

The Molecular Structure of the Diacid Species of $\alpha\beta\gamma\delta$ -Tetra-4-pyridylporphine and $\alpha\beta\gamma\delta$ -Tetraphenylporphine

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THERE continues to be a considerable amount of interest in the structure of the porphyrin nucleus, especially with regard to the cause of nonplanarity now observed in several systems.¹ We report the X-ray structural determination of the diacid species² of both $\alpha\beta\gamma\delta$ -tetra-4-pyridylporphine³ (Figure 1) and $\alpha\beta\gamma\delta$ -tetraphenylporphine.

Cell parameters for the TPYP-DA (space group $B2/b$) were determined as: $a = 19.89$, $b = 14.31$, $c = 19.26$ Å, and $\gamma = 133.50^\circ$, with 4 molecules in the unit cell. The present R -factor for 1430 observed reflections is 0.132. For the TPP-DA ($I4$), $a = b = 16.45$, $c = 7.32$ Å, and there are 2 molecules in the unit cell. The R -factor for 376 reflections is 0.098.

The H_4 TPP²⁺ molecule lies on a position of point group $\bar{4}$ (S_4), with the four-fold inversion axis perpendicular to the mean molecular plane at its centre. The point group of H_4 TPYP²⁺ is strictly 2 (C_2), although, having the same basic configuration as H_4 TPP²⁺, it exhibits pseudo- $\bar{4}$ symmetry. The Table shows deviations of the atoms comprising the porphyrin nucleus from the mean molecular plane. Figure 2 is a computer-drawn⁴ view of the H_4 TPYP²⁺ molecule, showing the configuration common to both diacid species.

These two diacid structures exhibit the greatest deviations from planarity thus far found in any porphyrin system. This distortion is almost certainly due to the mutual repulsion of the four hydrogen atoms on the inner nitrogens. The

distance between opposite nitrogen atoms in the tetragonal^{1b} TPP is 4.11 Å, just long enough to avoid interpenetration of the van der Waals radii of opposite hydrogens. To minimize this penetration the pyrrole rings are tilted (almost as rigid

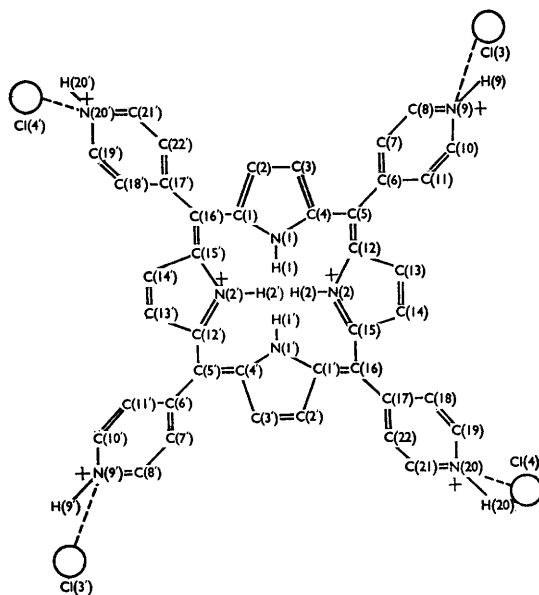


FIGURE 1. Skeletal structure of H_4 TPYP²⁺, showing numbering system used for both diacid species. Cl(1) and Cl(2) omitted for clarity.

bodies) alternatively up and down at 28° angles to the mean molecular plane.

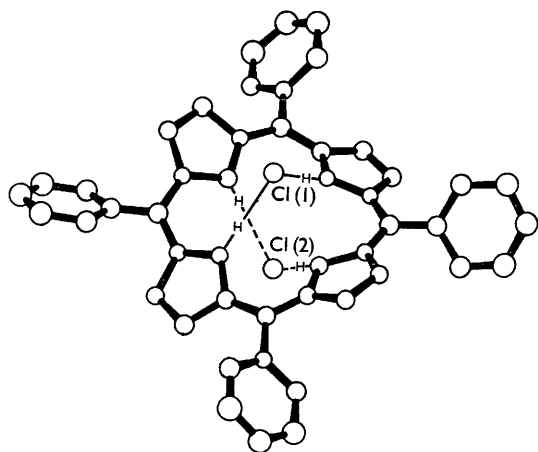


FIGURE 2. Molecular configuration of porphyrin diacids. Cl(1) and Cl(2) lie on the rotation axis, directly above and below the molecule. The size of the circles indicates the relative magnitude of isotropic temperature factors.

The large tilt of the pyrrole rings found in the diacid species may help explain the failure to detect the monocation,⁵ H_3TPyP^+ , upon protonation of the free base to the diacid. The energy barrier for the addition of the first proton may indeed be greater than that for the addition of the second, since presumably the first proton attacks a relatively planar molecule, with lone-pair electrons on the unprotonated nitrogens directed toward the centre of the ring, a sterically unfavourable location. Upon incorporation of the first proton to form the monoacid, the pyrrole rings probably tilt up and down as in the diacid, so that the opposite nitrogen's nonbonding electron pair is quite accessible to attack by a second proton.

Another important feature of the diacid configuration is that the phenyl or pyridyl rings are no longer constrained by hydrogen-hydrogen repulsions to be at least 60° from the plane of the

porphyrin ring, as they are in the TPP free base.^{1a} In the H_4TPyP^{2+} this angle is reduced to 32° , and

TABLE. Perpendicular displacements from the mean plane of the porphyrin nucleus

Atom	Displacement, Å	
	H_4TPyP^{2+} , ^a	H_4TPP^{2+} , ^b
N(1)	+0.12	+0.05
C(1)	-0.23	-0.19
C(2)	-0.83	-1.00
C(3)	-0.93	-1.16
C(4)	-0.23	-0.47
N(2)	-0.13	
C(12)	+0.18	
C(13)	+0.86	
C(14)	+0.87	
C(15)	+0.32	
C(5)	-0.10	-0.30
C(6)	-0.21	-0.49
C(7)	+0.37	-0.16
C(8)	+0.19	-0.42
N(9) [C(9)]	-0.60	-0.92
C(10)	-1.13	-1.19
C(11)	-0.98	-0.93
C(16)	-0.04	
C(17)	+0.19	
C(18)	-0.47	
C(19)	-0.19	
N(20)	+0.55	
C(21)	+1.07	
C(22)	+0.89	

^a Average standard deviation is 0.030 Å.

^b Average standard deviation is 0.035 Å.

in the H_4TPP^{2+} it is further reduced to 21° . Some resonance interaction of these rings with the porphyrin nucleus is thus allowed, and may be the reason why the diacid form of TPP and TPYP is green in solution, in contrast to the violet or red colour of other diacid porphyrin species.

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¹ (a) S. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, 1964, **86**, 927; (b) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1964, **86**, 1938; T. A. Hamor, W. S. Caughey, and J. L. Hoard, *ibid.*, 1965, **87**, 2305; (c) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, 1964, **86**, 2342; (d) L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, 1965, **43**, 3100.

² The diacids of the tetrapyrrolyl- and tetraphenyl-porphine molecule itself will be denoted as H_4TPyP^{2+} and H_4TPP^{2+} . The notation TPYP-DA and TPP-DA will be used to distinguish between the two crystalline systems studied.

³ E. B. Fleischer, *Inorg. Chem.*, 1962, **1**, 493.

⁴ C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations".

⁵ E. B. Fleischer and L. E. Webb, *J. Phys. Chem.*, 1963, **67**, 1131; it has been found that the monocation of several porphyrin species is observable in anionic detergents.