π-Cation Radical Generation *via* Aerial Oxidation of a Porphyrin

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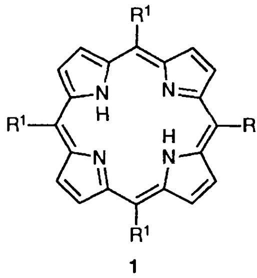
ESR spectroscopy and simulation suggest that *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin **1** undergoes aerial oxidation in acidified solutions to give a long-lived π-cation radical with a quasi-$^2A_{2u}$ ground state.

We have previously reported the facile two-electron aerial oxidation of **1** in basified solutions.[1] Oxidation proceeds *via* a radical intermediate whose strong triplet ESR spectrum is indicative of unpaired electron density localised over a 3,5-di-*tert*-butyl-4-phenoxy *meso*-substituent.[1e]

This radical subsequently decays with pseudo first-order kinetics[2] to the final ESR-silent product, shown by ^{1}H NMR spectroscopy to be the porphodimethene **2**[1a] in solution, and by X-ray crystallography to be the tautomeric tetraquinomethide xanthoporphyrinogen **3**[3] in the solid state.



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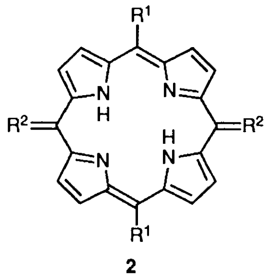

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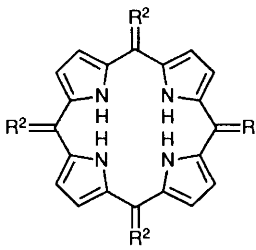

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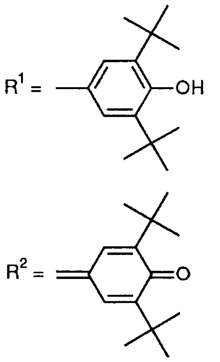

We now report that facile aerial oxidation of **1** also takes place in acidified solutions. This time, however, the radical is long-lived in the presence of air. We also present compelling evidence suggesting that the unpaired electron is delocalised over the macrocycle to form a porphyrin π-cation radical. As such, we believe this constitutes the first evidence for: (*i*) porphyrin π-cation radical generation *via* aerial oxidation, (*ii*) the generation of such a radical from a porphyrin dication.

A solution of porphyrin **1** (1.5×10^{-2} mol dm^{-3}) in 1,1,1-trichloroethane (TCE; 1 ml) in air, was acidified with 5 drops of trifluoroacetic acid (TFA). The solution immediately turned deep-green, typical of *meso*-tetraaryl porphyrin dications[4] (PH_4^{2+}), but also gave a singlet ESR spectrum [*g* 2.007, Fig. 1(*a*)] which did not decay appreciably over a 2 h period. This spectrum resembled those of *meso*-aryl-substituted metalloporphyrin ($MTPP^{+\bullet}$) π-cation radicals generated in the presence of oxygen.[5]

Deoxygenation of the above solution (by bubbling N_2) gave an ESR spectrum showing an extensive hyperfine structure of 29 lines [Fig. 1(*b*)] superimposed on the singlet envelope. Again, this resembles the ESR behaviour of deoxygenated $MTPP^{+\bullet}$ solutions, which show a hyperfine structure of nine lines superimposed on the singlet envelope.[6] Deoxygenation of the porphyrin solution *prior* to acidification with (degassed) TFA did not give an ESR spectrum.

$MTPP^{+\bullet}$ π-cation radicals have an unpaired electron density in a HOMO of a_{2u} symmetry,[6,7] (Fig. 2) so generating a quasi-$^2A_{2u}$ ground state. The nine-line ESR spectrum arises from an unpaired spin density interacting with four equivalent nitrogens ($I = 1$; $a_N \simeq 0.15$ mT)[6] and eight equivalent *ortho*-hydrogens ($I = \frac{1}{2}$; $a_H \simeq 0.03$ mT)[6] on the *meso*-aryl groups. This smaller interaction is thought to result from the spin density at the *meso*-positions[7] 'leaking' *via* hyperconjugative and inductive effects, onto the *meso*-substituents.[8]

Our simulation of the 29-line ESR spectrum derived from **1** [Fig. 1(*c*)] assumes a quasi-$^2A_{2u}$ ground state for the radical cation (*g* 2.007). It uses experimental ESR parameters for the four equivalent hydrogens attached to the central nitrogens ($a_{H(1)} = 0.05$ mT) and eight equivalent *ortho*-hydrogens attached to the *meso*-substituents ($a_{H(2)} = 0.0828$ mT), and a best-fit hyperfine splitting constant for the four equivalent nitrogens ($a_N = 0.0962$ mT).

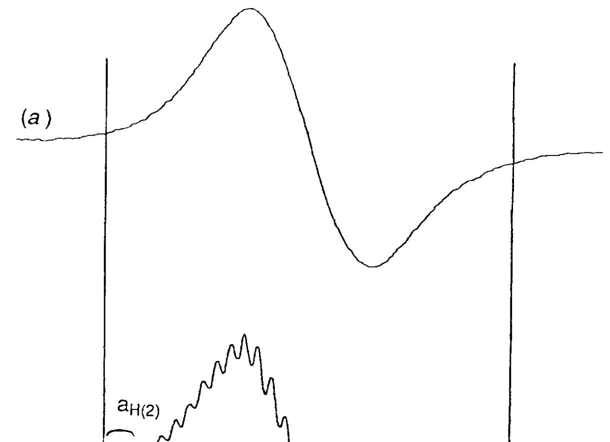

Fig. 1 (*a*) ESR spectrum obtained on addition of TFA (5 drops) to a TCE solution of porphyrin **1** (1.5×10^{-2} mol dm^{-3}) in the presence of air (*g* 2.007). (*b*) The same solution after degassing with nitrogen: $a_{H(1)} = 0.05$ mT; $a_{H(2)} = 0.0828$ mT. (*c*) Simulated ESR spectrum using best-fit nitrogen hyperfine splitting constant, $a_N = 0.0962$ mT; line-shape, 85% Gaussian/15% Lorentzian; spectral width, 0.07 mT cm^{-1}; half-width at half-height, 0.042 mT.

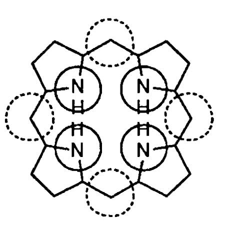

Fig. 2 The a_{2u} HOMO for a porphyrin dication (after Gouterman[4])

Interestingly, the simulated a_N and observed $a_{H(2)}$ hyperfine splitting constants differ markedly from those obtained for $MTPP^{+\bullet}$: there is a decrease in a_N and an increase in $a_{H(2)}$. Also, $a_{H(2)} > a_{H(1)}$, indicating that the unpaired electron interacts more strongly with the *ortho*-hydrogens on the *meso*-substituents than those on the central nitrogens. This is probably due to the radical (**PH**$_4^{3+\bullet}$) being derived from a porphyrin dication (**PH**$_4^{2+}$); the increased positive charge on

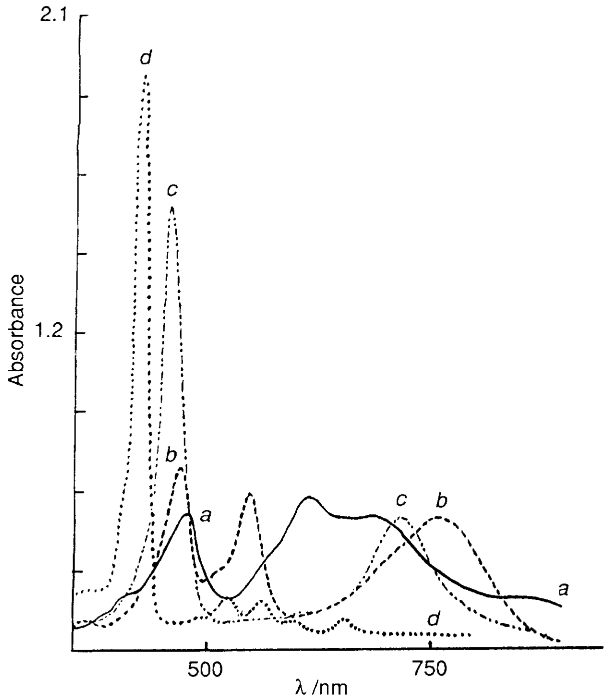

Fig. 3 UV–VIS spectra of a solution of porphyrin **1** (8×10^{-6} mol dm^{-3}) in CH_2Cl_2 (*a*) on addition of TFA (0.2 ml, >0.4 mol dm^{-3}) after 5 min; (*b*) on addition of TFA (0.2 ml, <0.04 mol dm^{-3}) after 5 min; (*c*) on addition of TFA (0.2 ml, <0.04 mol dm^{-3}) immediately; (*d*) neutral solution

the macrocycle (compared to MTPP$^{+\bullet}$) leading to a decrease in spin density over the central nitrogens.

meso-Aryl-substituted porphyrin dications also undergo extensive macrocyclic deformations[9] leading to a decrease in the dihedral angle between the aryl groups and the macrocyclic plane. In this context, it is worth noting that the two-electron oxidation of **1** in base generates a macrocycle with co-planar *meso*-substituents.[3] It is likely, therefore, that in the π-cation radical of **1**, the porphyrin and the *meso*-substituent π-systems are strongly coupled, allowing spin density at the *meso*-position to delocalise onto the aryl moieties.

UV–VIS spectroscopy of dilute acidified (8×10^{-6} mol dm^{-3}) solutions of **1** proved interesting. On addition of moderate to high concentrations (>0.4 mol dm^{-3}) of TFA, a UV–VIS spectrum was obtained that closely resembled those of MTPP$^{+\bullet}$ π-cation radicals [Fig. 3(*a*)].[10] However, addition of low concentrations (<0.04 mol dm^{-3}) of TFA initially gave the typical (unoxidised) porphyrin dication spectrum [Fig. 3(*c*)], which changes over 5 minutes to one that closely resembles the two-electron oxidised product, **2** or **3**, in acid [Fig. 3(*b*)].[1a] All this suggests that in acidified solutions direct one-electron aerial oxidation of **1** is not taking place.

$$PH_4{}^{2+} + PH_4{}^{4+} \rightleftharpoons 2\ PH_4{}^{3+\bullet} \qquad (1)$$

We speculate on a possible mechanism. On addition of acid, two-electron oxidation takes place first. At higher TFA concentrations, this product then undergoes further protonation, followed by conproportionation with the unoxidised dication of **1** to form the π-cation radical [see eqn. (1)], a precendent for which exists in the tetraquinocyclobutane series.[11] We shall report more fully on the mechanism of this oxidation elsewhere.

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