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RATE PROCESSES IN <u>meso</u>-TETRAPHENYLPORPHYRIN.

SLOW EXCHANGE BETWEEN <u>meso</u>-TETRAPHENYLPORPHYRIN AND ITS DIPROTONATED FORM

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We report herein the observation, by NMR spectroscopy, of a proton exchange which is abnormally slow, and is to our knowledge unique in the area of porphyrin chemistry. When trifluoroacetic acid (TFA) is added to <u>meso</u>-tetraphenylporphyrin (TPP) in deuteriochloroform solution, the ^{13}C resonances do not show a continuous shift characteristic of rapid exchange, but a new set of resonances grows until, at a mole ratio TFA:TPP of <u>ca</u>. 2:1, only this new set of resonances remains. We ascribe this observation to relatively slow exchange (on the NMR time-scale) between the uncharged and diprotonated species.

This interpretation was confirmed by measurements of the ^{1}H NMR spectrum at 100 MHz as a function of temperature, of a sample of TFA (0.03 M) and TPP (0.03 M) in deuteriochloroform. At these relative concentrations there exists approximately equal proportions of free base and diprotonated TPP in solution. The results are illustrated in the Figure for the temperature range +90° to -60°; at temperatures lower than -60° the solution solidified.

Two distinct rate processes are observed; the lower temperature coalescence (T_C <u>ca</u>. -46°; $\Delta G^{\ddagger}$ <u>ca</u>. 11.4 kcal./mole) occurs at the same temperature in TPP itself in chloroform, and has previously been observed and identified by Storm and Teklu[1] in carbon disulphide solution. This is due to the tautomeric exchange process $1 \rightleftharpoons 2$ in the uncharged species.

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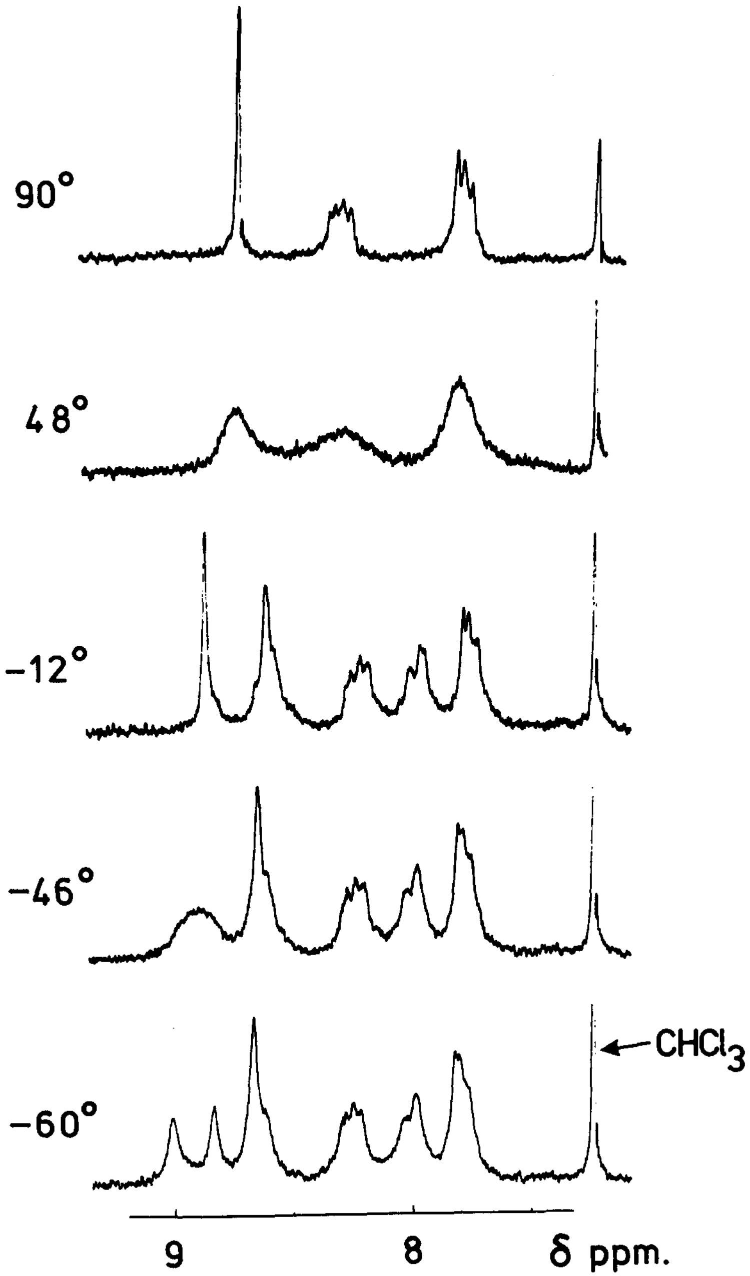
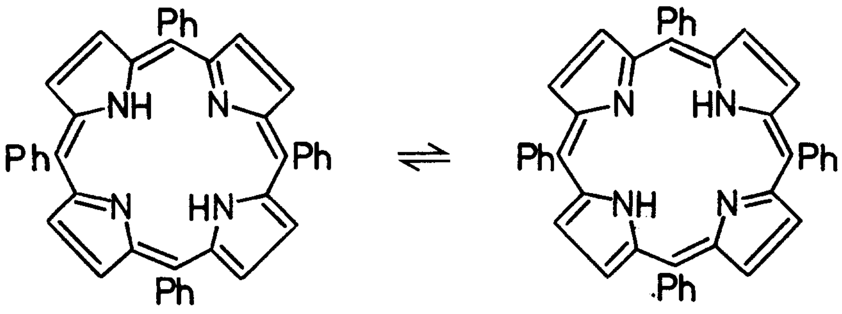


Figure: ^{1}H NMR Spectra (HA 100) of TPP and TFA in CDCl$_3$.



(1) (2)

The higher temperature coalescence (T_c *ca*. 48°; $\Delta G^{\ddagger}$ *ca*. 16.3 kcal./mole) is due to the two proton exchange between TPP and its dication:

$$\mathrm{TPP} + (\mathrm{TPPH_2})^{2+} \rightleftharpoons (\mathrm{TPPH_2})^{2+} + \mathrm{TPP}.$$

From a comparison of the individual spectra of TPP and $(\mathrm{TPPH_2})^{2+}$ in deuteriochloroform with the spectrum of partially acidified TPP, it is possible to completely assign the variable temperature spectra. For the uncharged species at -60°, signals at 9.01 and 8.84δ are due to the "ß-pyrrole" type (peripheral) protons, the lower field one on a 5-membered ring carrying a protonated nitrogen.[1] Multiplets at 8.25 and 7.80δ are due to the *ortho* and *meta* plus *para* protons respectively of the phenyl rings. For the diprotonated species, the multiplet at 8.67δ is due to the "ß-pyrrole" type protons plus the *ortho* phenyl protons, and the multiplet at 8.01δ is due to the *meta* plus *para* phenyl protons.

We have previously noted[2] that the coproporphyrin esters in deuteriochloroform show a continuous variation in the ^{13}C chemical shifts at 35° when titrated with TFA. It is therefore apparent that the barrier for proton exchange must be considerably higher for TPP than for the coproporphyrin esters. It is intriguing to postulate that the origin of this higher barrier in TPP may lie in the severe deformations from planarity of the porphyrin ring, and the significant change in the mean angle between the macrocycle and the phenyl ring planes induced by protonation of TPP.[3,4]

Throughout this study, no evidence of monoprotonated TPP species was obtained; this is in accord with the similar values of the two pK's, owing to the increased resonance stabilisation inherent in the symmetrical dication.[5]

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