

High Resolution Proton Magnetic Resonance Study on Metal-free Porphyrins

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High resolution (270 MHz) PMR spectra of metal-free tetraphenylporphyrin (I), *p*-methyltetraphenylporphyrin and octaethylporphyrin (II) have been recorded. Fine structure multiplets due to spin-spin coupling have been observed in their spectra. The dynamical effect of inner N-H proton tautomerism on the peripheral porphyrin protons has also been investigated through variable temperature measurements.

Metal-free tetraphenylporphyrin (TPPH₂, I) and octaethylporphyrin (OEPH₂, II) are synthetic porphyrins which resemble closely the natural porphyrins, and hence have been used as a model in NMR studies. Proton magnetic resonance (PMR) of both I and II have been reported at room temperature at 60 and 100 MHz and the spectra assigned¹⁻⁷. However certain features of their spectra are still obscure because of low resolution. For example, no well-resolved multiplet structure for the phenyl protons has been reported for I though it is, in fact expected in view of the possible spin-spin coupling between the protons. Lack of observation of such multiplet structure also makes the assignment of phenyl resonances uncertain. Thus the need for title investigation seems imperative. We have therefore recorded the high resolution (270 MHz) spectra of I, II and (*p*-CH₃)-I. We also report results of our temperature dependent PMR study on I and II to seek information on the effect of inner (N-H) proton

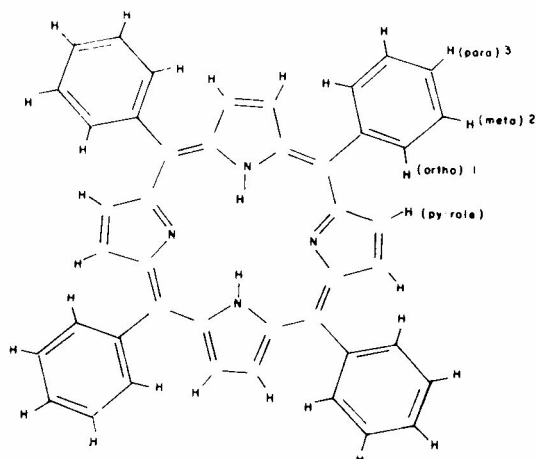
tautomerism on the peripheral protons, e.g. pyrrole or CH₂ protons.

Materials and Methods

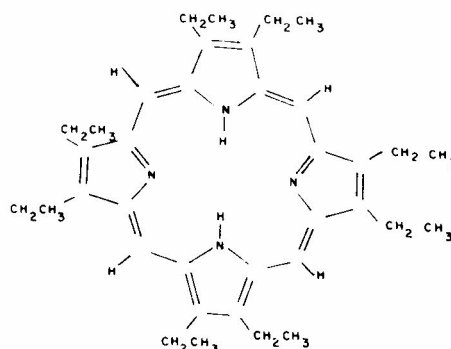
The PMR spectra of TPPH₂ (I), (*p*-CH₃)-I and OEPH₂ (II) were recorded in CDCl₃ on a Bruker FTNMR spectrometer working at 270 MHz in FT mode using 8/8 K data points in the frequency domain. Pulses of 5 μsec with repetition time of 3 sec were used. About 20 transients were sufficient to obtain well resolved spectra. A solution concentration of about 7 × 10³ mol dm⁻³ was used to avoid aggregation effect. For variable temperature work, the temperatures were kept constant within ± 1°. All shifts are with respect to TMS and are taken positive if the shift is downfield. The accuracy in the chemical shift measurement is estimated to be ± 0.001 ppm.

Results and Discussion

The general nature of the PMR spectra of these porphyrins is very similar to that reported earlier¹⁻⁴.



I



II

Table 1—Chemical Shifts and Coupling Constants for the Metal-free Porphyrins

[All shifts are in ppm]

N-H	Pyrrole-H	<i>ortho</i> -H	<i>meta</i> -H	<i>para</i> -H	<i>Meso</i> -H ^a	<i>J</i> ^a , (Hz)
TPPH ₂ (I)						
-2.785 ^a	8.848 ^a	8.241 ^a	7.759 ^a	7.766 ^a	—	<i>J</i> _{1,2} = 7.24
-3.33 ^b	8.75 ^b	8.30 ^b	7.80 ^b	7.80 ^b	—	<i>J</i> _{1,3} = 2.2
-2.76 ^c	8.84 ^c	8.22 ^c	7.78 ^c	7.20 ^c	—	<i>J</i> _{2,3} = 7.3
(<i>p</i> -CH ₃)TPPH ₂						
-2.780	8.852	8.096	7.549	2.730 (<i>p</i> -CH ₃)	—	<i>J</i> _{1,2} = 7.9
OEPH ₂ (II)						
-3.750	4.110 (CH ₂)	1.923 (CH ₃)	—	—	10.110	<i>J</i> _{CH₂} = 7.5

^(a)Present work; ^(b)ref. 3; and ^(c)ref. 8.

The spectrum of II displays a quartet at δ 4.11 resulting from the spin-spin coupling of the CH₂ protons with the CH₃. A coupling constant of $J_{\text{CH}_2} = 7.5$ Hz is deduced (Table 1), which agrees well with the previous value⁶. The -CH₃ protons show a triplet structure as expected.

The pyrrole protons in I and (*p*-CH₃)-I appear as sharp resonances $\sim \delta$ 8.85, indicating that methyl substitution at the *para*-position has little electronic

effect on the pyrrole protons. The phenyl protons in both appear as well-defined multiplets which have not been previously reported (Figs 1 and 2). The quadruplet centred at δ 8.24 in I has been assigned to *ortho*-proton, and the multiplet around δ 7.76 to *meta*- and *para*-protons (Fig. 1). The quartet evidently arises because of the coupling of the *ortho* with the *meta*- and *para*-protons. In mono substituted benzene J_{ortho} lies between 6 and 10 Hz, J_{meta} between 1 and 3 Hz and J_{para}

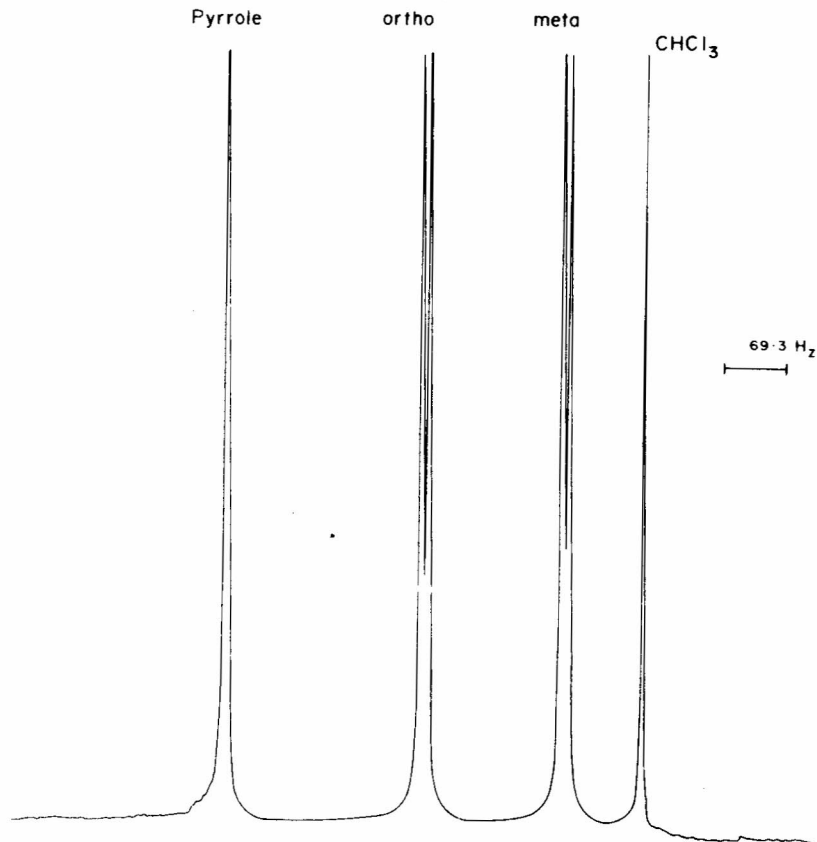


Fig. 1—Multiplet structure of the phenyl protons in TPPH₂ (I)

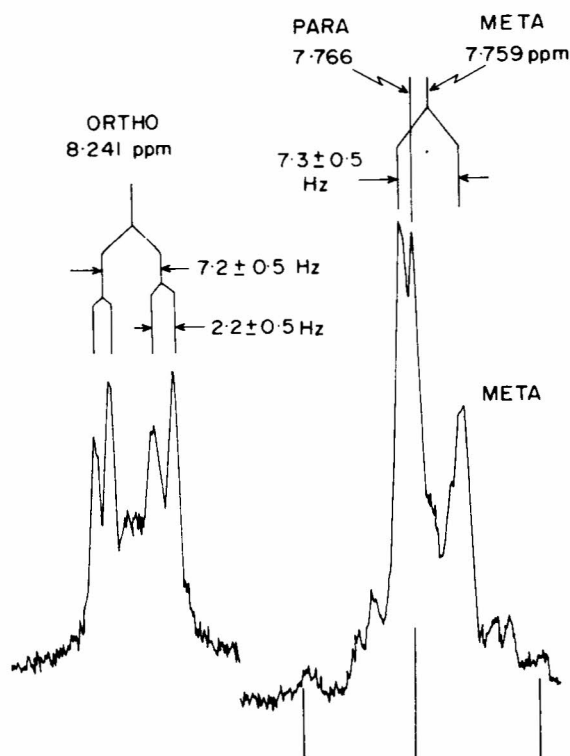


Fig. 2 PMR spectrum of (*p*-CH₃)TPPH₂ at room temperature [Only the pyrrole and phenyl proton region is shown]

between 0 and 1 Hz⁸. In the present case $J_{1,2}$ is estimated to be 7.24 Hz, $J_{1,3}$ 2.2 Hz, in close agreement with the above expected values (see structures I, II and Fig. 1 for assignment). The intense doublet of the multiplet structure centred around δ 7.76 has previously been assigned to *meta*-proton and the broad singlet to *para*-proton⁷. Since the *meta*-proton is expected to be spin-coupled with the *ortho*- and *para*-protons (see structure I), it is more likely that the broad singlet is a component of the resonance due to *meta*-proton doublet, the other component being one of the low-field doublet, with a separation of 7.3 Hz in close agreement with the expected coupling constant. The *para*-proton has a coupling with both *meta*- and *ortho*-protons and a total of nine resonances are expected. The fine structure observed on both sides of the multiplet at δ 7.76 together with the sharp line (all marked in Fig. 1) can then be assigned to *para*-protons. All the relevant data are included in Table 1.

The PMR spectrum of (*p*-CH₃)-I shows a clean doublet for the *ortho*- and *meta*-protons (Fig. 2). In this case the only significant coupling is that between the *ortho*- and *meta*-protons resulting in a doublet with $J_{1,2} = 7.9$ Hz. The difference in the $J_{1,2}$ between I and (*p*-CH₃)-I appears to be marginally real and may be indicative of the effect of methyl substitution. The coupling of the *meta*- and *ortho*-protons with the *p*-CH₃ proton is too weak to be observed in the present work.

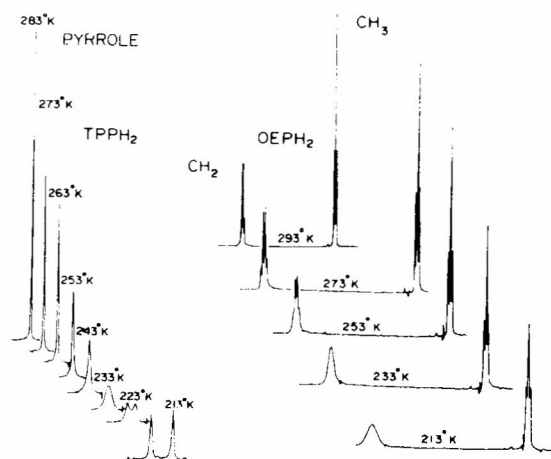


Fig. 3 Dynamical effect of N-H proton tautomerism in TPPH₂ (I) and OEPH₂ (II)

The inner N-H proton shifted upfield shows almost identical shift for I and (*p*-CH₃)-I, but is distinctly different for II (Table 1). The ethyl groups at the pyrrole positions in II have evidently marked effect on the inner N-H proton; in fact there is evidence of even coupling between the pyrrole and the N-H protons^{3,4}.

It is known that the two inner N-H protons in metal-free porphyrins 'exchange' very fast among the four pyrrole N-atoms resulting in a single resonance for the pyrrole protons. However, at lower temperatures the two N-H protons may get 'frozen' to their respective N-atoms, making the pyrrole protons (or the CH₂ protons) chemically inequivalent. The effect of this inequivalence on the pyrrole resonance and its dynamics are shown in Fig. 3 for I. The pyrrole protons showing a single resonance at higher temperatures split into two well-resolved resonances at lower temperatures where the two N-H protons have got 'frozen' in³. Similar effect in II for the corresponding CH₂ protons is however not seen down to 213 K though the broadening of the CH₂ resonance is clearly visible at and below 233 K (Fig. 3); for the CH₃ protons the effect is seen but to a lesser extent. Since the structural parameters of inner porphyrin core for I and II are almost identical^{9,10}, it is unlikely that the N-H protons in II may have greater mobility than those in I. The most likely explanation for the above difference between I and II may be that the CH₂ protons in II are one bond farther away from the pyrrole nitrogen than the pyrrole protons in I. This will ensure that the effect of inner N-H proton tautomerism on the CH₂ protons in II will be 'felt' at a lower temperature, and that on the CH₃ protons at a still lower temperature. Measurements at lower temperatures are required to experimentally verify it but the trend is apparent in Fig. 3. Measurement below 213 K in CDCl₃ solvent is, however, difficult.

Acknowledgement

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