5,10,15,20-Mesotetrakis(3,5-di-t-butyl-4-quinomethide)porphyrinogen: a Highly Puckered Tetrapyrrolic Macrocycle from the Facile Aerial Oxidation of a Phenolic Porphyrin

Andrew J. Golder,[a] Lionel R. Milgrom,*[b] Kevin B. Nolan,*[c] and David C. Povey[a]

[a] *Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, U.K.*
[b] *Department of Chemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH, U.K.*
[c] *Department of Chemistry, Royal College of Surgeons in Ireland, St. Stephen's Green, Dublin 2, Ireland*

The unusually highly puckered macrocyclic core of the title compound confirms proposed conformational changes which are essential for the facile aerial oxidation of phenolic porphyrins, such as *meso*-tetrakis(3,5-di-t-butyl-4-hydroxyphenyl)porphyrin (**1**).

Mediation of electron-transfer reactions by tetrapyrrolic macrocycles[1a] is the key to their biological function (*e.g.*, as chlorophyll in the photosynthetic light reaction[1b,c] and haem groups in haemoprotein redox enzymes[1d]) and their use as O_2 reduction catalysts,[2a] organic conductors and semiconductors,[2b] and tumour photonecrotic agents.[2c]

In trying to model this behaviour, we have investigated the ease of oxidation of phenolic porphyrins[3a—c] and their metal complexes.[3d] In particular, the free-base porphyrin (**1**) was shown to oxidise to the porphodimethene diquinomethide (**2**). Subsequently, these porphyrins were found to model the haem redox activity in peroxidases and cytochrome P450[3e] and also to make promising O_2-reduction catalysts.[3f] We proposed, and molecular models show, that facile aerial oxidation must involve appreciable overlap between the phenolate and macrocyclic π-systems, and that the oxidised product should contain coplanar, or nearly coplanar, *meso*-substituents with a puckered macrocyclic core.

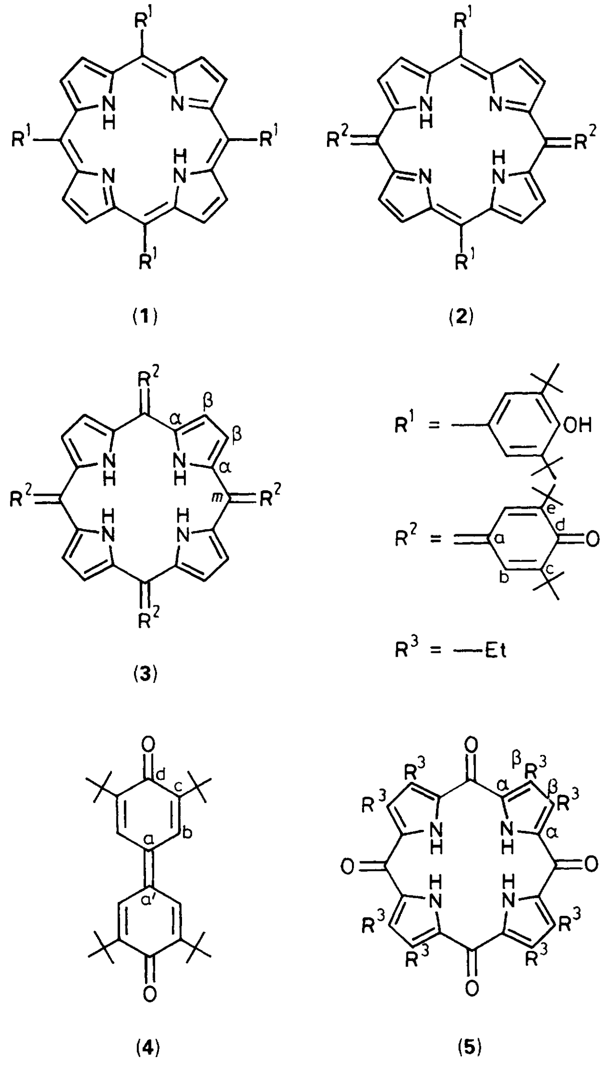
Crystallographic studies of both the Ni^{II} and Pd^{II} complexes of (**1**)[4a—c] partly support this view. Thus, the Ni^{II} complex, which has a substantially ruffled macrocyclic core,[5] undergoes facile aerial oxidation in basified solutions while the Pd^{II} complex, which has an essentially planar core, does not.[6]

We now present crystallographic data which show that the

Table 1. Representative bond lengths (Å) and bond angles (°).[a]

	(**3**)[b]	(**4**)	(**5**)	Pyrrole[c]
$N–C_\alpha$	1.36(2)	—	1.365(4), 1.384(4)	1.370(5)
$C_\alpha–C_\beta$	1.39(3), 1.46(3)	—	1.396(5), 1.401(5)	1.387(5)
$C_\beta–C_\beta$	1.44(3)	—	1.403(5)	1.420(5)
$C_\alpha–C_m$	1.43(2)	—	1.440(5)	—
$C_m–C_a$	1.40(2)	1.402(4)[d]	—	—
$C_a–C_b$	1.47(2)	1.440(2)	—	—
$C_b–C_c$	1.35(2)	1.345(3)	—	—
$C_c–C_d$	1.45(2)	1.479(3)	—	—
$C_d–O$	1.29(2)[e]	1.228(2)	1.235(5)[f]	—
$C_\alpha–N–C_\alpha$	110(1)	—	109.0(3)	109.8(5)
$N–C_\alpha–C_\beta$	107(2)	—	108.7(3)	107.7(5)
$C_\alpha–C_\beta–C_\beta$	105(2)	—	107.2(3)	107.4(5)
$C_a–C_b–C_c$	122(1), 123(1)	124.3(2)	—	—
$C_b–C_c–C_d$	118(2), 117(1)	118.1(2)	—	—
$C_c–C_d–C_e$	123(2)	119.2(2)	—	—
$N \cdots O(1)$	3.04(2)			
$O \cdots O(2)$	3.10(3)			
$O(2) \cdot\cdot O(2)$	3.00(3)			
$O(1) \cdot\cdot O(2)$	3.22(3)			

[a] Numbering system refers to Scheme 1 and Figures 1, 3, and 4. [b] Although refinement was difficult, and standard deviations large, it was possible to solve the structure. [c] See ref. 10. [d] $C_a–C_{a'}$ compound (**4**) in Scheme 1. [e] See ref. 9. [f] $C_m–O$, compound (**5**) in Scheme 1.



Scheme 1

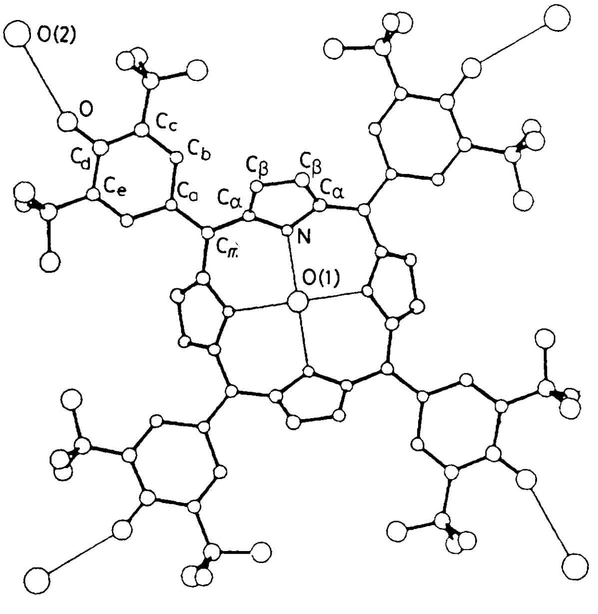


Figure 1. ORTEP diagram of the oxidised porphyrin (3).

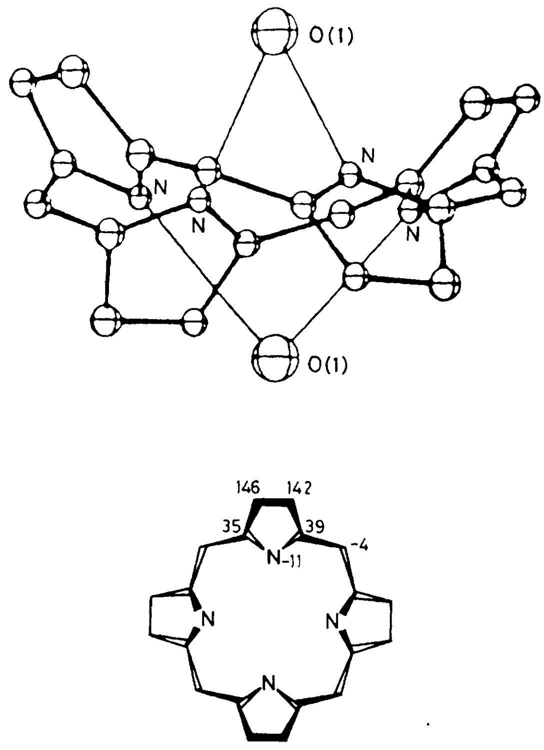


Figure 2. (Top) ORTEP diagram of the puckered macrocyclic core of the oxidised porphyrin (3) showing the hydrogen bonded O(1) water molecules and (bottom) deviations of the macrocyclic atoms from the mean plane in 0.01 Å units.

oxidised product of the metal-free porphyrin (**1**) has a highly puckered macrocyclic core and planar quinomethide *meso*-substituents, so vindicating our proposed explanation for the aerial oxidation of this phenolic porphyrin.

The oxidised porphyrin was obtained by a literature method[3a,b] and a solution of it in chloroform was slowly evaporated to afford flattened bipyramidal crystals with a deep green sheen. The product crystallises as the hexahydrate.

The crystal structure† shows that, in the solid state, the oxidised porphyrin has a porphyrinogen-type macrocyclic core, (**3**), which apart from being the most highly puckered of any tetrapyrrole prepared so far, is in contrast to the porphodimethene-like structure, (**2**), deduced from solution NMR studies.[3a] Bond distances and angles in the pyrrole rings and quinomethide *meso*-substituents of (**3**) are similar to those in free pyrrole[7a] and in the representative diquinomethide (**4**),[7b] respectively. These parameters for the pyrrole rings of (**3**) are also similar to those found in octaethylxanthoporphyrinogen (**5**),[7c] a similar structure, but with a less puckered core and no bulky *meso*-substituents (Table 1). The pyrrole rings of (**3**) have a larger angle of tilt (48°) away from the macrocyclic least-squares plane (Figures 1 and 2) than either (**5**)[7] or the

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† *Crystal data:* $C_{76}H_{92}N_4O_4{\cdot}6H_2O$, $M = 1233.7$, Enraf-Nonius CAD4, Cu-K_α ($\lambda = 1.54184$ Å); crystal ($0.20 \times 0.25 \times 0.04$ mm^3) mounted on a glass fibre; $T = 293$ K; tetragonal, space group $I\bar{4}$, $a, b = 19.487(3)$, $c = 9.923(2)$ Å, $U = 3768.0$ Å^3, $Z = 2$, $D_c = 1.087$ g cm^{-3}; structure solution by direct methods; 2873 measured reflections, 1489 unique, 702 with $[I > 3\,\sigma(I)]$, $\omega-2\theta$ scan mode, $\theta_{max} = 60°$, isotropic refinement for non-hydrogen atoms, H atom positions calculated and included in structure factor calculations, $R = 0.133$, $R_w = 0.078$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

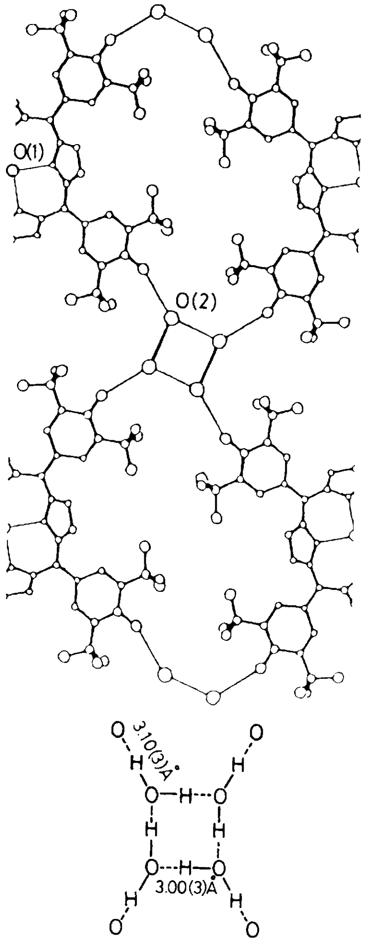

Figure 3. (Top) Packing diagram for the oxidised porphyrin (**3**) viewed down the *z* axis and showing the hydrogen bonded O(2) water molecules and (bottom) hydrogen bond distances.

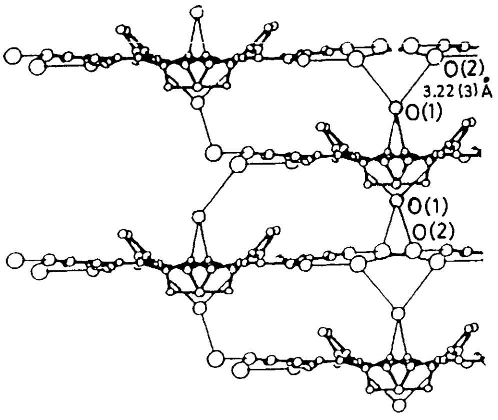

Figure 4. Packing diagram for the oxidised porphyrin (**3**) viewed down the *y* axis and showing the layers interconnected by hydrogen bonding between O(1) and O(2) water molecules.

dication of *meso*-tetraphenylporphyrin,[8] H_4TPP^{2+}, which are the two structures most resembling (**3**) and which have pyrrole ring tilt angles of 36.7 and 33° respectively. Also, the dihedral angle made by the quinomethide rings of (**3**) to this plane is virtually zero, compared to the 21° made by the phenyl rings of H_4TPP^{2+}.[8a,c]

A network of hydrogen bonds is partly responsible for the unusual amount of macrocyclic puckering and the clathrate-like solid-state structure of the oxidised porphyrin (Figures 2—4). Thus, two water molecules, O(1), are each H-bonded to hydrogen atoms on diagonally opposed central nitrogen atoms. Each of the remaining four water molecules, O(2), is H-bonded to the quinone oxygen atoms and to the O(2) water molecules attached to symmetry-related molecules of (**3**) giving rise to a layer structure. Hydrogen bonding, between O(1) water molecules of one layer and diagonally opposed O(2) water molecules of the next is responsible for holding the layers together. That the C–O bond distances in (**3**) are significantly longer than in (**5**), or the diquinomethide (**4**) (Table 1), probably reflects involvement in H-bonding.

On the basis of the data reported here, therefore, we believe that the structure of (**3**) confirms our explanation for the ease of aerial oxidation of (**1**), and some of its metal complexes, in terms of conformational changes occurring between the macrocyclic core and phenolate *meso*-substituents. Where these conformational changes are impeded, *e.g.*, by appropriate metal complexation, so facile aerial oxidation is curtailed.

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