Structural Consequences of Porphyrin Tautomerization. Molecular Structure of a Zinc Isoporphyrin

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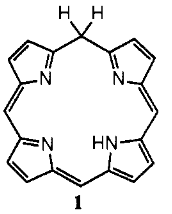
Isoporphyrins (**1**), tautomers of porphyrins with a saturated meso carbon, were originally postulated by Woodward.[2] Insertion of a divalent metal into **1** should yield a cation, and, indeed, the first metalloisoporphyrin was reported by Dolphin et al.,[3] who prepared zinc 5′-methoxy-5,10,15,20-tetraphenylisoporphyrin perchlorate by nucleophilic attack of methanol on the oxidized dication of zinc tetraphenylporphyrin. Since then, isoporphyrins, particularly tetraaryl derivatives, have been synthesized chemically, electrochemically, and photochemically.[4–7] The impetus for the studies arises from the occurrence of isoporphyrins in reactions of oxidized porphyrins with nucleophiles, as byproducts of heme oxidations, and as putative intermediates in the biosynthesis of chlorophylls.[3–7]



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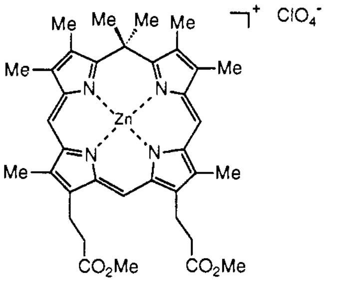
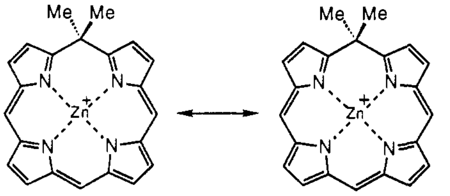


2

Although tetraaryl metalloisoporphyrins are readily synthesized, their chemistry is complicated by their tendency to revert to porphyrins.[3,4,6] The recently synthesized[8] zinc isoporphyrin **2** prevents the back tautomerization and should allow a fuller characterization of the chemical and electronic properties of isoporphyrins. During such studies, **2** was crystallized as the aquo perchlorate salt.[9] We report here the first crystallographic determination of an isoporphyrin which details the significant structural consequences of the porphyrin tautomerization.

The molecular structure of **2** is presented in Figure 1. The perchlorate counterion and the two methyl groups C21 and C22 at C5 confirm the cationic nature and the tetrahedral meso carbon features characteristic of a metalloisoporphyrin. As shown in Figure 2, the molecule exhibits near-mirror symmetry of bond distances along the C5–C15 axis. Most notable are the lengthening of C4-C5 and C5-C6 to canonical single bonds with average distances of 1.514(9) Å,[10] consonant with a tetrahedral carbon, and, moving away from C5, the alternation of short and long bonds along the inner π network comprised of the Cα, N, and meso atoms. This pattern breaks down only at C15, where C14-C15 and C15-C16 are equivalent, 1.385(9) and 1.384(9) Å, but intermediate in length from the equivalent pairs of Cα-Cm distances at C10 and C20, which average 1.423(9) and 1.354(9) Å. The two different N-Cα bonds in rings I and II average 1.327(8) and 1.412(8) Å, values distinctly different from those observed in rings III and IV, 1.385(8) and 1.356(8) Å, or the average values of 1.366(6) Å found in Zn octaethylporphyrins.[11] Also affected are the C3-C4 and C6-C7 distances in rings I and II, whose average value of 1.472(9) Å is longer than typical Cα–Cβ bonds in Zn porphyrins, 1.451(9) Å,[11] or the other Ca–Cβ bonds in **2**. The overall pattern of bond distances is thus most consistent with the resonance patterns shown below, in which the resonance forms of rings III and IV are interchangeable, while the rest of the resonance path is locked in a single configuration.



The isoporphyrin also displays distinctive bond angles when compared to porphyrins. The most obvious difference occurs at C5, where the C4C5C6 angle shrinks to 118.7(5)°, to be compared with the other three CαCmCα angles of 128.6(6)° or with average angles of 127.9(5)° in two ZnOEP complexes.[11] As well, the CβCαCm angles at C5 diminish to 122.7(6)°, in contrast to the other six angles, which are broader by 3° and agree well with literature porphyrin values.[11] The ZnNCα angles fall into three classes. Those in rings III and IV average 126.9(4)°, whereas, in rings I and II, those adjacent to C5 expand to 128.7(5)°, while those neighboring C10 and C20 contract to 124.2(4)°. Typical ZnNCα values in Zn porphyrins[11] range from 126.3(2)° to 126.7(3)°. The CαC5C21 and CαC5C22 angles with the methyl substituents are nearly tetrahedral and average 106.5(6)°.

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(1) (a) Brookhaven National Laboratory. (b) University of California, Davis.

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(9) Xie and Smith originally prepared the chloride salt of **2**.[8] The perchlorate derivative was prepared by metathesis with $AgClO_4$. The latter crystallizes from butyronitrile in space group $P\bar{1}$ with $a = 12.759(2)$ Å, $b = 13.296(3)$ Å, $c = 12.491(3)$ Å, $\alpha = 108.80(2)°$, $\beta = 90.50(2)°$, $\gamma = 62.85(2)°$, $V = 1760.7$ Å^3, $Z = 2$. Data were collected at 298 K on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu Kα radiation in the scan range $4 \leq 2\theta \leq 110°$. A total of 5089 reflections ($h \pm k \pm l$) were measured, with 4147 unique and 3247 with $F_o > 3\sigma(F_o)$. Anisotropic refinement of all non-hydrogen atoms using full-matrix least-squares yielded $R_F = 0.048$ and $R_{wF} = 0.061$. Hydrogens were included in the model in idealized locations. Additional details of the refinement, bonds angles, deviations from planarity, and packing diagrams are included in the supplementary material.

(10) The number in parentheses following each averaged distance or angle is the esd of the mean or the esd for an individual measurement, whichever is larger.

(11) Zn 2,3,7,8,12,13,17,18-octaethylporphyrin–pyridine (ZnOEP): Cullen, D. L.; Meyer, E. F. *Acta Crystallogr.* **1976,** *B32*, 2259. ZnOEP·1-methyl imidazole: Brennan, T. D.; Scheidt, W. R. *Acta Crystallogr.* **1988,** *C44*, 478. Zn 5,10,15,20-tetrapyridylporphyrin–pyridine: Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761.

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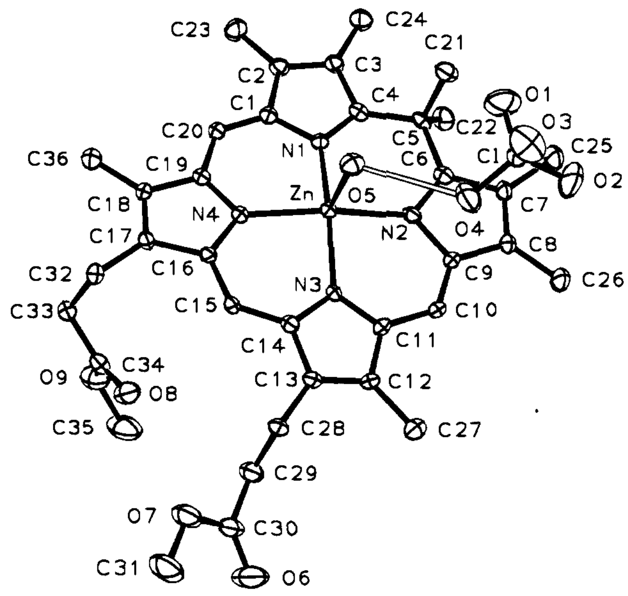

Figure 1. Molecular structure of **2**. The molecule crystallizes with a water (O5) bound to the Zn, and a perchlorate counterion hydrogen-bonded to the water along O5-O4. The thermal ellipsoids enclose 30% probability.

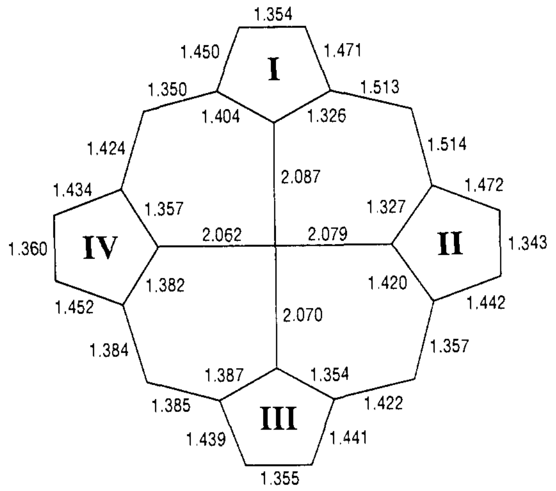

Figure 2. Bond distances in **2**. Esds are 0.009 Å for a typical C–C bond and 0.005 Å for the Zn–N bonds.

The Zn isoporphyrin cation is pentacoordinated with an adventitious water whose oxygen, O5, is bound to the Zn at 2.117(5) Å. One oxygen (O4) of the well-ordered perchlorate counterion lies 2.79 Å from the water oxygen, clearly indicative of a hydrogen bond. The Zn atom is displaced 0.31 Å from the plane of the four nitrogens and 0.34 Å from the average plane of the macrocycle. There is some asymmetry in the Zn-N distances which marginally distinguishes the bonding to rings I and II from that to rings III and IV. The average Zn-N1 and Zn-N2 distances are 2.083(5) Å, the Zn-N3 and Zn-N4 2.066(5) Å. All these values are comparable to those found in pentacoordinated Zn porphyrins.[11] The macrocycle itself is slightly ruffled, with the meso carbons moved above and below the macrocycle plane by 0.24, –0.18, 0.15, and –0.11 Å at C5, C10, C15, and C20, respectively, and the pyrrole rings are also slightly twisted above and below the plane, with maximum displacements ranging from 0.15 Å at C7 to –0.17 Å at C2. (Illustrations of the deviations from planarity[12] and of the crystal packing[13] are included in the supplementary material.)

The interrupted π system of **2**, evident from the crystallographic data, also profoundly affects its electronic properties. In butyronitrile, **2** undergoes three reversible redox changes at –0.61, –0.29, and 1.09 V (versus SCE). The difference between the oxidation and first reduction potentials, which reflects the energy difference between the HOMO and LUMO,[14] is 1.38 V, a gap considerably smaller than those reported for Zn porphyrins, $\sim$2.2 V.[14] As well, the first optical transitions of **2** in butyronitrile occur at 798 nm (1.55 eV) with a pronounced shoulder at 725 nm,[15] to be compared with transitions in the 530–610-nm (2.34–2.03 eV) region of Zn porphyrins.[16] Molecular orbital calculations (INDO/S[17]), based on the coordinates reported here, predict optical transitions at 844 and 769 nm, in reasonably good agreement (within 6%) with the experimental values.

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Supplementary Material Available: Experimental details, tables of bond angles and final positional parameters, and figures showing deviations from planarity and packing diagrams for **2** (8 pages). Ordering information is given on any current masthead.

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(12) The small conformational distortions in **2** contrast sharply with the pronounced rooflike folding observed in metalloporphodimethenes, in which two opposite meso positions are saturated: Dwyer, P. N.; Buchler, J. W.; Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 2789. Buchler, J. W.; Dreher, C.; Lay, K. L.; Lee, J. A.; Scheidt, W. R. *Inorg. Chem.* **1983**, *22*, 888 and references therein.

(13) The crystal lattice consists of two types of dimers. In the first, the Zn–Zn distances across a center of symmetry are 5.30 Å, and the mean planes of the molecules are separated by 4.00 Å with their respective waters pointing away from each other. In the second, centrosymmetrically-related Zn atoms are 7.96 Å apart, the mean plane separation is 3.52 Å, and the waters point toward each other. This arrangement allows possible weak hydrogen bonding between O5 of the waters and O7 of the methyl propionates and/or O8 of the keto groups at distances of 3.10 and 3.17 Å, which may enforce the different orientations of the propionate side chains.

(14) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 5, p 53.

(15) The distinctive optical features of the isoporphyrin are insensitive to solvent or counterion: the optical spectrum of the chloride salt in dichloromethane[8] is similar to those of the perchlorate salt in butyronitrile or dimethyl sulfoxide.

(16) Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 349.

(17) Intermediate neglect of differential overlap/spectroscopic. The method consists of a ground-state self-consistent-field calculation followed by configuration interactions between the 15 HOMOs and 15 LUMOs. Ridley, J.; Zerner, M. *Theor. Chim. Acta (Berlin)* **1973**, *32*, 111; 1976, *42*, 223. Thompson, M. A.; Zerner, M. C.; Fajer, J. *J. Phys. Chem.* **1991**, *95*, 5693.