N.M.R. SPECTROSCOPY OF METALLOPORPHYRIN RADICAL

CATIONS. ELECTRON DENSITY AND AGGREGATION EFFECTS

Jeremy K.M. Sanders[*] and Ian Baxter

University Chemical Laboratory,
Lensfield Road, Cambridge CB2 1EW

Metalloporphyrin radical-cations are important in many biological redox reactions but their mode of action is unclear.[1,2] E.s.r. studies of these species have provided some useful insights but the spectra are frequently complex and difficult to interpret. In this communication we apply an n.m.r. method[3] to these systems and demonstrate that electron density and aggregation information can be readily obtained.

Table 1 shows observed line broadenings at 100 MHz for the radical-cations of metalloporphyrins 1-3 in $CDCl_3$ solution.[4,5]
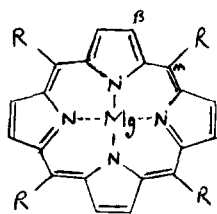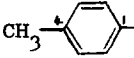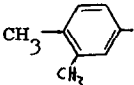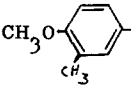

1-3
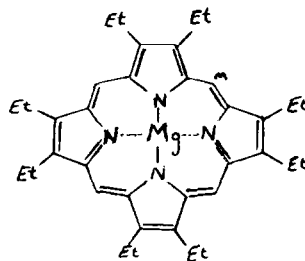
4 (MgOEP)

Table 1

Observed broadenings for some magnesium tetraphenylporphyrin cations[a]

in $CDCl_3$

No	R	Relative Broadening					
		H_2 (H_6)	H_5	$3-CH_3$	$4-CH_3$	$-OCH_3$	$\beta-H$
1	CH_3—⟨⟩—	1	~0.7	–	~0.9	–	<0.1
2	CH_3—⟨⟩— CH_3	1	~0.7	<0.1	~0.9	–	<0.1
3	CH_3O—⟨⟩— CH_3	1	~0.7	<0.1	–	<0.1	<0.1

[a] Generated by addition of iodine to neutral species.

Temperature and frequency dependence of the broadening confirm that the fast exchange condition holds for all resonances, and therefore broadening should directly reflect free electron density.[3] Clearly this is fairly evenly spread around the aromatic ring, but it is striking that in compound 2 delocalisation takes place into the 4-methyl group, and not into the 3-methyl group. Relative broadenings are not substantially changed in solutions containing up to at least 50% methanol or pyridine. These solvents coordinate strongly to the central metal ion.

In contrast, the effect of solvent on MgOEP[+.] is dramatic (Table 2): the ethyl resonances are strongly broadened in $CDCl_3$ solution (Figure) but not in the presence of methanol. Solutions with a high methanol concentration appear consistent with the expected[1] free electron density distribution, and since this distribution should not be very dependent on solvent the ethyl resonances in $CDCl_3$ solution must be suffering a dipolar (spin-label) broadening. Dipolar broadening occurs when the radical correlation time (τ_c) is sufficiently long that the radical field effects are not averaged out by tumbling and we deduce

therefore that $MgOEP^{+ \cdot}$ is aggregated in $CDCl_3$ solution. Preliminary measurements
of radical-induced T_1 changes indeed confirm[8,9] that τ_c (CH_2) is approximately
1×10^{-8} sec and τ_c (CH_3) is $\sim 5 \times 10^{-9}$ in $CDCl_3$ solution.
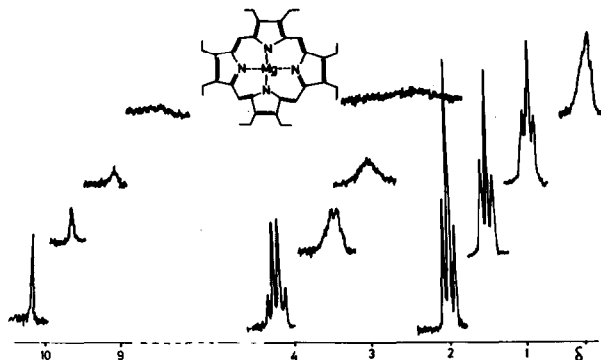
Figure: The effect of added iodine on the 100 MHz p.m.r. spectrum of MgOEP

   (0.007 M) in $CDCl_3$. Successive spectra are offset.

Table 2

Solvent dependence of broadenings in $MgOEP^{+ \cdot}$

Solvent		Relative Broadening		
%$CDCl_3$	%CD_3OD	meso-H	CH_2	CH_3
100	–	1	2.0 ± 0.5	~ 0.2
99	1	1	0.7 ± 0.3	~ 0.07
90	10	1	0.25 ± 0.05	~ 0.02
25	75	1	<0.07	<0.01

We conclude therefore that"

   (i)   MgOEP, $\underline{4}$, is aggregated in $CDCl_3$ solution.

  (ii)   The aggregates can be dispersed by methanol.

 (iii)   The substituted tetraphenyl porphyrins $\underline{1}$-$\underline{3}$ are not substantially

         aggregated in $CDCl_3$, presumably due to unfavourable steric inter-

         actions.

  (iv)   Radical-induced T_1 changes can be used to give information on

mobilities in various parts of a molecule.

Detailed studies of chlorophyll–derived radical-cations are in hand in an effort to define precisely both the electron density distribution and these mobility characteristics.

References

1.   D. Dolphin, R.H. Felton, Acc. Chem. Res., 1974, 7, 26.

2.   J.H. Furhop, Angew. Chem. Int. Ed., 1974, 13, 321.

3.a)   For a good guide to the theory and early literature see E. de Boer and C. Maclean, J. Chem. Phys., 1966, 44, 1334.

  b)   I. Baxter, J.K.M. Sanders, J.C.S. Chem. Comm., 1974, 255.

4.   Deuterochloroform was purified by passage over basic alumina.

5.   Porphyrins 1-3 were synthesised by the method of Adler et al[6] from pyrrole and the appropriate aldehyde. 3,4-dimethyl-benzaldehyde was prepared by a literature procedure.[7] MgOEP, 4, was a gift from Dr. E. McDonald.

6.   A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, J. Org. Chem., 1967, 32, 476.

7.   A. Rieche, H. Gross, E. Hoft, Chem. Ber., 1960, 93, 88.

8.   Method of T.L. James, M. Cohn, J. Biol. Chem., 1974, 249, 3519.

9.   We assume that there is no hyperfine contribution to T_2 changes, and that Solomon–Bloembergen equations are valid.[10]

10.   For discussion of these assumptions see R.A. Dwek, "NMR in Biochemistry", Oxford, 1973, chapters 9 and 12.

11.   For comparison see F.A. Walker, J. Mag. Res., 1974, 15, 201