On the Paramagnetism of Octaethyloxophlorin

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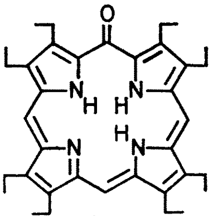
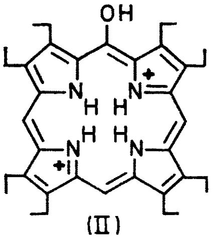
Summary The e.s.r. spectrum of octaethyloxophlorin in dry de-gassed tetrahydrofuran shows hyperfine structure: evidence is presented that this structure is due to coupling with *meso*-protons.

RECENT reports have indicated[1-3] that the oxophlorin system, which, as its iron complex, is thought to be involved in haem catabolism,[4] possesses paramagnetic character. We now summarise some e.s.r. observations with octaethyloxophlorin (I) which define this phenomenon more closely.†


(I)


(II)

(i) The polycrystalline material showed a single absorption (linewidth 11·5 gauss, $g = 2{\cdot}0029$).

(ii) A solution in tetrahydrofuran in the presence of air showed a broad signal with a hint of structure. On addition of trifluoroacetic acid to the solution, the signal disappeared. This loss of signal on acidification was reflected in the n.m.r. observations: in $CDCl_3$ only one broad signal (τ 8·63, Me) was observed (Figure 1a), while in $CF_3CO_2D/CDCl_3$ the spectrum of the oxophlorin dication (II, one canonical form drawn), was obtained.[3]

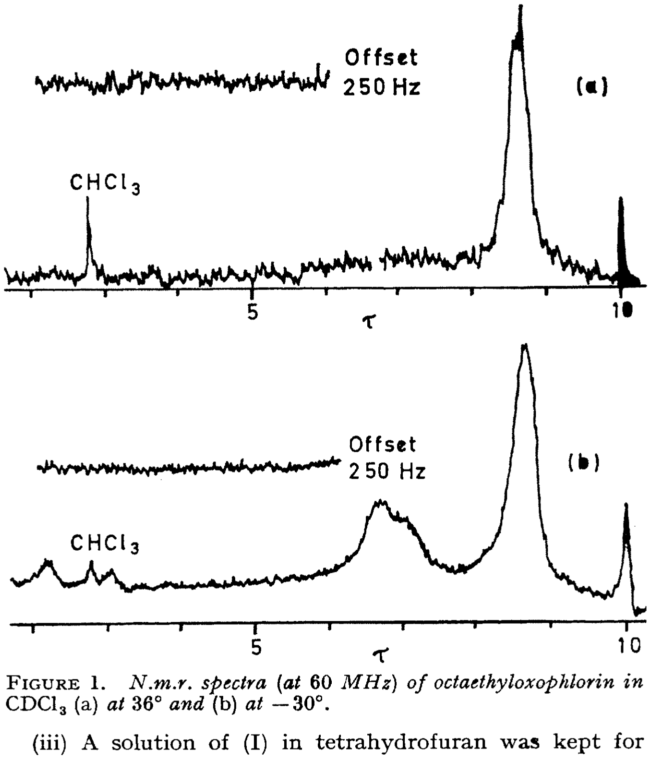


FIGURE 1. *N.m.r. spectra (at 60 MHz) of octaethyloxophlorin in* $CDCl_3$ (a) *at* 36° *and* (b) *at* −30°.

(iii) A solution of (I) in tetrahydrofuran was kept for several weeks (in air). The e.s.r. signal slowly decreased,

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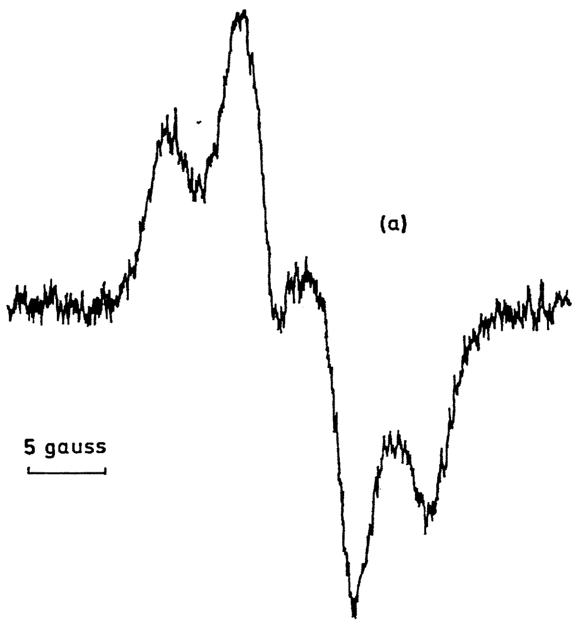
† A Decca X3 spectrometer incorporating a Newport Instruments M4X magnet system was used. Linewidth refers to peak-to-peak distance in the first derivative spectrum.

and the solution finally contained (t.l.c.) only a trace of oxophlorin. An as yet unidentified red compound was the major product.

(iv) In dry de-gassed tetrahydrofuran‡ the oxophlorin gave an e.s.r. spectrum possessing hyperfine structure, a quartet centred at $g = 2{\cdot}0025$ with a splitting of 4·5 gauss. The signal decreased in intensity as the temperature was lowered (Figure 2). This behaviour was again reflected in the n.m.r. spectrum: thus the spectrum in $CDCl_3$ at −30° (Figure 1b; contrast 1a) showed broad signals at τ 2·15, 3·02 (*meso*-H); 6·69, 7·02 (CH_2); and 8·62 (Me).

(v) 10,15,20-Trideuterio-octaethyloxophlorin[3] in dry degassed tetrahydrofuran gave a single line (linewidth 6·4 gauss, $g = 2{\cdot}0024$). On the basis of the observed proton coupling (see iv) a linewidth of *ca.* 4·5 gauss would be expected.

It is difficult to eliminate entirely the possibility that the observed e.s.r. spectrum is due to an impurity, or a reaction product arising from the oxophlorin, especially since the concentration of paramagnetic species is low (*ca.* 1% at 20°). However a direct photochemical process does not appear to be involved (a sample prepared as in iv, but in the dark, showed no change in signal on exposure to daylight). Autoxidation to give a radical species is a possibility, although the available evidence (items ii and iv) does not favour it.



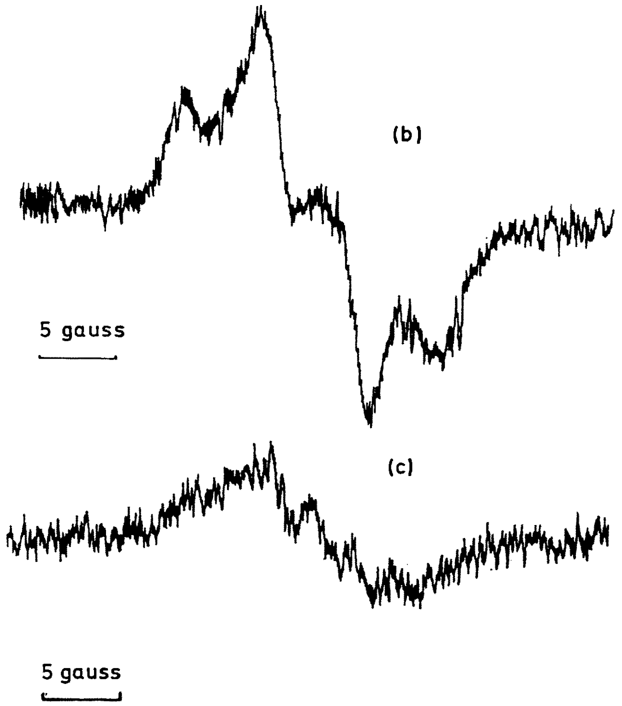


FIGURE 2. *E.s.r. spectra of octaethyloxophlorin in de-gassed tetrahydrofuran at* (a) 20°, (b) 0°, *and* (c) −60°.

We therefore suggest that the observed paramagnetism is an inherent property of the oxophlorin system, the temperature dependence of the e.s.r. signal being then ascribed (see also refs. 2 and 5) to the existence of a thermally-attainable triplet species estimated to be *ca.* 2·8 kcal. above the ground state. The deuteriation experiment indicates that the hyperfine structure is due principally to the three *meso*-protons, which give rise to the observed quartet. Some interaction with methylene protons must also occur (see Figure 1a) but interaction with nitrogen is absent or very small.

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‡ Sealed system, the tetrahydrofuran being distilled *in vacuo* from sodium–anthracene.

[1] P. S. Clezy, F. D. Looney, A. W. Nichol, and G. A. Smythe, *Austral. J. Chem.*, 1966, **19**, 1481; P. S. Clezy, A. J. Liepa, and G. A. Smythe, *ibid.*, 1970, **23**, 603.
[2] A. H. Jackson, G. W. Kenner, and K. M. Smith, *J. Chem. Soc.* (*C*), 1968, 302.
[3] R. Bonnett, M. J. Dimsdale, and G. F. Stephenson, *J. Chem. Soc.* (*C*), 1969, 564.
[4] R. Lemberg, *Rev. Pure and Appl. Chem.* (*Australia*), 1956, **6**, 1.
[5] M. J. Dimsdale, Ph.D. Thesis, London, 1968.