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The Oxidation of α-Amino-octaethylporphinatozinc to α-Imino-γ-oxoporphinogenatozinc

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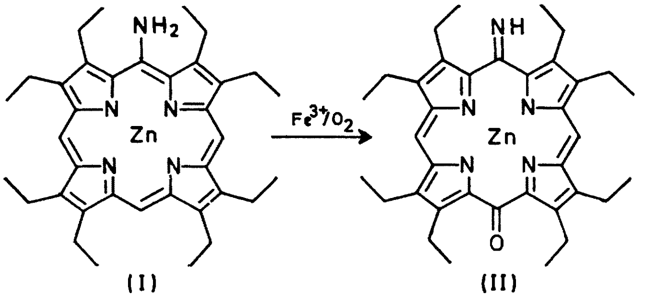
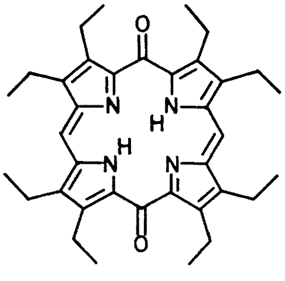
Summary The title reaction is thought to proceed *via* an imino-phlorin radical and to be analogous to the oxidation of aniline to *p*-benzoquinone.

THE oxidation of octaethylporphinatozinc with Fe^{3+} salts leads in a clean, reversible reaction to its cation radical.[1] The reaction has now been extended to include some *meso*-substituted porphin ligands, and with α-amino-octaethylporphinatozinc (I) an irreversible oxidation to α-imino-γ-oxoporphinogenatozinc (II) was observed when air was not excluded. (II) was characterized by its mass spectrum, molecular peak *m/e* 625,627,[2] ^{1}H n.m.r. spectrum, τ 3·53 and 3·19 (methine H), 0·27 (imine H), signal disappears with D_2O, i.r. spectrum, 3310 and 1602 cm^{-1}(=N–H), and electronic spectrum, λ_{max} ($CHCl_3$) 556 (ε 30,000) and 445nm (66,000). (II) was easily hydrolysed to αγ-dioxoporphinogenatozinc (III) [λ_{max} ($CHCl_3$) 576 (33,000) and 440 nm (78,000)] simply by leaving it in chloroform or during chromatography on active silica gel or aluminium oxide. (III) could be demetallized to αγ-dioxo-octaethylporphinogen in low yield by shaking its chloroform solution with diluted hydrochloric acid. Extensive ring opening of the porphinogenato-macrocycle was always observed, when (II), (III), or (IV) were exposed to hydrolytic conditions. The compounds (II)—(IV) could all be converted into octaethylporphin in 20—60% yield by 3% sodium amalgam in ethanol. (IV) [m.p. 272—274°, mass spectrum, molecular peak at *m/e* 564,566,[2] ^{1}H n.m.r. spectrum, τ 3·36 (methine H) electronic spectrum, λ_{max} ($CHCl_3$) 495 (ε 16,000) and 410 nm (71,000)] was also synthesized by oxidation with oxygen of dihydro-αγ-dioxo-octaethylporphinogen[3] and its zinc complex was identical with (III).



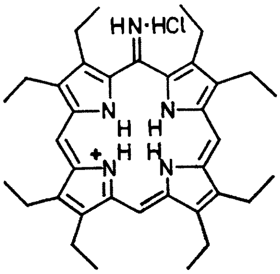
(I) (II)



(IV)
(III) *is the zinc complex of this porphinogen base.*

The oxidation (I) → (II) and its subsequent hydrolysis to (III) are thought to be analogous to the oxidation of aniline to *p*-benzoquinone. The course of the reaction may be rationalized as follows: the zinc-porphyrin (I) is first oxidized by Fe^{3+} to its cation radical, the positive charge of the macrocycle pulls an electron pair from the amino-nitrogen to the ring to form a phlorin radical, which is then stabilized by adding an oxygen atom. Direct evidence for the intermediacy of an iminophlorin radical could not be obtained, but an observation of Bonnett *et al.*[4] and Johnson *et al.*[5] indicates that the single electron pair of the amino-nitrogen is very likely to participate in bond formation to to the porphin macrocycle, when it is positively charged:

acidification of α-amino-porphyrin solutions leads quantitatively to green compounds with a phlorin-like spectrum. In these solutions the γ-methine proton is easily exchanged with deuterium, which is typical for phlorins.[6] α-Amino-octaethylporphin dihydrochloride could be crystallized and its analytical data are in agreement with structure (V) [electronic spectrum, λ_{max} ($CHCl_3$) 640 (ϵ 18,500), 588 (6400), and 428 nm (240,000), elemental analysis yields two chloro-anions per molecule]. An immediate result from these findings is that the amino-nitrogen is less basic than the pyrrolenine nitrogens of the macrocycle and that the porphin and phlorin ligands have similar stabilization energies. The first statement can be expanded by saying that the amino-protons are also more acidic than the N–H protons of the porphyrin macrocycle: upon dissolving α-amino-octaethylporphin in 20% tetramethylammonium hydroxide in methanol a phlorin-type spectrum appears (λ_{max} 730 and 420 nm) which indicates the formation of an imino-phlorin anion, whereas octaethylporphin itself does not loose a proton under these conditions. The second conclusion is in agreement with those of Jackson *et al.* on oxo-phlorins.[7]



(V)

(I) can also easily be photo-oxygenated irreversibly in benzene. The spectra of the resulting products resemble that of (II). An interesting aspect of the chemistry of *meso*-aminoporphyrins lies in the possibility that such compounds could be formed in Nature, apart from the main biosynthetic route, from porphobilinogen and play a rôle in such phenomena as "early bile pigment" formation and corrin synthesis.

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