

XeO<sub>3</sub>. Further support for this is given by the observation<sup>4</sup> that the electrical conductivity of the solution is very low.

The very weak Raman bands at 933, 524, and around 460 cm.<sup>-1</sup> must then be assigned to another molecular species of low concentration, that is, as yet, unknown.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

## Crystal and Molecular Structures of Some Metal Tetraphenylporphines<sup>1</sup>

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The crystal and molecular structures of copper tetraphenylporphine, palladium tetraphenylporphine, zinc tetraphenylporphine dihydrate, and ferric hydroxide tetraphenylporphine monohydrate were determined from three-dimensional X-ray diffraction data. These structures are all tetragonal. The space group of both copper tetraphenylporphine and palladium tetraphenylporphine is  $I\bar{4}2d$  with four molecules per unit cell. The other two porphyrins have two molecules per unit cell. The space group of the zinc porphyrin is  $I4/m$  and the molecular symmetry is  $4/m$ . The iron porphyrin has space group  $I4$  and a molecular symmetry of 4. The molecular configuration changes from a planar to a buckled, nonplanar one depending on the crystal packing and on the substituents attached to the porphine nucleus. Copper and palladium tetraphenylporphine are very nonplanar, while the porphine nucleus of the zinc compound is planar. The iron porphyrin is nearly planar except that the iron atom is 0.2 Å. above the plane of the four nitrogen atoms in the porphyrin ring.

### Introduction

Previous structural determinations have shown that although some phthalocyanines are planar,<sup>3</sup> nickel etioporphyrin I<sup>4</sup> and tetraphenylporphine<sup>5</sup> are nonplanar. We reported in a previous communication<sup>6</sup> that copper tetraphenylporphine is also nonplanar; this paper includes the details of this structure determination. Nickel etioporphyrin II<sup>7</sup> appears to be planar, but disorder in the crystal makes it impossible to detect suspected slight deviations from planarity.

A summary of some porphyrin crystal forms found by us and others<sup>8-10</sup> is given in Table I. The large number of different crystal forms can be partially explained by the wide variety of solutions from which the crystals were grown.

### Experimental

The metal tetraphenylporphines were prepared by the usual methods.<sup>11</sup> The PdTPP sample was kindly supplied by A. Martell.

TABLE I  
FORMS OF PORPHYRIN CRYSTALS

Compound	Form	Dimensions, Å.			Oblique angles, deg.			Density		Z <sup>a</sup>	Space group	Reference
		a	b	c	α	β	γ	Obsd.	Calcd.			
Porphine	Monoclinic	12.35	12.35	10.30						4	P2 <sub>1</sub> /a	8
TPP	Triclinic									1	P $\bar{1}$	<sup>d</sup>
TPP	Orthorhombic	12.0	19.2	14.7				1.26		4		9
TPP	Tetragonal	15.12	15.12	13.94						4	$I\bar{4}2d$	5
CuTPP	Tetragonal	15.04 <sup>c</sup>	15.04	13.993				1.40	1.43	4	$I\bar{4}2d$	<sup>b</sup>
PdTPP	Tetragonal	15.088	15.088	13.987				1.48	1.51	4	$I\bar{4}2d$	<sup>b</sup>
NiTPP	Tetragonal	15.04	15.04	13.92						4	$I\bar{4}2d$	<sup>b</sup>
ZnTPP	Triclinic	6.03	9.89	13.0	101	108	93	1.29		1	P1	9 <sup>b</sup>
ZnTPP	Orthorhombic	14.8	17.2	14.6				1.29		4	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<sup>b</sup>
ZnTPP·(H <sub>2</sub> O) <sub>2</sub>	Tetragonal	13.440	13.440	9.715				1.30	1.35	2	I4/m	<sup>b</sup>
FeTPPOH·H <sub>2</sub> O	Tetragonal	13.534	13.534	9.820				1.31	1.31	2	I4	<sup>b</sup>
Etio I	Monoclinic	10.3	19.5	6.75		98			1.17	2	P2 <sub>1</sub> /c	9, 10
Ni Etio I	Tetragonal	14.61	14.61	12.38				1.35	1.35	4	I4 <sub>1</sub> /amd	<sup>b</sup>
Ni Etio II	Tetragonal	14.68	14.68	12.51				1.5	1.37	4	I4 <sub>1</sub> /amd	7

<sup>a</sup> Molecules per unit cell. <sup>b</sup> This work. <sup>c</sup> Estimated uncertainties in Å. for a and c, respectively, are: CuTPP, 0.02 and 0.004; PdTPP, 0.002 and 0.001; FeTPPOH·H<sub>2</sub>O, 0.006 and 0.006; ZnTPP·(H<sub>2</sub>O)<sub>2</sub>, 0.006 and 0.01. <sup>d</sup> A. Tulinsky, private communication.

The present work was undertaken to determine if all tetraphenylporphines are nonplanar. This was accomplished by varying the metal atom in order to study the influence of changing the coordination number of the metal. The effects of changes in crystal packing were also studied. Tetraphenylporphine will be denoted by TPP, palladium tetraphenylporphine by PdTPP, etc.

Deep purple CuTPP and PdTPP crystals were grown from benzene, dark red ZnTPP·(H<sub>2</sub>O)<sub>2</sub> crystals from an acetone-ethanol solution, and dark red FeTPPOH·H<sub>2</sub>O crystals from a chloroform-ethanol solution.<sup>12</sup> All of the crystals were well formed tetragonal bipyramids. The edges of the pyramid base varied from 0.1 to 0.3 mm. in length.

A triclinic form of ZnTPP, listed in Table I, was grown from benzene. This crystal form decomposes slowly. Precession photographs taken a few days after preparation of the crystals showed evidence of decomposition.

(1) This research was supported by a Public Health Service Grant and the Louis Block Fund.

(2) NASA Predoctoral Fellow.

(3) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); 36 (1940).

(4) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963).

(5) J. I. Hoard, M. J. Hamor, and T. A. Hamor, *ibid.*, **85**, 2334 (1963).

(6) E. B. Fleischer, *ibid.*, **85**, 1353 (1963).

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

(8) C. Rimington, S. F. Mason, and O. Kennard, *Spectrochim. Acta*, **12**, 65 (1958).

(9) J. M. Goldstein, Ph.D. Dissertation, University of Pennsylvania, 1959.

(10) C. L. Christ and D. Harker, *Amer. Mineralogist*, **27**, 219 (1942).

(11) D. Thomas and A. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959), and references given therein.

(12) We gratefully acknowledge the help of Mrs. S. Choi, who skillfully grew the ZnTPP·(H<sub>2</sub>O)<sub>2</sub> and FeTPPOH·H<sub>2</sub>O crystals.

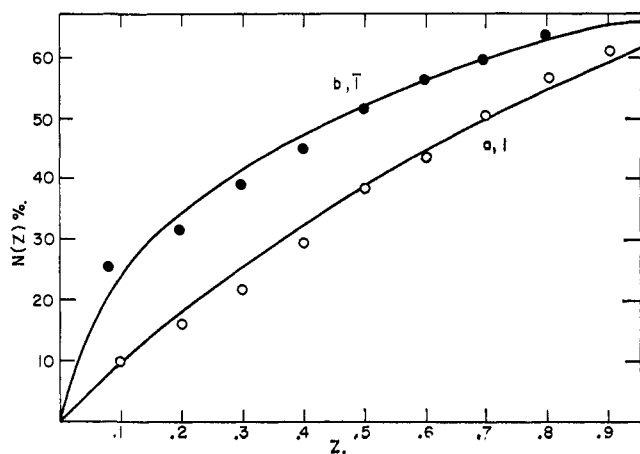


Fig. 1.—Statistical test for center of symmetry. Solid curve a is the theoretical curve for noncentric structures; solid curve b is the theoretical curve for centric structures. Open circles are data for copper tetraphenylporphine, solid circles for zinc tetraphenylporphine dihydrate.

The lattice constants, density, and number of molecules per unit cell for each compound are given in Table I. The densities were determined by the flotation method. The CuTPP lattice constants were measured on the G. E. XRD-5 Eulerian cradle. The powder method, with calibration by spinel ( $a = 8.0833 \text{ \AA}$ ),<sup>13</sup> was employed to determine the PdTPP lattice constants. The ZnTPP·(H<sub>2</sub>O)<sub>2</sub> and FeTPPOH·H<sub>2</sub>O lattice constants were obtained from Weissenberg *h0l* films and precession films calibrated with spinel powder.

**Determination of Structures.<sup>14</sup> CUTPP and PdTPP.**—Precession photographs showed that the Laue class is  $4/mmm$  and that the CuTPP and PdTPP have the same space group. The systematic extinctions are  $hkl: h + k + l = 2n$  and  $hhl: 2h + l = 4n$ . This allows two possible space groups,  $I4_1md$  and  $I4_2d$ . The  $I4_1md$  space group was tried first, but complete lack of agreement between the calculated and observed structure factors showed this choice to be incorrect. The final choice of the  $I4_2d$  space group was confirmed by the successful determination of the structure.

A scintillation counter was employed to collect all intensity data. An Eulerian cradle and Cu K $\alpha$  radiation were used to collect 465 CuTPP reflections, all nonzero. The intensities were obtained by the stationary crystal-stationary counter method, using balanced filters. A total of 475 nonzero PdTPP reflections were collected by the Weissenberg equi-inclination technique. Two sets of PdTPP data were collected, one with Mo K $\alpha$  radiation, the other with Cu K $\alpha$  radiation and a different crystal. The intensities were obtained by integrating the recorder scan of each peak with a planimeter.

Each independent intensity for both CuTPP and PdTPP is the average of two equivalent reflections.<sup>15</sup> Lorentz and polarization factor corrections were applied. The proportionality factor between each set of calculated and observed structure factor amplitudes was allowed to vary in the least-squares refinement calculations. These proportionality factors were used to put the two sets of PdTPP data on the same scale before averaging them. Absorption corrections were small enough to neglect. The scattering factors were obtained from Table 3.3.1A in the "International Tables for X-Ray Crystallography," Vol. III.

The space group fixes the metal atom at  $x = 0, y = 0, z = 0$  on a fourfold inversion axis. The metal atoms were used to calculate a first approximation to the phases of the structure factors in order

(13) J. V. Smith, private communication.

(14) The following computer programs were used for the calculations: A. Zalkin, "Fordap-3"; W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program" and "A Crystallographic Function and Error Program for the IBM 704" (Fortran revision). The intensity correction program was written by C. Knowles.

(15) Tables of calculated and observed structure factors of CuTPP, PdTPP, ZnTPP·(H<sub>2</sub>O)<sub>2</sub>, and FeTPPOH·H<sub>2</sub>O have been deposited as Document 7869 with the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting in advance \$6.25 for photoprints or \$2.50 for 35 mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.

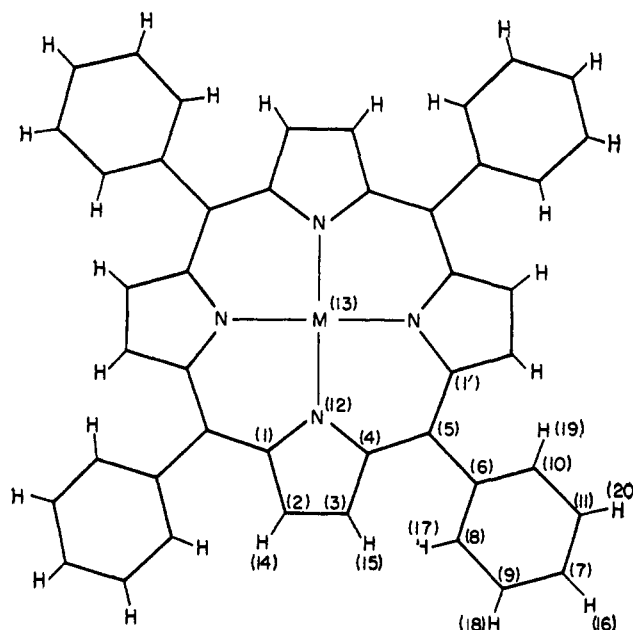


Fig. 2.—Atomic numbering system used for tetraphenylporphyrins. In the zinc and iron tetraphenylporphyrins, the oxygen below the metal atom is number 21; the oxygen above the metal atom is number 22.

to locate the other atoms. The final cycles of the least-squares refinement include anisotropic temperature factors and the hydrogen atoms. The observed CuTPP structure factors were weighted equally. For PdTPP, unit weights were used first. In the final stages of refinement, the observed structure factors were weighted according to the system of Hughes<sup>16</sup> ( $w = 1/|F|^2$  for  $|F|$  greater than  $4|F|_{\min}$  and  $w = 1/16|F|^2_{\min}$  for  $|F| \leq 4|F|_{\min}$ , where  $w$  is the weight). Comparison of data from the two PdTPP crystals indicated that the standard deviation of  $|F_{hkl}|$  was roughly proportional to  $|F_{hkl}|$ , making the Hughes weighting scheme reasonable. The differences between atomic coordinates found using different weighting schemes were small compared to the errors of the coordinates.

The final, conventional  $R$ -factor for CuTPP was 0.061, including all reflections. The PdTPP  $R$ -factor, not including unobserved reflections, was 0.051. Including all reflections, it was 0.161.

**ZnTPP·(H<sub>2</sub>O)<sub>2</sub>.**—The Laue group is  $4/m$  and the limiting condition on reflections is  $h + k + l = 2n$ . Space groups consistent with this are  $I4$  and  $I\bar{4}$ , which are noncentric, and  $I4/m$ , which is centric. The space group  $I4/m$  was chosen, since the structure could be successfully determined and refined using it. Furthermore, the usual statistical test for centric crystal structures<sup>17</sup> indicates that the space group is centric, as shown in Fig. 1.

Data were collected and the structure was determined in the way described above for PdTPP. The space group fixes the zinc atom at  $0,0,0$ . Mo K $\alpha$  radiation was used, and the absorption correction was small enough to neglect. The refinement included 569 nonzero structure factors and the Hughes weighting scheme<sup>16</sup> was used. The hydrogens and anisotropic temperature factors were included in the final stages of the refinement. The final  $R$  factor was 0.080 omitting unobserved reflections and 0.131 including unobserved reflections.

**FeTPPOH·H<sub>2</sub>O.**—This crystal has the same Laue group and systematic extinctions as ZnTPP·(H<sub>2</sub>O)<sub>2</sub>. As the results below indicate, the structure refined successfully with the space group  $I4$ . The molecular symmetry of this porphyrin will not fit into the space groups  $I\bar{4}$  or  $I4/m$ , allowing us to reject these space groups.

The structure factors were calculated from 399 independent nonzero reflections collected with Mo K $\alpha$  radiation as described above for PdTPP. The space group fixes the iron atom, the hydroxide oxygen, and the water oxygen at  $0,0,z$  on a fourfold axis. The  $z$  coordinate for the iron atom was set equal to zero and the positions of the other atoms were then found by using the iron

(16) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(17) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

TABLE II  
 FRACTIONAL COORDINATES AND TEMPERATURE FACTORS

A. COPPER TETRAPHENYLPORPHINE										C. ZINC TETRAPHENYLPORPHINE DIHYDRATE									
Atom	$x^a$	$y^a$	$z^b$	$B_{11}^c$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	Atom	$x^a$	$y^a$	$z^b$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cu(13)	0.0000	0.0000	0.0000	26	26	34	0	0	0	Zn(13)	0.0000	0.0000	0.0000	32	32	191	0	0	0
N(12)	.1140	.0659	-.0032	14	14	32	-1	5	-8	N(12)	.1477	-.0356	.0000	35	44	88	4	0	0
C(1)	.1971	.0316	.0186	17	29	31	-4	-5	-4	C(1)	.1881	-.1292	.0000	37	40	130	-5	0	0
C(2)	.2602	.1032	.0166	27	27	53	0	-11	-3	C(2)	.2936	-.1239	.0000	43	43	131	-3	0	0
C(3)	.2174	.1782	-.0064	32	25	50	7	-1	6	C(3)	.3187	-.0250	.0000	42	36	165	-2	0	0
C(4)	.1232	.1565	-.0169	19	28	36	-12	0	-6	C(4)	.2273	.0292	.0000	33	45	99	3	0	0
C(5)	.0573	.2171	-.0299	15	16	31	-3	1	6	C(5)	.2185	.1340	.0000	39	35	157	-3	0	0
C(6)	.0801	.3108	-.0543	26	14	27	1	1	7	C(6)	.3143	.1911	.0000	34	36	102	-5	0	0
C(7)	.1322	.4828	-.1011	56	25	73	-20	-7	18	C(7)	.4921	.2986	.0000	35	55	251	-6	0	0
C(8)	.1025	.3324	-.1471	61	12	50	-1	0	-6	C(10)	.3586	.2170	.1206	63	96	156	-30	-25	-15
C(9)	.1276	.4186	-.1722	52	38	52	-12	8	12	C(11)	.4508	.2685	.1188	52	98	244	-28	-14	-27
C(10)	.0872	.3761	.0166	64	23	42	-6	-5	-4	H(14)	.350	-.200	.000						
C(11)	.1106	.4637	-.0101	65	25	46	-1	3	2	H(15)	.390	-.020	.000						
H(14)	.333	.096	.051	<i>d</i>						H(16)	.570	.350	.000						
H(15)	.234	.237	.023							H(19)	.400	.240	.220						
H(16)	.144	.525	-.110							H(20)	.500	.290	.220						
H(17)	.127	.290	-.179							O(22)	.000	.000	.2519	284	284	301	0	0	0
H(18)	.159	.446	-.244																
H(19)	.046	.350	.087																
H(20)	.100	.531	.045																

<sup>a</sup> Estimated standard deviations for atoms 1 through 13 ranged from 0.00044 to 0.00101 and averaged 0.00071. The standard deviations were calculated by computer programs listed in ref. 14.

<sup>b</sup> Standard deviations ranged from 0.00068 to 0.00109 and averaged 0.00083. <sup>c</sup> The anisotropic temperature factors are defined by the expression,  $M = h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23}$ , where  $e^{-M}$  is the factor by which thermal vibration reduces the atomic scattering factor for the Bragg reflection,  $hkl$ . The values given are the experimental values multiplied by  $10^4$ . The range of the standard deviations for anisotropic temperature factors of these compounds is  $0.5 \times 10^{-4}$  to  $15 \times 10^{-4}$  with the majority between 0.0005 and 0.0010. <sup>d</sup> The isotropic temperature factor for the hydrogen atoms of all compounds was taken as 3.0.

B. PALLADIUM TETRAPHENYLPORPHINE									
Atom	$x^a$	$y^a$	$z^b$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Pd(13)	0.0000	0.0000	0.0000	27	27	58	0	0	0
N(12)	.1151	.0670	-.0022	35	35	55	3	-14	0
C(1)	.1974	.0328	.0159	25	34	92	7	-3	16
C(2)	.2613	.1037	.0161	22	39	87	-14	-7	-3
C(3)	.2179	.1794	-.0037	30	40	93	-11	-21	20
C(4)	.1266	.1565	-.0172	42	38	70	-5	5	1
C(5)	.0562	.2176	-.0273	36	22	48	8	-4	-2
C(6)	.0819	.3107	-.0535	39	23	70	-11	-1	8
C(7)	.1323	.4830	-.1030	45	55	102	-34	-8	23
C(8)	.1026	.3323	-.1464	48	23	70	6	9	-3
C(9)	.1261	.4189	-.1696	64	44	74	-14	6	6
C(10)	.0864	.3780	.0128	60	46	68	-11	5	3
C(11)	.1101	.4613	-.0073	70	25	92	0	-3	-3
H(14)	.327	.089	.048						
H(15)	.235	.238	.043						
H(16)	.166	.533	-.129						
H(17)	.116	.282	-.176						
H(18)	.155	.446	-.238						
H(19)	.074	.352	.089						
H(20)	.103	.532	.039						

<sup>a</sup> Standard deviations ranged from 0.00059 to 0.00195 with an average of 0.00081. <sup>b</sup> Standard deviations ranged from 0.00090 to 0.00160 with an average of 0.00117.

atom to determine the phases of the structure factors. The three-dimensional  $F_o-F_c$  synthesis indicates large anisotropic temperature factors, especially for the iron atom. Anisotropic refinement was attempted but was unsuccessful probably because the anisotropic vibration is so great and the atoms do not vibrate independently. Since it was not possible to locate the disordered hydrogens on the oxygens, the hydroxide was not differentiated from the water. The data were weighted according to the weighting system of Hughes,<sup>16</sup> and hydrogens were not included in the refinement. Final  $R$ -factors were 0.17 for nonzero reflections and 0.29 including the unobserved reflections.

### Discussion of Results

The atomic numbering system is given in Fig. 2. The final fractional coordinates and temperature factors are shown in Table II. As expected, the anisotropic temperature factors become larger as distance from the

### D. FERRIC HYDROXIDE TETRAPHENYLPORPHINE MONOHYDRATE

Atom	$x^a$	$y^a$	$z^b$	$B^c$
Fe(13)	0.000	0.000	0.000	3.9
N(12)	.1444	.0376	-.0211	3.3
C(1)	.2244	-.0227	-.0242	3.4
C(2)	.3119	.0306	-.0323	4.2
C(3)	.2889	.1277	-.0337	4.4
C(4)	.1825	.1322	-.0294	4.0
C(5)	.1291	.2193	-.0210	3.6
C(6)	.1834	.3154	-.0254	3.9
C(7)	.2904	.4896	-.0216	4.5
C(8)	.2116	.3593	-.1531	5.2
C(9)	.2644	.4505	-.1505	5.6
C(10)	.2085	.3588	-.0938	5.5
C(11)	.2618	.4454	.0890	5.2
O(21)	.0000	.0000	-.3005	4.4
O(22)	.0000	.0000	.2219	4.0

<sup>a</sup> Standard deviations of the atoms in the porphine ring (atoms 1-5, 12, and 13) ranged from 0.0013 to 0.0017 with an average of 0.0016. Standard deviations of the atoms in the phenyl rings (atoms 6-11) ranged from 0.0016 to 0.0044 with an average of 0.0026. <sup>b</sup> Standard deviations of atoms 1-5, 12, and 13 ranged from 0.0039 to 0.0044 with an average of 0.0042. Standard deviations of atoms 6-11 ranged from 0.0035 to 0.0049 with an average of 0.0042. <sup>c</sup>  $B$  is the individual isotropic temperature factor.

metal atom increases. The high degree of anisotropy supports the hypothesis of high deformability normal to the mean plane of the porphyrin ring, as pointed out by Hoard.<sup>5</sup> The attempted anisotropic refinements of the  $\text{FeTPPOH} \cdot \text{H}_2\text{O}$  structure indicated that the iron atom is held more loosely than the metal atoms in the other porphyrins.  $\beta_{11}$  for the iron is about 0.003, whereas  $\beta_{33}$  is about 0.048, which is much larger than any temperature factors found for other porphyrin metal atoms. The Fourier electron density maps indicate that the iron atom is definitely held on one side of the ring even though  $\beta_{33}$  is large.

The bond lengths and bond angles for CuTPP, PdTPP, ZnTPP  $\cdot$   $(\text{H}_2\text{O})_2$ , FeTPPOH  $\cdot$   $\text{H}_2\text{O}$ , and nickel etioporphyrin I are shown in Tables III and IV.

TABLE III  
INTRAMOLECULAR BOND LENGTHS IN Å.

Bond	Ni Etio I		CuTPP		PdTPP		ZnTPP·(H <sub>2</sub> O) <sub>2</sub>		FeOHTPP·(H <sub>2</sub> O)		Av. of all bond lengths
	Length	$\sigma^a$	Length	$\sigma$	Length	$\sigma$	Length	$\sigma$	Length	$\sigma$	
M-N	1.957	0.013	1.981	0.007	2.009	0.009	2.042	0.007	2.030	0.019	1.997
N-C <sub>1</sub>	1.396	.013	1.383	.012	1.369	.013	1.369	.010	1.356	.03	1.379
N-C <sub>4</sub>	1.396	.013	1.386	.012	1.377	.014	1.379	.011	1.383	.029	1.384
C <sub>1</sub> -C <sub>2</sub>	1.427	.016	1.461	.013	1.440	.014	1.421	.012	1.409	.03	1.437
C <sub>2</sub> -C <sub>3</sub>	1.335	.023	1.337	.014	1.346	.016	1.374	.012	1.352	.032	1.348
C <sub>3</sub> -C <sub>4</sub>	1.427	.016	1.436	.014	1.432	.016	1.429	.011	1.442	.031	1.431
C <sub>4</sub> -C <sub>5</sub>	1.398	.013	1.380	.013	1.413	.016	1.414	.012	1.386	.033	1.401
C <sub>5</sub> -C <sub>1</sub> '	1.398	.013	1.358	.013	1.386	.02	1.403	.012	1.442	.032	1.386
C <sub>5</sub> -C <sub>6</sub>			1.486	.014	1.502	.015	1.497	.011	1.494	.033	1.495
C <sub>6</sub> -C <sub>8</sub>			1.392	.015	1.376	.020	1.359	.012	1.439	.055	
C <sub>6</sub> -C <sub>10</sub>			1.393	.016	1.377	.019	1.360	.012	1.352	.053	
C <sub>6</sub> -C <sub>9</sub>			1.415	.015	1.391	.018	1.419	.010	1.426	.057	
C <sub>7</sub> -C <sub>9</sub>			1.346	.019	1.345	.021	1.344	.014	1.415	.063	
C <sub>7</sub> -C <sub>11</sub>			1.387	.020	1.419	.026	1.344	.014	1.299	.058	
C <sub>10</sub> -C <sub>11</sub>			1.395	.015	1.336	.019	1.419	.010	1.376	.061	
C <sub>2</sub> -H <sub>14</sub>			1.00	<sup>b</sup>	1.11	<sup>b</sup>	1.27	<sup>b</sup>			
C <sub>3</sub> -H <sub>15</sub>			1.19		1.13		0.96				
C <sub>7</sub> -H <sub>16</sub>			0.68		0.99		1.25				
C <sub>8</sub> -H <sub>17</sub>			1.22		0.87		1.15				
C <sub>9</sub> -H <sub>18</sub>			1.28		1.13		1.21				
C <sub>10</sub> -H <sub>19</sub>			0.86		1.15		1.15				
C <sub>11</sub> -H <sub>20</sub>			1.19		1.26		1.21				
M-O <sub>21</sub>							2.447	0.030	2.950	0.050	
M-O <sub>22</sub>							2.447	0.030	2.179	0.048	

<sup>a</sup> Standard deviations as calculated by computer programs listed in ref. 14. <sup>b</sup> Average standard deviation for C-H bonds is about 0.12 Å.

TABLE IV  
BOND ANGLES IN DEGREES

Angle <sup>a</sup>	CuTPP		PdTPP		ZnTPP·(H <sub>2</sub> O) <sub>2</sub>		FeTPPOH·H <sub>2</sub> O	
	Angle	$\sigma^b$	Angle	$\sigma$	Angle	$\sigma$	Angle	$\sigma$
1,12,13	125.7	0.6	126.3	0.8	126.9	0.6	128.4	1.6
4,12,13	126.0	.6	127.2	0.7	127.2	.6	126.7	1.5
1,12,4	107.8	.7	106.4	1.0	105.9	.7	104.9	1.8
2,1,12	107.6	.8	109.1	1.0	110.5	.7	111.7	1.9
5,1,12	127.3	.8	125.8	1.0	125.5	.7	124.2	2.1
2,1,5	124.8	.8	124.9	1.2	124.0	.8	124.1	2.2
1,2,3	107.5	.9	107.7	1.0	107.1	.7	108.0	2.1
2,3,4	108.6	.9	106.9	1.0	106.4	.7	105.7	2.0
3,4,12	108.1	.8	109.8	1.0	110.2	.7	109.6	2.0
5,4,12	127.3	.8	124.0	1.1	124.4	.7	126.1	2.1
3,4,5	124.8	.8	125.3	1.1	124.4	.7	123.9	2.1
1,5,4	123.1	.8	125.0	1.1	125.9	.8	124.1	2.1
1,5,6	119.8	.8	118.9	1.1	118.1	.7	116.7	2.0
4,5,6	117.0	.9	116.1	1.1	116.0	.7	118.8	2.0
5,6,8	122.0	.9	120.7	1.2	120.5	.5	121.0	3.6
5,6,10	119.1	1.0	122.6	1.3	120.5	.5	118.4	3.5
8,6,10	119.0	1.0	116.7	1.1	119.0	.5	120.5	2.2
9,7,11	121.2	1.2	118.1	1.2	119.0	.5	120.1	2.1
6,8,9	119.4	1.1	120.1	1.3	119.8	1.1	118.3	3.8
7,9,8	120.5	1.2	122.1	1.5	121.2	1.2	117.7	3.7
6,10,11	121.3	1.0	124.5	1.7	119.8	1.1	118.1	3.4
7,11,10	118.6	1.2	118.6	1.7	121.2	1.2	125.2	3.6

<sup>a</sup> Middle number is vertex of angle. <sup>b</sup> Estimated standard deviations calculated by computer programs listed in ref. 14.

A given bond distance, including the M-N distance, does not change significantly as the compound is changed, even though the substituents are different. Since C<sub>5</sub>-C<sub>6</sub> is nearly a single bond, conjugation of the benzene rings and the porphine nucleus must be small. These facts demonstrate the small effect of substituents on the bond distances of the porphine nucleus in these compounds.

The rather large number of porphyrins found to have nearly the same bond lengths allows one to obtain a reliable estimate of bond orders. Bond orders calcu-

lated from bond distances averaged over the Ni, Cu, Pd, and Zn porphyrins are given in Table V. The table shows that bond orders of porphyrins calculated by theoretical methods<sup>18,19</sup> vary widely in their agreement with the bond orders calculated<sup>20</sup> from our experimental bond lengths.

TABLE V  
AVERAGE BOND DISTANCES WITH THEORETICAL AND EXPERIMENTAL BOND ORDERS

Bond	Av. distance, Å <sup>a</sup>	Exptl. bond order <sup>b</sup>	Double bond character <sup>c</sup>	CAO-MO	
				Hückel model <sup>d</sup>	Four orbital model <sup>e</sup>
N-C <sub>1</sub>	1.38	0.3	0.25	0.58	0.22
C <sub>1</sub> -C <sub>2</sub>	1.44	.23	.25	.47	.61
C <sub>2</sub> -C <sub>3</sub>	1.35	.90	.75	.78	.62
C <sub>4</sub> -C <sub>5</sub>	1.40	.49	.50	.58	.62

<sup>a</sup> Average includes the experimental bond distances of nickel etioporphyrin I, copper tetraphenylporphine, palladium tetraphenylporphine, and zinc tetraphenylporphine dihydrate. <sup>b</sup> Calculated by a Pauling-type formula used by Cruickshank in ref. 20 and based on ethylene, benzene, and graphite bond distances and bond orders. An approximate correction for the smaller size of the nitrogen was made. <sup>c</sup> Pauling method; bond order given by proportion of the Kekulé structures in which a particular bond is double. <sup>d</sup> Application of simple Hückel model to porphine by Longuet-Higgins, Rector, and Platt in ref. 18. <sup>e</sup> Calculated by Gouterman and Wagnière in ref. 19.

The nonplanarity of CuTPP<sup>6</sup> and the isostructural tetragonal form of TPP<sup>5</sup> are described elsewhere. The TPP is as nonplanar as CuTPP, even though TPP has no metal atom. PdTPP has the same structure within experimental error. The benzene and pyrrole rings are flat within experimental accuracy. The angle between the plane of atoms 6, 8, and 10 of the benzene ring and the horizontal 001 plane is  $80.0 \pm 0.6^\circ$

(18) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(19) M. Gouterman and G. Wagnière, *J. Mol. Spectry.*, **11**, 108 (1963).

(20) D. W. J. Cruickshank, *Tetrahedron*, **17**, 155 (1962).

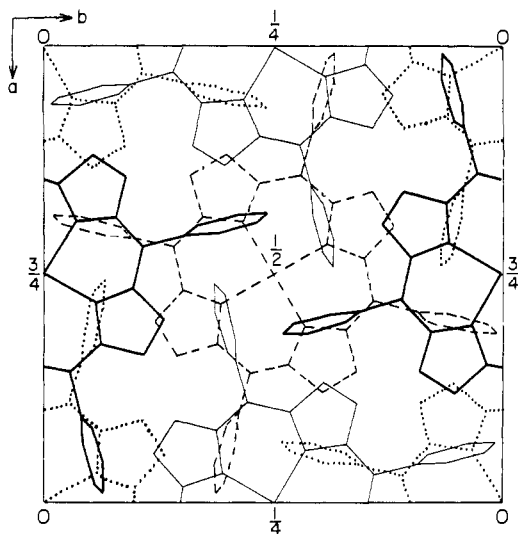


Fig. 3.—Projection of one unit of CuTPP on 001. Fractional  $z$ -coordinates of the metal atoms are shown. The CuTPP molecule at the center of the cell (dashed line) is bent toward negative  $z$  in the first and third quadrants, and toward positive  $z$  in the second and fourth quadrants. This correlates with the fact that a benzene ring from a neighboring molecule is directly above the first and third quadrants and directly below the second and fourth quadrants.

in both CuTPP and PdTPP. A model shows that this bending is caused by the interaction of benzene hydrogen, H(17), with pyrrole hydrogen, H(15), and the interaction of benzene hydrogen, H(19), with the pyrrole hydrogen equivalent to H(14). The plane of atoms 12, 1, and 4 of the pyrrole ring makes an angle of  $13.4 \pm 0.4^\circ$  with the 001 plane in CuTPP. The corresponding angle in PdTPP is  $12.3 \pm 0.6^\circ$ .

Tulinsky is now determining the structure of the triclinic form of TPP, which, interestingly, is much more planar than the tetragonal form of TPP.<sup>21</sup> The two hydrogens at the molecular center are bonded to two pyrrole rings, which are not equivalent to the other two pyrrole rings.<sup>21a</sup> It should be mentioned that in the tetragonal form of TPP, the pyrroles may also be non-equivalent. The molecules may, by random distribution, attain a statistical fourfold symmetry not inherent in the individual molecule.

By way of contrast to the other metal porphyrins, the porphine nucleus of ZnTPP·(H<sub>2</sub>O)<sub>2</sub> is in a mirror plane, within experimental error. The phenyl groups are perpendicular to this mirror plane. It is interesting to note that the zinc forms an octahedral rather than a tetrahedral complex, apparently because, at least in this crystal form, tetrahedral geometry would distort the ring too much. The Zn-H<sub>2</sub>O distance of 2.45 Å. is rather long, indicating that the water molecules are not bound tightly to the zinc.

FeTPPOH·H<sub>2</sub>O is nearly planar except that the iron atom is 0.2 Å. above the plane formed by the four nitrogen atoms, even though the Fe-N distance of 2.03 Å. is not significantly longer than metal to nitrogen distances in other porphyrins. This phenomenon has been observed by Kendrew<sup>22</sup> in myoglobin. The angle be-

tween the plane of atoms 6, 8, and 10 of the benzene ring and the horizontal 001 plane is  $89 \pm 2^\circ$ .

In FeTPPOH·H<sub>2</sub>O, the iron is in a field which is very asymmetric in the direction perpendicular to the plane of the four nitrogens, since the hydroxide oxygen carries much more negative charge than the oxygen in water. This asymmetry is shown by the fact that one of the oxygens, probably in the hydroxide, is 2.18 Å. from the iron while the other oxygen is 2.95 Å. away from the iron. It is possible that the asymmetry of charge changes the orbital geometry of the  $d_2sp_3$  hybridization of the iron atom. With this change in geometry, the  $d$ -orbitals of the iron may overlap better with the nitrogen orbitals when the iron is about 0.25 Å. above the nitrogen.

The extent of nonplanarity of the porphyrins discussed above can be illustrated by the distances of the atoms from the 001 plane, which passes through the metal atom. These distances, which are listed for several porphyrins in Table VI, also demonstrate the differences in the planarity of the various molecules.

TABLE VI  
DEVIATIONS OF ATOMS FROM THE 001 PLANE<sup>a</sup>

Atom	CuTPP	PdTPP	TPP <sup>b</sup>	Ni Etio I	FeTPP- OH·H <sub>2</sub> O	ZnT- PP·(H <sub>2</sub> O) <sub>2</sub>
M	0.00	0.00	0.00	0.00	0.00	0.00
N	-.04	-.03	-.04	-.07	-.20	.00
C <sub>1</sub>	.26	.22	.21	-.11	-.23	.00
C <sub>2</sub>	.23	.23	.22	-.25	-.31	.00
C <sub>3</sub>	-.09	-.05	-.07	-.25	-.33	.00
C <sub>4</sub>	-.24	-.24	-.22	.11	-.28	.00
C <sub>5</sub>	-.42	-.38	-.38	.00	-.20	.00
C <sub>6</sub>	-.75	-.75			-.24	.00
C <sub>7</sub>	-1.42	-1.44			-.21	.00

<sup>a</sup> Deviation in Å.

The many factors which act simultaneously make explanations of the widely varying shapes of porphyrin molecules difficult. Several hypotheses can be stated and considered in the light of the experimental evidence. The hypothesis that distortion of the ring by the metal atom is the main cause of the nonplanarity is not tenable, since the results discussed above make it apparent that absence of the metal atom does not necessarily decrease planarity and presence of a metal atom does not guarantee nonplanarity.

A second hypothesis is that nonplanarity is greatly increased when the molecules are packed so closely in the crystal that the porphyrin ring of each molecule is distorted by substituents of the nearest neighboring molecules. The following arguments indicate that this hypothesis best explains the results at present.

Two competing factors are operating. First, as Kitaigorodskii<sup>23</sup> has shown, organic molecules tend to pack in crystals as closely as their geometry allows, and porphyrins are no exception. In addition, the porphine nucleus will remain planar, if possible, in order to increase overlap of  $\pi$ -orbitals. When there are substituents bent at a sharp angle to the porphine nucleus, the molecules cannot close-pack and remain planar at the same time. The structure is the best compromise between these two competing factors.

CuTPP, for example, packs quite closely at the expense of loss of planarity. Three-dimensional models

(21) A. Tulinsky, private communication.

(21a) NOTE ADDED IN PROOF.—For results of this work see A. Tulinsky, *J. Am. Chem. Soc.*, **86**, 927 (1964).

(22) J. C. Kendrew, *Science*, **139**, 1259 (1963). Kendrew mentions that D. Koenig, while he was at Johns Hopkins University, noted the same phenomenon in hemin, by structural analysis.

(23) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1955.

show that the porphine skeleton of each molecule is distorted because of close contact with phenyl groups of neighboring molecules. These phenyl groups are directly above and below the porphine skeleton, as shown in Fig. 3.

ZnTPP·(H<sub>2</sub>O)<sub>2</sub>, on the other hand, cannot pack as closely as CuTPP because of the oxygen ligands, which are 2.45 Å. above and below the metal atom. The greater amount of void volume in the zinc porphyrin unit cell is illustrated by Fig. 3 and 4 which compare the ZnTPP·(H<sub>2</sub>O)<sub>2</sub> and CuTPP crystal packing in the *x*- and *y*-directions. In the *z*-direction, the shortest Zn-Zn distance is 4.86 Å., whereas the shortest Cu-Cu distance is 3.76 Å. Since the ZnTPP·(H<sub>2</sub>O)<sub>2</sub> molecules are farther apart, interference from phenyl groups is lessened and the porphyrin skeleton can remain planar. FeTPPOH·H<sub>2</sub>O, with the oxygen ligands above and below the ring, packs in about the same way as the ZnTPP·(H<sub>2</sub>O)<sub>2</sub> and is thus almost planar.

The packing and molecular interactions of nickel etioporphyrin I<sup>4</sup> are illustrated by the 001 projection of isomorphous nickel etioporphyrin II given by Crute.<sup>7</sup> There are no oxygen ligands above and below the ring, and close contact between neighboring molecules is possible. The close packing occurs with a slight loss of planarity. The ethyl and methyl groups, which are attached to atoms 2 and 3 of the pyrrole ring, are bent out of the plane of the ring. The interactions of these groups with neighboring molecules contribute to bending of the porphine nucleus. The interaction of overlapping pyrrole rings from neighboring molecules may also contribute to the nonplanarity.

The evident conclusion is that the porphine skeleton

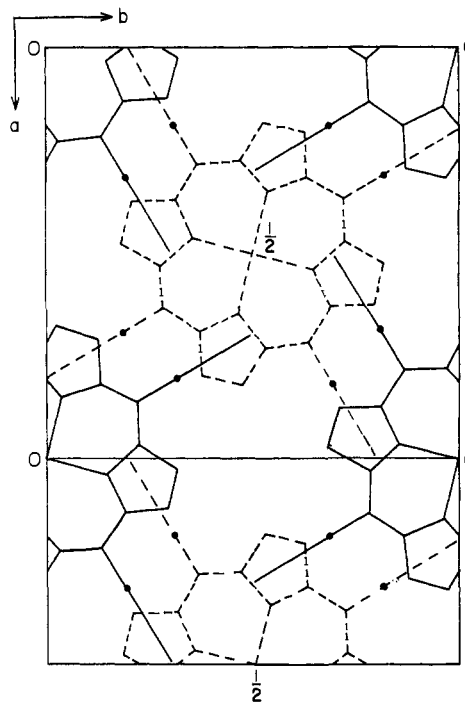


Fig. 4.—Projection of 1½ unit cells of ZnTPP·(H<sub>2</sub>O)<sub>2</sub> on 001. The scale is the same for both the CuTPP and ZnTPP·(H<sub>2</sub>O)<sub>2</sub> projections.

is quite flexible, since crystal packing forces can bend it easily. The shape of a particular porphyrin in a crystal appears to depend on the substituents and the type of packing. Porphine, since it has no substituents, would be expected to be nearly planar. The X-ray analysis of this compound is in progress.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

## Molecular Addition Compounds of Amines and Iodine. Evidence for the Existence of a 2 : 1 Triethylamine-Iodine Complex

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Calorimetric studies of the triethylamine-iodine system in *n*-heptane revealed that the measured heat of reaction of the amine and iodine to form a 1:1 complex was strongly dependent upon the amine concentration. This result is explained in terms of the existence of a second iodine(I) complex, [(Et<sub>3</sub>N)<sub>2</sub>I<sup>+</sup>][I<sup>-</sup>], which is in equilibrium with the 1:1 complex. The molar heats of reaction that accompany the formation of 1:1 complexes were measured for seven amine-iodine systems in *n*-heptane by the method of thermometric titration and found to compare favorably with those values obtained by spectroscopic techniques. The sensitivity of iodine(I) compounds to hydrolysis and disproportionation is discussed.

### Introduction

Numerous studies have been made of the interaction of the halogens and interhalogens with nitrogen-containing bases.<sup>1</sup> The large heats of reaction that accompany the formation of 1:1 complexes of alkylamines and iodine<sup>2-4</sup> and pyridine and iodine<sup>5</sup> indicate that interaction is appreciable. The trialkylamine-iodine complexes<sup>3,4</sup> are formed with the largest enthalpy loss (~12 kcal.) of all the iodine complexes for which thermodynamic constants have been measured.

Additional information germane to this study has been obtained from conductance studies and spectral investigations. The increase in conductance of pyridine with the addition of iodine,<sup>6,7</sup> and of acetonitrile with the addition of iodine or iodine monochloride,<sup>8,9</sup> leaves no doubt that ionic species are present. The nature of the ionic species as yet has not been established with certainty. Spectral evidence indicates that in solutions of iodine or iodine monochloride which contain a Lewis base, there exists one or more type of iodine(I) cation. Popov and co-workers<sup>10,11</sup> have made

(1) See I. J. Andrews and R. M. Keefer, *Advan. Inorg. Chem. Radiochem.*, **3**, 91 (1961).  
 (2) H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960).  
 (3) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).  
 (4) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).  
 (5) C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954).

(6) L. F. Audrieth and E. J. Birr, *ibid.*, **55**, 668 (1933).  
 (7) G. Kortum and H. Wilski, *Z. physik. Chem. (Leipzig)*, **202**, 35 (1953).  
 (8) A. I. Popov and W. A. Deskin, *J. Am. Chem. Soc.*, **80**, 2976 (1958).  
 (9) A. I. Popov and N. E. Skelly, *ibid.*, **77**, 3722 (1955).  
 (10) A. I. Popov and R. T. Pflaum, *ibid.*, **79**, 570 (1957).  
 (11) A. I. Popov and R. H. Rygg, *ibid.*, **79**, 4622 (1957).