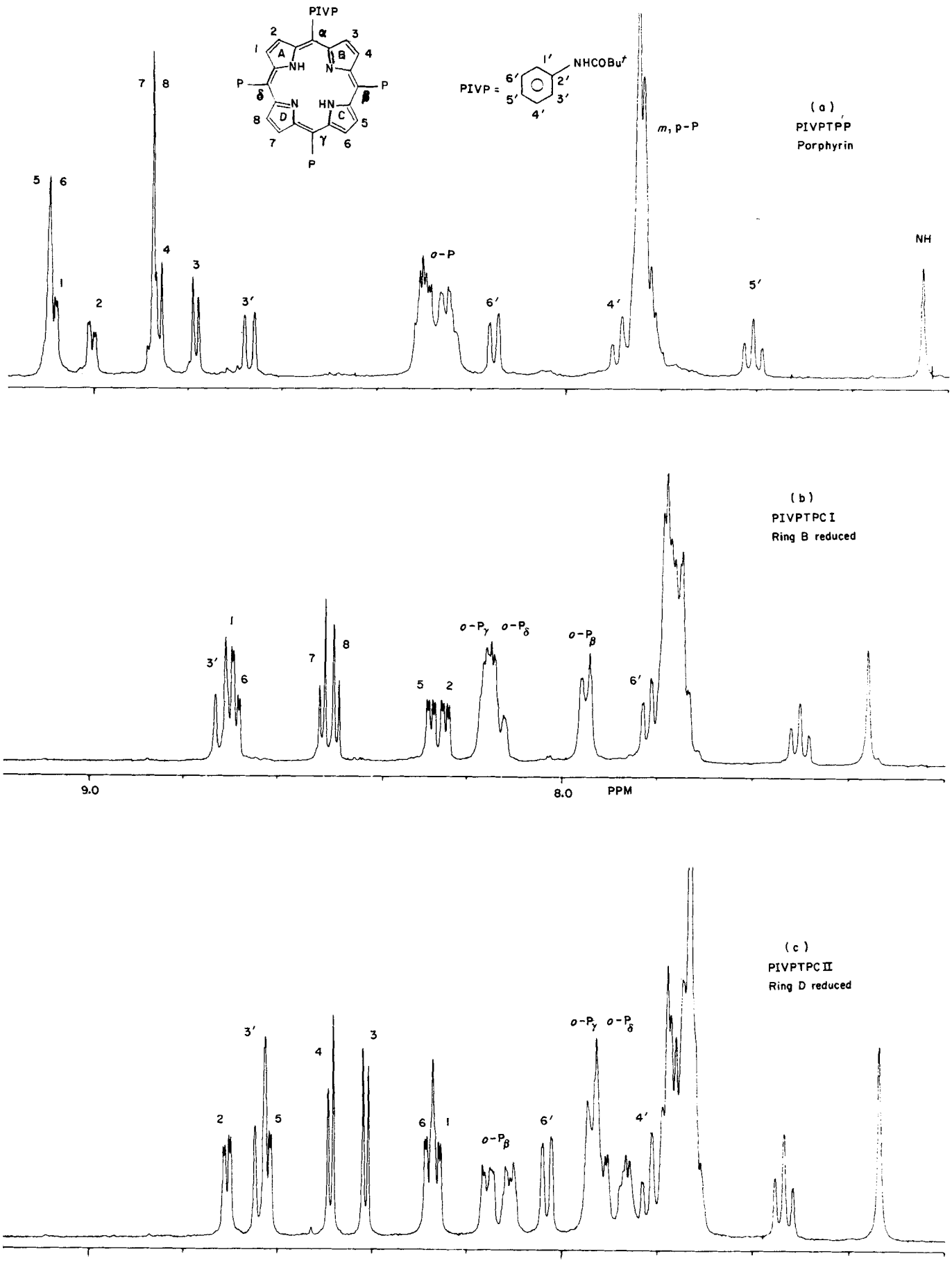


Figure 3. 400 MHz proton spectra at 192 K of free base PIVPTPP (a) and the related chlorins (b and c) in CD_2Cl_2.

Table 3. Proton chemical shifts (δ) and chemical shift differences (Δδ) between 2-chloropivaloylamidobenzene (4) and PIVTPP and the parent compounds

				Amide shifts		Ring current shifts	
Proton	δ(4)[a]	δ(C_6H_5Cl)[b]	δ(TPP)[c]	Δδ(4)[d]	Δδ(PIVTPP)[e]	Obs.[f]	Calc.
H-3′	8.36	7.24	7.80	1.12	0.86	0.30	0.48
H-4′	7.28	7.17	7.80	0.11	0.02	0.54	0.47
H-5′	7.04	7.24	7.80	−0.20	−0.27	0.49	0.48
H-6′	7.39	7.29	8.30	0.10	−0.23	0.68	0.80
tert-Bu	1.32	—	—			−1.22	−1.47
NHCO	7.97	—	—			−0.81	−0.18

[a] CD_2Cl_2 soln., 250 MHz.
[b] CCl_4 infinite dilution, from Ref. 26.
[c] $CDCl_3$ solution, from Ref. 20.
[d] δ(4) − δ(C_6H_5Cl).
[e] δ(PIVPTPP) − δ(TPP).
[f] δ(PIVPTPP) − δ(4).

intense singlet at δ 0.101 is assigned intuitively to the *tert*-butyl group, and shows a similar chemical shift to that found in Collmans 'picket fence' porphyrin.[17] The *ortho*-phenyl (*o*-P) protons are seen as a broad multiplet at δ 8.205 and the *meta*- and *para*-protons are assigned to the multiplet at δ 7.771. These shifts are similar to those observed in TPP.[20]

PIVPTPC-I. Reduction of one of the pyrrole rings, provisionally assigned to ring B for PIVPTPC-I, removes the element of symmetry present in the porphyrin and all the β positions would now be expected to be non-equivalent. The three AB systems thus predicted for the β protons of the chlorin are observed (Fig. 2b), and two of these are clearly broadened with respect to the other. In the chlorins, the N—H protons are more localized on the nitrogen atoms adjacent to the reduced ring.[2,19,20,27] The broadened resonances are thus assigned to the protons on rings A and C, broadening as before being due to long-range coupling to the nitrogen protons. Indeed, even at room temperature, the β-pyrrole nitrogen proton coupling is observable for some of the β signals. This localization is evident from the two broad singlets observed for the N—H resonances (δ −1.406; δ −1.296) which, as expected, show a downfield shift with respect to the porphyrin. Considerable shifts from the porphyrin β proton signals are observed, and the upfield doublets are assigned to H-2 [δ 8.179, ^3J(HH) = 4.99 Hz] and H-5 [δ 8.213: ^3J(HH) = 4.92 Hz] because of their position relative to the reduced ring. H-1 (δ 8.611) and H-6 (δ 8.589) are thus assigned to the downfield broadened doublets. The assignment for each AB system was confirmed by decoupling experiments, and the pairs of protons are assigned as given because the shift difference for H-1 and H-2 is expected to be more than that for H-5 and H-6 because of their position relative to the pivaloyl ring. The remaining sharp AB system is thus assigned to the ring D protons. The reduced ring protons of PIVPTPC-I consist of two complex multiplets at δ 4.172 and 3.948 of relative intensities 3 : 1, respectively. The upfield signal is tentatively assigned to the reduced ring proton closest to the amide function. The multiplicity of the reduced ring protons is discussed below in terms of the general assignment of PIVPTPC-I and PIVPTPC-II, having rings B and D reduced, respectively.

The pivaloyl phenyl protons were assigned by direct comparison with the parent porphyrin, and all show an upfield shift because of the proximity of the reduced pyrrole ring. Although H-3′, H-5′, H-6′ and the amide proton are still clearly distinguishable, H-4′ is now obscured by the *meta*- and *para*-protons of the phenyl rings and is thus assigned the same chemical shift. The *tert*-butyl signal is shifted downfield with respect to the porphyrin. The *ortho*-phenyl protons now show two clearly distinct sets of signals of relative intensity 2 : 1. The upfield multiplet is assigned to the *o*-P_β protons, because of their position relative to the reduced ring, and the downfield broadened multiplet to *o*-$P_{\gamma,\delta}$ which shows a similar chemical shift to that observed for the *ortho* phenyl protons in the parent porphyrin. The upfield signal is approximately first order and consists of two distinct protons, each with an evident *ortho*, *meta* and *para* coupling. That a sharp signal is observed for the *o*-P_β protons may be due to a restricted rotation of the phenyl group imposed by the adjacent reduced ring, and the chemical shift difference of the two *ortho* protons presumably reflects the asymmetry of the two sides of the porphyrin macrocycle introduced by the anisotropy of the amide group.

So that meaningful comparisons with the low-temperature spectrum of PIVPTPP may be made for the ring current calculations, a spectrum of PIVPTPC-I at 192 K was also obtained (Fig. 3b). Apart from minor shift differences (approximately 0.05–0.1 ppm downfield shifts for all signals except the chlorin N—H protons, which shift upfield by approximately 0.17 ppm) and broadening of resonances, no difference is observed from the room temperature spectrum. However, the β-pyrrole nitrogen proton coupling is now clearly distinguishable for the β protons of rings A and D [^4J(HH) = 4.94 Hz], although some overlapping is observed between H-1, H-6 and H-3′. No further coupling is seen for the β protons of ring D (H-7, H-8), confirming the previous assignment.

Surprisingly, the shift difference seen for the *o*-P_β protons at room temperature (approximately 11 Hz) is

not observed at 192 K. This presumably is due to the accidental equivalence of the two *ortho*-phenyl protons at this temperature, perhaps because of a change in the conformation of the carbonyl function. At room temperature it was proposed that smaller shifts of H-3′ compared with the equivalent proton in the chloro derivative was because some degree of rotation about the phenyl nitrogen bond was allowed in the porphyrin. At 192 K all the pivaloyl phenyl protons are shifted downfield with respect to the room temperature spectrum, but the value for H-3′ is approximately 0.015 ppm greater than those H-4′, H-5′ and H-6′. Although this is a very small increase in chemical shift, it is consistent with the tentative suggestion that the carbonyl moiety is now 'locked' in a position coplanar with the pivaloyl phenyl ring, remote from the adjacent phenyls, and thereby having a minimal effect on the o-P_β protons.

PIVPTPC-II. The assignments for PIVPTPC-II followed directly from those observed for the type I chlorin. Thus H-2 (δ 8.605), partially obscured by H-3′, and H-5 (δ 8.530) are assigned to the low-field broadened doublets and H-1 (δ 8.226) and H-6 (δ 8.215) overlap to form the high-field triplet structure, the AB systems again being identified by decoupling (Fig. 2c). The remaining sharp AB system is thus assigned to H-3 (δ 8.338) and H-4 (δ 8.408) and the shift difference, as expected from their proximity to the amide function, is greater for these protons than for H-7 and H-8 in PIVPTPC-I. The assignment of H-3 (and H-8 for the type I chlorin) to the upfield signal of the AB system is tentatively given on the basis of position with respect to the pivaloyl group, in view of the upfield shift observed for one of the reduced ring protons of PIVPTPC-I.

The pivaloyl phenyl protons of PIVPTPC-II, now more remote from the reduced ring compared with the type I chlorin, all show more similar chemical shifts to the parent porphyrin although a slight, upfield shift is again observed. H-4′ is no longer obscured and all the protons are distinguishable. The *tert*-butyl signal is again shifted downfield with respect to the porphyrin, but to a lesser extent than in PIVPTPC-I. The *ortho*-phenyl protons again show two distinct sets of resonances, but the ratio of the downfield to upfield intensities is now reversed (1:2) compared with the type I chlorin. Thus, the sharp upfield signals are assigned to the o-P_γ and o-P_δ protons adjacent to the reduced ring, and the downfield signal to o-P_β. The non-equivalence across the plane of the porphyrin is again seen in the broadened signals of the o-P_β protons, but a larger separation is now observed than for PIVPTPC-I (Table 1), the broadening presumably being due to a rotational effect of the phenyl group.

The low-temperature spectra (Fig. 3c) again showed the β-pyrrole nitrogen proton coupling for H-1, H-2, H-5 and H-6, with no further coupling for H-3 and H-4, and the broad signal observed for the N—H protons at room temperature is now resolved into two singlets. The separation of the o-P_β protons, although slightly smaller than at room temperature (approximately 18 Hz) is still clearly evident, but the o-P_γ and o-P_δ protons now show two sets of signals (approximately 25 Hz separation) of relative intensities 3:1. These observations must lead to some doubt about the proposed hypothesis for the low-temperature effects observed in the type I chlorin of an amide orientation more coplanar with the pivaloyl ring. Indeed, the downfield shift again observed for all the pivaloyl ring protons compared with the room temperature spectrum is now less for H-3′ (approximately 0.03 ppm) than for H-4′, H-5′ and H-6′. Obviously, the actual explanation is complicated, as solvent or association effects may be important at the two temperatures, and no further interpretation of the results was attempted.

The general assignment for PIVPTPC-I and PIVPTPC-II having rings B and D reduced, respectively, is thus supported by three independent observations:

1. Multiplicity of reduced ring protons. The complex multiplet observed for PIVPTPC-I compared with the singlet seen for PIVPTPC-II is consistent with the greater asymmetry introduced by the amide group around ring B than ring D.
2. The relative positions of the six *ortho*-phenyl protons. The downfield to upfield ratios for the *ortho*-phenyl protons of I and II are 2:1 and 1:2, respectively, again consistent with the given assignment.
3. The shifts of the pivaloyl ring and *tert*-butyl protons relative to the parent porphyrin. The shifts are less pronounced for the type II than the type I chlorin, indicating that the reduced pyrrole ring is remote from the pivaloyl phenyl ring in PIVPTPC-II.

Zinc complexes

All the zinc complex spectra were obtained with approximately 1–2 equivalents of pyrrolidine added to eliminate aggregation effects. Apart from minor shift differences, the zinc complexes showed little change from the free base proton spectra, and assignment followed directly. The β proton signals for the zinc complexes were all much sharper than those for the free base, owing to the removal of the β-pyrrole and nitrogen proton coupling. In all the metallochlorin spectra a small amount of Zn-PIVPTPP (<5%) was observed, presumably being formed by oxidation of the chlorin in the metal insertion reaction. No attempt at separation of the zinc porphyrin was made.

Chiral base studies

Because of our interest in the development of a diamagnetic chiral shift reagent for the determination of enantiomeric purities by NMR spectroscopy, chiral base studies with the zinc complexes of the two optically active chlorins were carried out. The use of zinc porphyrins as diamagnetic shift reagents for nitrogenous bases has been described, and their advantages over lanthanide shift reagents (LSR) in terms of specificity with multifunctional ligands have been discussed.[1,10,11] A recent review[15] describes the use of chiral LSR for the determination of optical purity, and shows the considerable advantages of the method

compared with the more classical techniques of chemical conversion[28,29] or use of a chiral solvent.[30] Thus, the development of a diamagnetic chiral shift reagent is thought to be desirable.

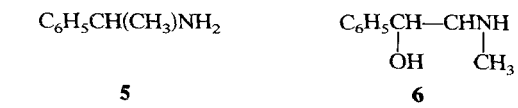
Although ideally we should like to separate the two enantiomers of the chlorins and run optically pure metallochlorin with the racemic mixture of the base, it is possible to check whether differential spectra are observable by using enantiomerically pure base with the racemic mixture of the chlorin. Under normal conditions the equilibrium between the substrate and zinc chlorin is rapid on the NMR time scale,[10] and a time-averaged spectrum results. There are two possible equilibria:

$$(R)\text{-base} + (R)\text{-chlorin} \overset{K_R}{\rightleftharpoons} (R)\text{-base-}(R)\text{-chlorin}$$

$$(R)\text{-base} + (S)\text{-chlorin} \overset{K_S}{\rightleftharpoons} (R)\text{-base-}(S)\text{-chlorin}$$

The *R–R* and *R–S* complexes are diastereomeric and can have different averaged chemical shifts. We might therefore expect to see differential spectra on addition of enantiomerically pure base.

On addition of approximately two equivalents of *d*(+)-α-methylbenzylamine (**5**) to a chloroform solution of Zn-PIVPTPC-II, changes are observed in the β proton signals compared with the uncomplexed zinc chlorin (Fig. 4). As can be seen, doubling up of all the β proton signals except H-4 occurs, the size of the splitting varying from *ca* 10 Hz for H-5 to *ca* 21 Hz for H-2. This doubling up was also seen for other protons in the chlorin, particularly for H-6′, but was complicated by considerable overlapping of signals. In contrast, however, the base signals, although exhibiting upfield shifts, were broad and ill-resolved and no further multiplicity from the free spectrum could be observed.



5 **6**

An interesting effect is seen in the difference in shifts between the uncomplexed and complexed species. On addition of the asymmetric base all the proton signals exhibit small upfield shifts of between 0.01 to 0.05 ppm, except H-3′ and the amide proton, which are shifted approximately 0.18 and 0.08 ppm downfield, respectively, compared with the uncomplexed species. A possible explanation of these observations is a participation via hydrogen bonding of the amide group with the complexing base.

Thus, the amide would be 'locked' into coplanarity with the phenyl ring causing a larger, downfield shift for H-3′ compared with the uncomplexed species, the usual hydrogen-bonded downfield shift being seen for the amide proton.

The optical base experiment was also carried out with (−)-ephedrine (**6**) for both types of metallochlorin, and again further multiplicity was seen for H-1, H-5 and H-6 for Zn-PIVPTPC-I and H-2 and H-5 in Zn-PIVPTPC-II. Extensive broadening of the base

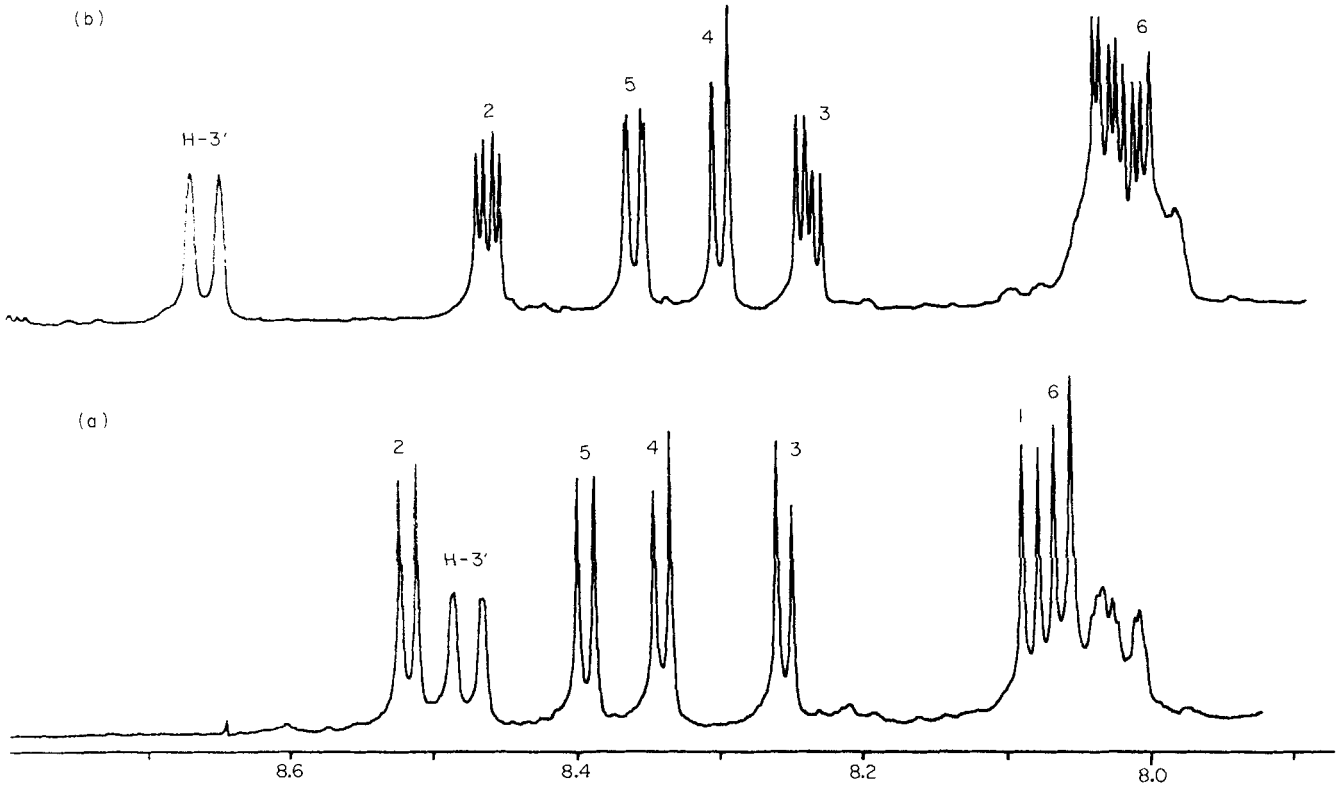


Figure 4. 400 MHz proton spectra of uncomplexed Zn-PIVPTPC-II (a), and with addition of approximately 2 equivalents of *d*(+)-α-methylbenzylamine (b) in $CDCl_3$.

signals was once more observed, and an attempt to 'freeze out' the equilibrium by cooling to −53 °C was made. Although larger upfield shifts of the ephedrine signals were seen compared with the room temperature spectrum, indicating that the equilibrium had certainly slowed, if not stopped, broadening of the signals was still evident, making resolution of the two diastereomeric forms impossible.

Enantiomeric base additions were also made for the parent zinc porphyrin, which showed increased multiplicity compared with the pyrrolidine addition. For *d*(+)-α-methylbenzylamine the resonances for H-5 to H-8 and H-2 and H-3 showed a multiplicity of 2 compared with the pyrrolidine spectrum. This is also seen for the (−)-ephedrine addition, in which all the β protons are doubled up, although slight overlapping is evident. This increased multiplicity is assigned to the removal of the plane of symmetry present in the metalloporphyrin by coordination of asymmetric base. It was also noticed that the base signals of *d*(+)-α-methylbenzylamine with the zinc porphyrin were now slightly sharper than for the metallochlorin addition. This leads us to the tentative suggestion that broadening may, at least in part, be due to exchange effects of the active base between the *d* and *l* forms of the racemic metallochlorin.

Therefore, although the results obtained are disappointing in that we were unable to observe the diastereomeric forms in the base signals, the fact that differences were observable for the porphyrin spectra encourages our search for a diamagnetic chiral shift reagent. At present, work is being carried out on the development of a chiral porphyrin which allows insertion of cobalt(III), impossible with the chlorins owing to oxidation effects, in which exchange between base and porphyrin is slow on the NMR time scale.[31-33] Thus, the induced shifts are much larger than the zinc complexes and, hopefully, any broadening due to exchange effects will be eliminated.

Ring current calculations

The double dipole model[9,10] has previously been described both for the porphyrin and 7,8-dihydro macrocycle ring current, and has proved successful in predicting the chemical shift differences of chlorophyll derivatives and their parent porphyrin structures.[14] We wish simply to apply this model to the two tetraarylchlorins described, and compare the observed and calculated shifts on reduction of the porphyrin macrocycle.

The model considers the porphyrin ring to be broken down into a number of current loops which are replaced by their equivalent dipoles. Symmetry allows only two kinds of equivalent dipole, those due to the pyrrole rings (μ_P) and the hexagons (μ_H), and the ring current shift at any point (R) is given by the summation of the individual dipoles using the standard dipole equation to give Eqn (1):

$$\delta_R = \sum_{i=1,8} \mu_{Hi} f(iR) + \sum_{j=1,8} \mu_{Pj} f(jR) \qquad (1)$$

where $f(iR)$ depends only on the coordinates of R. A close-range approximation is also included to allow for calculations within the ring current loop where the equivalent dipole approximation breaks down.[13]

The ring current shift differences ($\delta_{porphin} - \delta_{chlorin}$) of the chlorins have been shown to give good agreement with experimental values simply by removal of the dipole in the reduced ring and a general 10% reduction of the remaining dipoles.[14]

The calculated ring current shifts were obtained using a modified version of DIPCALC,[10] which includes the close range approximation.[14] The geometry of PIVPTPP was obtained directly from the known porphin geometry of TPP;[10] the amide group was assumed to adopt a coplanar, *cis*-carbonyl conformation with respect to the phenyl ring, the amide bond lengths and angles being taken from reported values for acetanilide.[34] A standard *tert*-butyl geometry was assumed (CC 1.54 Å, CH 1.09 Å) using tetrahedral carbons.

As a test both for the ring current model and the conformation of the amide group the calculated ring current shifts ($\Delta\delta$) for the pivaloyl ring were compared with observed values taking the shifts for 2-chloropivaloylamidobenzene (**4**) as the reference compound ($\Delta\delta_{obs} = \delta_{porphyrin} - \delta_{reference}$), in which the amide group adopts the same approximate conformation as that assumed for PIVPTPP, but where there is no external ring current. The observed and calculated shifts are shown in Table 3.

In view of the limitations of the chloroamide as a suitable reference compound, the agreement between observed and calculated ring current shifts is surprisingly good. In particular, the large upfield shift of the *tert*-butyl group induced by the ring current is well reproduced. This agreement, together with the deshielding effect of the carbonyl group on H-3′ (see earlier), substantiates the given conformation of the amide moiety. That the amide proton shows a large discrepancy between observed and calculated values is to be expected, because of large differences in hydrogen bonding effects between the reference and porphyrin compounds. These results were obtained with a C-*meso*, C-1, C-2 angle of 120°, and we were interested to determine whether the pivaloyl phenyl ring might tilt to relieve steric interactions of the *tert*-butyl group with the porphyrin. However, a computational search of the above angle between 110° and 130° gave very little variation of the RMS error between calculated and observed $\Delta\delta$ values, and the value of 120° for the above angle was assumed both for the porphyrin and its reduced products.

The observed and calculated chemical shift differences ($\delta_{porphyrin} - \delta_{chlorin}$) for the two reduced products are shown in Table 4. The calculated values for I and II are obviously the same and only vary positions because of the different locations of the reduced ring in the two chlorins. Both are included for ease of comparison.

We shall first consider the two pyrrole rings A and C, adjacent to the reduced ring in each chlorin. As can be seen, good agreement is seen for the protons remote from the reduced ring in I (H-1, 6) and the averaged value for II (H-2, 5), although we are unable to explain the large difference in the observed values

Table 4. Observed and calculated proton chemical shift differences ($\delta_{porphyrin} - \delta_{chlorin}$) of PIVPTPP and its two reduced products

	PIVPTPC-I				PIVPTPC-II			
	Observed		Calculated		Observed		Calculated	
Proton	Free base[a]	Zn complex[b]	[c]	[d]	Free base[a]	Zn complex[b]	[c]	[d]
H-1	0.39	0.45	0.46	0.42	0.81	0.84	0.55	0.53
H-6	0.41	0.47			0.83	0.88		
H-2	0.76	0.85	0.55	0.53	0.30	0.33	0.46	0.42
H-5	0.82	0.90			0.48	0.53		
H-3	—	—			0.37	0.55	0.42	0.38
H-4	—	—			0.37	0.57		
H-7	0.37	0.60	0.42	0.38	—	—		
H-8	0.40	0.61			—	—		
H-3′	−0.05	0.06	0.14	0.16	0.03	0.10	0.07	0.09
H-4′	0.13	0.16	0.14	0.16	0.08	0.09	0.07	0.09
H-5′	0.10	0.12	0.14	0.16	0.07	0.09	0.07	0.09
H-6′	0.34	0.36	0.20	0.24	0.13	0.18	0.13	0.16
o-P_β	0.32	0.38	0.20	0.24	0.14	0.16	0.13	0.16
o-P_γ	0.13	0.18	0.13	0.16	0.38	0.41	0.20	0.24
o-P_δ	0.13	0.16			0.38	0.36		
m,p-P	0.08	0.11	0.11	0.13	0.09	0.10	0.11	0.14
tert-Bu	−0.17	−0.31	−0.39	−0.45	−0.05	−0.14	−0.13	−0.17
NHCO	−0.11	−0.13	0.01	−0.05	−0.09	0.08	0.06	0.00
N—H	−1.46	—	−0.87	−2.36	−1.30	—	−0.87	−2.36

[a] CD_2Cl_2; −81 °C.
[b] $CDCl_3$; ambient temperature.
[c] 10% overall reduction in μ_H and μ_P.
[d] 25% reduction in μ_H.

for these protons. However, for the protons adjacent to the reduced ring, large discrepancies between calculated and observed values are seen. We have reported similar observations for the corresponding protons of TPP and TPC,[35] and the same explanation of a different orientation of the phenyl groups adjacent to the reduced ring in the chlorin compared to the porphyrin is used here. This seems a reasonable assumption in view of the puckered nature of the pyrrolenine ring in the chlorin compared to the planar porphyrin, and is also consistent with the discrepancies observed for the *ortho*-phenyl protons adjacent to the reduced ring in both I and II. The protons on the pyrrole rings remote from the reduced ring, 7 and 8 for I, 3 and 4 for II, show good agreement between observed and calculated values for the free base. However, discrepancies are seen for the zinc complexes, which show a constantly larger observed shift difference of approximately 0.2 ppm for the corresponding protons compared with the free base. We are unable to find a satisfactory explanation for this anomaly, although incomplete elimination of aggregation effects, more pronounced for the zinc complexes than the free base, may be important. The difference could not reasonably be assigned to either a solvent or temperature effect, because of the generally good agreement for the remaining protons of the free base and zinc complexes.

The *meta* and *para* protons and the *ortho*-phenyl protons remote from the reduced ring all show good agreement between calculated and observed shift differences, although a discrepancy is seen for H-3′ in PIVPTPC-I. This presumably reflects the sensitivity of H-3′ to the anisotropic effect of the carbonyl moiety which may undergo a slight change in conformation for I, in view of the proximity of the pyrrolenine ring, compared to II and the parent porphyrin.

The negative observed shift differences for the *tert*-butyl and nitrogen protons are well reproduced in the calculated values, although again differences are seen between the free base and zinc complexes. The shifts of the amide proton are presumably sensitive to solvation and conformational effects and are not discussed further.

We are interested to see if Woodward's alternative approach[8,8a] to the macrocycle ring current, in which the pyrrole rings as independent aromatic subunits would remain unchanged on formation of the chlorin, could give better agreement between the observed and calculated N—H shifts. It was thus decided to keep the pyrrole dipoles constant and arbitrarily vary the hexagon dipoles until good agreement between experimental and observed shifts could be seen for the β protons remote from the reduced ring, as these protons did not show the discrepancies discussed earlier. A reduction of 25% in the hexagon dipoles gave good agreement, not only for the remote β protons but also for the remaining protons (Table 4), although the usual discrepancy is seen for the β and *ortho*-phenyl protons adjacent to the reduced ring. The N—H protons now show considerably larger calculated shifts (approximately 1 ppm) compared with the experimental values. The difference between the calculated and observed values could be due to a decrease in NH---N hydrogen bonding in the chlorin compared with the more basic porphyrin.

Alternatively, precise agreement with the observed NH shifts could be obtained by suitable manipulation

of the hexagon and pyrrole dipoles. However, without a further check, such calculations would not be definitive.

EXPERIMENTAL

Syntheses

5-(*o*-Aminophenyl)-10,15,20-triphenylporphyrin[16] (AMPTPP). Benzaldehyde (30.6 ml), *o*-nitrobenzaldehyde (22.65 g) and pyrrole (31 ml) were added simultaneously to refluxing propionic acid (1.25 l) and the mixture was boiled under reflux for 25 min. On cooling, the black, tarry product was collected at the pump, dissolved in dichloromethane and purified by filtration through a bed of TLC-grade silica to remove excessive base-line material. The mixture of nitroporphyrins obtained was reduced to aminoporphyrins with concentrated HCl (350 ml) and ground tin(II) chloride (32.5 g of the dihydrate) at reflux for 30 min. The mixture was carefully neutralized with concentrated aqueous ammonia and the porphyrins were extracted into chloroform. The desired product was obtained by column chromatography (Grade 1 alumina; toluene–ethyl acetate eluent) as the second fraction. Recrystallization from dichloromethane–methanol gave dark purple crystals (3.41 g, 4.9% based on pyrrole): NMR ($CDCl_3$) (for numbering system see Fig. 1) 8.897 (d, H-1,4); 8.850 (d, H-2,3); 8.842 (s, H-5,6, H-7,8); 8.201 (m, *o*-P); 7.879 (d of d, H-6); 7.731 (m, *m*, *p*-P); 7.567 (t of d, H-4′); 7.151 (t of d, H-5′); 7.064 (d of d, H-3′); 3.509 (bd. s, $—NH_2$); −2.740 (s, N—H).

5-(*o*-Pivaloylaminophenyl)-10,15,20-triphenylporphyrin (PIVPTPP). AmPTPP (1.2 g), pivaloyl chloride (3.6 ml) and pyridine (3.6 ml) were stirred in dichloromethane (250 ml) for 1.5 h at room temperature. The reaction mixture was then washed first with dilute aqueous ammonia and then twice with water. After drying over anhydrous magnesium sulphate the porphyrin was reduced to dryness on a rotary evaporator and purified by column chormatography (Grade 1 alumina; toluene–ethyl acetate eluent). Recrystallization from dichloromethane–methanol give a fine purple solid (1.10 g, 81.1%), m.p. >300 °C; $\lambda_{max.}$ (CH_2Cl_2) 418 nm (ε 371000), 514 (17500), 549 (6800), 589 (5400), 646 (3800). Mass spectrum: *m/e* 713 (M^+). Elemental analysis: calc. for $C_{49}H_{39}N_5O$: C, 82.4; H, 5.5; N, 9.8%. Found: C, 81.45; H 5.49; N, 9.83%.

3,4-Dihydro-5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (PIVPTC-1) and 7,8-dihydro-5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (PIVPTPC-II). A mixture of PIVPTPP (0.52 g, 0.73 mmol), *p*-toluenesulphonylhydrazine (0.3 g), anhydrous potassium carbonate (1.0 g) and dry pyridine (40 ml) was heated with stirring at 105 °C under nitrogen. Five further additions of 0.3 g of the hydrazine were made over a total period of 8.5 h, the course of the reaction being followed spectrophotometrically. The reaction mixture was then added to a mixture of benzene (500 ml) and water (250 ml) and digested on a steam-bath for 1 h. The separated benzene layer was washed with cold 3 M hydrochloric acid, water and saturated sodium hydrogen carbonate solution. Analysis of the visible spectrum of the benzene solution showed it to be a mixture of the chlorin (80.6%) and bacteriochlorin (19.4%) ($\lambda_{max.}$ and ε values were estimated from literature values of tetraphenylchlorin and tetraphenylbacteriochlorin[36–38]).

o-Chloroanil (42 mg, 0.17 mmol) was then added to the benzene solution and the mixture stirred at room temperature for 1 h. The benzene solution was washed with 5% aqueous sodium hydrogen sulphite solution, 5% sodium hydroxide solution, 250 ml of 70% (w/w) phosphoric acid (to remove residual PIVPTPP), water and saturated sodium hydrogen carbonate solution, dried over anhydrous magnesium sulphate and reduced to dryness on a rotary evaporator. The mixture of chlorins was recrystallized from dichloromethane–methanol to give a purple powder (0.33 g, 63.6%). No trace of PIVPTPP was observed in the ^1H NMR and UV–visible spectrum of the mixture, indicating that the reduction was complete. The mixture of chlorins (0.31 g) was separated using column chromatography (Grade II alumina; toluene eluent), PIVPTPC-I being collected as the first fraction. An initial 100 g column was required to provide a rough separation, followed by two 50 g columns for each chlorin to give pure samples of PIVPTPC-I and PIVPTPC-II. The chlorins were recrystallized from dichloromethane–methanol to give PIVPTPC-I (0.10 g, 32.3% from the mixture) and PIVPTPC-II (0.14 g, 45.2% from the mixture).

PIVPTPC-I: $\lambda_{max.}$ (CH_2Cl_2) 417 nm (ε 77500), 517 (6200), 543 (4500), 597 (2400), 650 (15700). Mass spectrum: *m/e* 715 (M^+). Elemental analysis: calc. for $C_{49}H_{41}N_5O$: C, 82.2; H, 5.8; N, 9.8%. Found: C, 81.53; H, 5.86; N, 9.82%.

PIVPTPC-II: $\lambda_{max.}$ (CH_2Cl_2) 420 nm (ε 175000), 519 (14400), 545 (9000), 598 (5700), 653 (32000). Mass spectrum: *m/e* 715 (M^+). Elemental analysis: calc. for $C_{49}H_{41}N_5O$: C, 82.2; H, 5.8; N, 9.8%. Found: C, 81.77; H, 6.03; N, 9.86%.

Zinc-5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin[2] (Zn-PIVPTPP). To PIVPTPP (0.2 g) in dichloromethane (100 ml) a saturated solution of zinc acetate in methanol (10 ml) was added and the mixture boiled under reflux for 30 min. The metalloporphyrin was obtained by addition of methanol (100 ml) and slow evaporation of the dichloromethane on a rotary evaporator to give purple crystals (0.21 g, 96.5%). $\lambda_{max.}$ (CH_2Cl_2) 418 nm (ε 414000), 510 (2900), 548 (22000), 585 (3100).

Zinc-3,4-dihydro-5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (Zn-PIVPTPC-I) and zinc-7,8-dihydro-5-(*o*-pivaloylaminophenyl)-10,15,20-triphenylporphyrin (Zn-PIVPTPC-II).[18] Zinc acetate (35 mg) was added to the chlorin (35 mg) in dimethylformamide (100 ml) and the mixture boiled under reflux under nitrogen for 1 h. The reaction mixture was cooled and distilled water (100 ml) added. The precipitated porphyrin was extracted into dichloromethane and the separated organic layer washed with water (3 × 100 ml), dried over

anhydrous magnesium sulphate and reduced to dryness on the rotary evaporator. The metallochlorin was recrystallized from dichloromethane–hexane to give a dark green powder. Purification of Zn-PIVPTPC-II by column chromatography (Grade III alumina, toluene-ethyl acetate eluent) was required to give an adequate sample. The UV–visible spectra (values below) were similar to the literature values for Zn-TPC.[36]

Zn-PIVPTPC-I: $\lambda_{max.}$ (CH_2Cl_2) 620 nm (ε 50000); 582 (13600); 550 (11400); 513 (10700); 415 (370000).

Zn-PIVPTPC-II: $\lambda_{max.}$ (CH_2Cl_2) 624 nm (ε 55000); 585 (15700); 552 (13500); 517 (13500); 418 (300000).

Spectral measurements

The ^{1}H NMR spectra were recorded on a Bruker WH400 (400.13 MHz) instrument at approximately 21 °C. The spectra were obtained in $CDCl_3$ at a concentration of approximately 2.8×10^{-2} M, the solvent providing the internal deuterium lock. Typical conditions for the ^{1}H spectra were a spectra width of 7000 Hz, using 32K data points for acquisition and a pulse width of 5 μs (45°). A Lorentzian–Gaussian conversion was applied to the FID before Fourier transformation. NMR tubes of 5 mm o.d. were used and all chemical shifts were measured relative to TMS.

Acknowledgements

We thank Drs B. E. Mann and C. Spencer for the ^{1}H NMR spectra run on the Bruker WH400 spectrometer on the SERC service. We also acknowledge the use of the University of Liverpool computing facilities and J.E.P. acknowledges an SERC CASE award.

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Received 26 March 1983; accepted 23 May 1983