Carbon-13 Nuclear Magnetic Resonance in Isotopically Enriched High-spin Iron(III) Porphyrins: π-Electron Spin Distribution

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The ^{13}C n.m.r. spectrum of high-spin chloro(5,10,15,20-tetraphenylporphyrinato)iron(III) has been unambiguously assigned using porphyrins isotopically enriched at selected positions. The unexpected linewidth of the resonances of the porphyrin core carbons is explained by the dipolar interaction of the carbon nuclei with the ligand unpaired π-electron spin densities. This interaction is the dominant mechanism of relaxation for the *meso* carbons and the pyrrole β carbons. The relative contribution of this mechanism increases for nuclei farther from the iron ion. As a result, it is also the dominant mechanism for the relaxation of the porphyrin protons. The π spin distribution on the porphyrin ring has been derived from the dipolar contribution to the linewidth for the carbon nuclei. Furthermore, the experimental β proton resonance linewidth can be interpreted only by considering a normalized iron spin density lower than unity. A value of 3.5/5 is proposed in good agreement with earlier molecular-orbital calculations. This analysis provides a set of self-consistent data for the quantitative description of the various contributions to the observed shifts, including the ligand-centred pseudo-contact contribution, and to the linewidth for both the proton and the carbon nuclei.

VALUABLE insight into the magnetic and electronic properties of the active site of haem proteins can be afforded by ^{13}C n.m.r. spectroscopy of iron porphyrin complexes in their various redox and spin states.[1-3] The carbon atoms of the porphyrin skeleton are of particular interest. In a recent paper [3] we reassigned some resonances in high-spin iron(III) ($S = \frac{5}{2}$) complexes using a 5,10,15,20-tetra(*p*-tolyl)porphyrin (ttp) selectively enriched at the *meso* carbon position. At natural abundance, the ^{13}C resonances of the α and β pyrrolic carbons were not observed, due to severe broadening in the chloro- as well as in the iodo-complexes. These resonances have been observed by Phillippi and Goff [4] in a dimeric sulphate complex which exhibits relatively narrow lines in the high-spin iron(III) state. However, they could not be assigned conclusively, thus preventing any interpretation in terms of electronic structure.

We have now synthesized 5,10,15,20-tetraphenylporphyrins (tpp) selectively enriched in ^{13}C at the α and β positions providing straightforward assignments and permitting the analysis of both paramagnetic shifts and linewidths mainly in terms of π-electron spin delocalization.

EXPERIMENTAL

5,10,15,20-Tetraphenylporphyrin was prepared by the usual condensation reaction of pyrrole and benzaldehyde.[5] The *meso* enriched compound was prepared as previously reported [3] using benzaldehyde enriched at the aldehyde group. The synthesis of pyrrole enriched at the α [C(2) and

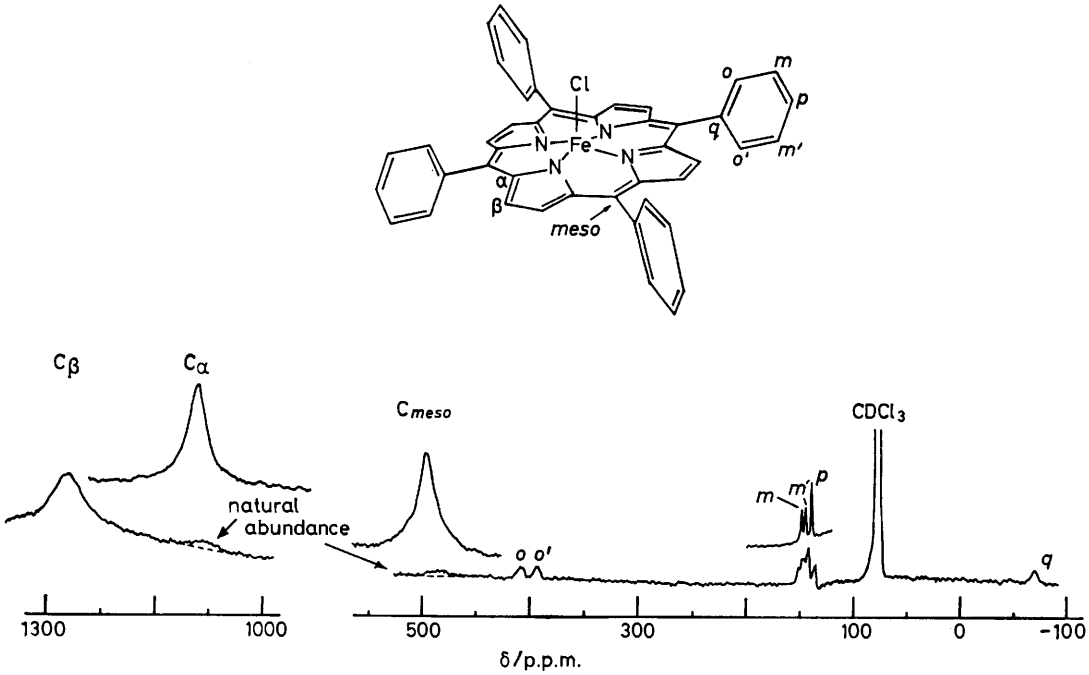
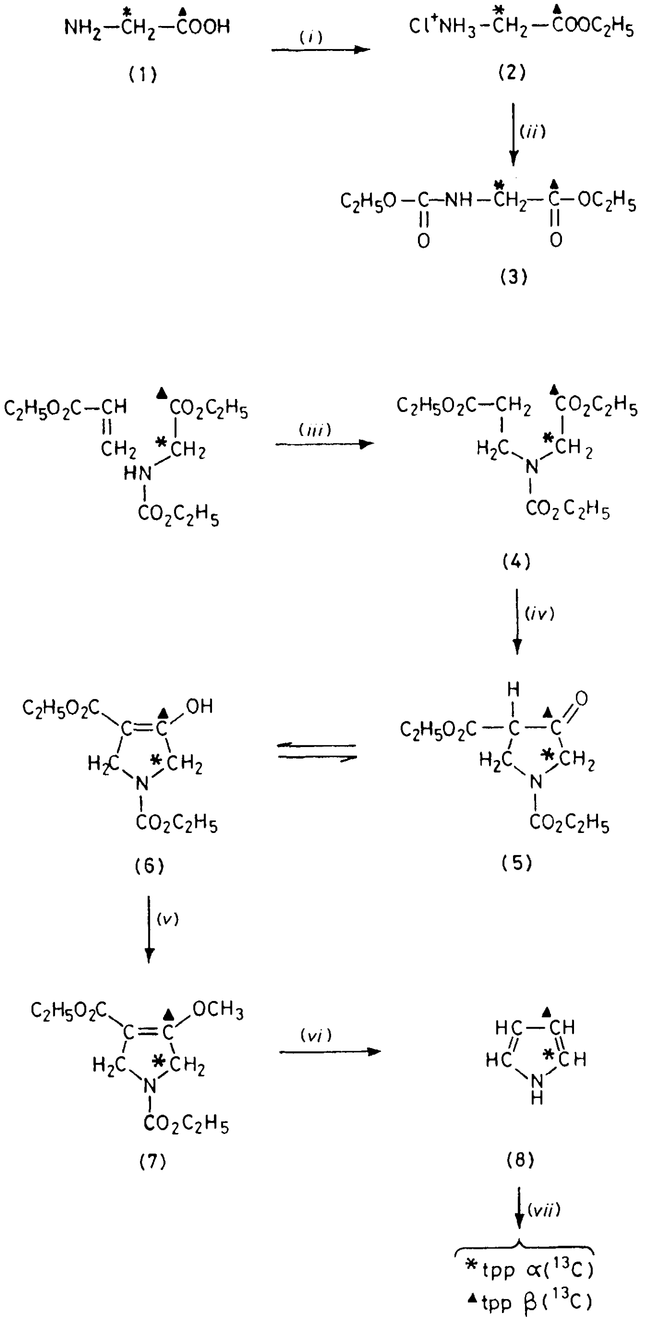


FIGURE 1 Carbon-13 n.m.r. spectra of [Fe^{III}(tpp)Cl] with complete assignment, at 34 °C

C(5)] or the β [C(3) and C(4)] position followed a modified Rapoport's method [6,7] starting from glycine selectively enriched at C(1) or C(2) (90%; Merck, Sharp and Dohme Co., Canada) and following the Scheme.

Glycine (1) was transformed into the *N*-ethoxycarbonylglycine ethyl ester (3) by esterification and subsequent acylation of the amino-group with ethyl chloroformate in a dichloromethane–water heterogeneous mixture at 0 °C in the presence of an excess of magnesium oxide. The Michael condensation of (3) with ethyl acrylate gave the triester (4) which undergoes a Dieckmann ring closure in refluxing benzene with sodium to yield diethyl 4-hydroxy-Δ^3-pyrroline-1,3-dicarboxylate (6) in 92% yield *via* diethyl 1,4-bis(ethoxycarbonyl)pyrrolidin-3-one (5).[8] The 4-methoxypyrroline derivative (7) was then prepared from (6) by using dimethylsulphate in dry acetone in the presence of $K_2[CO_3]$ (79.5% yield after distillation). This procedure was preferred to the diazomethane technique which gives the methoxy-derivative in lower yield (53%). Attempts to remove the methoxy- and the *N*-ethoxycarbonyl group of (7) to obtain ethyl pyrrole-3-carboxylate by aqueous $Ba[OH]_2$ according to Rapoport and Willson [7] were unsuccessful. However, the desired unsubstituted pyrrole (8) may be obtained in high yield (67%) in a single-step reaction. Saponification, demethoxylation, decarboxylation, and distillation occur directly by heating (7) with sodium hydroxide in diethylene glycol from 70 to 180 °C.



SCHEME (*i*) HCl, C_2H_5OH, 97.5%; (*ii*) $ClCO_2Et$, MgO, 94%; (*iii*) Michael condensation, Na; (*iv*) Dieckmann ring closure, 92%; (*v*) Me_2SO_4, $K_2[CO_3]$, 79.5%; (*vi*) Na[OH], H_2O, diethylene glycol, 67%; (*vii*) PhCHO, 23% yield

Anaerobic insertion of iron into the labelled porphyrins to give chloro(5,10,15,20-tetraphenylporphyrinato)iron(III), $[Fe^{III}(tpp)Cl]$, was carried out as described by Rothemund and Menotti.[9] Treatment of the μ-oxo-iron(III) dimer by hydroiodic acid provided the monomeric iodo-complex, $[Fe^{III}(tpp)I]$.

The ^{13}C n.m.r. spectra were recorded on a Varian XL 100 spectrometer operating at 25.2 MHz in the Fourier-transform mode using 2×10^{-3} mol dm^{-3} solutions in deuteriated chloroform (99.5%; from CEA, France) and 10-mm diameter sample tubes. The built-in 22-kHz single sideband crystal filter was used in the intermediate frequency stages and homemade five-pole Tschebychev external filters with a bandwidth of 18 or 30 kHz were used in the audio frequency stage. These filters and a spectral width of 20 kHz permitted the observation of resonances up to *ca.* 1 500 p.p.m. from $SiMe_4$. Typically, 5×10^4 transients were accumulated at a rate of 5—10 s^{-1} in 4K data points. Hydrogen-1 decoupling was avoided because it creates temperature inhomogeneities which broaden the resonances due to the large temperature dependence of the paramagnetic shifts. The variable-temperature experiments were carried out using the usual gas-flow technique and monitoring the temperature with a calibrated red LED probe.[10]

RESULTS

The ^{13}C n.m.r. data for the labelled carbons of the chloro- and iodo-iron(III) complexes are collected in Table 1. The paramagnetic shifts are referenced to those of the diamagnetic $[Zn^{II}(tpp)]$ complex.[1] The linewidth of the components of the β-carbon resonances, which are split by coupling to the pyrrolic protons (J = 175 Hz), was obtained by simulation of the observed line assuming a Lorentzian lineshape. Spin–spin couplings at other positions are negligible relative to the resonance linewidth (Figure 1).

TABLE 1

Isotropic hyperfine shifts and linewidths (at 34 °C) of the ^{13}C resonances of the porphyrin core in high-spin iron(III) complexes referenced to diamagnetic $[Zn^{II}(tpp)]$ (δ is positive to low field). For the β pyrrole carbon, the value indicated in parentheses is the measured linewidth without proton spin decoupling

Carbon	$[Fe^{III}(tpp)Cl]$		$[Fe^{III}(tpp)I]$	
atom	δ/p.p.m.	λ/Hz	δ/p.p.m.	λ/Hz
α Pyrrole	1 010	450	950	180
β Pyrrole	1 150	900 (950)	1 110	330 (460)
meso	374	450	358	180

The linewidth, λ, which is related for a Lorentzian lineshape to the spin–spin nuclear relaxation time by [11] equation (1) is not simply correlated to the iron-nucleus distance [12]

$$\pi\lambda = t_2^{-1} \qquad (1)$$

nor to the square of the corresponding shift.[13] In both complexes, the linewidth of the α-carbon resonances is surprisingly small relative to that of the *meso*- and especially the β-carbon resonances. This already suggests that one must add the dipolar coupling of the nuclear spins with the unpaired ligand electron-spin densities [14-16] to the more usual mechanisms of relaxation, *i.e.* the dipolar interaction with the iron electron spin [12] and Fermi contact interaction.[12]

DISCUSSION

A quantitative analysis of the n.m.r. data in terms of unpaired electron-spin distribution requires the experimental estimate of the contact and the dipolar contributions to the paramagnetic shifts and linewidths. The delocalized π-electron spin density at the various carbon atoms of the porphyrin ring will be derived finally from the dipolar contribution to the ^{13}C relaxation. This contribution can be evaluated from the experimental linewidth once the contact coupling constant, $A/\hbar$, involved in the hyperfine exchange relaxation mechanisms is known. This isotropic relaxation mechanism cannot be neglected for ^{13}C [11] and is given by equation (2)

$$t_{2c}^{-1} = \tfrac{1}{3}S(S+1)(A/\hbar)^2\Sigma_c J(\omega,\tau) \qquad (2)$$

where the spectral density function is defined according to equation (3) due to a slow rotational correlation time

$$\Sigma_c J(\omega,\tau) = [1 + (1 + \omega_s^2 t_{1e}^2)^{-1}]t_{1e} \qquad (3)$$

($\tau_r \simeq 10^{-10}$ s) and assuming $t_{1e} \simeq t_{2e}$. For a high-spin d^5 iron(III) complex,[17] $A/\hbar$ can be obtained from the contact contribution δ_c to the observed paramagnetic shifts [equation (4)]. The first step of this analysis is therefore the estimate of the pseudo-contact shifts.

$$\delta_c = \left(\frac{35\beta}{6\gamma_c kT}\right)(A/\hbar) \qquad (4)$$

Metal- and Ligand-centred Pseudo-contact Shifts.—The metal-centred pseudo-contact shift δ_p^M is [17] given by equation (5) where D is the zero-field splitting parameter,

$$\delta_p^M = -\frac{112D\beta^2}{9(kT)^2}\left(\frac{3\cos^2\theta - 1}{r_M^3}\right) \qquad (5)$$

assuming an isotropic $g = 2$ value. The value of D has already been determined from the susceptibility anisotropy of the chloro-complex and equals 5.9 cm^{-1}.[18] The geometrical factor can be calculated from the crystallographic data [19] for the various nuclei.

The ligand-centred contribution is due only to the non-zero averaging of the dipolar hyperfine interaction of the unpaired π-electron spin with the corresponding carbon nucleus, the contribution of π-electron spin density at neighbouring atoms being negligible. The one-centre term for a non-orbitally degenerate $^6A_1$ state is still proportional to the susceptibility anisotropy, equation (6).

$$\delta_p^L = -\frac{56D\beta}{9\gamma_c(kT)^2}(2b/\hbar)\rho \qquad (6)$$

TABLE 2

Contributions to the hyperfine shift and linewidth of the ^{13}C resonances in the high-spin iron(III) chloro-complex and theoretical contributions to the linewidth of the pyrrole proton (the experimental value for λ_H is 250 Hz); λ_M is the metal-centred contribution, $\lambda_L + \lambda_{LM}$ the total contribution from the ligand spin densities (ligand-centred plus ligand–metal-centred), and λ_c is the contact contribution. ρ Values are the normalized π spin densities obtained with $t_{1e} = 10.5 \times 10^{-12}$ s and $\rho_{Fe} = 3.5/5$

		α(^{13}C)	β(^{13}C)	*m*(^{13}C)	β(^1H)
δ_p^M/p.p.m.		24	9	17	
δ_p^L/p.p.m.		−38	−70	−67	
δ_c/p.p.m.	π	< −350	430	424	
	σ direct	> 1 400	781	assumed 0	
	total	1 024	1 211	424	
λ_M/Hz		136	18	66	84
$(\lambda_L + \lambda_{LM})$/Hz		16	467	333	151
λ_c/Hz		298	415	51	16
$\lambda_{tot.}$/Hz		450	900	450	251
ρ *		5.0×10^{-3}	9.2×10^{-3}	8.8×10^{-3}	

* The ρ values are normalized to 1.

The value of the z component, $2b/\hbar$, of the anisotropic hyperfine interaction for a carbon atom has been taken as 1.35×10^9 rad s^{-1} for a unit spin density.[20]

The corresponding pseudo-contact contributions to the shifts are given in Table 2. They cannot be neglected, especially for the *meso* carbons, but they are not sufficient to induce a noticeable curvature of the temperature dependence of the observed shifts which still extrapolate linearly to the origin in a Curie plot (Figure 2).

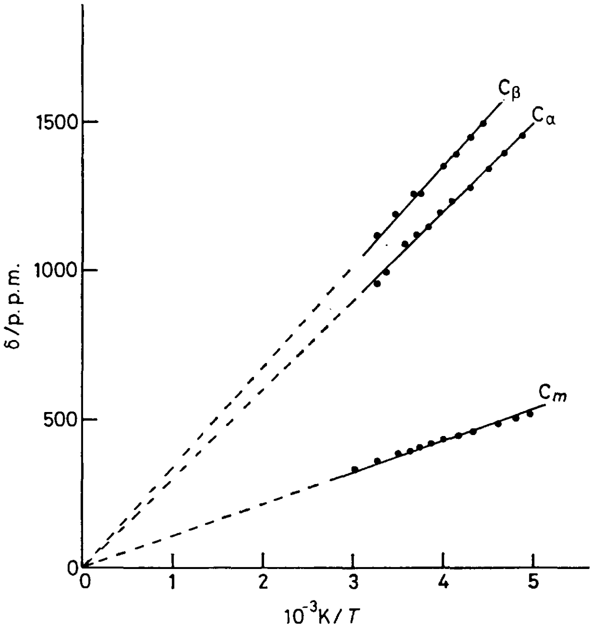


FIGURE 2 Temperature dependence of the hyperfine shifts of the porphyrin core carbon resonances

Mechanism of the Paramagnetic Dipolar Relaxation of the Porphyrin Ring-carbon Nuclei.—Any dipolar contribution of the unpaired electron spin to the nuclear relaxation is roughly proportional to the square of the spin density and to the inverse sixth power of the distance.

In order to be comparable to the effect of the metal-centred spin, the effect of the ligand-centred spin should correspond to spin densities of at least 10^{-2}.[21] The σ spin densities in the sp^2 hybridized carbon orbitals cannot be expected to contribute noticeably to the linewidth since the spin density in the carbon 2*s* orbitals, estimated from the contact shifts, is at most 2.7×10^{-4} [20] ($\delta_c = 1\,200$ p.p.m. at 307 K, $A/\hbar = 6.3 \times 10^6$ rad s^{-1}).

The contribution of the ligand π-electron spin density and of the metal electron spin is given in terms of normalized spin densities ρ_i and atomic orbitals $u_i(r)$ by expression (7a) [15] where the spectral density function is equation (8) (subscript d = dipolar).

$$t_{2d}^{-1} = \tfrac{1}{15}\, S(S+1)\gamma_N^2(g\beta)^2 \left[\frac{4\pi}{5}\sum_{\nu=-2}^{2}|\Sigma\rho_i\!\int F_2^{\nu}(r')|u_i(r)|^2 dr|^2\right]\Sigma_d J(\omega,\tau) \quad (7a)$$

$$\Sigma_d J(\omega,\tau) = [7 + 13(1 + \omega_s^2 t_{1e}^2)^{-1}]t_{1e} \quad (8)$$

The integrals in equation (7a) are components of the dipolar interaction of the nuclear spin with the unpaired electron spin involving the iron orbitals (two-centre integrals) and the carbon orbitals (one- and two-centre integrals). The former are approximated by point dipole expressions because the electron dipole in a high-spin iron(III) ion has a quasi-spherical distribution. The two-centre integrals involving $2p_z$ carbon orbitals, *i.e.* the effect of the spin density on neighbouring atoms, have been neglected for ^{13}C, but not for ^{1}H. The dominant ^{13}C one-centre integral is expressed in terms of the dipolar hyperfine interaction of a unit $2p_z$ spin density with the nuclear spin ($\frac{2}{5}g\beta\gamma\langle r^{-3}\rangle_{2p}$ with $\langle r^{-3}\rangle_{2p} = 1.34 \times 10^{25}$ cm^{-3} [20]). Then, the dipolar contribution to the ^{13}C relaxation is given by (7b).

$$t_{2d}^{-1} = \tfrac{1}{15}\, S(S+1)\gamma_C^2(g\beta)^2 [\rho_{Fe} r_M^{-6} + \tfrac{4}{25}\langle r^{-3}\rangle^2_{2p}\rho^2 - \tfrac{2}{5}\langle r^{-3}\rangle_{2p}\rho\rho_{Fe} r_M^{-3}]\, \Sigma_d J(\omega,\tau) \quad (7b)$$

Combining the expressions for the linewidth and the relaxation as described above, the total linewidth for a carbon nucleus can thus be expressed as a second-order polynomial of the π-electron spin density, ρ, borne by, and only by, the considered carbon. The ρ values can be derived from the experimental data if t_{1e} and ρ_{Fe} are known. One must therefore add two independent equations for a unique solution for the spin densities.

Iron Spin Density.—The contribution to the linewidth of the resonance of the pyrrole protons of the π-electron spin density on the attached carbon can be calculated using the same theory.[15] In Figure 3, the total proton linewidth has been calculated for various values of ρ_{Fe} as a function of t_{1e}, within limits compatible with the carbon resonance data for expected ρ values, $0 \leqslant \rho \leqslant 10^{-2}$. The experimental proton resonance linewidth of 250 Hz can be fitted only with $\rho_{Fe} < 1$. The derived ligand spin densities already indicated that *ca.* 0.75 π-electron spin is delocalized on the porphyrin carbons (Table 2). ENDOR experiments [22] have also shown the presence of a large unpaired spin on the counter ion and on the porphyrin nitrogen atoms. The best final fit is obtained with $\rho_{Fe} = 3.5/5$, in good agreement with molecular-orbital calculations of Mallick *et al.*[23] ($\rho_{Fe} = 3.24/5$). The small difference could be taken into account by our neglect of the contribution to the relaxation of the unpaired spin delocalized on the chloride ion.

Electron Relaxation Time.—The opposite sign of the contact shift of the *meso* carbons and of the shift of the quaternary phenyl carbons or of substituted protons in the parent chloro(octaethylporphyrinato)iron(III) is consistent with a dominant π–σ polarization mechanism at this position.[3] Assuming that this is the only contribution to the contact hyperfine interactions for these *meso* carbons, the corresponding coupling constant can be described by the Karplus–Fraenkel equation,[24] (9), with $Q_1 = 5.30 \times 10^8$ and $Q_2 = -2.46 \times 10^8$ rad s^{-1}.

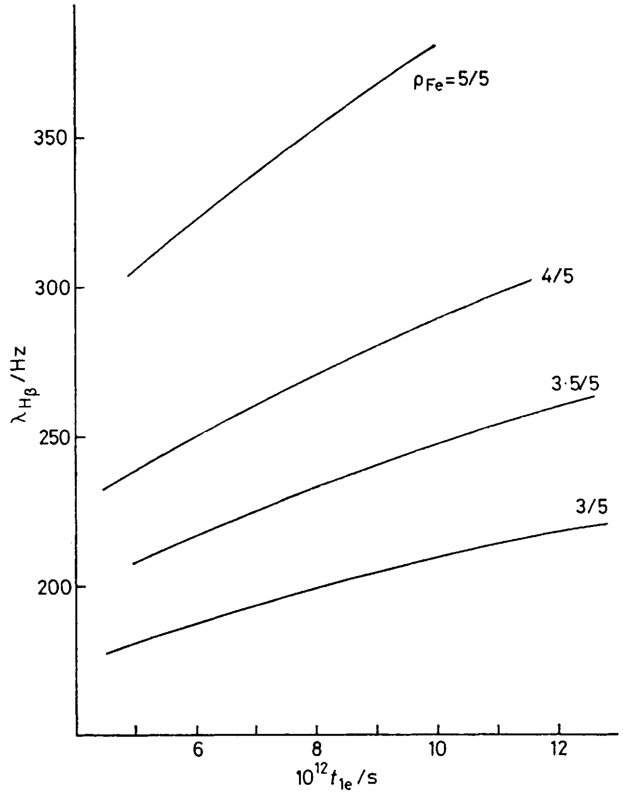


FIGURE 3 Computed linewidth of the pyrrolic proton resonance as a function of t_{1e}. The range of values for t_{1e} is compatible with the linewidth observed for the carbon nuclei. ρ_{Fe} is the normalized total iron spin density

$$A/\hbar = Q_1\rho_{C_m} + 2Q_2\rho_{C_\alpha} \quad (9)$$

Combining this equation with the three equations derived from equation (7b) for the porphyrin carbons gives a value for t_{1e} of 10.5×10^{-12} s together with a single set of values for ρ (Table 2). It should be noted that the neglect of a direct σ contribution of ±100 p.p.m. to the shift of the *meso* carbons does not introduce an error on the estimate of ρ_{C_α} larger than 20% and only of 8, 5, 4, and 9% for ρ_{C_β}, ρ_{C_m}, ρ_{Fe}, and t_{1e} respectively.

Origin of the Contact Shifts.—The experimental determination of the unpaired π-electron spin distribution allows one to separate the ^{13}C contact shift into contributions from π–σ polarization at the observed carbon and its direct neighbouring atoms[24] ($\delta_c{}^{\pi}$) and from direct σ delocalization ($\delta_c{}^{\sigma}$). The absolute value of $\delta_c{}^{\pi}$ for the α carbons (Tables 2 and 3) is a lower limit since it does not take into account the π–σ polarization from the nitrogen spin density. The unexpected larger shift observed for the α carbons as compared to the β carbons is clearly interpreted. The total contact shift of the β-carbon resonance is the sum of two contributions of same sign: a π–σ polarization mainly due to the large π-electron spin density at this position and a direct σ delocalization. On the contrary, each α carbon bears a smaller π-electron spin density but is surrounded by a *meso* carbon, a β carbon, and a nitrogen atom with higher π-electron spin densities. Thus, the π–σ polarization at these neighbouring atoms reduces the shift contributions of the direct π–σ polarization and of σ delocalization since they are opposed in sign.

TABLE 3

Hyperfine shifts and linewidths of the ^{13}C resonances in the high-spin iron(III) iodo-complex. Symbols as in Table 2. t_{1e} is 3.1×10^{-12} s and $\rho_{Fe} = 3.5/5$. The experimental β-proton linewidth is 95 Hz

		α(^{13}C)	β(^{13}C)	*m*(^{13}C)	β(^{1}H)
$\delta_p{}^{M}$/p.p.m.		40	15	28	
$\delta_p{}^{L}$/p.p.m.		−72	−112	−114	
δ_c/p.p.m.	π	< -240	341	349	
	σ direct	$> 1\,200$	866	95	
	total	981	1 207	444	
λ_M/Hz		63	8	30	38
$(\lambda_L + \lambda_{LM})$/Hz		11	162	128	60
λ_c/Hz		106	160	22	6
$\lambda_{tot.}$/Hz		180	330	180	104
ρ		5.2×10^{-3}	8.1×10^{-3}	8.2×10^{-3}	

We can predict from the π-electron spin density at the *meso* carbons a shift of −166 p.p.m. at 29 °C for an hypothetical proton substituted at these positions, assuming that this contact shift still originates mainly from π–σ polarization. As a matter of fact, the observed contact shift for the *meso* protons in chloro(octaethylporphyrinato)iron(III) is only −80 p.p.m.[25] This may be against the hypothesis of the lack of significant direct σ delocalization at this position. It should be noticed however that the *meso* carbons in this complex exhibit a paramagnetic shift of only 282 p.p.m.[2,3] as compared to the shift of 384 p.p.m. in [Fe^{III}(tpp)Cl]. A clear interpretation is the decrease of the π-electron spin density at the *meso* carbons upon removal of the phenyl substituents. In [Fe^{III}(tpp)Cl], the large contribution of direct σ delocalization to the β-carbon shift is consistent with the observation of a large downfield shift of the corresponding proton resonance (60 p.p.m. at 34 °C).

An analysis similar to that for the chloro-complex has been carried out for the iodo-complex (Table 3). A D value was not available for [Fe^{III}(tpp)I], but it has been assumed that the ratio D_{Cl}/D_{I} for the tpp complexes is equal to that measured directly by i.r. spectroscopy in the iron(III) complex of deuteroporphyrin IX (2,7,12,18-tetramethylporphyrin-13,17-dipropionic acid).[26] For consistency, t_{1e} was chosen to be proportional to D^{-2},[27] *i.e.* $D = 11$ cm^{-1} and $t_{1e} = 3.1 \times 10^{-11}$ s. As expected, the direct σ delocalization at the *meso* carbons is small (95 p.p.m.). The calculated linewidth for the β protons (104 Hz) is in good agreement with the experimental (95 Hz), still using $\rho_{Fe} = 3.5/5$. The best agreement is found with $\rho_{Fe} = 3.3/5$, but the decrease in ρ_{Fe} is perhaps not significant owing to the uncertainty in t_{1e} and the approximation of the spin distribution over the iron and counter ions to a spherical distribution of dipoles. The spin distribution pattern over the porphyrin ring is however very similar in both complexes. Such a conclusion has been reached by molecular-orbital calculations[23] and by nitrogen ENDOR spectroscopy[22] for complexes with various halogeno-ligands (Cl, F, or Br). This justifies the use of the relative proton resonance linewidths as probes for the electronic relaxation in iron(III) high-spin complexes[28] without knowledge of the spin densities.

Conclusion.—The observation of the ^{13}C n.m.r. in labelled iron porphyrins has provided an unambiguous assignment of the resonances and accurate data about the metal–porphyrin ligand electronic interaction derived only from experimental measurements. The remaining uncertainties on delocalized spin densities concern only the pyrrole nitrogens. The major result obtained from the ^{13}C n.m.r. analysis is the evidence for large π-electron spin density on the pyrrole β carbons which escaped observation by proton n.m.r. because of the superimposition of the effect of direct σ spin delocalization. On the contrary, this large π-electron spin density dominates the relaxation of the carbon nucleus.

At other positions, close to the porphyrin centre, the contributions of the ligand spin densities to the relaxation are less important. This is due not only to the increased dipolar interaction with the metal ion ($r_M{}^{-6}$), but also to the negative (for ^{13}C) metal–ligand centred cross term[15] in equation (7b) which is proportional to $r_M{}^{-3}$.

A precise estimate of the unpaired spin densities in natural porphyrins, which are not substituted on the *meso* carbons, should require a complete analysis of the shifts and linewidths for both ^{1}H and ^{13}C resonances. Preliminary results with iron(III) complexes of octaethylporphyrin and deuteroporphyrin IX indicate that the spin distribution pattern is, at least qualitatively, similar to that in the tetraphenylporphyrin derivatives. This pattern corresponds neither to that of the highest degenerate pair of filled π orbitals of e_g symmetry[29] nor to the lowest empty π orbitals of the same symmetry. Pure mixing of the metal d_{π} orbitals with the former ones should correspond to an absence of π-electron spin on the *meso* carbons, whereas pure mixing with the latter ones should result in a π spin density at this position approximately three times larger than that on the β carbons. The metal–porphyrin ligand binding corresponds therefore to a large π covalency but the corresponding π-electron charge transfer cannot be described simply as a transfer from the metal ion to the antibonding e_g porphyrin orbitals.

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