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Core protonation of *meso*-tetraphenylporphyrin with tetrafluoroboric acid: unusual water-mediated hydrogen bonding of H_4tpp^{2+} to the counterion

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Abstract

N-Protonation of *meso*-tetraphenylporphyrin (H_2tpp) with tetrafluoroboric acid gives a hydrated porphyrin dication of the formula $[H_4tpp](BF_4)_2{\cdot}2H_2O{\cdot}CHCl_3$, in which the saddled $[H_4tpp]^{2+}$ moiety is hydrogen bonded to the counterions through the two water molecules. Apparently, the formation of this unusual porphyrin diacid serves to optimize the hydrogen bonding. Rather than the tetrafluoroborate ion hydrogen bonding to the two N–H's of $[H_4tpp]^{2+}$, the water molecules interact with $[H_4tpp]^{2+}$ and then with the BF_4^- counterions. The average pyrrole tilt angle with the N4 plane is 23.37° and an essentially saddled porphyrin core structure, with insignificant ruffling of the porphyrin core, is observed.

Keywords: *meso*-Tetraphenylporphyrin; Dication; Hydrogen bonding; Saddled conformation; HBF_4

N-Protonation of porphyrins with various inorganic and organic acids is of interest.[1] The two pyrrolenine nitrogen atoms bearing lone pairs of electrons can be protonated easily with acids such as trifluoroacetic acid. Several spectral signatures of the porphyrin macrocycle have been shown to be affected significantly by the non-planar deformation of the core.[2] Protonation of the porphyrin core is one of the influencing factors in porphyrin deformation which results in out-of-plane twisting, often saddling, of the macrocycle.[1] Protonation and deprotonation of the imino nitrogens of porphyrin-type photosensitizers have been shown to effect the charge and lipophilicity properties of drugs which regulate cellular uptake and localization.[3]

Usually, dications of *meso*-tetraalkyl- or -arylporphyrins with acids such as CF_3COOH, H_2SO_4, $HClO_4$, and HX (X = F, Cl, Br, I) consist of a saddled diprotonated porphyrin moiety which is hydrogen bonded to the counterion.[1a–e] The optimization of the hydrogen bond interactions between the halides (F^-, Cl^-, Br^-, and I^-) and $[H_4tpp]^{2+}$ has been suggested as a factor in determining the actual degree of saddling of the porphyrin core of the diacids of *meso*-tetraphenylporphyrins with HX as well as the requirement for up- and down-tilting of neighboring N–H bonds due to the restricted size of the porphyrin core.[1g]

Porphyrins react with various organic and inorganic acids to give a distorted porphyrin dication, usually attached directly to the counterion formed from the original acid.[1a–e,g] X-ray crystallographic studies of a series of β-fluorinated *meso*-tetraarylporphyrins (aryl = phenyl or pentafluorophenyl) protonated with $HClO_4$ have shown that only in the case of H_2F_8tpp have two water molecules mediated between $[H_4F_8tpp]^{2+}$ and the counterions in the solid state.[1f]

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H_2tpp was prepared and characterized by a previously described method.[4] Excess HBF_4 (beyond a 1:2 ratio of H_2tpp/HBF_4) was added to a $CHCl_3$ solution of H_2tpp in a narrow tube. Very slow evaporation of the solvent at room temperature, after two weeks, produced usable crystals.[5] Interestingly, diprotonation of H_2tpp with HBF_4 gave a diacid in which there was no direct hydrogen bonding between $[H_4tpp]^{2+}$ and BF_4^- (Fig. 1). Instead, two water molecules bridge the dication and tetrafluoroborate ions from above and below the porphyrin mean plane. This unusual water-mediated hydrogen bonding between the counterions and the dication of H_2tpp cannot be attributed to the size of the counterion—such structures have not been observed for counterions larger than BF_4^-, for example, ClO_4^-.[1e]

Fluorine is expected to form stronger hydrogen bonds than oxygen or nitrogen atoms.[12] The hydrogen bond between H and F is so strong that it persists partially in the vapor state below 80 °C in a ring hexamer, $(HF)_6$, but the F forms a total of only two hydrogen bonds so that even crystalline HF contains zigzag chains of hydrogen bonded HF molecules.[13] Water forms four hydrogen bonds in the solid state.[14] The preferred structure of $[H_4tpp](BF_4)_2{\cdot}2H_2O$ suggests that boron-bound fluorine is not an efficient hydrogen bond acceptor to bond simultaneously to the two N–Hs of $[H_4tpp]^{2+}$ from below or above the mean plane. Accordingly, it is reasonable to conclude that the formation of such an unusual porphyrin diacid results from optimization of the hydrogen bond interactions. This structure allows the formation of a well-defined set of four unequivalent hydrogen bonds around each water molecule and a single one around the boron-bound fluorine atom.

Various dihedral angles for $[H_4tpp](BF_4)_2{\cdot}2H_2O$ and $[H_4TPP](ClO_4)_2$[1e] are listed in Table 1. The average crystallographic bond lengths and bond angles are given in Table 2. The average pyrrole tilt angle with the N_4 plane is 23.37° in the former and 27.89° in the latter. The difference between the deviations of adjacent C_βs of pyrrole rings relative to the N_4 plane are 0.03 Å (C_9–C_{10}), 0.01 Å (C_{14}–C_{15}), 0.06 Å (C_{19}–C_{20}), and 0.05 Å (C_4–C_5), which demonstrate very little ruffling of the porphyrin core.

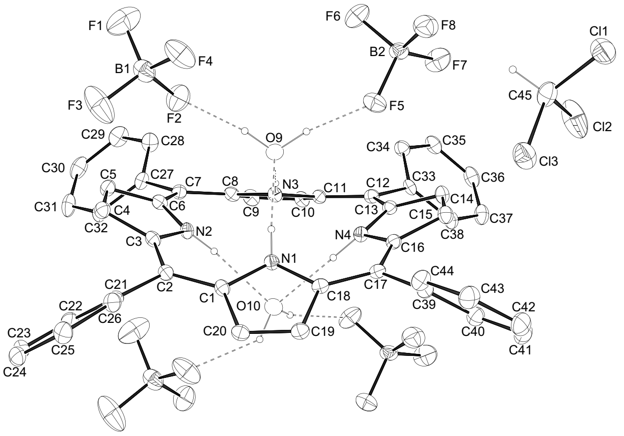


Fig. 1.

Table 1
Pyrrole-porphyrin and phenyl group-porphyrin dihedral angles in $[H_4tpp](BF_4)_2{\cdot}2H_2O$ and $[H_4TPP](ClO_4)_2$

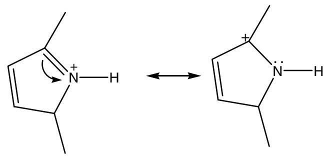
	$[H_4tpp](BF_4)_2{\cdot}2H_2O$	$[H_4TPP](ClO_4)_2$[1e]
Pyrrole 1	24.8 (1)	31.94
Pyrrole 2	22.2 (1)	22.55
Pyrrole 3	23.8 (9)	29.91
Pyrrole 4	22.7 (1)	27.16
Phenyl 1	38.8 (8)	23.43
Phenyl 2	37.9 (9)	26.99
Phenyl 3	34.3 (8)	28.19
Phenyl 4	38.4 (9)	27.35

Table 2
Average crystallographic bond lengths (in Å) and bond angles for $[H_4tpp](BF_4)_2{\cdot}2H_2O$, $[H_4TPP](ClO_4)_2$, and H_2tpp

	$[H_4tpp](BF_4)_2{\cdot}2H_2O$	$[H_4TPP](ClO_4)_2$[1e]	H_2tpp[7]
N–H	0.88 (3)	0.89 (7)	0.93 (1.006)[1g]
NH···O	2.03	2.12	—
N–H···O	174.5°	165°	—
N–C_α	1.379 (3)	1.390 (9)	1.369
C_α–C_β	1.424 (4)	1.431 (11)	1.442
C_β–C_β	1.392 (4)	1.366 (11)	1.356
C_α–C_{meso}	1.406 (4)	1.414 (11)	1.400
C_α–N–C_α	109.7 (2)°	110.3 (10)°	107.7
N–C_α–C_β	106.6 (2)°	106.1 (8)°	108.8
N–C_α–C_{meso}	125.8 (2)°	125.9 (6)°	126.1
C_α–C_β–C_β	107.5 (2)°	108.7 (9)°	107.4
C_α–C_{meso}–C_α	124.8 (2)°	123.2 (7)°	125.6
C_{meso}–C_α–C_β	126.2 (2)°	127.9 (5)°	125.0

It has been shown that the degree of saddling for $H_4tpp(X)_2$ ($X = F^-$, Cl^-, Br^-, and I^-) increases with the increasing size of halide, suggesting that the optimization of hydrogen bond interactions between the halides and the dication is an additional factor in determining the actual degree of saddling of the porphyrin core.[1g] Therefore, the greater tilting angle of the porphyrin core of $[H_4TPP](ClO_4)_2$ relative to $[H_4tpp](BF_4)_2{\cdot}2H_2O$ (Table 1) may be due to the larger size of ClO_4^- relative to that of the water molecule bridged between the counterion and the dication in $[H_4tpp](BF_4)_2{\cdot}2H_2O$. The N–H bond, on the other hand, is shorter than that in the free base porphyrin. It may be concluded that the N–H···O hydrogen bond in $[H_4tpp](BF_4)_2{\cdot}2H_2O$ or $[H_4TPP](ClO_4)_2$ is weaker than the intramolecular N–H···N bond in the free base porphyrin.[15]

The average dihedral angle between the phenyl groups and the porphyrin mean plane in $[H_4tpp](BF_4)_2{\cdot}2H_2O$ is ca. 37° which is smaller than that in the free base porphyrin (60–81.5°).[1d,16,17] In the diacid, the saddling of the porphyrin core allows the phenyl group to rotate toward the porphyrin plane making a decreased angle with it, which leads to a strong interaction between the phenyl group and the a_{2u} orbital of the porphyrin[1a,d] Although this interaction



Scheme 1. A possible explanation for the weakening of C_α–N bonds upon the protonation of pyrrolenine nitrogens.

might be expected to cause a significant decrease in the C_{meso}–C(phenyl) bond length with respect to that of H_2tpp, the average length of the bond is ca. 1.49 Å (see Supplementary data) which is very similar to that of H_2tpp (1.504 Å).[1c,4] It should be noted that the greater degree of saddling of the porphyrin core in $[H_4TPP](ClO_4)_2$ causes larger coplanarity of the phenyl groups with the mean porphyrin plane (ca. 27°) (Table 1).

The increased length of the N–C_α bond upon diprotonation of H_2tpp (Table 2) is probably due to the enhanced polarity of the bond resulting from the protonation of the pyrrolenine nitrogens which in turn leads to a contribution from the resonance forms shown in Scheme 1. This may also explain the weakening of the C_β–C_β bond and strengthening of the C_α–C_β bond; a consequence of delocalization of the pyrrole π-system to compensate for the positive charge on the nitrogen atom. This observation may also be due to the decreased ring current of the porphyrin core.

It is observed (Table 2) that the diprotonation of H_2tpp with HBF_4 is accompanied by changes in all the bond lengths and bond angles as well as the saddling of the porphyrin core. The view that the large red shifts seen in the UV–vis spectra of non-planar porphyrins are the result of substituent-induced changes in the porphyrin bond lengths and bond angles, termed in-plane nuclear reorganization (IPNR), has recently been challenged by Shellnut and co-workers[2] on the basis of using non-planar deformations along the high-frequency $2B_{1u}$ and $3B_{1u}$ normal coordinates of the macrocycle. Further theoretical work is required to reveal how much IPNR is responsible for the observed shifts of the Soret and Q bands of porphyrins upon diprotonation with different acids.[1a,g]

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.11.140.

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$$wR_2 = \left\{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right\}^{1/2}$$

$$\text{GOF} = \left\{\sum w(F_o^2 - F_c^2)^2 / (n - p)\right\}^{1/2}$$

where n = the number of reflections and p = the number of parameters refined.

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