The Crystal Structure of 5-Benzoyloxyoctaethylporphyrin. An Example of a Distorted Porphyrin Ring

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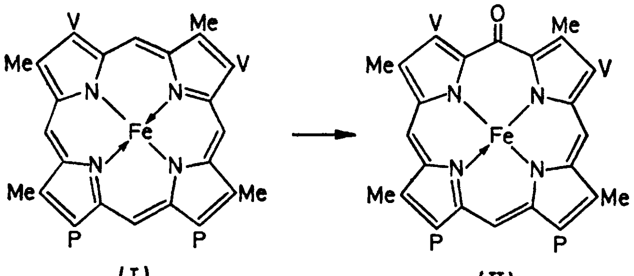
Summary The X-ray structure determination of 5-benzoyloxyoctaethylporphyrin is reported; the porphyrin skeleton is significantly ruffled, with an alteration in geometry of the central 'hole', compared to that in porphyrin itself.

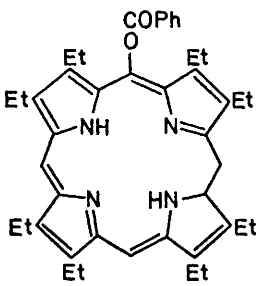
It has been well established that the degradation of the haem group in haemoglobin and other haemoproteins results in the formation of the open-chain tetrapyrroles (the bile pigments[1]). There is no generally accepted mechanism for this catabolism. A likely postulate however, is that the initial reaction is *meso*-hydroxylation of a haem,[2] such as (I), to give an iron(III) oxophlorin derivative (II).



(I)

(II)

V = vinyl
P = propionic acid
(axial ligands not shown)



(III)

Bonnett *et al.*[3] have suggested that this reaction is a free-radical one, and have shown that a major product of the reaction of the model compound octaethylporphyrin with benzoyl peroxide, is the *meso*-benzoyloxyporphyrin (III). This is just the stabilised ester of the hydroxy-porphyrin tautomeric with the oxophlorin system.

We report an X-ray analysis of compound (III). It crystallises as purple lustrous prisms, in the space group $P2_1/n$, with cell dimensions $a = 15{\cdot}105$, $b = 20{\cdot}729$, $c = 12{\cdot}721$ Å, $\beta = 112{\cdot}05°$, and four molecules of $C_{43}H_{50}N_4O_2$ in the unit cell. The intensities of 5410 reflections, to a limit of 60° in θ, were collected on a Siemens AED diffractometer, employing Cu-K_α radiation. A total of 4151 reflections were considered to be statistically significant. The structure was solved by direct methods,[4] to a current value of $R = 0{\cdot}077$; refinement is being continued. Standard deviations for non-hydrogen bond lengths average 0·008 Å, and 0·6° for valence angles. The Figure shows the overall structure.

This is the first reported structure determination of a metal-free porphyrin with a single *meso* substituent. It is evident that the introduction of a benzoyl group in this position has markedly altered the geometry from that observed in porphyrin itself,[5] which is virtually completely planar, to give a ruffled molecule. (It is well known that porphyrins are easily deformable).[6] This ruffling is most marked for pyrrole rings A and B; these rings are inclined at angles of 6·4° and 3·9° to the mean plane of the four nitrogen atoms, and are at an angle of 9·9° to each other. Atom O(25) is 0·397 Å out of the mean plane. These deformations can probably be attributed to interactions between O(25) and the hydrogen atoms on C(36) and C(38).

The geometry of the central 'hole' is significantly different from that in both porphyrin itself, and all the metal–porphyrin complexes so far examined.[6] These all have a square 'hole', with a nitrogen–nitrogen distance of 2·90 Å in porphyrin, whereas compound (III) has a distinctly rectangular arrangement. The N(22)–N(23) and N(21)–N(24) distances are 2·969 and 2·960 Å, and the N(21)–N(22) and N(23)–N(24) ones are 2·828 and 2·837 Å, respectively. These differences are highly significant in view of the standard deviations involved.

The central hydrogen atoms have been located, as four 'half-atoms', each attached to a nitrogen. This effect has often been observed in the porphyrin series;[5,6] it is not clear whether it reflects either static or dynamic disorder of the hydrogen atoms.

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One of us (S.N.) is an ICI Research Fellow of the University of London.

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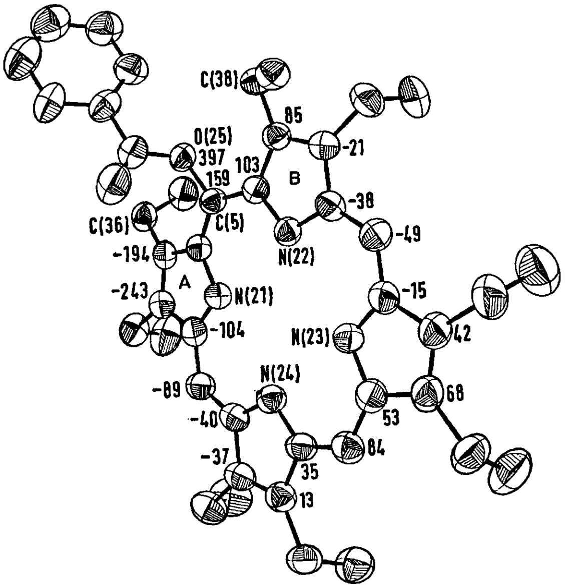

FIGURE. *A molecule of 5-benzoyloxyoctaethylporphyrin. The thermal ellipsoids are scaled to include 50% probability. The deviations of various atoms from the mean plane of the four nitrogen atoms are shown, in* Å × 10^3.

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[1] For a recent review, see, for example, C. Ó. Heocha in "Porphyrins and Related Compounds," ed. T. W. Goodwin, Academic Press, London and New York, 1968, p. 91.

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[6] E. B. Fleischer, *Accounts Chem. Res.*, 1970, **3**, 105.