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THE FACILE AERIAL OXIDATION OF A PORPHYRIN

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Abstract: Meso-tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin (1a) undergoes rapid, non-photosensitised, aerial oxidation in basic solutions. The product (3) is shown by NMR, UV/visible and Fast-atom Bombardment spectroscopy, to be a novel tetrapyrrolic macrocycle, possessing an extended diphenoquinoid conjugated system in place of the porphyrin aromaticity.

Photosensitised oxidation of porphyrins by singlet dioxygen generally leads to the destruction of the macrocycle.[1,2] In this respect, metalloporphyrins[3,4] and porphyrin dianions[5] are more susceptible to photo-oxidation than the free-base porphyrins[2] unless the molecule contains unsaturated photo-labile side-chains,[6] e.g., protoporphyrin IX. In the absence of light, however, porphyrins are stable to oxygen. This paper reports, for the first time, the facile, non-photosensitised oxidation of a porphyrin by molecular di-oxygen, in which the macrocyclic framework of the molecule survives.

Meso-tetrakis(4-hydroxyphenyl)porphyrin (2a) was recently shown to be a useful synthon in the production of novel porphyrin sensitisers for studies in solar-energy conversion.[7] Reaction proceeds via the green tetraphenoxide (2b), produced by the action of KOH in methanol or K_2CO_3 in DMF. Further reaction with suitable substituents was followed by the reappearance of the porphyrin red colour. In order to broaden this procedure for the synthesis of sterically-hindered porphyrin sensitisers, the synthon, meso-tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin (1a) was prepared. Reaction with methanolic KOH momentarily gave a green intermediate (1b), which rapidly turned blue in air. (Exclusion of oxygen from the reaction, however, maintained the green colour of (1b)). Neutralisation of the blue product did not reform the porphyrin (1a). Subsequent separation and investigation of the blue principle, indicated that the porphyrin (1a) had undergone a facile two-electron oxidation to (3).

Results and Discussion

Condensation of 3,5-di-tert-butyl-4-hydroxy-benzaldehyde with pyrrole, inrefluxing propionic acid,[8] afforded the porphyrin (1a) in 13% yield. A dichloromethane solution of (1a), in methanolic KOH (10% w.v.), gave a green solution of the tetraphenoxide (1b), which rapidly turned deep blue in air, under illumination or in the dark. Neutralisation with trifluoracetic acid converts the blue solution to a purple colour which, following work-up, afforded (3) as a dark-green amorphous powder in 60% yield. A similar series of changes was observed for the zinc chelate of porphyrin (1a) (Figure 1).

The UV/visible spectra of (3), in acidic, basic, and neutral media, are characterised by loss of the intense porphyrinic B band at 420 nm, and by strong broad absorbances in the

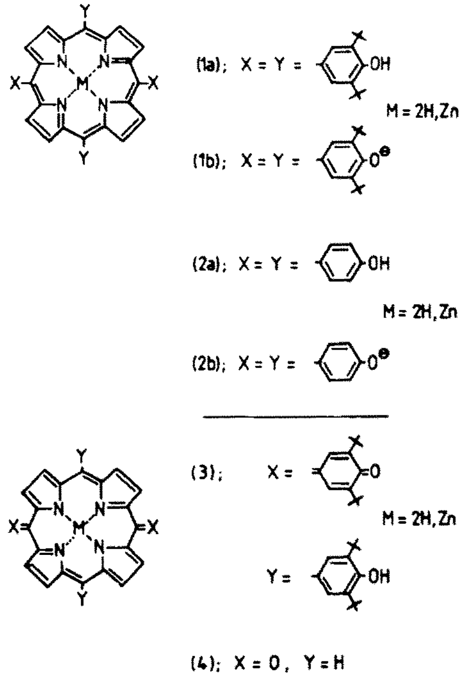


Figure 1

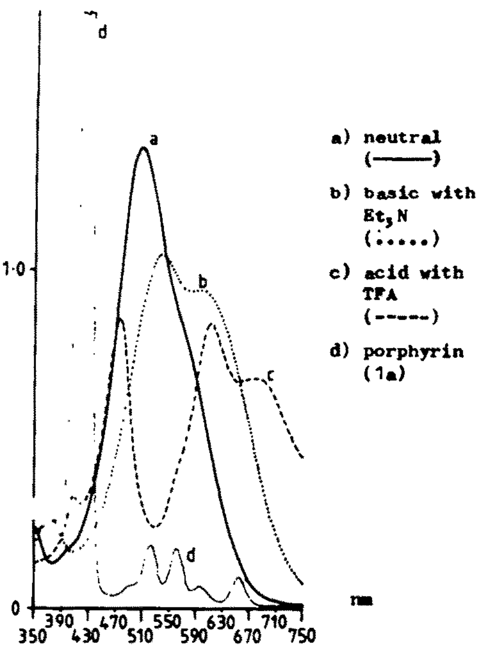


Figure 2. UV/visible spectra of (3) in CH_2Cl_2

range 450 - 750 nm (Figure 2). In the ^{1}H-NMR spectrum of (3), the N-H protons appear at very low field (δ_H = 9.5 ppm). This is in contrast to those of the porphyrin (1a) which, by virtue of diamagnetic shielding,[9] appear at high field relative to TMS (δ_H = -2.6 ppm). Also, the tert-butyl protons appear as two singlets (δ_H = 1.3 and 1.6 ppm) at higher field than the lone tert-butyl singlet of the porphyrin (1a) (δ_H = 1.7 ppm). This indicates that the tert-butyl protons of (3) have two different chemical environments. On addition of d_5-pyridine, the two tert-butyl singlets of (3) collapse to one (δ_H = 1.4 ppm) and the N-H protons are shifted further downfield (δ_H = 11.0 ppm).

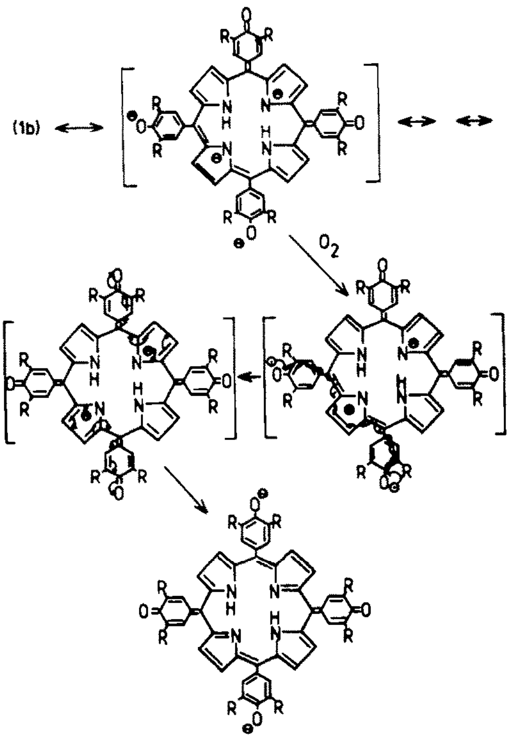
The Fast-atom Bombardment spectrum of (3) shows an M^+ ion at m/z = 1124 (compared to the M^+ ion for porphyrin (1a) at m/z = 1126) indicating a loss of two protons from the porphyrin following oxidation.

The compound (3) gave no observable ESR signal and solutions were visibly non-fluorescent.

Reduction of (3) with lithium aluminium hydride restored the typical porphyrinic UV/visible spectrum of (1a), i.e., an intense B band at 420 nm and four weak Q bands between 500 and 700 nm. The red fluorescence emission of (1a) was also restored. Both these observations demonstrates the survival of the macrocyclic skeleton of (1a) following oxidation.

All this spectroscopic data suggests that the aromaticity of (1a) is interrupted after oxidation. A plausible mechanism for the formation of (3) involves an intramolecular oxidative coupling of two phenoxide meso-substituents on (1a). Phenoxy radicals are first formed, followed by electronic re-arrangement to form the 'trans' (i.e., on opposite sides of the macrocyclic skeleton) extended diphenoquinoid system (Scheme). The ^{1}H-NMR data would seem to support this hypothesis. A precedent exists in the well-known intermolecular oxidative coupling of 2,6-di-tert-butylphenol, in base, to 2,2',6,6'-tetra-tert-butyldiphenoquinone.[10]

The compound (3) bears certain resemblances to the α,γ-dioxoporphodimethenes (4), obtained by chemical and photochemical oxidation of oxophlorins,[11] and meso-aminoporphyrins.[12] Thus, (4) has broad absorbtions in its electronic spectrum and the intense porphyrin B band is missing. Also, in the ^{1}H-NMR spectrum of (4), the N-H protons appear at low field (δ_H = 10 ppm)[13,14] indicating a lack of porphyrinic aromaticity.



(3)

Scheme

A preliminary investigation into the generality of this reaction for the meso-tetrakis(4-hydroxyaryl)porphyrin series was encouraging. Thus, the tetraphenoxide (2b) is air-stable in methanolic KOH solution. When treated with bromine (1drop), however, the green colour of (2b) was immediately replaced by purple with the same UV/visible spectroscopic features as (3), i.e., loss of the intense porphyrin B band absorbtion at 420 nm and strong, broad absorbances in the range 450 - 750 nm. Addition of hydroquinone restored the porphyrin spectrum. Similar spectroscopic changes were observed for the green tetraphenoxide of meso-tetrakis(3,5-dimethoxy-4-hydroxyphenyl)porphyrin, when treated with basic potassium ferricyanide solution (1drop). The porphyrinic spectrum was restored with sodium borohydride.

It is anticipated that this novel redox behaviour for the porphyrin series, could be exploited in new oxygen-reduction catalysts (for in vivo biosensors, fuel-cells, air-batteries, and photochemically-driven solar-energy conversion) and organic conductors and semi-conductors.[15]

Experimental

^{1}H-NMR spectra were recorded at 250 MHz on a Bruker WM 250 instrument, using $CDCl_3$ as solvent and TMS as internal reference. UV/visible spectra were recorded on a Pye Unicam SP8-400 spectrophotometer. Fast-atom bombardment spectra were obtained using a Vacuum Generators High Field ZAB instrument. Chromatographic separations were performed on columns made from slurries of neutral alumina (Brockmann activity grade III, BDH). Solvents were used as supplied.

5,10,15,20-Tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin (1a) - Pyrrole (Aldrich; 6.7gm, 0.1mol) was added to a refluxing solution of 3,5-di-tert-butyl-4-hydroxybenzaldehyde (Aldrich; 23.4gm, 0.1mol) in propionic acid (Aldrich; 500ml). After 1½ hours, the mixture was concentrated to one-fifth its volume and cooled. The solid was filtered, taken into chloroform and chromatographed on alumina, eluting with chloroform. The eluant was concentrated and crystallised with light petroleum (b.p. 60 - 80°C) to afford the porphyrin (1a) as purple microcrystals (3.7gm, 13%), m.p. = >300°C. (Microanalysis as zinc chelate. Found: C = 74.6; H = 7.8; N = 4.4%. $C_{76}H_{92}N_4O_4Zn.2H_2O$ requires C = 74.43; H = 7.83; N = 4.57%). UV/visible spectrum (see 'd' in Figure 2):

λ_{max}nm (ϵ mmol l^{-1}) in CH_2Cl_2; 426(330), 522 (14), 560(13), 597(5), 654(7).
^{1}H-NMR (250MHz, $CDCl_3$) δ_H(ppm); -2.6 (2H, br s, N-H), 1.7 (72H, s, t-butyl), 5.6 (4H, s, -OH), 8.1 (8H, s, Ar), 8.9 (8H, s, pyrrole-H).
FABS: found M^+, m/z = 1126, requires m/z 1126.

5,15-Di-(3,5-di-tert-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-tert-butyl-4-quinomethene) porpho-10,20-dimethene (3) - The previous porphyrin (1a) (500mg, 0.44mmol) in dichloromethane (250ml) was stirred with 10% (w/v) methanolic KOH (10ml) for 24 hours. The solution was then neutralised with a few drops of trifluoracetic acid and then washed with water in a separating funnel. The lower, dichloromethane layer was run off, dried over magnesium sulphate (anhydrous), filtered, evaporated to dryness, and recrystallised from dichloromethane and light petroleum (b.p. 60 - 80°C). The intense dark-green microcrystals were filtered, washed with ether, and dried. (300mg, 60%) m.p. > 300°C.
(Found: C = 77.5; H = 8.1; N = 4.7%.
$C_{76}H_{92}N_4O_4 \cdot 3H_2O$ requires C = 77.42; H = 8.32; N = 4.75%)

λ_{max}nm (ϵ mmol l^{-1}) in neutral CH_2Cl_2 (see 'a' in Figure 2); 406(23), 508(109), 578(63 sh): in CH_2Cl_2 + Et_3N (see 'b' in Figure 2); 367 (17), 530(89), 590(73 sh): in CH_2Cl_2 + TFA (see 'c' in Figure 2); 347(17), 476(68), 608 (53 sh).

^{1}H-NMR (250 MHz, $CDCl_3$) δ_H(ppm); 1.3 (36H, s, t-butyl), 1.6 (36H, s, t-butyl), 6.8 (8H, s, Ar), 7.6 (8H, s, pyrrole-H), 9.5 (2H, br s, N-H). With d_5-pyridine; 1.4 (72H, s, t-butyl), 6.7 (8H, s, Ar), 7.5 (8H, s, pyrrole-H), 11.0 (2H, br s, N-H).

FABS: found M^+, m/z = 1124, requires m/z 1124.

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