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The Molecular and Crystal Structure of Porphyrin Diacids

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Abstract: The crystal and molecular structures of two porphyrin diacid species have been determined. The $\alpha,\beta,\gamma,\delta$-tetra(4-pyridyl)porphine diacid and the $\alpha,\beta,\gamma,\delta$-tetraphenylporphine diacid structures were studied by three-dimensional X-ray analysis. $\alpha,\beta,\gamma,\delta$-Tetra(4-pyridyl)porphine–6-(hydrogen chloride) has a space group B2/b with the cell constants $a = 19.89$, $b = 14.31$, $c = 19.26$ Å, $\gamma = 133.5°$, and $\alpha,\beta,\gamma,\delta$-tetraphenylporphine($2H^+$, Cl^-,$FeCl_4^-$) has a space group of $I\bar{4}$, $a = 16.45$, $c = 7.32$ Å. The porphine nuclei of both of these structures are similar—the porphine is very nonplanar with the molecule having a $\bar{4}$ symmetry. The tilting of the pyrroles from the mean plane of the nitrogens is understandable in terms of the van der Waals repulsion of the inner hydrogen atoms of the porphyrin ring. Some of the physical and chemical properties of the porphyrin diacid are discussed in terms of the observed structure.

The porphyrin and metalloporphyrin molecules are an interesting and important class of compounds. The details of the chemical and physical properties of these molecules are becoming an understandable area of scientific research.[2] There are still portions of porphyrin chemistry where detailed studies have not as yet been carried out. This paper discusses the chemistry and structural aspects of one of these relatively unexplored areas, porphyrin diacid systems.

Porphyrin compounds which contain two hydrogens in the central positions (Figure 1a) are called free bases. The addition of one proton forms the monoacid, or monocation (Figure 1b), and the diacid, or dication (Figure 1c), is that species with all inner nitrogens protonated. It should be noted that the terms "monocation" and "dication" refer only to the charge associated with the 24-atom porphyrin nucleus and do not include any charge conventionally associated with substituent groups. Free base, monoacid, and diacid porphyrins will often be symbolized by H_2P, H_3P^+, and H_4P^{2+}, respectively. Displacement of the two central hydrogen atoms of the porphyrin free base by a metal cation produces the metalloporphyrins.

Synthetic porphyrins with substituents at the methine bridges are now common. These are called *meso*-substituted porphyrins, and the four positions are often designated by α, β, γ, and δ.

The two porphyrins whose crystal structures are described in this paper are the diacid forms of the *meso*-substituted $\alpha,\beta,\gamma,\delta$-tetra(4-pyridyl)porphine (TPyP) and $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (TPP). The skeletal structure of the chloride salt of the former porphyrin dication is shown in Figure 2. Note that a total of six formula weights of HCl has added to the porphyrin, four associated with the pyridyl groups and two with the inner nitrogens. The numbering system in Figure 2 is that used in the crystallographic determination. These cationic molecules will be symbolized by H_4TPyP^{2+} and H_4TPP^{2+}, respectively, and H_2TPyP and H_2TPP will be used when referring specifically to the free base forms. The notations TPyP-DA and TPP-DA will be used to refer to the *entire* crystalline systems investigated, which, of course, include the anions and solvent molecule found to be present.

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(1) Uniroyal Fellow. (b) Alfred P. Sloan Fellow.

(2) See the following for review of porphyrins and metalloporphyrins: J. N. Phillips, *Rev. Pure. Appl. Chem.*, 10, 35 (1960); G. P. Gurnovich, A. N. Sevchenko, and K. N. Solov'ev, *Soviet Physics Usp.*, 6, 67 (1963); P. S. Braterman, R. C. Davies, and R. J. P. Williams, *Advan. Chem. Phys.*, 7, 359 (1964); J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.

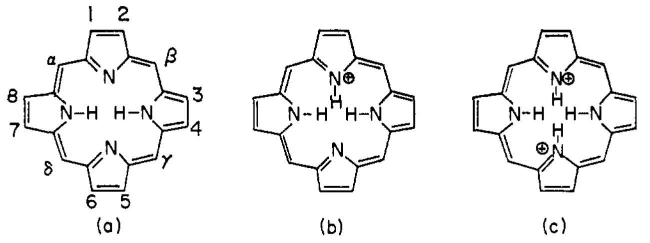

Figure 1. Skeletal structure of porphine (a) free base, (b) monoacid, and (c) diacid. Conventional labeling system for porphyrins is shown in (a).

Previous Structural Studies

There have by now been a number of X-ray structural determinations of both metallo- and free-base porphyrins. Although some of these studies have been complicated by possible stacking disorder[3–7] of the porphyrin molecule, the essential structural features of the molecule have been elucidated. Fleischer and coworkers have observed a slightly ruffled porphyrin nucleus in nickel etioporphyrin-I,[6] CuTPP,[7] and PdTPP,[7] the latter two structures being isomorphous. Similarly ruffled skeletons have also been found for nickel(II) diacetyldeuteroporphyrin-IX,[8] methoxyiron(III) mesoporphyrin-IX dimethyl ester,[9] and chlorohemin.[10] (In the last two compounds the iron atom was found to be 0.45 and 0.48 Å, respectively, out of the mean porphyrin plane.) On the other hand, the more loosely packed ZnTPP · H_2O[7] and copper tetra(*p*-chlorophenyl)porphine[11] molecules are almost planar. Fleischer, *et al.*,[7] have interpreted these results to indicate that the porphyrin molecule is naturally planar, but that it has a low energy barrier to out-of-plane distortions, and thus is particularly sensitive to the packing environment. The very accurate determination of porphine[12] to be almost planar would also seem to support this view. It has been argued[8] that the ruffling is due not to packing effects, but to the strain in the σ-bonding network of the porphyrins, which is reduced by the observed ruffling. Either of the two explanations could account for the small (less than 0.2 Å) out-of-plane deviations of the atoms in these compounds. Aside from porphine itself, the only other porphyrin free base whose structure has been crystallographically determined is TPP. Both a triclinic[13] and tetragonal[4] crystalline form of that compound have been studied. The triclinic modification exhibits small but significant tilts of the pyrrole rings to which the hydrogens are attached.

This paper describes the structure of the dications of TPyP and TPP and discusses certain of their chemical properties in terms of the observed structures. The precise structure of the dication is of interest because the positions of the four inner hydrogen atoms are uncertain. Indeed, it was not even certain that all the inner hydrogens could be discretely bonded to the nitrogen atoms, since models showed that four hydrogens in the center of the plane cause a great deal of steric crowding.

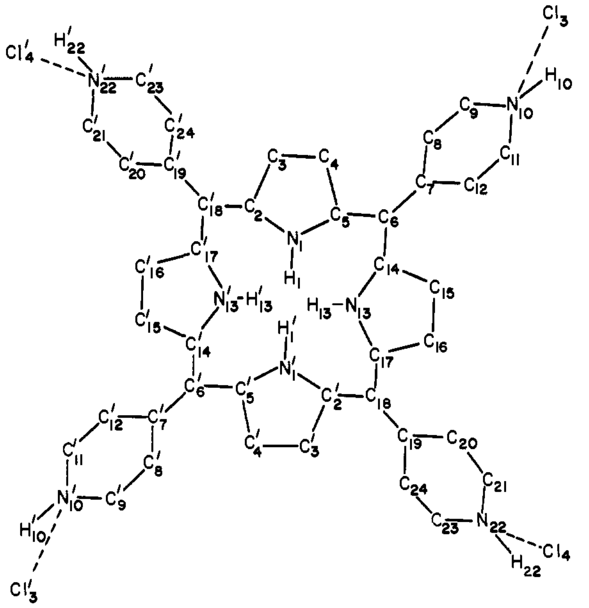

Figure 2. Skeletal structure of α,β,γ,δ-tetra(4-pyridyl)porphine diacid (chloride salt), showing numbering system. The structure and numbering system (see text) used for α,β,γ,δ-tetraphenylporphine diacid are analogous.

Experimental Section

Crystallographic. Tetrapyridylporphine Diacid. Preliminary. Dark green octahedral-shaped crystals of the diacid species of α,β,γ,δ-tetra(4-pyridyl)porphine were grown by slow, room-temperature evaporation of an aqueous solution of H_2TPyP[14,15] in ~1.0 *N* hydrochloric acid. A crystal of dimension 0.37 × 0.25 × 0.25 mm was used for the X-ray analysis. The space group of the TPyP-DA was determined to be B2/b.[16] The unit cell dimensions were determined as $a = 19.89 \pm 0.02$, $b = 14.31 \pm 0.02$, $c = 19.26 + 0.02$ Å, and $\gamma = 133.5 + 0.1°$.[17]

The density of the TPyP-DA crystals was determined by flotation in a mixed solution of hexane and carbon tetrachloride to be 1.440 g/cm³. If one assumes the tetrapyridylporphine diacid composition to be $H_2TPyP \cdot 6HCl$ (molecular weight (*M*) 837.7), application of the formula $Z = dVN_0/M$ gives 4.09 molecules per unit cell. For four molecules per unit cell, the calculated formula weight becomes 856.8. At this point, the inclusion of one molecule of water per porphyrin molecule, which would raise the formula weight to 855.7, was suspected. The subsequent X-ray analysis verified the presence of four $H_2TPyP \cdot 6HCl \cdot H_2O$ units per cell.

Intensity Measurements.[18] The first of two sets of intensity data collected on different tetrapyridylporphine diacid crystals

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(3) M. B. Crute, *Acta Cryst.*, 12, 24 (1959).

(4) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Am. Chem. Soc.*, 86, 1938 (1964).

(5) J. L. Hoard, G. H. Cohen, and M. D. Glick, *ibid.*, 89, 1992 (1967).

(6) E. B. Fleischer, *ibid.*, 85, 146 (1963).

(7) E. Fleischer, C. Miller, and L. Webb, *ibid.*, 86, 2342 (1964).

(8) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *ibid.*, 87, 2305 (1965).

(9) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, 87, 2312 (1965).

(10) D. F. Hoenig, *Acta Cryst.*, 18, 663 (1965).

(11) E. Fleischer, S. Shapiro, R. Dewar, S. Hawkinson, and A. Stone, submitted for publication.

(12) L. E. Webb, Ph.D. Dissertation, The University of Chicago, 1965.

(13) S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, 86, 927 (1964); S. Silvers, Ph.D. Dissertation, Yale University, 1964.

(14) E. B. Fleischer, E. Choi, P. Hambright, and A. Stone, *Inorg. Chem.*, 3, 1284 (1964).

(15) E. B. Fleischer, *ibid.*, 1, 493 (1962).

(16) "International Table for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1952.

(17) It is conventional to define the unit cell so that $\gamma < 120°$ and the *b* axis is unique. The space group would then become I2/n, with $a = 19.89$, $b = 19.26$, $c = 10.39$ Å, and $\beta = 90.0°$.

(18) The observed and calculated structure factors for $H_2TPyP \cdot 6HCl$ and $H_2TPPClFeCl_4$ which were submitted with the manuscript as Tables I and II, respectively, have been deposited as Document No. 9808 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and remitting $5.00 for photoprints or $2.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

was taken on the XRD-5 diffractometer. This set was used in the actual solution of the structure. The stationary crystal–stationary counter technique[19] was employed, using nickel-filtered Cu Kα (λ 1.5418) radiation. Intensity measurements of 10-sec duration were taken on each reflection after maximization on 2θ. Intensities were also maximized on φ for each new φ setting. The (600) reflection was measured at least three times a day as a monitor. It was found to vary within a range of 10% of its initially recorded intensity (7918), but no time trend was noticed. The rather large intensity variation of the monitor peak is believed due to small movements of the crystal, perhaps a result of using moisture-sensitive shellac as an adhesive. In any case, small corrections to the goniometer arcs, which increased the monitor intensity, were made twice during the data collection. A total of 1851 reflections were examined, of which 1430 (77%) were determined "observable" (at least greater than twice the background).

Peak intensities (I_p) were used in the solution of the structure and initial stages of refinement but were corrected to integrated intensities (I_i) in the last least-squares refinement calculation. This correction was performed by applying the factor I_i/I_p to the observed peak intensities. Appropriate values of I_i/I_p were taken from Webb's[12] plot of I_i/I_p *vs.* 2θ. For $2\theta \leq 100°$, his plot is quite close to the theoretical plot of Alexander and Smith,[20a] and experimentally observed on a number of other compounds.[20b] An empirical correction for an absorption was made.[21]

The second set of data taken from the tetrapyridylporphine diacid was collected with the PAILRED[22] automatic single-crystal diffractometer on a different crystal of the same dimensions. This second set was collected to serve as a check on the newly acquired instrument and also to minimize the large absorption effect encountered with copper radiation on the XRD-5. Intensities were collected using Mo Kα radiation (λ 0.7107) reflected from the (111) face of a silicon crystal monochromator. The use of molybdenum instead of copper radiation reduces the absorption by more than a factor of 10. (For copper the linear absorption coefficient $\mu = 44.3$ cm^{-1} and $\mu R = 0.67$; for molybdenum, $\mu = 3.4$ cm^{-1} and $\mu R = 0.05$.) Integrated intensities were acquired using the ω-scan (moving crystal–stationary detector)[22] technique.

Backgrounds were measured as an average of 20-sec stationary counts 1.5° on either side of the peak. Peaks were scanned over a 3° range in ω at a speed of 2.5°/min. Reflections whose integrated intensity was less than 1000 counts were rescanned once or even twice. A total of 2552 reflections were examined within the sphere bounded by $2\theta \leq 47.5$ ($d \geq 0.88$), of which 1336 (52%) were determined nonzero by a data reduction program which classified a reflection as unobserved if (1) $I_{\text{peak}} - I_{\text{background}} \leq 0$ or (2) the counting error involved in the measurement, defined as $E_{\text{cnt}} = \Delta I/I = (T + t^2B)^{1/2}/(T - tb)$ where T = total counts for peak, t = ratio of time spent counting peak intensity to that spent counting backgrounds, and B = sum of background counts, calculated greater than 0.5. In addition, a few reflections were initially rejected if (1) the two background measurements differed by more than a factor of 2.0, and (2) the ratio of the calculated peak using B_1 (smaller background) to that calculated using B_2 was greater than 1.10. The imposition of condition 2 ensures that strong reflections will not be rejected because of large but insignificant background fluctuations.

Since this second set of data was to be used solely for refinement and not to solve the structure, and since absorption was relatively small here, no *a priori* absorption correction was applied. Instead, the method used by Uehi, Zalkin, and Templeton[23] was tried.

Tetraphenylporphine Diacid. Preliminary. Dark blue crystals of what was determined to be the diacid species of tetraphenylporphine (TPP-DA) appeared upon slow evaporation (3 days) of a chloroform solution of H_2TPP ($\sim 2.0 \times 10^{-5}$ M) and anhydrous ferric chloride (~ 0.2 M).[24]

Precession photographs placed this crystal in the tetragonal system and determined the Laue group to be 4/m. The only systematic extinction found was $h + k + l + 1 = 2n$ for all hkl, limiting the possible space groups to I4, I$\bar{4}$ (both noncentric), or I$\bar{4}$/m (centric). (I$\bar{4}$ was later found to be correct.) Cell dimensions calculated from the precession pictures are $a = b = 16.45 \pm 0.03$ and $c = 7.32 \pm 0.02$ Å.

The density of the TPP-DA crystal was determined by flotation in a carbon tetrachloride–hexane mixed solution to be 1.424 g/cm^3. Two formula units per cell requires a weight of 849.0, which is in good agreement with the formula weight of 847.4 calculated for $[H_4TPP^{2+}][Cl^-, FeCl_4^-]$, the species found to be present.

Intensity data for this crystal were collected on the PAILRED in the manner described for the second set of TPyP-DA data. A scanning rate of 2.5°/min was employed, with a scan range of 1.5° for the zero and first layers, 2° for the second layer, and 2.5° for the third, fourth, and fifth layers. All reflections within the sphere bounded by $2\theta \leq 43°$ ($d \geq 0.97$ Å) were examined on these layers. Unfortunately, no reflections on the sixth and higher layers could be found, so the real data set consists of a flattened section of the quadrant. The effect of this incomplete data set upon the final refinement will be discussed later.

Altogether, 1220 distinct pieces of data were collected by PAILRED, of which 752 were considered nonzero; these were then averaged to give a set of 376 independent nonzero reflections.

Solution and Refinement of the Structures[25,26]

Tetrapyridylporphine Diacid. Phase Determination.[27] The structure of the tetrapyridylporphine diacid was determined by symbolic addition procedures.[28–32]

An initial structure factor calculation based on only the chlorine atoms and the carbon atoms in the porphyrin nucleus produced an R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.38. A Fourier map calculated from these phases revealed all 29 nonhydrogen atoms in the asymmetric unit including the oxygen atom of a water molecule on the twofold axis at (0, $^1/_4$, 0).

Refinement. All refinement was done by the method of least squares using the full-matrix, least-squares program of Busing, Martin, and Levy,[26] which minimizes a weighted R factor given by $R_w = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$. Scattering factors used for carbon, hydrogen, oxygen, nitrogen, and chloride ion were

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[19] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

[20] (a) L. E. Alexander and G. S. Smith, *Acta Cryst.*, **15**, 983 (1962); (b) J. D. Wright and R. B. K. Dewar, private communication.

[21] U. W. Arndt and B. T. M. Willis, "Single Crystal Diffractometry," Cambridge University Press, London, 1966, pp 241–243.

[22] Phillips Automatic Indexing Linear Reciprocal-Space Exploring Diffractometer; see *Norelco Reptr.*, 12, No. 2 (1965).

[23] T. Uehi, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **19**, 157 (1965).

[24] These crystals were the result of an attempt to grow stable crystals on the iron "sitting-atop" species.[14] Apparently the $CHCl_3$ or "anhydrous" $FeCl_3$ contained enough water to promote the reaction

$$2FeCl_3 + H_2TPP + 2H_2O \rightleftharpoons FeCl_4^- + Cl^- + Fe(OH)_2Cl + H_4TPP^{2+}$$

as a subsequent X-ray analysis determined the crystalline composition to be $[H_4TPP^{2+}][FeCl_4^-, Cl^-]$, The equilibrium constant for the reaction $2FeCl_3 \rightleftharpoons FeCl_2^+ + FeCl_4^-$ has been studied in a number of nonaqueous solvents (see T. B. Swanson and V. M. Laurie, *J. Phys. Chem.*, **69**, 244 [1965]) and found to lie far to the right in some. For example, in a 0.01 F solution of $FeCl_3$, the equilibrium concentration of $FeCl_4^-$ was found to vary from ~ 0.005 M in acetonitrile and nitromethane to 0.0007 M in dimethyl sulfoxide. In general, K for this equilibrium decreased with decreasing dielectric constant of the solvent.

[25] W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 7090 Computer," CBRL-22M-62, Esso Research and Engineering Co., Linden, N. J., 1962.

[26] W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge, Tenn., 1962.

[27] For interesting details of various approaches and failures to solve this structure, see A. Stone, Ph.D. Thesis, University of Chicago, 1967.

[28] D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

[29] M. Woolfson, *ibid.*, **7**, 61 (1954).

[30] J. Karle and I. Karle, *ibid.*, **21**, 849 (1966).

[31] The symbolic addition procedure was carried out with the computer program MAGIC: E. Fleischer, "Transactions of the American Crystallographic Association," Vol. 2, W. Bradley and H. Hanson, Ed., American Crystallographic Association, Pittsburgh, Pa., 1966, p 75; E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, *ibid.*, Vol. 3, 1967.

[32] For a general review of methods of applying symbolic addition methods to both centric and acentric space groups see R. Dewar, Ph.D. Thesis, University of Chicago, 1968.

those derived from self-consistent field or variational wave functions.[33] The refinement for the XRD-5 set of TPyP-DA data proceeded as follows. Two cycles of least-squares refinement on all 29 atoms in the asymmetric unit were calculated, with individual atomic temperature factors, positional coordinates, and a scale factor allowed to vary. This gave an R factor for all observed reflections of 0.160. A difference map calculated at this point indicated the chlorine atoms to be vibrating anisotropically to a great extent. A subsequent least-squares calculation was thus made, assigning anisotropic temperature factors defined by the expression

$$M = h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2hl\beta_{23}$$

where e^{-M} is the factor by which the thermal vibrations reduce the scattering factor. Only the chlorine atoms were allowed to vary anisotropically. All atomic coordinates were varied. The resulting coordinate shifts were all less than one standard deviation (about 0.03 Å at this time), but the residual underwent a statistically significant[34] reduction to 0.132. A final difference map revealed a number of peaks with a height equivalent to about one electron, but the noise level was such that only about two-thirds of these were in reasonable positions to be hydrogen atoms. The refinement on this set of data was terminated at this point, in anticipation of more fruitful results with the PAILRED-collected set of data.

The PAILRED data were refined with a weighting scheme

$$F_o \leq 32, \sigma = 1.0$$

$$F_o > 32, \sigma = 1.0 + 0.5(F_0 - 32)/32$$

A final isotropic cycle of least-squares refinement, including 1308 observed reflections, gave an R factor of 0.124.

Tetraphenylporphine Diacid. Phase Determination. The solution of the structure of the tetraphenylporphine diacid crystal (unit cell composition $[H_4TPP^{2+}][FeCl_4^-, Cl^-]$; space group either I4/m, I$\bar{4}$, or I4) was quite straightforward. Application of the Z test for measuring the statistical distribution of measured intensities determined the crystal to be noncentric and thus belonging to space group I4 or I$\bar{4}$. The presence of only two iron atoms in the unit cell fixes the iron positions at $(0, 0, 0)$ and $(^1/_2, {}^1/_2, {}^1/_2)$ in space group I$\bar{4}$ and $(0, 0, z)$ and $(^1/_2, {}^1/_2, {}^1/_2 + z)$ in I4. Since there is no symmetry element in I4 at a specific height in z, this coordinate may be arbitrarily taken as zero. A structure factor calculation based on the irons at $(0, 0, 0)$ and $(^1/_2, {}^1/_2, {}^1/_2)$ produced an R factor of 0.31. The subsequent Fourier summation with structure factors phased with respect to only the iron atoms showed the highest noniron peak to be in a general position at a distance of 2.2 Å from the origin. Assuming this peak to be the bonded chlorine atom of the $FeCl_4^-$ anion, trial R factors were calculated for the iron and chlorine atoms in both space groups I4 and I$\bar{4}$. The residual was 0.40 in I4 and 0.38 in I$\bar{4}$, indicating the space group to be I$\bar{4}$. It was also thought to be more reasonable for the iron atom to be on a position of point group symmetry $\bar{4}$ than one of symmetry 4. The subsequent refinement verified the space group as I$\bar{4}$. A second Fourier calculation using structure factors phased by the iron and chlorine atoms revealed the porphyrin molecule centered on the fourfold inversion axis at $(0, {}^1/_2, {}^3/_4)$, with a configuration similar to that found for the H_4TPyP^{2+} molecule. An additional peak whose height corresponded to a chloride ion was also found on the axis at $(0, {}^1/_2, {}^1/_4)$. At this point the structure was considered solved.

Refinement. Two cycles of least-squares refinement on all atomic positional parameters and temperature factors for the 15 atoms in the asymmetric unit produced an R factor of 0.118. It was immediately noticed at this point that the average estimated standard deviation (esd) in the z coordinate was about 0.04 Å, while that in both the x and y coordinates was about 0.03 Å. This is the expected result of the collection of a nonspherical set of data, no reflections with $l > 6$ being recorded. A difference map calculated at this point showed a disturbing peak of a height equivalent to about two electrons, situated at a distance of 1.4 Å from the uncoordinated chloride ion on the fourfold inversion axis. This was especially surprising because the experimentally derived molecular weight of 849.0 agreed quite well with that of what was already found in the unit cell, namely $[H_4TPP^{2+}][FeCl_4^-, Cl^-]$ (molecular weight 847.4). From a consideration of the distance of this extraneous peak from the chloride ion, it was thought to represent an oxygen of a perchlorate group, substituted interstitially for the chloride. The unit cell composition would then be $[H_4TPP^{2+}][FeCl_4^-, (Cl^-)_{1-n}(ClO_4^-)_n]$. From the height of the peak on the difference map, it is reasonable to assume that $n \approx {}^1/_6$. The absence of any detectable band in the infrared characteristic of ClO_4^- precludes the possibility of n being much greater than this value. Several cycles of isotropic least-squares refinement, including the fractional oxygen atom, lowered the R factor to 0.095; the same refinement without the oxygen gave an R factor of 0.112. Allowing the iron atom and the two chlorines to vibrate anisotropically, these residuals were reduced to 0.092 and 0.111, respectively. Bond lengths calculated at this point both with and without the fractional oxygen atom agreed to within 0.02 Å.

The final least-squares refinement of the TPP-DA structure, with hydrogen atoms placed in reasonable positions and including the zeros, gave $wR = 0.150$ for all reflections and $wR = 0.118$ for observed F's only. The inclusion of the unobserved reflections again had almost no effect on the atomic positions, although the average temperature factor increased by about 0.30 Å^2.

A final difference map calculated at this point had a "noise level" approaching one electron, and therefore the hydrogen atoms could not be located with certainty. One of the highest peaks in the difference map, however, corresponded to the same position of the inner hydrogen atom found in the TPyP-DA structure.

For the purpose of calculating intramolecular distances which seemed of significance, hydrogen atoms were placed in reasonable positions with respect to the other atoms, assuming normal sp^2 hybridization and C–H bond lengths of 1.08 Å and N–H lengths of 0.99 Å.[35]

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(33) Reference 3, Vol. 3, 1962, p 202.

(34) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(35) Hydrogen atoms were placed in reasonable positions with respect to the other atoms using the program PLHA, written by S. Shapiro.

Results and Discussion

Structures of the Diacid Molecules. Atomic Parameters. The results, as well as the subsequent discussion, of the crystal structure determinations of the two porphyrin dications will be presented concurrently in order to facilitate comparison of their structural features. The atomic labeling system used in the discussion of the TPyP-DA structure is shown in Figure 2. Not shown in that figures are Cl_1 and Cl_2, the chloride ions found on the twofold axis, directly above and below (respectively) the porphyrin molecule. Also absent is the oxygen atom (O) of the water molecule, situated below Cl_2 on the rotation axis. Atoms N_1, C_2, C_3, C_4, C_5 constitute the pyrrole ring designated as pyrrole I, and N_{13}, C_{14}, C_{15}, C_{16}, C_{17} make up pyrrole II. Similarly, atoms C_7, C_8, C_9, N_{10}, C_{11}, C_{12} and C_{19}, C_{20}, C_{21}, N_{22}, C_{23}, C_{24} comprise pyridyl rings I and II, respectively.

The labeling system employed for the tetraphenylporphine diacid molecule is identical with that shown in Figure 2 for tetrapyridylporphine, except that N_{10} in the TPyP-DA structure becomes C_{10} for TPP-DA. Also, the chloride anions (Cl_1 through Cl_4) in the TPyP-DA structure are replaced by $FeCl_4^-$ and Cl^- in TPP-DA, with Cl_1 there denoting the uncoordinated chloride ion and Cl_2, the chloride ion coordinated to the iron atom. Atoms numbered 1–12 comprise the complete asymmetric unit in the tetraphenylporphine diacid molecule. All hydrogen atoms in both structures are assigned the number of the atom to which they are bonded.

Table I. Fractional Atomic Coordinates and Isotropic Temperature Factors for $\alpha,\beta,\gamma,\delta$-Tetra(4-pyridyl)porphine Diacid

	Coordinates and standard deviations[a] ($\times 10^4$)						
Atom	x	σ_x	y	σ_y	z	σ_z	B, Å^2 [b]
O_1	0	..	2500	..	−157	15	9.5
Cl_1	0	..	2500	..	4998	3	3.4
Cl_2	0	..	2500	..	2509	3	3.4
Cl_3	3358	3	−541	4	4829	3	4.6
Cl_4	6074	3	11983	4	2623	3	4.6
N_1	1417	7	3406	9	3828	6	2.4
C_2	2118	8	4665	12	3624	8	2.6
C_3	2830	9	4756	12	3293	8	2.9
C_4	2554	10	3623	13	3339	9	3.3
C_5	1644	8	2721	11	3654	7	2.1
C_6	1111	9	1404	12	3786	8	3.1
C_7	1553	10	951	13	3841	9	3.2
C_8	2410	11	1699	14	4213	10	3.7
C_9	2810	11	1200	15	4290	10	4.0
N_{10}	2395	9	53	12	4019	8	4.2
C_{11}	1610	11	−630	15	3648	9	4.1
C_{12}	1197	10	−204	14	3541	9	3.6
N_{13}	454	8	4329	10	3716	7	3.1
C_{14}	148	9	502	12	3916	8	2.8
C_{15}	438	9	5742	12	4226	8	2.7
C_{16}	1323	9	6299	12	4192	8	2.9
C_{17}	1353	9	5429	12	3861	8	2.8
C_{18}	2124	10	5624	14	3725	9	3.5
C_{19}	3031	8	6988	12	3639	8	2.6
C_{20}	3087	10	7855	13	3266	9	3.4
C_{21}	3899	11	7091	15	3177	10	4.1
N_{22}	4684	10	9491	13	3466	9	5.0
C_{23}	4668	11	8704	16	3873	10	4.5
C_{24}	3848	10	7439	14	3964	9	3.5
H_1	834		3004		4084		3.0
H_3	3507		5616		3074		4.0
H_4	2926		3361		3141		4.0
H_8	2736		2633		4406		4.0
H_9	3453		1744		4595		4.0
H_{11}	1310		−1555		3424		4.0
H_{12}	558		−777		3221		4.0
H_{13}	255		3537		3503		3.0
H_{15}	193		6171		4437		4.0
H_{16}	1921		7294		4412		4.0
H_{20}	2454		7574		3069		4.0
H_{21}	3924		9782		2917		4.0
H_{23}	5269		9091		4164		4.0
H_{24}	3843		6807		4255		4.0

[a] Standard deviations were not calculated for the hydrogen atoms since no refinement on their coordinates was performed. Standard deviations are also absent for coordinates fixed by symmetry considerations. [b] Hydrogen atom temperature factors were arbitrarily assigned.

The fractional atomic coordinates and their estimated standard deviations as calculated from the final least-square refinement on TPyP-DA are given in Table I. Also shown are the atomic isotropic temperature factors. Table II lists the corresponding parameters for TPP-DA. The hydrogen coordinates are those calculated from the positions of the nonhydrogen atoms, assuming normal trigonal hybridization of the atom to which the hydrogen is bonded.

Table II. Fractional Atomic Coordinates and Isotropic Temperature Factors for $\alpha,\beta,\gamma,\delta$-Tetraphenylporphine Diacid

	Coordinates and standard deviations[a] ($\times 10^4$)						
Atom	x	σ_x	y	σ_y	z	σ_z	B, Å^2 [b]
Fe	0	..	0	..	0	..	2.5
Cl_1	0	..	5000	..	2500	..	4.7
Cl_2	645	4	860	4	1722	13	4.4
N_1	3779	9	210	9	2572	30	1.8
C_2	3213	11	−413	11	2252	40	1.7
C_3	2580	12	−80	13	1168	41	2.5
C_4	2730	13	715	13	898	41	3.0
C_5	3470	11	918	11	1832	40	1.9
C_6	3787	11	1691	11	2124	40	2.2
C_7	3330	11	2429	11	1833	37	1.7
C_8	2494	17	2454	16	2261	53	2.9
C_9	2041	15	3156	15	1963	52	4.2
C_{10}	2454	16	3864	16	1262	50	4.2
C_{11}	3258	16	3827	17	889	52	4.0
C_{12}	3670	12	3128	13	1194	41	2.9
H_1	4309		134		3188		3.0
H_3	2053		−412		624		4.0
H_4	2358		1130		105		4.0
H_8	2203		1901		2829		4.0
H_9	1381		3169		2195		4.0
H_{10}	2121		4438		1077		4.0
H_{11}	3579		4341		281		4.0
H_{12}	4330		3107		1026		4.0
O[c]	20	12	4220	12	3343	44	5.9

[a] Standard deviations were not calculated for the hydrogen atoms since no refinement on their coordinates was performed. Standard deviations are also absent for coordinates fixed by symmetry considerations. [b] Hydrogen atom temperature factors were arbitrarily assigned. [c] Fractional oxygen atom of postulated perchlorate anion. B is dependent upon multiplicity. When varied simultaneously, multiplicity = 0.60 and B = 5.9.

Figure 3 is a computer-drawn[36] perspective view of the tetrapyridylporphine diacid molecule showing the location of the ionically bound chlorines (Cl_2 is directly beneath Cl_1). With the exception of the location of the chlorine atoms, this basic configuration is *common to both diacids*. The most noticeable feature is the large deviation from planarity, which will be discussed shortly. Although the H_4TPyP^{2+} molecule exhibits strict point group symmetry $2(C_2)$, with the twofold

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(36) C. K. Johnson, "ORTEP, A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge, Tenn., 1965.

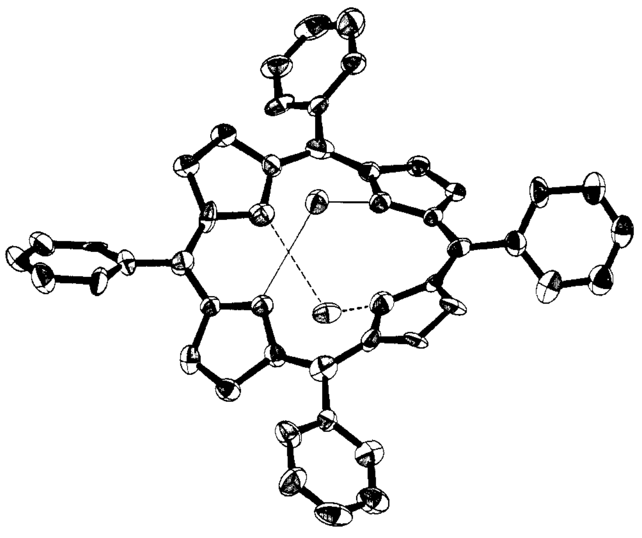

Figure 3. Anisotropic vibration in TPyP diacid.

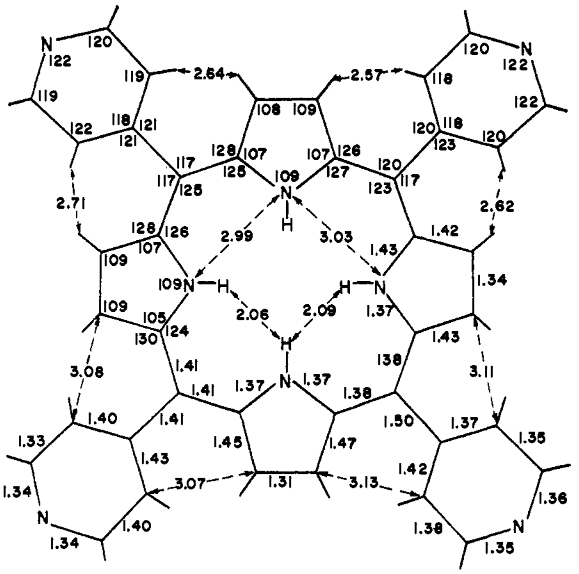

Figure 4. Bond length and angles in TPyP diacid. Some important intramolecular distances are also given. Average standard deviation in a bond length is 0.019 Å and in a bond angle 1.2°.

axis perpendicular to the mean molecular plane and intersecting Cl_1 and Cl_2, it is evident from Figure 3 that the molecule has pseudo-point symmetry $\bar{4}$ (S_4). The tetraphenylporphine molecule is required by space group considerations to also possess point group symmetry $\bar{4}$. Both molecules are expected to exhibit $\bar{4}$ symmetry in solution (assuming no flipping is taking place; see section on chemical properties).

Inspection of Tables I and II shows that temperature factors for both diacids generally increase going toward the periphery of the molecule and are greatest for the atoms in the pyridyl (or phenyl) rings, especially C_9, N_{10} (C_{10}), and C_{11}. Figure 3 shows the ellipsoids representing the anisotropic thermal motion of the atoms in the H_4TPyP^{2+} molecule. The shape of the atomic ellipsoids cannot readily be explained by any thermal motion of the molecule as a whole. That is, there is no evidence of any general tangential oscillation about the rotation axis or widespread out-of-plane vibrations. Most of the atoms, in fact, exhibit relatively isotropic vibration. The marked anisotropic vibration of C_{12}, which is inconsistent with that of its neighboring atoms, is almost undoubtedly caused by experimental errors and serves to illustrate the large effect that these errors—systematic and random—can have on the anisotropic parameters. Figure 3 is, in fact, intended to give only a rough, qualitative picture of the nature of the thermal vibrations. The least-squares calculated values of the anisotropic temperature factors for TPyP-DA are listed in Table III.

Table III. Anisotropic Temperature Factor Coefficients in TPyP-DA

	(Parameters)^{a,b} × 10^4					
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O_1	114	220	64	109	0	0
Cl_1	37	60	15	28	0	0
Cl_2	44	71	22	41	0	0
Cl_3	46	81	35	39	−7	3
Cl_4	50	100	36	52	10	15
N_1	28	55	16	27	0	0
C_2	16	43	27	14	−2	−7
C_3	27	59	19	24	0	−3
C_4	32	66	24	33	−13	−16
C_5	25	49	14	24	0	0
C_6	25	35	28	16	−3	−6
C_7	35	78	24	41	3	2
C_8	41	74	41	46	0	8
C_9	50	115	31	61	6	1
N_{10}	45	108	29	54	14	10
C_{11}	36	85	36	37	12	7
C_{12}	46	62	22	36	29	28
N_{13}	37	71	21	35	0	0
C_{13}	39	45	33	34	−19	−19
C_{15}	51	75	−3	47	0	11
C_{16}	17	49	18	12	7	0
C_{17}	27	45	23	23	−3	1
C_{18}	36	65	21	27	−7	−1
C_{19}	30	41	17	24	0	−6
C_{20}	51	72	14	40	−2	−10
C_{21}	33	62	36	18	4	−11
N_{22}	40	60	33	15	10	−5
C_{23}	51	72	45	41	1	6
C_{24}	27	68	33	26	−1	−13

[a] The β_{ij} are coefficients of the quadratic form $\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl$. [b] Standard deviations estimated from the least-squares calculation average about 30% of the reported parameters.

Although stacking disorder has proven to be a common phenomenon in crystals of naturally occurring porphyrins, the relatively small magnitude of the isotropic temperature factors found for these structures indicates little or no such disorder. This is not surprising in view of the fact that the type of stacking (or statistical) disorder thought to exist in free base or metalloporphyrin crystals requires a 90° rotation about a pseudo-fourfold axis. No such axis exists in the markedly nonplanar diacids.

Bond Lengths and Angles. The bond lengths and bond angles as calculated from the final least-squares of both diacid structures are given in Figures 4 and 5. The crystal structure determinations of both a triclinic[13] and tetragonal[4] form of tetraphenylporphine free base (TPP-FB) have been mentioned. The calculated standard deviations of C–C bonds averaged about 0.01 Å in these studies. No structural determination of the TPyP free base has been reported. Standard deviations for C–C bonds average 0.019 Å in TPyP-DA and 0.032 Å in TPP-DA. These larger errors hamper a detailed comparison of bond lengths of the diacid porphyrins with those of the free bases.

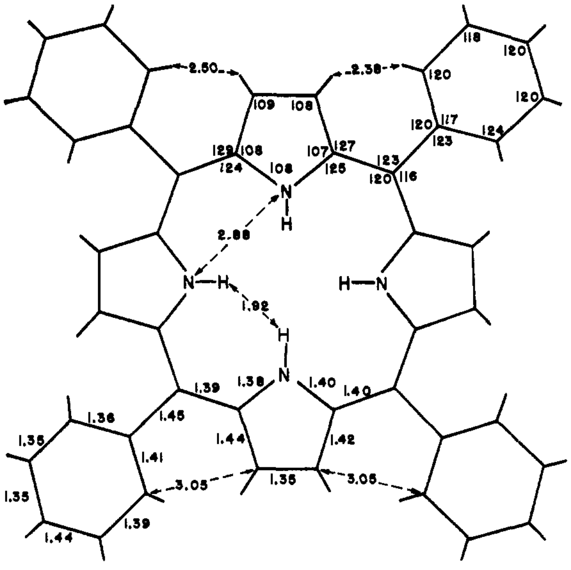

Figure 5. Bond lengths and angles in TPP diacid. Some important intramolecular distances are also given. Average standard deviation in a bond length is 0.032 Å and in a bond angle 2.0°.

The lower precision obtained for the bond lengths in the diacid structures can be somewhat nullified by taking an average of chemically equivalent bonds. For this purpose it is preferable to calculate a weighted average, given by $d_{av} = (\Sigma d_i/s_i^2)/(\Sigma 1/s_i^2)$,[37] where the d_i's are the individual bond lengths and the s_i's are their associated standard deviations. Figure 6 shows the weighted average bond lengths in each diacid molecule for the four chemically distinct bonds constituting the porphyrin nucleus. The average distance between the methine carbon and the substituted pyridyl or phenyl ring (C_6–C_7) is also shown. The corresponding distances for the free base tetraphenylporphine (triclinic form) are given for comparison purposes.

Table IV gives the bond lengths in the pyridyl and phenyl rings. The average C–C bond length for the phenyl ring, 1.384 Å, is within one standard deviation of the commonly accepted value of 1.395 Å.[38] The difference in length between the C_α–C_β and C_β–C_γ bonds of the phenyl ring cannot be considered significant. The average C–N distances in both pyridyl rings agree well with the value of 1.342 Å found in the microwave determination of pyridine.[39] In pyridine itself no significant difference between the C_α–C_β and C_β–C_γ distance was found, the former averaging 1.391 Å and the latter, 1.398 Å. The same type of C–C bond length variation in the pyridyl rings as is indicated in Table IV was found by Hanic[40] for the pyridoxine hydrochloride structure, where C_α–C_β bonds averaged 1.363 ± 0.005 Å and C_β–C_γ bonds, 1.394 ± 0.005 Å. The C_α–N bonds averaged 1.335 Å in that structure.

The bond angles found for the two diacid nuclei are quite similar and, moreover, close to those found in the TPP free base despite the radically altered configuration of the diacid. The good agreement between bond angles in pyrrole I and pyrrole II in the TPyP-DA structure suggests that these two rings are equivalent, in spite of bond-length differences which approach three standard deviations.

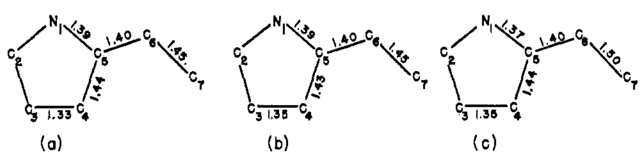

Figure 6. Bond lengths in (a) TPyP diacid, (b) TPP diacid, and (c) TPP free base (triclinic form), averaged over chemically equivalent bonds. The nuclear bond lengths in tetragonal TPP free base are all within 0.02 Å of those in triclinic TPP-FB.

Table IV. Average Bond Lengths in Pyridyl and Phenyl Rings

	TPyP-DA					
	Pyridyl I		Pyridyl II		TPP-DA	
Bond	d_{av}	σ_{av}	d_{av}	σ_{av}	d_{av}	σ_{av}
C–C[a]	1.390	0.011	1.380	0.010	1.384	0.014
C_α–N[b]	1.340	0.014	1.356	0.015		
C_α–C_β[b]	1.365	0.016	1.367	0.015	1.373	0.025
C_β–C_γ[b]	1.417	0.016	1.394	0.014	1.390	0.016

[a] Includes all four C–C bonds in pyridyl rings and all six bonds in phenyl rings. [b] Subscripts refer to positions relative to the end nitrogen or carbon atom (*i.e.*, N_{10} and C_{10}).

The Inner Hydrogen Atoms and Hydrogen Bonding. It must be mentioned at this point that the positions of both inner hydrogen atoms were not absolutely determined. As indicated in the refinement section, the experimental data were not sufficiently exact to produce a well-defined difference map from which all the hydrogens could be located. The inner hydrogens, moreover, might not be expected to appear as hydrogen atoms but could each have a formal positive charge as great as $+{}^1/_2$ in the dication. (As will be mentioned later, there is reason to believe that this formal charge resides on the nitrogen atoms or the nucleus itself, and that the hydrogen atoms may be considered to be neutral.)

In spite of the high noise levels in the difference maps, they were useful in determining the positions of most of the hydrogen atoms in the TPyP-DA structure. A comparison of difference syntheses calculated with the XRD-5 and PAILRED data before the hydrogen atoms were included in the refinement revealed only 19 peaks *common to both maps* of height greater than 0.5 e/Å^3. Of these 19 peaks, ten are in appropriate positions for hydrogen atoms, and another two peaks are "close" to expected hydrogen positions. Table V compares the fractional coordinates of the 14 hydrogen atoms in the asymmetric unit, as calculated assuming trigonal hybridization, with the coordinates of 12 of the highest common peaks in the difference maps. The hydrogen atoms of special interest are, of course, H_1 and H_{13}, the hydrogens on the inner nitrogen atoms. Table V shows that the peak corresponding to H_1 is in precisely the position calculated assuming normal sp^2 hybridization of the pyrrole nitrogen atom. The peak corresponding to H_{13}, however, is quite far from its predicted location. The difference map calculated for the TPP-DA structure was no better than either of the difference maps found for TPyP-DA, but a peak of height 0.8 e/Å^3 was found within 0.2 Å of the position calculated for the inner hydrogen in that structure.

(37) "Interatomic Distances," The Chemical Society, Burlington House, London, 1958, p S1.

(38) Reference 3, Vol. 3, 1962, p 276.

(39) B. Bak, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, 22, 2013 (1954).

(40) F. Hanic, *Acta Cryst.*, 21, 332 (1966).

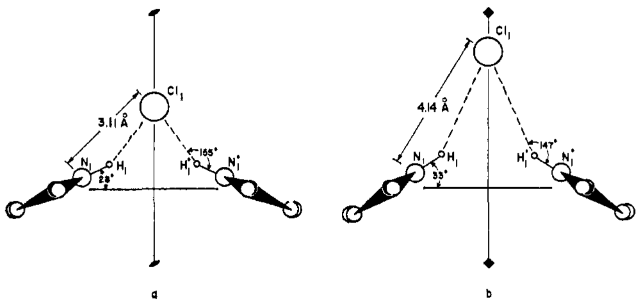

Figure 7. N–H···Cl hydrogen bonding in the (a) TPy-DA and (b) TPP-DA structures. View is perpendicular to the molecular rotation axes.

Figure 7a is a cross-sectional diagram of the tetrapyridylporphine diacid nucleus, showing the N–H···Cl hydrogen bonding. The N_1–Cl_1 distance of 3.11 for this nearly linear bond is in the lower range of reported N–H···Cl^- distances, indicating a fairly strong bond. The average length of this type of hydrogen bond is about 3.21 Å,[41] although values as low as 3.06 Å (for pyridoxine hydrochloride) have been found. Figure 7b is a cross section of the tetraphenylporphine diacid nucleus. The larger N_1–Cl_1 distance of 4.14 Å here discounts the possibility of any significant hydrogen bonding. A combination of stoichiometric and packing requirements in the TPP-DA cell have virtually eliminated the chance of a hydrogen bond.

Table V. Hydrogen Coordinates in TPyP-DA as Found from Difference Maps and as Calculated from Positions of Other Atoms

	Fractional coordinates						Peak
	Difference map			Calculated			electron density,
Atom	*x*	*y*	*z*	*x*	*y*	*z*	e/Å^3
H_1	0.083	0.300	0.400	0.083	0.300	0.408	0.8
H_3	0.350	0.567	0.333	0.351	0.561	0.307	0.8
H_4	0.300	0.333	0.266	0.292	0.336	0.314	0.5
H_8	0.266	0.250	0.467	0.273	0.263	0.441	0.7
H_9[a]	...	...	...	0.345	0.174	0.459	...
H_{11}	0.150	−0.133	0.333	0.131	−0.155	0.342	0.7
H_{12}	0.184	0.734	0.433	0.192	0.725	0.441	0.8
H_{13}	0.033	0.400	0.316	0.025	0.354	0.350	0.8
H_{15}	0.033	0.617	0.450	0.019	0.617	0.444	0.6
H_{16}	0.184	0.734	0.433	0.192	0.725	0.441	0.8
H_{20}[a]	...	...	...	0.245	0.757	0.307	...
H_{21}	0.383	0.983	0.284	0.392	0.978	0.292	0.7
H_{23}	0.284	0.800	0.300	0.245	0.757	0.307	0.6
H_{24}	0.383	0.700	0.433	0.384	0.680	0.425	0.8

[a] No peaks in the difference maps were found corresponding to these hydrogen atoms.

Deviation from Planarity. As seen in Figure 3, the most remarkable feature of the diacid configuration is the distortion from planarity. These two diacid structures exhibit the greatest deviations from planarity thus far found in any porphyrin system. In both TPyP-DA and TPP-DA the pyrrole rings are tilted alternately up and down, almost as rigid bodies. The angles of tilt[42] of these rings from the mean molecular plane are 28.2° for pyrrole I and 27.3° for pyrrole II in TPyP-DA and 33.0° for the pyrrole ring in TPP-DA. The porphyrin nuclear least-squares (NLS) plane for the H_4TPyP^{2+} molecule is given by the equation $z = 0.385c$ and fixed by symmetry to be $z = 0.250c$ for H_4TPP^{2+}. Deviations from the NLS planes for the diacids and a number of other porphyrin systems are given in Table VI. Table VII gives some of the planes in the porphyrin structures.

This reveals a small sideways tilt, or ruffling, of the pyrrole rings *superimposed* on the large vertical tilt. While a vertical tilting of such magnitude is unique to these diacid structures, it was mentioned that the sideways ruffling has been found in other porphyrins, including the free base[4] and copper tetraphenylporphine.[7] The conclusion that the ruffling is dependent upon crystal packing forces is supported by the much more pronounced ruffling in the H_4TPP^{2+} molecule than in H_4TPyP^{2+}. Specific packing interactions in the two crystal structures will be discussed in the section on molecular packing.

The cause or causes of the pronounced tilting of the pyrrole rings in the dications is of considerable interest. Upon initial consideration there seemed to be at least three possible causes: (1) the steric hindrance that would result if all four inner hydrogen atoms were coplanar, (2) the electrostatic repulsion of the inner nitrogen atoms, assuming each of them to have a charge of $+^1/_2$, and (3) general packing effects.

Causes 1 and 2 apply to the molecule in solution as well as in the solid state, while cause 3 is applicable only to the solid state. More precisely, if the nonplanarity is due to cause 3, then it may be specific to certain crystalline forms of diacids.

The stability gained by the nearly linear N–H···Cl hydrogen bonds is not considered to be a necessary condition for the establishment of the nonplanar configuration, because strong hydrogen bonding is not, in fact, common to both diacids. While the N_1–Cl_1 distance in the TPyP-DA is a short 3.11 Å, indicating strong hydrogen bonding, the corresponding distance in the TPP-DA is 4.14 Å, too long for any significant hydrogen bonding. Yet, it was seen that the angular tilt of the pyrrole rings was slightly greater in the TPP-DA structure. Hydrogen bonding is thus not required to stabilize the nonplanar molecule.

It is probable that the nonplanarity is due to a combination of reasons 1 and 2. With regard to reason 1, Figure 8 illustrates the degree of steric hindrance that would exist between four coplanar hydrogen atoms in the center of the molecule. The effective van der Waals radii of hydrogen atoms is between 1.10 and 1.20 Å.[43] For an N–H distance of 0.93 Å[44] and a hydrogen van der Waals radii of 1.15 Å, opposite hydrogen atoms in the free base porphyrin would just contact one another. However, it is seen from the cross-hatched area that there is a great amount of interpenetration for four hydrogens in the plane. The distance between adjacent hydrogen atoms would be 1.50 Å for the planar configurations. The tilting of the pyrrole rings allows this distance to increase to an average of 2.08 Å in TPyP-DA and 1.92 Å in TPP-DA. These latter values are comparable to the contact distance between diagonally

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(41) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., New York, N. Y., 1960, pp 295–293.

(42) The values given are the angles between the molecular rotation axis and the normals to the pyrrole rings as defined by the nitrogen and the two β-carbon atoms.

(43) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961, p 7.

(44) This is the observed N–H distance found for free base TPP in ref 4.

Table VI. Deviations from Nuclear Least-Squares Plane for Some Porphyrins[a]

Atom[c]	Out-of-plane distance,[b] Å						
	CuTPP	Cu(*p*-Cl)TPP	Porphine	TPP(tri)	TPP(tet)	TPP-DA	TPyP-DA
Metal	0.00	0.00	...	...	...	...	...
N_1	0.04	−0.02	0.00	0.01	0.04	0.05	0.13
C_2 (α)	0.24	−0.06	0.01	0.00	0.22	−0.19	−0.22
C_3 (β)	0.09	−0.02	0.01	−0.05	0.07	−1.00	−0.82
C_4 (β)	−0.23	0.04	−0.02	−0.03	−0.22	−1.16	−0.92
C_5 (α)	−0.26	0.04	−0.02	0.01	−0.21	−0.47	−0.22
C_6 (m)	−0.42	0.07	−0.03	0.05	−0.38	−0.30	−0.09
N_{13}	−0.04	0.00	0.01	0.16	−0.04	−0.05	−0.12
C_{14} (α)	−0.24	0.00	−0.02	0.07	−0.22	0.19	0.19
C_{15} (β)	−0.09	−0.08	−0.01	−0.07	−0.07	1.00	0.87
C_{16} (β)	0.23	−0.04	0.02	−0.10	0.22	1.16	0.88
C_{17} (α)	0.26	0.00	0.03	0.04	0.21	0.47	0.33
C_{18} (m)	0.42	0.06	0.03	−0.03	0.38	0.30	−0.03
N_1'	0.04	0.02	−0.01	−0.01	0.04	0.05	0.13
C_2' (α)	0.24	0.06	0.00	0.00	0.22	−0.19	−0.22
C_3' (β)	0.09	0.02	0.00	0.05	0.07	−1.00	−0.82
C_4' (β)	−0.23	−0.04	−0.02	0.03	−0.22	−1.16	−0.92
C_5' (α)	−0.26	−0.04	−0.02	−0.01	−0.21	−0.47	−0.22
C_6' (m)	−0.42	−0.07	−0.01	−0.05	−0.38	−0.30	−0.09
N_{13}'	−0.04	0.00	0.02	−0.16	−0.04	−0.05	−0.12
C_{14}' (α)	−0.24	0.00	0.00	−0.07	−0.22	0.19	0.19
C_{15}' (β)	−0.09	0.08	−0.01	0.07	−0.07	1.00	0.87
C_{16}' (β)	0.23	0.04	0.00	0.10	0.22	1.16	0.88
C_{17}' (α)	0.26	0.00	0.01	−0.04	0.21	0.47	0.33
C_{18}' (m)	0.42	−0.06	0.02	0.03	0.38	0.30	−0.03

[a] Taken in part from L. E. Webb, Ph.D. Dissertation, The University of Chicago, 1965, p 44. [b] Numbering system is that of Figure 2. The asymmetric unit for these porphyrins is as follows: CuTPP, unprimed atoms numbered 1–6; Cu(*p*-Cl)TPP, all unprimed atoms; porphine, all atoms; TPP(tri), all unprimed atoms; TPP(tet), unprimed atoms 1–6; TPP-DA, unprimed atoms 1–6; TPyP-DA, all unprimed atoms. [c] The notations α and β indicate those positions on a pyrrole ring; m denotes a *meso* position on the porphyrin ring.

Table VII. Equations of Pyrrole and Pyridyl Planes in TPyP-DA and TPP-DA and Atomic Displacements from These Planes

Structure	Plane	Equation of plane[a]				Atomic out-of-plane displacements, Å
		A	*B*	*C*	*D*	
TPyP-DA	Pyrrole I	7.8165	−1.5260	17.1744	7.1588	N_1 = 0.003, C_2 = 0.008, C_3 = −0.017, C_4 = 0.019, C_5 = −0.013
	Pyrrole II	4.5246	−6.2344	17.2431	3.8971	N_3 = 0.017, C_{14} = −0.015, C_{15} = 0.008, C_{16} = 0.002, C_{17} = −0.012
	Pyridyl I	5.6677	2.0161	−16.1579	−5.1084	C_7 = −0.027, C_8 = 0.010, C_9 = 0.011, N_{10} = −0.017, C_{11} = −0.001, C_{12} = 0.023, Cl_3 = −0.900[b]
	Pyridyl II	−10.2243	7.8278	15.7178	8.1126	C_{19} = −0.021, C_{20} = 0.013, C_{21} = 0.010, N_{22} = −0.025, C_{23} = 0.016, C_{24} = 0.007, Cl_4 = −0.820[b]
TPP-DA	Pyrrole	−8.2123	3.5648	6.1423	−1.4220	N_1 = −0.027, C_2 = 0.018, C_3 = −0.003, C_4 = −0.013, C_5 = 0.024
	Phenyl	3.3800	4.8801	6.8454	3.5765	C_7 = −0.012, C_8 = 0.011, C_9 = −0.006, C_{10} = −0.001, C_{11} = 0.006

[a] The equation of the plane is defined as $Ax + By + Cz = D$, where x, y, and z are fractional coordinates of the direct lattice axes. [b] Atom not included in the calculation of the least-squares plane.

situated hydrogen atoms in the triclinic TPP free base (2.10 Å). Hydrogen–hydrogen contact distances as low as 1.82 Å (in biphenyl)[45] have been reported.

As mentioned previously, the porphyrin skeleton is known to be quite flexible toward out-of-plane deformation. It was mentioned that some investigators feel that one might expect the molecule to be ruffled in the gaseous state, since there exists a considerable amount of angular strain in the σ-bonding system of a strictly planar porphyrin nucleus. In spite of this, the possibility that the nonplanarity might be due to cause 3, the packing in the crystal, can probably be eliminated. As will be seen from the packing diagrams, the diacid molecules in the two structures are *quite differently packed*, yet exhibit the same basic conformation. Furthermore, there are *no* close contact distances in TPyP-DA which might be cited to contribute to the nonplanarity. However, packing forces may explain why the pyrrole rings of H_4TPyP^{2+} are not tilted as much as they were in H_4TPP^{2+} (see section on molecular packing).

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(45) A. I. Kitaigorodskii, ref 43, p 9.

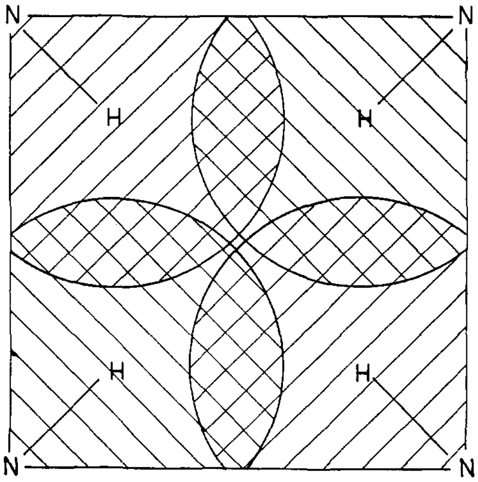

Figure 8. Interpenetration of hydrogen-hydrogen van der Waals spheres for a prophyrin diacid with four coplanar hydrogen atoms. Cross-hatched area shows extent of interpenetration of spheres.

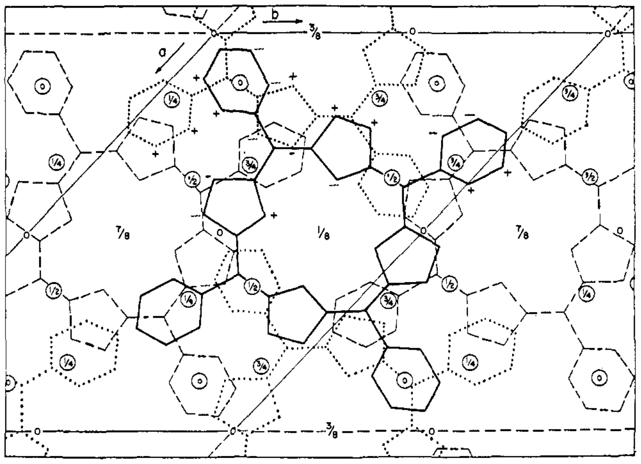

Figure 9. Molecular packing in the TPyP-DA structure. View is a projection on the (001) plane. Fractions at the center of the molecules indicate fractional z coordinates. Diacid molecules centered on the twofold axes at (0, $^3/_4$, $^5/_8$) and (1, $^3/_4$, $^5/_8$) have been omitted for clarity. Only those molecules close to the molecule at ($^1/_2$, $^3/_4$, $^1/_8$) (solid lines) are shown. Also omitted is the water molecule which does not have significant close contacts with any porphyrin molecule. The symbols "+" and "−" show the directions of tilt of pyrrole and phenyl rings. Circles containing fractions denote chloride ions and their fractional z coordinates.

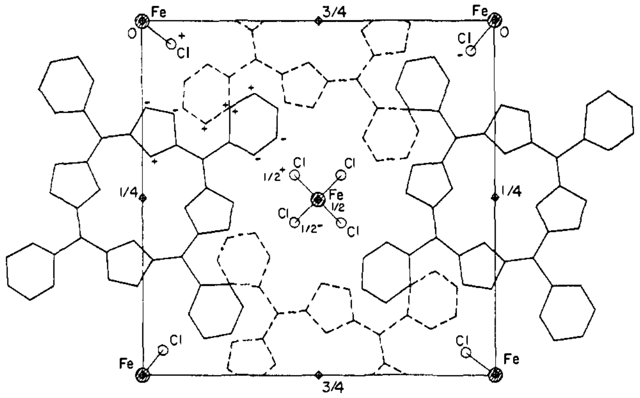

Figure 10. Molecular packing in the TPP-DA structure. View is a projection on the (001) plane. The entire unit cell contents are shown. The symbols "+" and "−" show the directions of tilt of the pyrrole and phenyl rings in the asymmetric unit.

Molecular Packing in the Diacid Structures. A good deal of crystallographic evidence has accumulated in support of the hypothesis that the porphyrin molecule is a highly flexible aromatic system, with low-energy barriers to a variety of angular distortions. The best examples of packing effects playing a prominent role in determining porphyrin molecular configurations are seen in (1) the conformational differences of the tetragonal and triclinic forms of α,β,γ,δ-tetraphenylporphine, and (2) the lack of ruffling in the more loosely packed Cu(p-Cl)TPP compared to that in CuTPP (see Table VI). The above-mentioned differences cannot, of course, be explained by chemical effects. With the knowledge that the packing environment can have a pronounced effect on porphyrin structures, it was thought necessary to closely examine this environment in the diacid crystals.

Unit cell contents and packing arrangements for TPyP-DA and TPP-DA are shown in Figures 9 and 10, respectively. These figures are projections down the rotation axis (z), perpendicular to the molecular planes. The fractions at the centers of the molecules indicate their fractional z coordinates. It is immediately apparent that the packing situation in the diacid molecules is completely different in the two crystals. Specifically, there is no actual overlap between two symmetry-related molecules in TPP-DA, while there is overlapping in TPyP-DA. The large $FeCl_4^-$ anion has the effect of "spreading out" the H_4TPP^{2+} molecules. Close intermolecular contact distances in both structures are listed in Tables VIII and IX. All of the close nonchlorine contacts in TPyP-DA are between molecules related by either the b-glide plane (at $z - {}^1/_4$ and $^3/_4$) or the inversion centers; all those in TPP-DA are between molecules related by the twofold screw axes ($e.g.$, at $(x,y) = ({}^1/_4, {}^1/_4)$, Figure 10).

Structure of the Tetrachloroferrate(III) Anion. An interesting but unintentional by-product of the TPP-DA study is the structural determination of the $FeCl_4^-$ anion. This complex was found to possess point group symmetry $\bar{4}$, with an Fe–Cl distance of 2.171 ± 0.009 Å. Within experimental error, the chlorines exhibit perfect tetrahedral coordination to the iron atom. The Cl–Fe–Cl′ angles of 109.1 ± 0.5° and 109.7 ± 0.3° are both within one standard deviation of the tetrahedral angle of 109.47°. The two symmetry-distinct Cl–Cl′ distances are 3.536 ± 0.016 and 3.548 ± 0.017 Å, identical within the error of their calculations. It should be emphasized that the requirement of $\bar{4}$ point symmetry does not in itself ensure perfect tetrahedral geometry, since the Cl–Fe–Cl′ angle is not fixed by symmetry.

To the authors' knowledge, there have been only two other crystallographic determinations of $FeCl_4^-$. One was done by Zaslow and Rundle,[46] who crystallized the tetrachloroferrate(III) ion with the bulky tetraphenylarsonium cation. These authors reported an Fe–Cl distance of 2.19 ± 0.03 Å for the ($[(C_6H_5)_4As^+][FeCl_4^-]$) structure. The large bond-length error is a consequence of the fact that only two-dimensional data sets (hk0 and h0l) were collected in this determination. Although the iron atom was also on a position of $\bar{4}$ symmetry in that crystal, the Cl–Fe–Cl′ angles were 107.0 and 114.5° with esd's of 1.5°. The other tetra-

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[46] B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).

Table VIII. Close Intermolecular Contact Distances in TPyP-DA[a]

Contact atoms[b]	Distance,[c] Å	Contact atoms[b]	Distance,[c] Å
Cl_3–C_{20}[d]	3.59	Cl_2–H_3[e]	2.52
Cl_3–C_{21}[d]	3.51	Cl_1–H_{15}[f]	2.44
Cl_3–N_{22}[d]	3.70	H_{12}–C_4[e]	2.91
Cl_2–C_{23}[e]	3.47		
Cl_2–C_{24}[e]	3.61	C_{21}–H_{21}[e]	2.92
C_8–Cl_3[f]	3.51	C_{24}–H_9[f]	2.87
C_{15}–Cl_1[f]	3.51	H_{12}–H_{21}[e]	2.42
C_3–Cl_2[e]	3.62	H_{24}–H_9[f]	2.33
Cl_3–C_{16}[d]	3.62	O–H_{24}[e]	2.48
C_{16}–C_8[f]	3.57	O–H_{23}[e]	2.73
C_4–C_{20}[e]	3.46		
C_{15}–C_{14}[f]	3.60		
C_3–C_3[e]	3.58		
C_{24}–C_9[f]	3.70		
C_{12}–C_{21}[e]	3.73		
O–C_{24}[e]	3.20		
O–C_{23}[e]	3.33		

[a] Includes all C–C and C–Cl distances less than 3.7 Å and C–H distances less than 3.0 Å. [b] Atoms without superscripts are those in the asymmetric unit, with coordinates given in Table III. Atoms with superscripts have coordinates (x', y', z') derivable from Table III by the transformations (x, y', z') equal those values given in footnotes *d*, *e*, and *f*. [c] The average estimated standard deviation for C–C contact distances is 0.025 Å. [d] (x, $-1 + y$, z). [e] ($^1/_2 - x$, $1 - y$, $^1/_2 - z$). [f] (x, $^1/_2 + y$, $1 - z$).

Table IX. Close Intermolecular Contact Distances in TPP-DA[a]

Contact atoms[b]	Distance,[c] Å	Contact atoms[b]	Distance, Å
C_3–Cl_2	3.56	H_3–Cl_2[d]	2.63
C_3–Cl_2[d]	3.65	H_4–Cl_2	3.09
C_4–Cl_2	3.49	H_{11}–Cl_2[e]	2.92
C_{11}–Cl_2[e]	3.58	N_1–H_{10}[f]	3.02
C_{12}–Cl_2[e]	3.84	H_8–C_{10}[f]	2.86
C_7–C_8[e]	3.61	H_8–C_{11}[f]	2.65
C_8–C_8[e]	3.66	H_8–C_{12}[f]	2.85
C_{11}–C_8[e]	3.60		
C_{12}–C_8[e]	3.58		
C_9–C_4[e]	3.45		
C_{10}–C_4[f]	3.48		

[a] Includes all C–C and C–Cl distances less than 3.7 Å and C–H distances less than 3.0 Å. [b] Atoms without superscripts are those in the asymmetric unit, with coordinates given in Table IV. Atoms with superscripts have coordinates (x', y', z') which are derivable from Table IV by the transformations (x', y', z') equal those values given in footnotes *d*, *e*, and *f*. [c] Estimated standard deviations for C–C distances average 0.035 Å. [d] (y, $-x$, $-z$). [e] ($^1/_2 - x$, $^1/_2 - y$, $z - {}^1/_2$). [f] ($^1/_2 - x$, $^1/_2 - y$, $z + {}^1/_2$).

chloroferrate(III) determination was in $NaFeCl_4$.[47] The $FeCl_4^-$ anion in this crystal also exhibited significant tetrahedral distortion, with Cl–Fe–Cl′ angles ranging between 104.9 ± 0.4 and 112.7 ± 0.5°. The iron atom in that case did not lie on a special position. Fe–Cl bond distances in $NaFeCl_4$ varied between 2.18 and 2.22 (±0.01) Å, and nonbonding Cl–Cl′ distances, between 3.50 and 3.66 (±0.01) Å. The authors attributed the distortion to electrostatic interactions of the chlorines with neighboring sodium ions.

There is a substantial amount of chemical evidence indicating that $FeCl_4^-$ ions are perfectly tetrahedral (T_d) in solution. Clark and Dunn[48] found a single sharp Fe–Cl stretching absorption at 378 cm^{-1} in the infrared spectrum of $[NEt_4^+][FeCl_4^-]$ in Nujol mull. A tetrahedral configuration in solution is also indicated by Raman spectra.[49] As one would not expect a tetrahedral d^5 system to experience a Jahn–Teller distortion,[50] that distortion found in $[(C_6H_5)_4As^+][FeCl_4^-]$ can almost certainly be attributed to packing effects and the irregularities in $NaFeCl_4$ to packing and/or electrostatic interactions. A perfectly tetrahedral $FeCl_4^-$ has therefore not been found in any crystallographic determination prior to that of the TPP-DA. It is significant that the $FeCl_4^-$ anion is free of distortion in TPP-DA in that it is a further clue to the nature of the packing in that crystal. If the tetrachloroferrate(III) played a *major* role in pushing the pyrrole rings out of the plane, one would expect it to be somewhat distorted itself. The fact that it is undistorted suggests that it has a minimal effect on the conformation of the diacid molecule.

Effect of the Structure of the Porphyrin Diacids on Some of Their Chemical Properties. This section is an attempt to interpret some of the chemical properties of porphyrin dications in general—and those of TPP and TPyP in particular—in relation to their observed structures in the solid state. The section is by no means an exhaustive review of the chemical and physical properties of porphyrin dications. It might be mentioned at this point that while there is an abundance of literature on free base and metalloporphyrins, conspicuous gaps are seen with respect to the properties of the dications. For example, no infrared spectra of porphyrin diacids could be found in the literature.

Two questions must be answered before proceeding further. The first is: Is the basic configuration found for the diacids of TPyP and TPP general for all porphyrins? Until further structural studies (preferably of porphine dication) are undertaken, this question cannot be answered conclusively. One can say, however, that the observed "fourfold" symmetry and equivalence of pyrrole rings is probably general to all diacids. This conclusion is based on the fact that the absorption spectra of all porphyrin dications are qualitatively similar. They all exhibit a very intense band (Soret band) in the near-ultraviolet region and two much weaker absorptions in the visible range,[51] between 550 and 650 mμ. With respect to the observed deviations from planarity, one would expect a similar configuration in all dications upon consideration of the proposed causes of the nonplanarity, since these would be operative in all porphyrins. However, certain anomalies observed in the visible and nmr spectra of H_4TPyP^{2+} and H_4TPP^{2+}, which will be mentioned shortly, imply that the nonplanarity may be more pronounced in these dications than the dication of porphine itself.

A second question to be answered concerns the actual state of the dication in solution. There is the possibility that in acidic solution the pyrrole rings are flipping up and down, although always in alternating directions. This flipping would amount to an inversion through a center of symmetry and would change the average point symmetry of the molecule from S_4 to D_{4h}. Such a motion is conceivable only if there occurs an ex-

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(47) R. R. Richards and N. W. Gregory, *J. Phys. Chem.*, **69**, 239 (1965).

(48) R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).

(49) J. A. Woodward and M. J. Taylor, *ibid.*, 4473 (1960).

(50) L. E. Orgel, "An Introduction to Transition Metal Chemistry: Ligand Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p 65.

(51) In the dication of porphine itself, one of these bands is quite weak, so that the visible spectrum seems single banded; *cf.* A. Stern and H. Wenderlein, *Z. Physik. Chem.*, **A175**, 405 (1936).

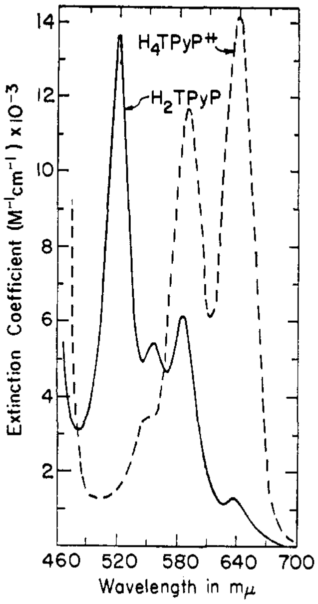

Figure 11. Visible spectra of free base and diacid α,β,γ,δ-tetrapyridylporphine in aqueous hydrochloric acid solution: free base, pH 2.3; diacid, pH 0.0.

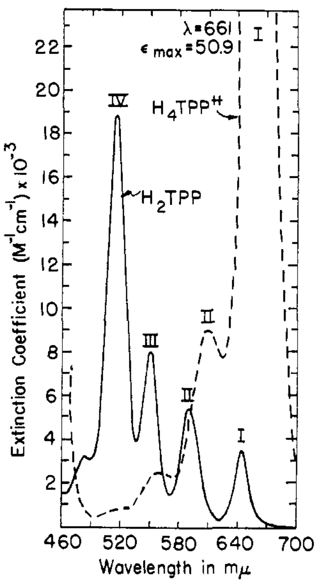

Figure 12. Visible spectra of free base and diacid α,β,γ,δ-tetraphenylporphine in chloroform.

change to the inner hydrogens with solvent protons. A rapid exchange (with a half-life of the order of seconds, or faster) of these hydrogens with D_2O has been reported for free base porphyrins[52] and methyl pheophorbides.[53] Also, a high-field peak observed at τ 11.89 ppm in the nmr spectrum of etioporphyrin-I in trifluoroacetic acid is missing when the solid is dissolved in deuterioacetic acid.[54] It has been shown that the porphyrin exists mainly as the dication in this acidic solvent,[55] in which the N–H protons are evidently being rapidly exchanged for deuterium. It is not unlikely that such an exchange also occurs in acidic aqueous solutions.

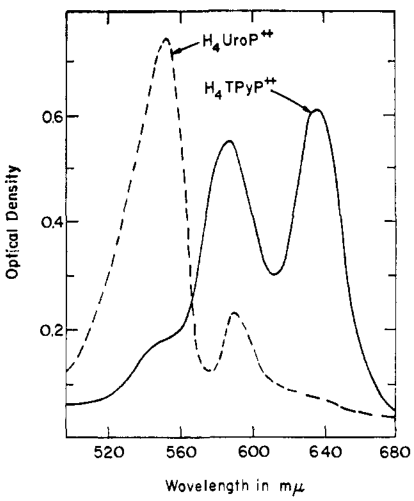

Figure 13. Comparison of the visible spectra of the diacids of tetrapyridylporphine and uroporphyrin.

An experiment which had the potential of clarifying both of the above questions was performed. *If* the nonplanar configuration of the dication extended to the asymmetrically substituted protoporphyrin-IX in solution, and *if* no fast flipping occurred (*i.e.*, if the half-life were of the order of ~30 min or more at room temperature), then protoporphyrin-IX dication should be resolvable into stereoisomers.[56] The free base of this porphyrin is not optically active. Also, the diacid species of the symmetrically substituted TPP and TPyP cannot exhibit optical activity because there exists a mirror plane through each pair of opposite nitrogen atoms.

Ultraviolet, Visible, and Infrared Spectra. A list of the absorption bands in the ultraviolet and visible spectra of a number of porphyrin free bases and diacids, including TPyP and TPP, is given in Table X. The Soret band (400–420 mμ in the free base) is found in all fully conjugated tetrapyrrole systems including porphyrins, phthalocyanines, chlorins, etc. In general, varying the solvent produces only small wavelength shifts (<3–4 mμ) in porphyrin spectra[57] (except if it coordinates with the metals in metalloporphyrins) but may affect the intensity markedly. The visible spectra for TPyP free base and diacid and TPP free base and diacid are given in Figures 11 and 12.

One apparent anomaly observed previously in the spectra of the tetrapyridyl- and tetraphenylporphine dications can now probably be explained in terms of the observed structure. The diacid forms of TPyP and TPP are green in solutions, in contrast to the violet or red color of other diacid porphyrin species.[58] A comparison of the spectra of H_4TPyP^{2+} and H_4UroP^{2+} (Figure 13) shows quantitatively the bathochromic shift observed in the spectra of the former. The diacids of TPP and its phenyl-substituted derivatives[59] and of

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(52) J. Mason, *J. Chem. Soc.*, 976 (1958).

(53) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963).

(54) J. Ellis, A. H. Jackson, G. W. Kenner, and J. Lee, *Tetrahedron Letters*, No. 2, 23 (1960).

(55) A. Neuberger and J. J. Scott, *Proc. Roy. Soc.* (London), A123, 307 (1952).

(56) An experiment to test this hypothesis was performed but was negative.

(57) G. D. Dorough, J. R. Miller, and E. M. Huennekens, *J. Am. Chem. Soc.*, 73, 4315 (1951).

(58) E. B. Fleischer and A. L. Stone, *Chem. Commun.*, 332 (1967).

(59) N. Datta-Gupta and T. J. Bardos, *J. Heterocyclic Chem.*, **3**, 495 (1966).

Table X. Absorption Spectra of Various Porphyrin Free Bases and Dications[a]

Porphyrin		Free Base					Dication		
		Soret	IV	III	II	I	Soret	II	I
Meso-IX dimethyl ester[c]	λ[b]	399	498	599	569	624	404	549	592
	ε[d]	208	11.9	9.2	7.1	5.3	406	15.2	6.6
Proto-IX dimethyl ester[c]	λ	408	505	540	578	633	412	557	602
	ε	151	14.1	11.7	6.8	6.4	282	15.1	6.8
Deutero-IX dimethyl ester[c]	λ	398	497	526	567	623	402	549	589
	ε	195	15.2	9.2	8.1	5.3	394	14.7	5.7
2,4-Diacetyldeutero-IX dimethyl ester[c]	λ	423	517	552	584	639	421	565	610
	ε	100	9.2	6.0	5.0	1.8	192	11.4	4.6
Octophenylporphine[e]	λ	423	514	550	583	635	440	570	615
	ε[f]	36.0	4.0	2.5	2.0	1.0	38.0	2.0	1.0
α,β,γ,δ-Tetraphenylporphine[g]	λ	419	515	548	592	647	445	608	661
	ε	478	18.7	8.1	5.3	3.4	431	9.0	50.9
α,β,γ,δ-Tetrapyridylporphine[h]	λ	420	518	553	585	638	442	588	639
	ε	201	13.5	5.3	6.2	1.3	287	11.7	14.2

[a] Values given are taken from Falk,[2] Appendix I, except where noted. [b] Wavelength at maximum absorption (mμ). [c] Solvent is aqueous sodium dodecyl sulfate. Wavelength shifts of less than 4 mμ are observed for the nonesterified dications in aqueous hydrochloric acid. [d] Extinction coefficient (l./mole cm) × 10^{-3}. [e] From M. Friedman, Ph.D. Dissertation, The University of Chicago, 1962, p 32. Solvent is chloroform, acidified with HCl for diacid. [f] Extinction ratios. [g] Was done in this laboratory. Solvent is chloroform, saturated with gaseous HCl for diacid. [h] Was done in this laboratory. Solvent is aqueous hydrochloric acid; pH 2.3 for free base, pH 0.0 for diacid.

TPyP are the only ones in which the intensity of band I is greater than that of band II. Inspection of Table X shows that even the free-base forms of TPP and TPyP have absorptions which are shifted 10–15 mμ to the red compared to the free bases of most of the naturally occurring porphyrins. This is consistent, however, with a small electron-withdrawing effect of the phenyl and pyridyl rings. It should be noted that the free base spectrum of 2,4-diacetyldeuteroporphyrin-IX, which also has electron-withdrawing substituents, is quite similar to those of free base TPyP and TPP. Upon the addition of two protons, we see that all the bands in the ultraviolet–visible spectra of H_4TPP^{2+} and H_4TPyP^{2+} are shifted 20–40 mμ to the red of even those of the dication of diacetyldeuteroporphyrin-IX. This is interpreted to be evidence of increased resonance interaction of the phenyl and pyridyl rings with the porphyrin nucleus in going from the free base to the diacid, which would be allowed by the tilting of the pyrroles observed in the solid state. That the bathochromic shift is more pronounced in H_4TPP^{2+} than H_4TPyP^{2+} is consistent with the structural observation that the phenyl rings in H_4TPP^{2+} were more nearly coplanar with the porphyrin nucleus than were the pyridyl rings in H_4TPyP^{2+}. However, it must be remembered that the *enhanced* nonplanarity found in H_4TPP^{2+} might also be due to packing effects.

The infrared spectra of the free base and diacid forms of TPP are shown in Figure 14. Detailed band assignments in free base TPP have been proposed by Thomas and Martell[60] and Mason.[52] The two spectra in Figure 14 are qualitatively similar, the main difference being the previously mentioned general collapsing of bands in the diacid. The region of greatest difference in the ir spectra of the free base and diacid is 1100–1500 cm^{-1}. Many of the bands corresponding to stretching and bending modes of the pyrrole ring occur in this region, and the fewer bands and reduced intensities noted in the diacid here probably arise from the equivalence of the pyrrole rings. In particular we see that the intense band at 1350 cm^{-1} in the free base, attributed to a C–N stretch, is almost absent in the diacid. A characteristically strong band at 1225 cm^{-1} observed in the porphyrin dications, which is present but much less intense in the free base, has, unfortunately, not yet been assigned. The main observation one can make is that the diacid ir spectrum is simpler than the free base spectrum which is what is expected from the higher symmetry of the former species.

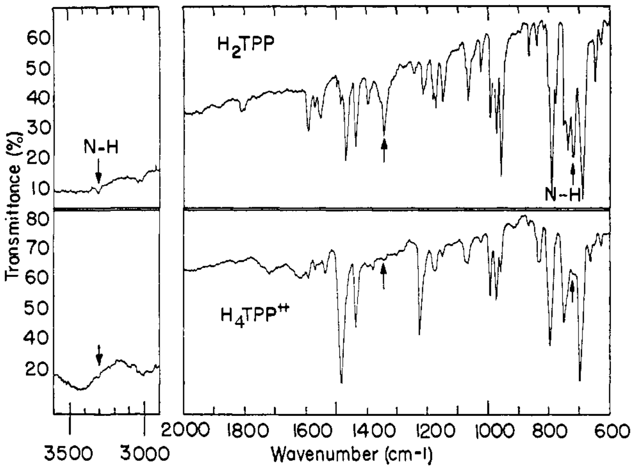

Figure 14. Infrared spectra of free base and diacid tetraphenylporphine.

Free Base–Diacid Equilibrium. Free base porphyrins, having two unprotonated nitrogen atoms, are capable of exhibiting the following acid–base equilibria.

$$H_4P^{2+} \rightleftharpoons H_3P^+ + H^+ \qquad K_1 \qquad (1)$$

$$H_3P^+ \rightleftharpoons H_2P + H^+ \qquad K_2 \qquad (2)$$

A number of workers have studied the above equilibria for various porphyrins, using potentiometric or spectrophotometric techniques. Among the first such investigators were Aronoff and Calvin,[61] whose colorimetric study of three porphyrins in sulfuric acid–pyridine mixtures failed to show a spectrum distinct from those of H_2P and H_4P^{2+}. They were thus led to the rather remarkable conclusion that the monocation

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(60) D. Thomas and A. Martell, *J. Am. Chem. Soc.*, **78**, 1338 (1956).

(61) S. Aronoff and M. Calvin, *J. Org. Chem.*, **8**, 205 (1943).

H_3P^+ could exist over only a very limited pH range. This conclusion has since been verified for protoporphyrin[62] in aqueous hydrochloric acid solutions, where it was found that, within the experimental error of the method of continuous variations, the two protons added simultaneously. Aronoff[63] later found, however, that upon titration of several porphyrins with perchloric acid in nitrobenzene, a distinct spectrum assumed to be that of the monocation was found for some porphyrins, while such a spectrum was totally absent for others. He also listed a third class of porphyrins, including tetraphenylporphine, for which an intermediate spectrum was indicated by small shifts in isosbestic points. Even in the cases where an intermediate spectrum was detected, however, K_2 was calculated to be at least three times greater than K_1. It should be mentioned that while the monosalts have never been isolated, there is now sufficient spectral evidence supporting their existence in anionic detergents,[2] which evidently stabilize the singly charged species with respect to the free base. There has been no conclusive proof that the monocations exist in detectable concentrations in aqueous solutions, although Neuberger and Scott[55] have presented spectra of what they claim to be the monoacids of a number of porphyrins in buffered, aqueous solutions. However, their results have been questioned because of their use of buffer solutions containing alkali ions and because the porphyrins they used contained carboxylic and sulfonic acid groups, whose pK's are in the pH range at which the supposed monocations appeared.

A careful study of porphyrin free base–diacid equilibria was undertaken on the water-soluble H_2TPyP[24] system. Excellent isosbestic points were obtained upon changing the pH of an aqueous hydrochloric acid solution from 2.30, at which point 98% of the porphyrin is in the free base form, to 0.00, where essentially all of the porphyrin is in the diacid form. In addition, the observed change in optical density was quantitatively consistent with the single equilibrium

$$H_4TPyP^{2+} \rightleftharpoons H_2TPyP + 2H^+ \qquad K = K_1K_2$$

A value of 5.4×10^{-3} (moles/l.)^2 was reported for K.

Thus, the bulk of the experimental evidence indicates that the second proton is added (or abstracted) much more easily than the first. This, of course, is contrary to what is found for most dibasic acids, in which successive proton transfers occur with increasing difficulty as a result of the accumulating charge. The relative instability of the monoacid had previously been explained solely in terms of the loss of symmetry, which decreased the resonance stabilization. Undoubtedly, this factor is important, and perhaps, even predominant in reducing the relative stability of the monoacid. However, the nonplanar configuration found in the diacids affords a second explanation. The energy barrier for the addition of the first proton may be greater than that for the addition of the second, because the first proton attacks a relatively planar molecule, with lone-pair electrons on the unprotonated nitrogens directed toward the center of the ring, a sterically unfavorable location. Upon incorporation of the first proton to form the monoacid, the pyrrole rings are probably tilted 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.[64]

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The Crystal and Molecular Structure of Octahydroxycyclobutane

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Abstract: Octahydroxycyclobutane crystallizes in the monoclinic system $P2_1/n$, a_0 = 7.525 Å, b_0 = 5.472 Å, c_0 = 7.491 Å (all ±0.005 Å), β = 90.00 ± 0.05°. The structure was solved by the symbolic addition method. The two molecules in the unit cell lie on centers of symmetry and thus require the cyclobutane ring to be planar. The average carbon–oxygen bond length is 1.385 Å and the carbon–carbon bond length is 1.562 Å. The average O–C–O bond angle is 111.8°. The structure is held together by a loose three-dimensional network of hydrogen bonds involving all of the hydroxyls in the system.

The synthesis of the novel compound octahydroxycyclobutane was first reported by West, Niu, and Ito[1] in 1963. The original workers on the compound predicted a planar structure for the cyclobutane ring on the basis of infrared data; however, the possibility of slight torsional deformation was not ruled out.

The variability of conformation in cyclobutane rings has been reviewed by Lambert and Roberts,[2] and from their work it would seem that there is no *a priori* way of predicting the conformation of the ring skeleton after substitution. The purpose of this study is to establish exactly the conformation of this molecular structure.

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