PORPHYRIN NUCLEAR MAGNETIC RESONANCE SPECTRA*

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THE nuclear magnetic resonance spectra[2] of porphyrins show a number of

uncommon features, of which the most noteworthy is a peak at very high

field. The spectrum of aetioporphyrin I*** in trifluoroacetic acid (TFA)

is shown in the figure; in this strongly acidic medium the porphyrin is

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* Some of the results recorded in this paper were presented at
the XVLLth International Congress of Pure and Applied Chemistry
(Section on Natural Pigments and their Biogenesis) in Munich,
September, 1959. Spectra of several porphyrin esters in
deuterochloroform solution have been described recently;[1] the
published interpretation of these results agrees with this
communication.

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*** 1:3:5:7- Tetramethyl-2:4:6:8-tetraethylporphin.

[1] E.D. Becker and R.B. Bradley, J.Chem.Phys. In press; we thank
Dr. Becker for sending us his manuscript.

[2] A Varian V-4300-B 40.00 Mc/sec spectrometer was employed, together
with a sample spinner, field stabiliser and Varian recorder.
Tetramethyl silane was used as an internal reference, and spectra
were calibrated by the side-band method.
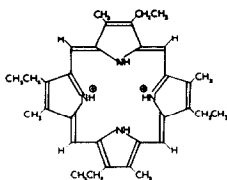
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PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF

AETIO-PORPHYRIN I
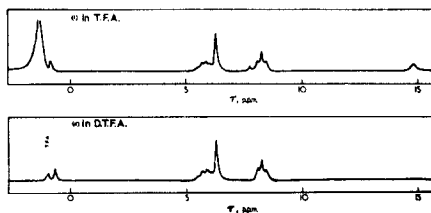
presumably present as the di-cation (I) in which all four nitrogen atoms

are protonated[3]. We assign the high-field peak at 14.89[4] to the NH protons,

because this peak is absent from the spectrum of aetioporphyrin I in

deuterotrifluoroacetic acid (DTFA) (in which one would expect the NH protons

to be exchanged for deuterium). [In TFA, γ-phylloporphyrin XV[*] shows three

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[*] 1:3:5:8:γ-Pentamethyl-2:4-diethyl-7-carboxyethylporphin

[3] A.Neuberger and J.J. Scott, Proc.Roy.Soc. A 213, 307 (1952)

[4] Numerical values of the chemical shifts recorded in this paper
are in parts per million, and are referred to the τ -scale, on
which the tetramethylsilane peak is taken as +10.00 by defini-
tion (see G.V.D. Tiers, J.Phys.Chem. 62, 1151 (1958)

peaks in the high field region at 13.64(1), 13.84(1), 14.43(2) (the figures in parentheses indicate relative integrated intensities); these may arise from the non-equivalence of the NH groups.]

The peak at 6.30, the quadruplet centred at 5.80, and the triplet at 8.22 are clearly due to the ring-methyl, ring methylene, and side-chain methyl group resonances respectively, although they are shifted slightly from the normal positions. The low-field peak in DTFA solution at -0.69 (present in TFA at -0.88 on the edge of the solvent band) must therefore be due to the methine protons; the neighbouring peak at -0.97 shows the TFA produced by exchange of the NH protons as well as a trace in the DTFA. On the other hand there is no obvious explanation for the peak at 7.73, although it must be connected in some way with the presence of TFA, (see below).

These assignments have been confirmed with other porphyrins. For example, the spectrum of octamethyl porphin in TFA shows peaks at -0.71 (methine), 6.2 (methyl), 7.77 and 14.90 (NH); the peaks at 7.77 and 14.90 are both absent from the spectrum in DTFA.

Simple porphyrins, (especially octamethylporphin) are not sufficiently soluble for their spectra to be measured in chloroform, whilst concentrated sulphuric acid solutions are too viscous and too dilute to give good spectra. On the other hand the esters of the more complex porphyrins are often sufficiently soluble for good spectra to be obtained in chloroform, as well as in TFA and DTFA. Thus the spectra of both the free porphyrin ester and the salts of the corresponding acids can be obtained. The behaviour of coproporphyrin III methyl ester* when dissolved in chloroform

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* 1:3:5:8-Tetramethyl-2:4:6:7-tetracarboxyethylporphin tetramethyl ester.

and in DTFA shows an interesting contrast; in the former case the methine

peak is at 0.04, in the latter at -0.82. This effect of the additional

central protons recalls the effect of electronegative substituents in

aromatic compounds.[5]

A fairly sharp high-field peak at 13.89 has been observed for

coproporphyrin I methyl ester[*] in deuterochloroform, but with chloroform

solutions we find broad high-field bands doubtless caused by intermediate

rates of ^{14}N quadrupolar relaxation. Solvent-solute chemical exchange

is presumably responsible for the sharper peaks in TFA solutions.

The band at 7.7-7.8, present in the spectra of all TFA solutions of

porphyrins, is absent from spectra taken in either DTFA or chloroform

solutions; it thus apparently arises from the presence of TFA although its

precise origin remains uncertain.

The unexpected positions of the low-field peak (due to the methine

protons) at 5.5 p.p.m. lower than ethylene and the very high field peak

(NH protons, 12 p.p.m. high than pyrrole NH[6]) can be attributed on

theoretical grounds to the effect of ring currents[7] in the large conjugated

porphyrin ring system, whereby the NH protons are much more highly

shielded than the NH proton of pyrrole, and the methine protons less

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[*] 1:3:5:7-Tetramethyl-2:4:6:8-tetracarboxyethlporphin tetramethyl ester.

[5] J.A.Pople, W.G.Schneider and H.J.Berstein, High Resolution Nuclear Magnetic Resonance pp. 258 ff. McGraw-Hill, New York (1959).

[6] R.J. Abraham and H.J.Berstein, Canad.J.Chem. 37, 1056 (1959).

[7] J.A.Pople, W.G.Schneider and H.J.Bernstein, High Resolution Nuclear Magnetic Resonance pp. 180,251. McGraw-Hill, New York (1959).

shielded than those of ethylene. It has been reported[1] that the magnetic ring model[8] can account semi-quantitatively for the methine peak, but the calculated position of the NH peak is then far too high. Our own calculations (with 1.28 Å current loop spacing) agree; for example, an assumed ring of 18 electrons with a radius of 3.0 Å locates the methine peak at -1.2, but the NH peak is then at 29.3. In order to fit these calculations to the observations it is necessary to assume an effective number of 9.4 free electrons in a ring of radius 3.7 Å.

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[8] C.E. Johnson and F.A. Bovey, J.Chem.Phys. 29, 1012 (1958).