

## Carbon-13 nuclear magnetic resonance studies on high spin iron(III) porphyrins

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**Abstract.** Carbon-13 NMR studies on a series of high spin iron(III) porphyrins, namely tetraphenylporphyrin iron(III) halides [Fe(TPP) X, X = Cl, Br, I] in CDCl<sub>3</sub> solution are reported. As expected the <sup>13</sup>C shifts are found to be an order of magnitude larger than the corresponding proton shifts. The dipolar contribution, which is quite important for the proton NMR, becomes much less significant for the <sup>13</sup>C shifts. No systematic variation in the <sup>13</sup>C shift across the series is observed, except for the meso-carbon which shows a small but gradual decrease in going from the chloro to the iodo complex. The <sup>13</sup>C shift for the various carbon atoms of the porphyrin ligand shows interesting pattern which is discussed in terms of spin delocalisation mechanisms.

**Keywords.** Nuclear magnetic resonance ; high spin iron(III) porphyrins ; C-13 shifts.

### I. Introduction

Nuclear magnetic resonance (NMR) studies on synthetic iron porphyrins have been very useful in understanding the magnetic and electronic properties of iron in haem proteins (Wuthrich and Baumann 1973a,b, 1974; Goff 1978, 1981; LaMar and Walker 1979). Most of the NMR studies on iron porphyrins have been done on proton nucleus. <sup>13</sup>C NMR is, however, a more direct, sensitive and accurate probe for paramagnetic complexes. Besides being a direct probe to the distribution of unpaired spin across the porphyrin skeleton, <sup>13</sup>C NMR has an additional advantage over proton NMR. Since the <sup>13</sup>C shifts are generally an order of magnitude larger than the corresponding proton shifts (Horrocks 1973; Doddrell and Gregson 1974; Mitra 1977) the dipolar contribution to the <sup>13</sup>C shifts is expected to be usually negligible, which makes the interpretation of the data easier.

We have recently reported (Behere *et al* 1982) a detailed proton NMR study on a series of five coordinated high spin tetraphenylporphyrinato iron(III) halides, [Fe(TPP)X, X = Cl, Br, I (figure 1)]. These studies confirmed the dominant

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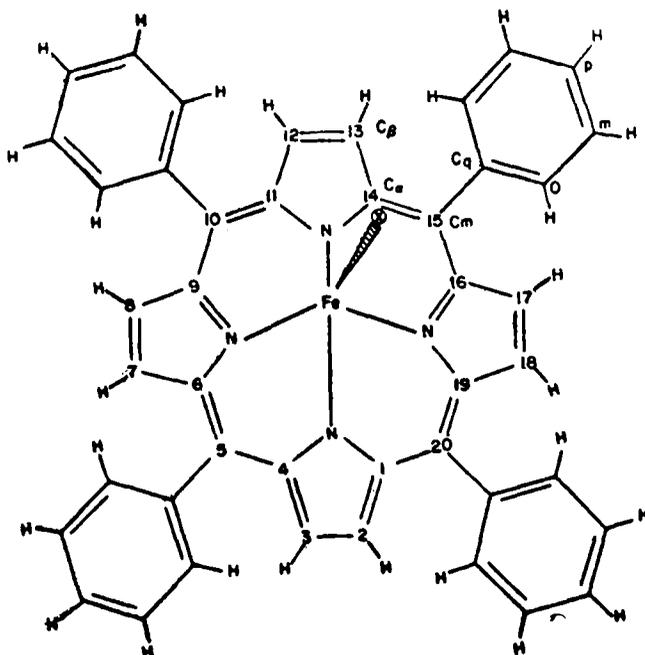


Figure 1. Molecular geometry of Fe(TPP)X.

influence of the porphyrin ligand on the shift pattern, since the changes in the axial halide ligand were found to have minimal effect on the shifts of the various protons. Based on the pattern of the unpaired spin density distribution across various proton sites, a mechanism for the delocalisation of the unpaired spin across the porphyrin ligand was suggested (Behere *et al* 1982). The present  $^{13}\text{C}$  NMR study is an extension of our proton NMR study (Behere *et al* 1982) and forms a part of our research programme on metalloporphyrins (Behere and Mitra 1979, 1980; Behere *et al* 1977, 1979, 1981, 1982).  $^{13}\text{C}$  NMR on Fe(TPP)Cl had been reported earlier by Goff (1978) but a subsequent study by Mispelter *et al* (1979) proved that the previous assignments were grossly in error.

## 2. Experimental

The Fe(TPP)X samples were prepared by the previously reported methods (Adler *et al* 1970).  $^{13}\text{C}$  NMR in natural abundance was recorded at 67.89 MHz on Bruker FT NMR spectrometer. Deuterated chloroform solutions having solute concentrations in 30–60 mM were used. Since aggregation effect often complicates the  $^{13}\text{C}$  NMR results on metalloporphyrins, a study at different concentrations was done to determine the optimum concentration range. Spectral width of about 50,000 Hz were employed. About 30,000–40,000 transients were collected. Pulses of  $15\ \mu\text{sec}$  width were applied at a rate of 0.4 sec repetition. The spectra were run under conditions of proton broad band decoupling with use of 8/8 K memory points in quadrature detection mode. Because of proton decoupling the temperature of the sample was considerably raised and found to be around  $40^\circ\text{C}$ .

### 3. Results

A typical  $^{13}\text{C}$  NMR spectrum of  $\text{Fe}(\text{TPP})\text{Br}$  is shown in figure 2. The resonances were assigned following Mispelter *et al* (1979, 1981). The resonances due to all but pyrrole carbon atoms were observed. The pyrrole carbon resonances are believed to be shifted to 1000-1400 ppm down-field and hence could not be observed simultaneously along with other resonances. As in the proton NMR study the two ortho and meta carbons of the phenyl ring show inequivalence with respect to the iron atom which lies out of the mean porphyrin plane. Table 1 summarises the relevant  $^{13}\text{C}$  shifts on the three complexes; the data were corrected for diamagnetic shifts using the corresponding values of  $\text{ZnTPP}$  (Wuthrich and Baumann 1973a). The proton NMR shifts are included in table 1 for comparison.

The  $^{13}\text{C}$  shifts consist of both dipolar and contact terms. The dipolar contribution is given in axial symmetry by

$$\left(\frac{\Delta H}{H}\right)_D = \frac{1}{3N} (K_L - K_{||}) \left[ \frac{3\cos^2\theta - 1}{r^3} \right], \quad (1)$$

where  $(K_L - K_{||})$  is the paramagnetic anisotropy and  $\theta$  and  $r$  are the structural parameters as defined by Horrocks (1973). Both these informations are available on the  $\text{Fe}(\text{TPP})\text{X}$  series (Behere *et al* 1982). The dipolar term can therefore be easily calculated for pyrrole, meso and quaternary phenyl carbon atoms, but for the other phenyl carbons slight complication is involved due to the rotation of the phenyl ring in solution, which will affect the evaluation of  $r$  and  $\theta$ . Hence we calculated  $r$  and  $\theta$  at an interval of every  $10^\circ$  by rotating the phenyl ring through  $\pm 40^\circ$  with respect to porphyrin plane and used an average value for the calculation of the dipolar terms. The dipolar and contact terms so obtained are included in table 1.

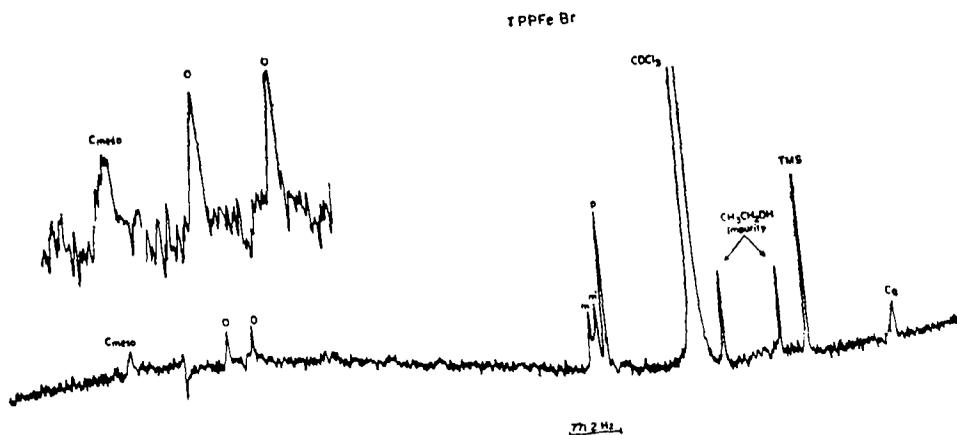


Figure 2. A typical  $^{13}\text{C}$  spectrum of  $\text{Fe}(\text{TPP})\text{Br}$  at room temperature. All the carbon resonances are labelled.

Table 1.  $^{13}\text{C}$  shifts for Fe(TPP)X

	Fe(TPP) Cl				Fe(TPP) Br				Fe(TPP) I			
	$\delta_{\text{C}}^{\text{ISO}}$	$\delta_{\text{C}}^{\text{DIP}}$	$\delta_{\text{C}}^{\text{CON}}$	$\delta_{\text{H}}^{\text{CON}}$	$\delta_{\text{C}}^{\text{ISO}}$	$\delta_{\text{C}}^{\text{DIP}}$	$\delta_{\text{C}}^{\text{CON}}$	$\delta_{\text{H}}^{\text{CON}}$	$\delta_{\text{C}}^{\text{ISO}}$	$\delta_{\text{C}}^{\text{DIP}}$	$\delta_{\text{C}}^{\text{CON}}$	$\delta_{\text{H}}^{\text{CON}}$
Meso (Cm)	-329.8	-15.8	-314.0	..	-334.7	-32.6	-302.1	..	-311.5	-35.7	-275.8	..
Quaternary phenyl (q)	+177.9	-5.2	+183.1	..	+182.6	-11.2	+171.4	..	+177.3	-12.3	+189.6	..
Ortho (o)	-260.1	-2.7	-257.4	..	-272.1	-5.8	-266.3	+5.0	-278.1	-7.5	-270.6	+3.65
Ortho (o')	-246.1	-2.2	-243.9	..	-255.1	-5.2	-249.9	+5.20	-255.1	-6.2	-248.1	..
Meta (m)	-22.9	-1.6	-21.3	-4.10	-25.0	-3.8	-21.2	-3.25	-27.0	-4.1	-22.9	-4.37
Meta (m')	-19.3	-1.3	-18.0	-3.24	-20.5	-2.4	-18.1	-2.83	-20.8	-3.6	-17.2	-3.57
Para (p)	-13.3	-1.3	-12.0	+2.35	-14.6	-3.0	-11.6	+3.06	-15.8	-33	-12.5	+2.01

The shifts are relative to TMS and corrected for diamagnetism (see text). All negative shifts are 'down-field' with respect to TMS.

#### 4. Discussion

Table 1 shows several interesting results. As expected  $^{13}\text{C}$  shifts are much larger than the corresponding proton shifts. This is true not only for pyrrole but for phenyl carbon shifts as well. In view of the large shifts, the dipolar contributions which lie in the range of 1-40 ppm appear insignificant. This is an encouraging result as it allows the neglect of dipolar contribution for the analysis of  $^{13}\text{C}$  shifts. This is contrary to the situation for proton NMR where the dipolar contribution plays a significant role in the interpretation of the data (Mitra 1977; Behere *et al* 1982).

The variation in the  $^{13}\text{C}$  shifts across the  $\text{Fe}(\text{TPP})\text{X}$  does not show any definite trend, though the systematic decrease in the meso-carbon shift from chloride to the iodide complex appears to be real. It is interesting that a very recent theoretical calculation on five coordinated high spin iron(III) porphyrin predicts just a similar variation in the meso-carbon shift (Mun *et al* 1981). Nevertheless the effect of variation in the axial halide on the  $^{13}\text{C}$  shift of the basal porphyrin ring is small and for most cases difficult to discern.

We shall now discuss the spin delocalisation mechanisms responsible for the observed contact shifts of the various carbons and protons in this series. We observe from table 1 that the meso-carbon shows a large down-field shift while the phenyl quaternary carbon bonded to it is considerably up-field shifted. The shift pattern of the phenyl ortho, meta and para carbons and protons is quite interesting. The  $^{13}\text{C}$  shifts for these nuclei show a sharp decrease in magnitude in going from ortho to meta to para but the sign of the shift remains the same. This is in contrast to the situation for the corresponding proton shifts which show alternation in sign but no attenuation.

The ferric ion in the  $\text{Fe}(\text{TPP})\text{X}$  series has unpaired electrons in all the five  $d$ -orbitals of  $\pi$  and  $\sigma$  symmetry. The unpaired electrons can therefore delocalise over the porphyrin ring through its  $\pi$  and  $\sigma$  molecular orbitals. It has recently been shown that the meso-carbon shift arises mainly through the unpaired spin-density in the  $\pi$  molecular orbitals (Mispelter *et al* 1981). This unpaired spin-density in the  $\pi$ -MO can induce an unpaired spin density at the phenyl quaternary carbon either through  $\pi$ - $\sigma$  correlation (Carrington and McLachlan 1967; LaMar 1973) or through direct  $p_{\pi}$ - $\sigma_{\pi}$  interaction (LaMar 1973). The latter contribution is expected to be small because of the orientation of the phenyl rings. Nevertheless both these mechanisms will induce at the phenyl quaternary carbon a spin density opposite in sign to that at the meso-carbon, as is experimentally observed. The unpaired spin density induced at the phenyl quaternary carbon in both  $\sigma$  and  $\pi$  MO propagates over the phenyl rings. The proton contact shifts found earlier (Behere *et al* 1982) are consistent with the spin delocalisation in predominantly  $\pi$ -MO of the phenyl rings. The  $^{13}\text{C}$  contact shifts of the phenyl carbons however show typical variation expected of  $\sigma$ -delocalisation resulting from the unpaired spin density in the  $\sigma$ -atomic orbitals of these carbon atoms. While these simple arguments explain qualitatively the unpaired spin density at various carbon sites, a quantitative description may be much more complicated (Carrington and McLachlan 1967).

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