Carbon-13 Nuclear Magnetic Resonance in High Spin Iron(III) Porphyrins: a Reassignment

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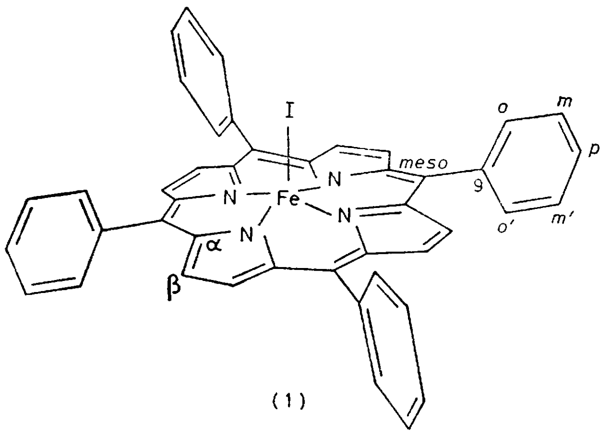
Summary The observation of a new resonance in the ^{13}C n.m.r. spectrum of a high spin iron(III) *meso*-tetraphenylporphyrin, the resolution of previously unresolved spin–spin splittings, and the synthesis of a ^{13}C enriched porphyrin permit a complete reassignment of the spectrum which shows unexpectedly large paramagnetic shifts of the *ortho* phenyl carbon resonances previously assigned to pyrrolic carbon signals.

Goff has recently reported[1] the ^{13}C n.m.r. spectra of high spin iron(III) porphyrins. The spectrum of the iron(III) tetraphenylporphyrin chloride (Fe^{III}TPP Cl) exhibits, outside the diamagnetic range, a resonance at -76 p.p.m. and two resonances near $+400$ p.p.m. assigned, respectively, to the *meso* carbons (high field) and the α and β pyrrolic carbons (low field).

We have synthesized a *meso* ^{13}C enriched *p*-tolyl porphyrin by acid condensation with pyrrole[2] of a ^{13}C tolaldehyde prepared[3] from 90% enriched ^{13}CO (Mound Lab.). Its high-spin iron(III) chloride complex exhibits a resonance at $+498$ p.p.m. with a linewidth of 400 Hz at 34 °C. This resonance does not correspond to any of the reported ones.



(1)

Reinvestigating the ^{13}C n.m.r. spectrum of Fe^{III}TPP Cl at natural abundance, using a 18 mm probe on a Varian XL 100 spectrometer, we could indeed observe this broad resonance, the spectrum being otherwise identical to the previously published one.[1]

We used an earlier suggestion of La Mar *et al.*[4] for improving the resolution by a judicious choice of axial ligand, the iodo complex being expected to give the sharpest lines owing to larger zero field splitting. The ^{1}H n.m.r. spectrum of Fe^{III}TPP I (**1**) is indeed completely resolved allowing the observation of the two inequivalent phenyl *ortho* protons at δ 12 and 6·5 at 34 °C.[4,5] Furthermore, the carbon resonances near 400 p.p.m. both exhibit a resolved splitting of *ca.* 120 Hz characteristic of a $^{1}J_{CH}$ coupling. Selective decoupling of each *ortho* phenyl proton, facilitated by the good resolution of the proton spectrum, permits direct assignment of these resonances to the corresponding *ortho* phenyl carbons (Figure). The inequivalence in the proton as well as in the carbon spectra is due to the out of plane displacement of the iron ion.[6] In the former case this inequivalence arises mainly from the difference in the dipolar interaction with the electron spin, with the 'upper' proton shifted to low field. Contrary to previous statements,[1] we observed only three resonances near 150 p.p.m. assigned by selective decoupling to the two inequivalent *meta* carbons (156 and 149 p.p.m.) and the *para* carbon (144 p.p.m.) of the phenyl ring. The *meso* carbon resonance, at 475 p.p.m., is now clearly resolved (Figure). The last observed resonance at -72 p.p.m. has a line width of only 80 Hz and does not exhibit any resolved J_{CH} coupling. The lack of narrowing upon irradiation of the β protons indicates that this resonance should correspond either to the α pyrrole or to the quaternary phenyl carbons. Owing to its small linewidth as compared to the *meso* carbon one (200 Hz) the assignment to the quaternary phenyl carbons is obvious. A search for other resonances was unsuccessful in the range $+850$ to -250 p.p.m.

The isotropic shifts of the observed resonances have been referenced to the diamagnetic ZnTPP complex[7] (Table 1).

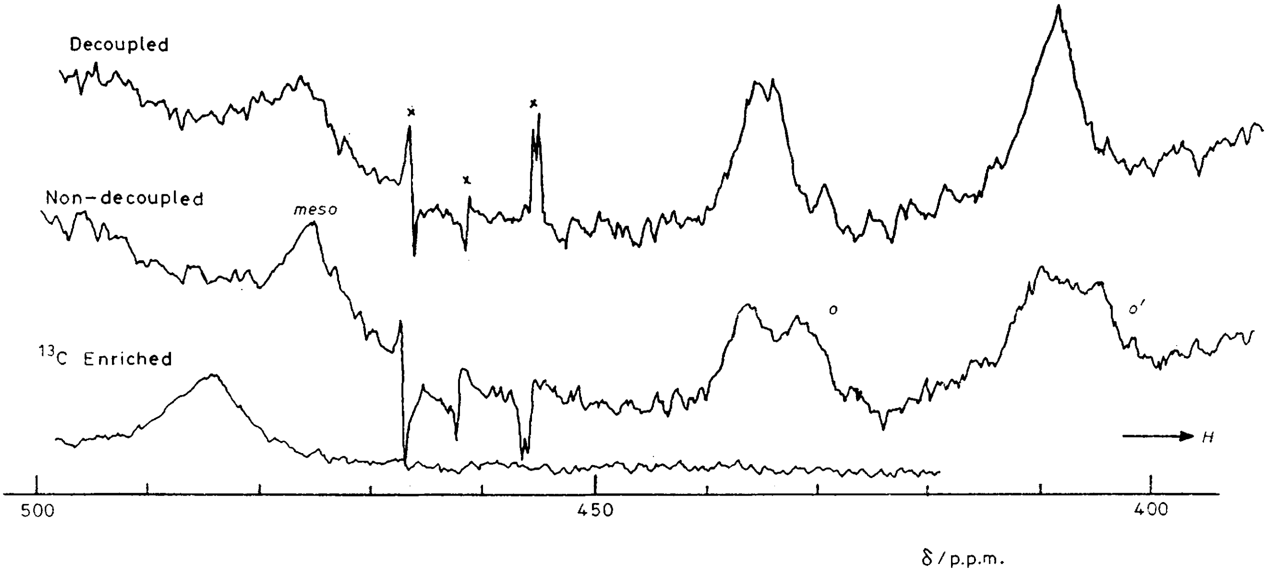


Figure. Low field part of the 25 MHz ^{13}C n.m.r. spectrum of Fe^{III}TPP I, at natural abundance ($3{\cdot}7 \times 10^{-2}$ M in CDCl$_3$, 300 000 transients, full spectral width of 12 000 Hz, and acquisition time of 0·17 s) with (32 °C) and without (34 °C) phenyl proton decoupling and of a *meso* ^{13}C enriched (90%) sample (4×10^{-3} M in CDCl$_3$, 8000 transients). The shift of 10 p.p.m. to high field of the *meso* carbon resonance of the unlabelled compound is probably due to association effects. The crosses indicate spurious signals corresponding to folded over high field resonances.

TABLE 1. Paramagnetic isotropic shifts δ_p in p.p.m. (positive to low field) of the observed ^{13}C resonances in Fe^{III}TPP I and estimated metal centred dipolar contribution δ_d, at 34 °C.

Position	*meso*	Quaternary phenyl	*ortho*		*meta*		*para*
δ_p	353	−215	299	273	28·5	21·5	16
δ_d	32	11	7	5·3	3·7	3·1	2·9

The metal centred dipolar contribution to these shifts was estimated from equation (1) which holds for a pure high spin d^5 complex,[8] where D is the zero field splitting parameter, T the absolute temperature, and $(3\cos^2\theta - 1)/r^3$ the geometrical factor which can be calculated from crystallographic data.[6] D was estimated to be *ca.* 18·5 cm^{-1} from the ^{1}H n.m.r. data of the iodo complex.[4] The resulting contact contributions, including perhaps the ligand centred dipolar terms, are given in Table 2 and compared with the proton contact shifts. The contact shifts of the proton substituted at the *meso* carbons in the octaethylporphyrin have the same sign as those of the quaternary phenyl carbons in TPP. They both have a sign opposite to that of the shift of the *meso* carbons, agreeing with a mechanism of dominant π spin delocalization on that position of the porphyrin ring.[5] In contrast, the phenyl carbon shifts do not correlate with the corresponding proton shifts, in disagreement with a π-type delocalization in the phenyl ring suggested by the alternation of sign of the proton contact shifts.[5] In particular, the contact shift which is unexpectedly 43 times larger for the *ortho* phenyl carbons as compared to the corresponding protons and the drastic decrease of this shift for the *meta* carbons suggest a strong mixing of the σ-type orbitals of the phenyl group with the $2p_z$ orbitals of the *meso* carbon atoms.

$$(\Delta\nu/\nu)_{\text{dip.}} = K(D/T^2)\,(3\cos^2\theta - 1)/r^3 \qquad (1)$$

Such a shift pattern of the phenyl carbons results from the presence of a positive π spin density at the *meso* carbon atoms. In fact, a similar pattern, with sign reversal occurs in unliganded (S=1) iron(II) porphyrins (Table 2) owing to the fact that the *meso* carbon in this reduced state bears a negative π spin density.[10,11] In both systems, the contact shifts of the quarternary and *ortho* phenyl carbons are nearly equal, but opposite in sign, confirming definitely the assignment of the observed high field resonance to the quaternary phenyl carbons.

TABLE 2. Comparison of the ^{1}H and ^{13}C contact shifts in p.p.m. (positive to low field), including the ligand centred dipolar contribution, in Fe^{III}TPP I and a derivative of Fe^{II}TPP at 34 °C.

Position	*meso*	Quaternary phenyl	*ortho*		*meta*		*para*
^{1}H Fe^{III}	−80[c]	—	−6·1	−6·9	3·4	2·6	−3·4
^{13}C Fe^{III}	321	−226	292	268	25	18	13
^{13}C Fe^{II}[a]	−137	47	−45			−1·6	−1·5
^{1}H Fe^{II}[b]	22[c]	—	1·58			−0·4	+0·03

[a] From ref. 9. [b] From ref. 10. [c] The *meso* proton shifts are those observed in an octaethylporphyrin complex.

The resonance observed near 400 p.p.m. in natural iron(III) porphyrins[1] must therefore be assigned to the protonated *meso* carbons rather than to the β pyrrole carbons. The resonances of the β-carbons, as well as those of the α pyrrole carbons, should be broadened beyond observation or shifted out from the accessible experimental range.

The financial aid of the Institut National de la Santé et de la Recherche Médicale is acknowledged.

(*Received*, 17*th May* 1979; *Com.* 526.)

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