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Experimental Procedure

Multibilayer cast films were prepared by casting aqueous bilayer dispersions of **1** onto quartz plates or fluoropore membrane filters as described previously [3, 4]. Cast films of **1** were first dipped in an aqueous solution of potassium tetracyanonickel (100 mM) for 5 d at room temperature to effect exchange with bromide ion. The resulting I-Ni films were rinsed with deionized water, then dipped in an aqueous solution of copper nitrate (100 mM) for 5 d, and finally dipped in pure water for 10 min to remove unreacted copper ion (I-Ni-Cu film). Atomic absorption analysis of Ni and Cu was conducted for the cast films, after they had been dispersed by ultrasonication in aqueous hydrogen chloride (0.1 N) containing 0.25% sodium hypochlorite.

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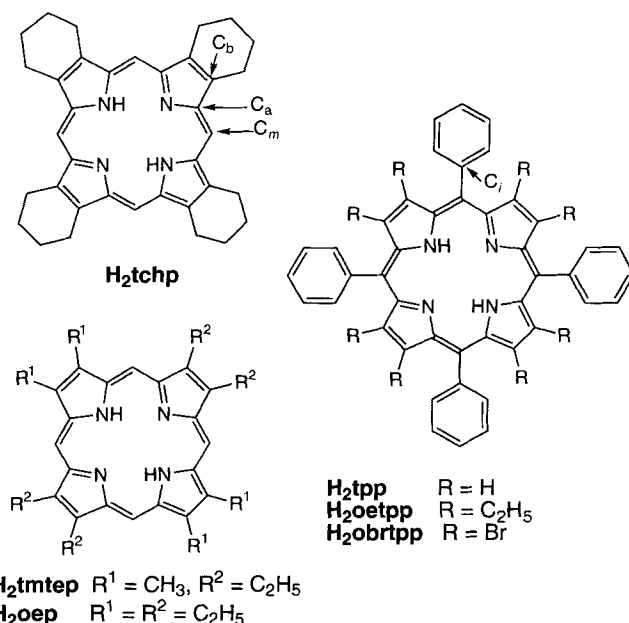
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Sterically Strained Porphyrins—Influence of Core Protonation and Peripheral Substitution on the Conformation of Tetra-*meso*-, Octa- β -, and Dodeca-Substituted Porphyrin Dications**

Mathias O. Senge,* Timothy P. Forsyth,
Liem T. Nguyen, and Kevin M. Smith

The study of nonplanar porphyrin conformations is currently under active scrutiny with regard to the possible role different macrocycle conformations play in biological processes such as respiration, electron transfer, photosynthesis, and enzyme catalysis.^[1a] The synthesis of porphyrins bearing large and sterically interacting substituents at the porphyrin periphery has been used successfully to yield tetrapyrroles with significantly distorted macrocycles.^[1, 2] Such compounds were mostly characterized by steric overload of the porphyrin periphery, for example, dodecasubstitution of the *meso*-carbon and β -pyrrole positions. In addition, core substitutions by either protonation of the two hydrogen-free pyrrole nitrogens (porphyrin dications)^[3] or preparation of *N*-alkyl or *N*-aryl porphyrins^[4] have been shown to lead to significantly distorted macrocycles, owing to steric congestion in the porphyrin core. We were interested in testing how far the macrocycle nonplanarity in dodeca-substituted porphyrins can be increased by a combination of both strategies.

namely, core *and* peripheral substitution. Spectroscopic evidence already indicated that compounds such as 22,24-dihydrododecaphenylporphyrin dication are nonplanar in solution, but no detailed structural data were available.^[2b] Additionally, only a few crystal structures of tetra-*meso*- or octa- β -substituted porphyrin dications were available for comparison with those of dodecasubstituted porphyrins. These included [H₄tp⁺]²⁺ (H₂tp⁺ = tetraphenylporphyrin, Scheme 1), which exhibits a nonplanar saddle conformation with pyrrole tilt angles of 33° and β -pyrrole displacements of 0.9–1.16 Å with respect to the mean plane.^[3a] In contrast, the porphyrin skeleton in [H₄oep][RhCl₂(CO)₂]₂ (H₂oep = octaethylporphyrin) has a planar conformation.^[3b]



Scheme 1. Structures of the investigated porphyrins.

The macrocycle of $[\text{H}_4\text{tchp}][\text{CF}_3\text{COO}]_2 \cdot 2\text{CF}_3\text{COOH} \cdot 2\text{H}_2\text{O}$ (H_2tchp = tetracyclohexa[*b, g, l*]porphyrin) is, surprisingly, almost planar (Fig. 1).^[5, 6a] Two trifluoroacetate (TFA) anions are hydrogen-bonded to the pyrrole hydrogens in a monodentate fashion, with one carboxyl oxygen bonded to two neighboring N–H units on the same face of the porphyrin. In this unique structure, the neighboring pyrrole units are displaced pairwise above and below the mean plane. On the basis

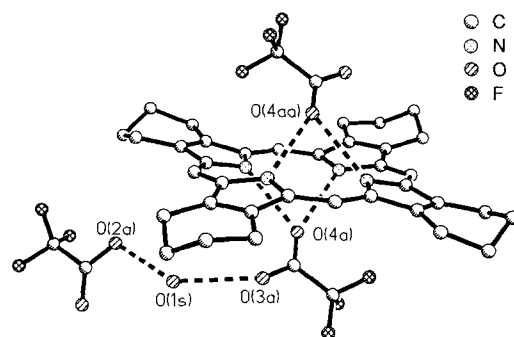


Fig. 1. Crystal structure of $[H_4tchp][CF_3COO]_2 \cdot 2CF_3COOH \cdot 2H_2O$. The associated solvent chain is shown for only one face of the porphyrin. Dashed lines indicate hydrogen bonds. Selected bond lengths (Å): N(21)–O(4a) 2.727, N(22)–O(4a) 2.760, O(3a)–O(1s) 2.778, O(1s)–O(2a) 2.510.

[*] Dr. M. O. Senge,¹⁺¹ T. P. Forsyth, L. T. Nguyen, Prof. Dr. K. M. Smith
Department of Chemistry, University of California
Davis CA 95616 (USA)

[*] New address: Institut für Organische Chemie der Freien Universität
Takustrasse 3, D-14195 Berlin (FRG)
Telefax: Int. code + (030)838-4248

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of earlier structural data, alternating up-and-down displacement of the N–H units was predicted for all porphyrin dications; this conformation minimizes the steric interaction of the four core hydrogens.^[3, 7] The 24 macrocycle atoms show an average deviation from the porphyrin mean plane of 0.129 Å, which is comparable to that found in some sterically unencumbered free-base porphyrins.^[8]

In the related compound $[H_4tmtp][ClO_4]_2 \cdot CH_3OH$ (H_2tmtp = tetraethyltetramethylporphyrin), the average deviation from the porphyrin mean plane is 0.173 Å for the macrocycle atoms and 0.37 Å for the C_b atoms; this represents a rather moderate degree of distortion.^[6b, 9] In contrast, $[H_4oep][CF_3COO]_2 \cdot 2 CF_3COOH$ (Fig. 2)^[6c] contains a signifi-

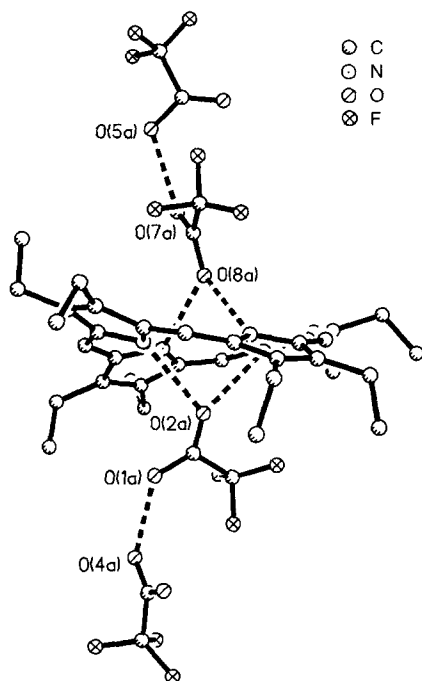


Fig. 2. Crystal structure of $[H_4oep][CF_3COO]_2 \cdot 2 CF_3COOH$. Dashed lines indicate hydrogen bonds. Selected bond lengths [Å]: N(21)–O(8a) 2.871, N(23)–O(8a) 2.802, N(22)–O(2a) 2.798, N(24)–O(2a) 2.862, O(1a)–O(4a) 2.501, O(5a)–O(7a) 2.523.

cantly saddle-distorted macrocycle: the average deviation of the C_b atoms from the mean plane is 0.72 Å (0.333 Å for all 24 macrocycle atoms), which is about 30% smaller than that found in $[H_4tpp]^{2+}$.^[3b] On each porphyrin face, a TFA ion acts as a monodentate ligand and binds through a carboxyl oxygen to two opposing N–H protons. The pyrrole rings are twisted with respect to each other by 30.7°; the corresponding value for $[H_4tchp]^{2+}$ is 17°. Thus, octa- β -alkyl-substituted porphyrin dications can have varying degrees of macrocycle distortion, depending on the geometry of the central N–H units. In contrast, all tetra-*meso*-arylporphyrin dications so far studied show similar nonplanar saddle conformations with C_b displacements of about 1–1.2 Å.^[10]

The complex $[H_4oetpp][CH_3COO]_{3/2}[CF_3COO]_{1/2} \cdot 4 CH_3COOH \cdot H_2O$ (H_2oetpp = octaethyltetraphenylporphyrin) is an example of a dodeca-substituted porphyrin dication combining both the structural characteristics of oep and tpp with core substitution (Fig. 3).^[6d] The dication has a severely distorted macrocycle with C_b atom displacements of 1.357 Å from the porphyrin mean plane (0.612 Å for all macrocycle atoms). The pyrrole rings are tilted by 39.2° with respect to the

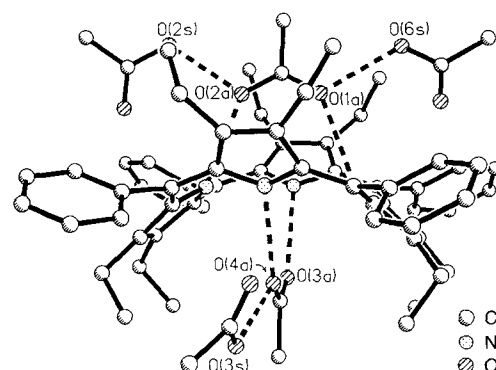


Fig. 3. Crystal structure of $[H_4oetpp][CH_3COO]_{3/2}[CF_3COO]_{1/2} \cdot 2 CH_3COOH \cdot H_2O$. The minor TFA component, presumably due to contamination from a prior crystallization, is not shown. Dashed lines indicate hydrogen bonds. Selected bond lengths [Å]: N(21)–O(1a) 2.744, N(23)–O(2a) 2.759, N(22)–O(4a) 2.781, N(24)–O(3a) 2.758, O(4a)–O(3s) 2.596, O(1a)–O(6s) 2.592, O(2a)–O(2s) 2.559. The compound contains an additional acetic acid and water residue (not shown), which are hydrogen-bonded to each other: O(8')–O(9s) 2.288 Å.

macrocycle plane and by 53.1° with respect to each other. On each porphyrin face, an acetate ion acts as a bidentate ligand and binds through each carboxyl oxygen atom to an N–H proton. Initial studies on other oetpp dications indicate that the type of anion and the geometry of the hydrogen bonding to the core protons do not exert a major influence on the observed conformation in porphyrin dications.^[10]

The dodeca-substituted free bases and metalloporphyrins have conformations which are about as distorted as or slightly more distorted than the tpp dications. Thus, it might be expected that no further distortion is necessary to accommodate the four pyrrole hydrogens in the corresponding dications. Nevertheless, the $[H_4oetpp]^{2+}$ dication is about 30% more distorted than the corresponding free base, H_2oetpp .^[11, 12] It is possible that porphyrins that are already nonplanar due to peripheral steric strain undergo further distortion more easily upon core protonation than do "normal" planar porphyrins. A special feature of *meso*-arylporphyrin dications is the large degree of in-plane rotation of the *meso*-aryl groups (e.g., 21° in $[H_4tpp]^{2+}$).^[3a, 10] This feature has been used to account for the increased resonance interaction between the π electron system of the porphyrin macrocycle and the *meso*-aryl groups. This explains the bathochromic shifts of the absorption bands of the tpp dications vs. those of oep dications.^[3a, 13] However, inspection of all the structures bearing *meso*-aryl groups^[11] yields no evidence for shortening of the C_m – C_i bonds compared to those in the planar H_2tpp .^[8c] Thus, the spectroscopic differences between the oep and tpp series reside solely in the electronic effects of the substituents and/or macrocycle conformations. Interestingly, the phenyl tilt angle in $[H_4oetpp]^{2+}$ (39.2°) is actually larger than that observed in $[H_4tpp]^{2+}$, which shows a smaller deviation from planarity. Similarly, compounds like $[Cu(oetpp)]$ show tilt angles of approximately 46°. ^[12c] Thus, a linear correlation between *meso*-aryl tilt and porphyrin nonplanarity is not possible on the basis of the present data. In general terms, porphyrins that deviate strongly from planarity seem, however, to show a more coplanar arrangement of the aryl rings, which is significantly enhanced by core protonation.

The porphyrin conformation with the largest deviation from planarity observed so far is found in $[H_4obrtpp][CF_3COO]_2 \cdot 0.5 CHCl_3$ ($H_2obrtpp$ = octabromotetraphenylporphyrin; Fig. 4).^[6e] Overall, the structure is very similar to that of $[H_4oetpp]^{2+}$, with bidentate binding of the TFA carboxyl oxygens to opposing N–H hydrogens. The average deviation of the

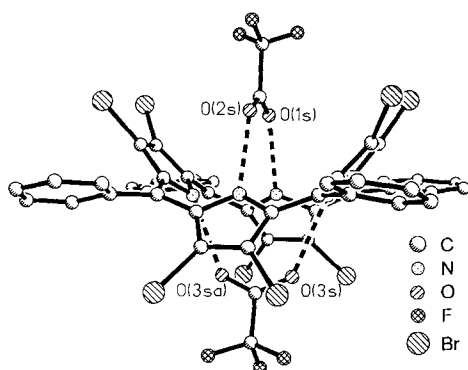


Fig. 4. Crystal structure of $[H_4obrtpp][CF_3COO]_2 \cdot 0.5CHCl_3$. Dashed lines indicate hydrogen bonds. Selected bond lengths [Å]: N(21)–O(2s) 2.744, N(23)–O(1s) 2.648, N(22)–O(3s) 2.685, N(22')–O(3s) 2.658. The compound contains two additional chloroform molecules (not shown) per unit cell.

24 macrocycle atoms from the mean plane is 0.689 Å; the corresponding figure for the C_b atoms is 1.521 Å. The distortion is about 63% greater than in the related octabromotetramesityl free base derivative.^[12c] The increase upon protonation of $H_2obrtpp$ is even larger than that observed upon going from H_2oetpp to $[H_4oetpp]^{2+}$. The extreme degree of nonplanarity is also reflected in the angles between the pyrrole rings of 62.1° and those between pyrrole rings and the macrocycle plane of 46.3°. Very surprising is the large in-plane rotation of the phenyl rings with tilt angles as small as 8.8° (average value 10.9°); the aryl rings are almost coplanar with the porphyrin plane. Even at this degree of coplanarity, no evidence for C_m – C_i bond shortening was found. Hence, the phenyl tilt observed in nonplanar porphyrins does not influence the spectroscopic characteristics of the nonplanar porphyrins. Disregarding electronic effects of different substituents or counterions, the bathochromic shifts of the absorption maxima are solely the result of increased macrocycle nonplanarity.

Correlations also exist between increasing macrocycle nonplanarity and selected geometrical characteristics: while most bond lengths and angles remain unaffected by comparison with those of planar porphyrins, increasing nonplanarity leads to a decrease in the N– C_a – C_m and C_a – C_m – C_s angles and an increase in the C_m – C_a – C_b and C_a – C_m – C_i angles. These structural correlations are independent of the way the macrocycle distortion is induced: the same trends are observed in the octa- β -substituted porphyrin dications, whose structure is determined solely by core strain, as in porphyrins with only peripheral steric strain.^[2b, d, g–f, 11] These trends are no different in dodeca-substituted porphyrin dications possessing both peripheral and core strain. Since all nonplanar porphyrins described here have the same saddle-shaped distortion, the trends described are the result of the macrocycle distortion alone and not due to local effects of individual substituents, be they core hydrogen atoms or peripheral bulky substituents.

So far no structures of dodeca-substituted porphyrin dications have been found that are not more strongly distorted than the corresponding free base (unlike some oep derivatives). This indicates that sterically strained porphyrins with both β -alkyl and *meso*-aryl substituents behave conformationally like the sterically unencumbered tpp series upon protonation and not like the octaalkyl series. A detailed analysis of the exact geometry of the hydrogens in the core and their influence on the conformation will, especially in the case of the oep series, have to await neutron diffraction studies.

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