

able and/or high ionic strength. Though there may be many criticisms which may be expressed concerning these equations, the empirical value is clear from the results illustrated in the data presented. These results seem to justify the arguments set forth in the derivation. Other systems such as mixed uni-uni- and di-univalent ( $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ , etc.) inert electro-

lytes as well as noncharged reducible species have been investigated and are to be presented in subsequent communications.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

## The Structure of Crystalline Tetraphenylporphine. The Stereochemical Nature of the Porphine Skeleton<sup>1,2</sup>

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Analysis of all three-dimensional X-ray diffraction data photographically recordable with Cu  $K\alpha$  radiation from tetragonal single crystals of tetraphenylporphine provides a definitive description of the atomic arrangement. The space group is  $I4_2d$ , the required molecular symmetry is  $S_4$ , and "half-atom" peaks for hydrogen attached to nitrogen are clearly resolved by Fourier difference synthesis; the implication that stacking disorder does not seriously affect accuracy is supported also by other evidence, e.g., the high yield of observable reflections, ca. 91% of theoretical. Bond lengths obtained for the porphine skeleton are thought to be the most accurate values thus far reported. Simple theory suggests that at sufficiently low temperature the equilibrium configuration of the unconstrained porphine skeleton is somewhat ruffled, but the energy barrier to reflection of configuration through the mean plane is so low that at ordinary temperatures the skeleton is quasi-planar and easily deformable. Thus a mutual accommodation of the observed ruffling of the porphine skeleton (Fig. 1) in crystalline tetraphenylporphine with the observed parallel stacking of quasi-planar molecules in the crystalline phthalocyanines is achieved.

### Introduction

As a prelude to attack upon the structural problems encountered in the naturally occurring porphyrins, one attempts first to determine the stereochemical characteristics of the central porphine skeleton. X-Ray diffraction analysis of crystalline structure, with utilization of three-dimensional intensity data from good single crystals, can provide the needed fundamental information for subsequent theoretical digestion. The classic determinations of structure for the crystalline phthalocyanines,<sup>3</sup> achieved by X-ray zonal analysis, display essentially flat molecules tightly packed in parallel arrays; they provide bond parameters which, although lacking the authority of data now obtainable, are generally reasonable. Very recent determinations of crystalline structure for nickel etioporphyrin-I,<sup>4</sup> copper tetraphenylporphine,<sup>5</sup> and tetraphenylporphine<sup>6</sup> itself assign markedly ruffled configurations to the porphine skeletons of the respective molecular species. The *a priori* grounds for anticipating easy deformation of the porphine skeleton normal to its mean plane—leading, indeed, to the conclusion that a somewhat ruffled or bent configuration should be stable for a free porphyrin molecule at sufficiently low temperatures—were outlined in the most recent communication<sup>6</sup>; this matter, together with the supporting experimental evidence, are to be further developed herein.

The bond parameters obtained from our three-dimensional analysis of *tetragonal* crystals of tetraphenylporphine afford, we believe, the most accurate stereochemical description of a porphyrin molecule thus far published. A virtually concurrent determination of structure for *triclinic* crystals of tetraphenylporphine carried out at Yale University has come recently to our attention.<sup>7</sup> The two studies are in gratifyingly good agreement on all major points, although there are inevitably some differences (*vide infra*) at the center of the molecule; *i.e.*, in the disposition of the nitrogen atoms and the hydrogen atoms attached thereto. With some help also from the copper tetraphenylporphine study, it becomes feasible to appraise the importance of  $\pi$ -bonding in the porphine skeleton and in the molecule as a whole. A molecular orbital treatment of the bonding pattern in the porphine skeleton is simultaneously in progress.<sup>8</sup>

### Experimental

The crystals of tetraphenylporphine used for determination of structure were kindly supplied by Adler and Shergalis.<sup>2</sup> The final stages of purification and of crystal growth were effected by carefully controlled techniques of vacuum sublimation.

The unit cell of tetragonal tetraphenylporphine has  $a = 15.125 \pm 0.025$ ,  $c = 13.94 \pm 0.02$  Å, and contains four molecules; the calculated and measured densities are, respectively, 1.28 and 1.27 g./cc. The X-ray symmetry is that of the point group  $D_{4h}-4/m$ , but tests for piezoelectricity are positive. Systematic vanishings of spectra<sup>9</sup> are those demanded by the (non-centrosymmetric) space groups<sup>9</sup>  $D_{2d}^{12}-I4_2d$  and  $C_{4v}^{11}-I4_1md$ .

Three-dimensional X-ray data were recorded photographically on multiple films in a Weissenberg equi-inclination camera. The crystal specimen was a tetragonal bipyramid having diameters along  $a$  and  $c$ , respectively, of 0.35 and 0.32 mm. With a linear absorption coefficient of 7.0  $\text{cm}^{-1}$  for Cu  $K\alpha$  radiation, no

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(2) The very pure crystals of tetraphenylporphine used in our study were supplied by A. A. Adler and W. Shergalis, Department of Chemistry, University of Pennsylvania, with support from the U. S. Signal Corps (Grant DA-SIG-36-039-61-G9).

(3) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); 236 (1940).

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

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

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

(7) A. Tulinsky, private communication.

(8) H. Kobayashi and M. Gouterman, private communication.

(9) "International Tables for X-Ray Crystallography, Vol. I. Symmetry Groups," The Kynoch Press, Birmingham, England, 1952.

corrections for variation of absorption with scattering angle or specimen shape were deemed necessary. Some 981 independent  $\{hkl\}$  of a theoretical total of 1025 lying within the Cu  $K\alpha$  limiting sphere were examined, and 892 of these were recorded above background. Intensities were estimated by visual comparison with specially prepared scales. The intensities of  $(hkl)$  and  $(\bar{h}\bar{l})$  from each form  $\{hkl\}$  were estimated independently, and were found to conform satisfactorily to tetragonal symmetry. Inverse polarization and Lorentz factors appropriate<sup>10</sup> to the equi-inclination technique then were applied to the  $\{hkl\}$  intensities to give relative  $|F|^2$  data for structure determination.

**Determination of Structure.**—The space groups  $I4_1md$  and  $I\bar{4}2d$  both would require (1) the four molecules of tetraphenylporphine within a cell to be structurally equivalent, and (2) the mean plane of every molecule to be parallel to  $(001)$ .  $I4_1md$  would utilize the positions  $4(a)$ <sup>9</sup> of point group symmetry  $mm2$ , and would require either the nitrogen atoms or the methine carbon atoms along with the axial carbon atoms of the phenyl groups to lie in symmetry planes.  $I\bar{4}2d$  would utilize either of the sets of positions  $4(a)$  or  $4(b)$ <sup>9</sup> of point group symmetry  $\bar{4}$  with equal satisfaction, and would allow a general orientation of the molecule with respect to the secondary axes of the cell. Only the first possibility based upon  $I4_1md$  would permit the hydrogen atoms attached to nitrogen to occupy a unique set of positions conforming to rigorously applied space group theory.

It soon developed that neither of the specialized orientations of the molecule demanded by  $I4_1md$  were compatible with the experimental data, and that the structural arrangement was in fact based upon  $I\bar{4}2d$ . We had determined approximate positions for the carbon and nitrogen atoms of the porphine skeleton, and for the axial carbon atoms of the phenyl group, when Fleischer's communication<sup>8</sup> on copper tetraphenylporphine appeared. Taking advantage of the nearly isostructural character of the two crystals, we were enabled to pass immediately to the stage of refining structure for tetraphenylporphine.

In our description of the structure, the molecules are centered in  $4(a)$ :  $000$ ;  $0\frac{1}{2}1\frac{1}{4}$ ;  $1\frac{1}{2}1\frac{1}{2}1\frac{1}{2}$ ;  $1\frac{1}{2}0\frac{3}{4}$ , and all other atoms lie in the general positions  $16(e)$ <sup>9</sup> of  $I\bar{4}2d$ , namely

$$xyz; \bar{x}\bar{y}\bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{4} - z; x, \frac{1}{2} - y, \frac{1}{4} - z$$

$$\bar{y}\bar{x}\bar{z}; y\bar{x}\bar{z}; y, \frac{1}{2} + x, \frac{1}{4} + z; \bar{y}, \frac{1}{2} - x, \frac{1}{4} + z$$

and each of the foregoing plus  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ . The asymmetric unit of structure is one-quarter of the molecule, and, for ready comparison, the eleven structurally distinct classes of carbon atoms are numbered in accordance with the published description<sup>8</sup> of copper tetraphenylporphine.

Refinement of structural parameters was carried out for the most part by diagonal least squares procedures<sup>11</sup> using programs for the Control Data 1604 computer kindly supplied by R. A. Jacobson and F. A. Muller of Princeton University. The function minimized was  $\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$ , with  $w^{1/2} = 1$  for  $|F_o| < 4|F_{min}|$ , and  $w^{1/2} = 16|F_{min}|^2 / |F_o|^2$  for  $|F_o| > 4|F_{min}|$ . Form factors from the "International Tables"<sup>12</sup> were employed. Seventeen cycles of least squares refinement which used individual isotropic thermal parameters for carbon and nitrogen, and included calculated contributions from hydrogen atoms assigned uniformly a  $B$  of  $4.0 \text{ \AA}^2$ , reduced the value of  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  to 0.177. Following introduction of anisotropic thermal parameters for carbon and nitrogen (and an indicated increase to  $5.5 \text{ \AA}^2$  in the value of the isotropic  $B$  assigned to the calculated contributions of hydrogen atoms), 26 cycles of least squares refinement produced stable values of the parameters and reduced  $R$  to 0.111. Refinement was then completed with three cycles of difference synthesis.<sup>11</sup> No very significant changes from the least squares results were indicated, but convergence of refinement was convincingly demonstrated, and hydrogen positions were more or less satisfactorily determinable directly from Fourier difference maps as follows.

Peaks having electron densities of 0.47 and  $0.34 \text{ electron/\AA}^3$  were clearly attributable to hydrogen atoms attached at 1.00 and

(10) Cf. "International Tables for X-Ray Crystallography, Vol. II. Mathematical Tables," The Kynoch Press, Birmingham, England, 1959, p. 266.

(11) Cf. H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, London, 1953.

(12) "International Tables for X-Ray Crystallography. Vol. III. Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962.

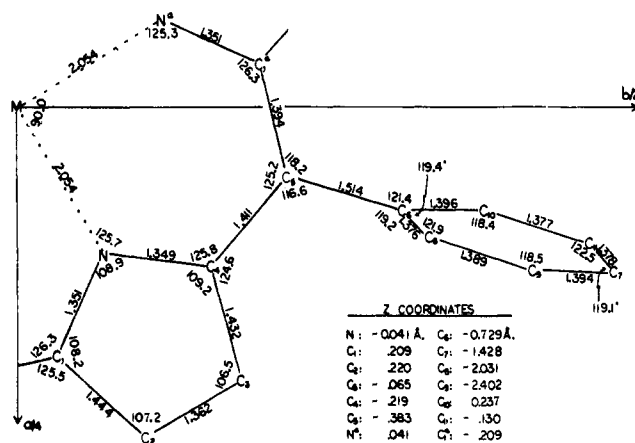


Fig. 1.—Diagram in true projection along the  $\bar{z}$  axis of a portion of the tetraphenylporphine skeleton and, with the addition of the dotted lines, of its metal derivative. Ruffling of the skeleton is to negative  $Z$  in the first and third quadrants, to positive  $Z$  in the second and fourth.

$1.03 \text{ \AA}$ , respectively, to the carbon atoms  $C_2$  and  $C_3$  of the pyrrole ring (Fig. 1). A peak of  $0.29 \text{ electron/\AA}^3$  lying  $0.95 \text{ \AA}$  from each nitrogen atom in the plane of the pyrrole ring gave an unexpectedly clear representation of the "half-hydrogen" atom (*vide infra*) attached to each nitrogen. The positions of hydrogen atoms in the phenyl group were much less satisfactorily indicated, presumably in consequence of the larger thermal motions on the periphery of the molecule. All peak densities saving that of  $H_9$  rose above  $0.33 \text{ electron/\AA}^3$ , but the  $C_9-H_9$  and  $C_{11}-H_{11}$  distances of  $1.46$  and  $1.30 \text{ \AA}$ . were much too large, while the  $C_7-H_7$  distance of  $0.93 \text{ \AA}$ . was somewhat small. In the final calculation of structure amplitudes, positions of phenyl hydrogen atoms were taken each  $1.1 \text{ \AA}$ . from the appropriate carbon atoms. The final  $R$  of 0.108 is actually quite good considering that it is based upon 91% of all reflections theoretically obtainable with Cu  $K\alpha$  radiation and, consequently, includes a large proportion of reflections too weak for accurate estimation of intensities.

### Discussion of Results

Table I lists positional coordinates for carbon and for nitrogen atoms, each with standard deviation esti-

TABLE I  
PARAMETER DATA<sup>a</sup> FOR TETRAPHENYLPORPHINE

Atom type	(Coordinate $\pm$ std. dev.) $\times 10^4$			$B, \text{ \AA}^2$
	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	
N	$1171 \pm 3$	$687 \pm 3$	$-29 \pm 3$	3.8
C <sub>1</sub>	$1977 \pm 3$	$339 \pm 3$	$150 \pm 4$	3.8
C <sub>2</sub>	$2613 \pm 3$	$1051 \pm 3$	$158 \pm 6$	4.9
C <sub>3</sub>	$2166 \pm 4$	$1809 \pm 3$	$-46 \pm 6$	4.9
C <sub>4</sub>	$1256 \pm 3$	$1567 \pm 3$	$-157 \pm 4$	4.3
C <sub>5</sub>	$555 \pm 3$	$2173 \pm 3$	$-275 \pm 4$	3.8
C <sub>6</sub>	$808 \pm 3$	$3114 \pm 3$	$-523 \pm 4$	3.9
C <sub>7</sub>	$1310 \pm 5$	$4823 \pm 3$	$-1024 \pm 7$	5.9
C <sub>8</sub>	$1020 \pm 5$	$3320 \pm 3$	$-1457 \pm 5$	5.1
C <sub>9</sub>	$1284 \pm 5$	$4164 \pm 4$	$-1723 \pm 6$	6.0
C <sub>10</sub>	$808 \pm 5$	$3780 \pm 4$	$170 \pm 5$	5.4
C <sub>11</sub>	$1088 \pm 5$	$4611 \pm 3$	$-93 \pm 6$	5.6

<sup>a</sup> Complete amplitude data have been submitted as Document No. 7801 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance \$1.25 for photoprints or \$1.25 for 35-mm. film by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

mated by doubling the figure claimed by the least squares refinement program. This procedure gives estimates of accuracy which are in line with Cruickshank's original suggestions.<sup>11</sup> It then turns out that no pair of chemically quasi-equivalent bond parameters differ by an objectively significant amount (*vide infra*).

Table I lists also isotropic thermal parameters for individual atoms as computed from the anisotropic parameters. It is seen that just three carbon atoms, all situated at branch points in the over-all ring system, have averaged thermal parameters as small as that of the nitrogen atom which is not thus constrained.

Table II describes the thermal ellipsoid of each atom by listing the thermal parameters which correspond to the principal axes and the angles made by these latter with the crystal axes. These data are best considered in conjunction with Fig. 1, which is a diagram in true projection of the asymmetric unit of structure, *i.e.*, of one-fourth of the tetraphenylporphine molecule. The

TABLE II  
TEMPERATURE FACTORS OF THE ATOMS ALONG THE PRINCIPAL AXES OF THEIR THERMAL ELLIPSOIDS

Atom	$B, \text{\AA}^2$	—Angle <sup>a</sup> between axis of ellipsoid and—		
		$a$	$b$	$c$
N	4.4	96°	88°	6°
	3.9	25	103	68
	3.1	76	25	70
C <sub>1</sub>	5.2	95	77	14
	4.4	58	144	76
	1.5	148	122	87
C <sub>2</sub>	6.7	95	86	6
	4.5	55	144	84
	2.7	36	54	89
C <sub>3</sub>	6.0	103	89	13
	4.2	60	31	82
	3.9	36	124	80
C <sub>4</sub>	5.2	96	105	16
	3.9	15	82	77
	3.3	104	18	78
C <sub>5</sub>	4.5	97	99	12
	3.4	69	25	78
	3.3	152	62	88
C <sub>6</sub>	5.1	94	90	4
	3.7	62	28	89
	2.3	28	118	86
C <sub>7</sub>	7.9	106	77	21
	5.8	18	94	73
	3.4	97	166	78
C <sub>8</sub>	7.4	37	97	54
	4.9	112	48	50
	3.0	118	137	61
C <sub>9</sub>	9.0	49	80	43
	4.9	139	75	52
	3.7	95	162	73
C <sub>10</sub>	8.2	161	71	88
	5.1	88	90	2
	3.2	71	19	86
C <sub>11</sub>	7.7	27	116	84
	6.4	98	90	8
	2.2	65	26	87

<sup>a</sup> Each ellipsoid axis is taken as positive when it makes an acute angle with (positive)  $c$ . All angles listed are between the positive directions of the ellipsoid and the crystallographic axes.

ruffling of the porphine skeleton in agreement with  $\bar{4}$  is indicated by the  $Z$ -coordinates listed in Fig. 1. Maximum deviations from the mean plane  $Z = 0$  occur at methine carbon atoms  $C_5$ , for which  $Z$  alternates between  $-0.38$  and  $+0.38 \text{ \AA}$ . for each rotation of  $90^\circ$  about  $c$ . One sees (Table II) that the thermal vibrations of nitrogen, and of all carbon atoms out to and including the first carbon,  $C_6$ , of the phenyl group, are markedly anisotropic, with the direction of largest amplitude for each atom making a small angle ( $4$ – $16^\circ$ ) with the normal ( $c$ ) to the mean plane of the molecule.

These data suggest easy deformation of the porphine skeleton normal to the mean plane. Subsequent analysis of ring strain will be seen to yield a similar conclusion.

Inasmuch as just two nitrogen atoms of each molecule carry hydrogen, the molecular symmetry,  $S_4\bar{4}$ , required in the crystal is achieved statistically by utilizing one or more stereochemical species in two or more orientations. The stereochemical species in which the hydrogen atoms are attached to a diagonally opposed pair of nitrogen atoms is especially probable; the H–H separation is then  $\geq 2.1 \text{ \AA}$ ., corresponding to mild repulsion.<sup>13</sup> Statistical distribution of this species between two orientations differing by a  $90^\circ$  rotation about  $c$  suffices to meet the space group requirements. Neither the comparatively sharp definition of "half-hydrogen" positions obtained by Fourier difference synthesis (*vide supra*) nor the pattern of apparent thermal vibrations for nitrogen (Table II) suggest any strong dependence of the experimentally derived atomic coordinates (Table I) on the statistical distribution of hydrogen atoms. No stacking disorder of major consequence is consistent with the high yield of observable reflections throughout the Cu  $K\alpha$  limiting sphere.

The C–C bond lengths (Table III) in the phenyl group average to  $1.385 \pm 0.010 \text{ \AA}$ ., as compared with the recommended value<sup>14</sup>  $1.395 \pm 0.003 \text{ \AA}$ .. The difference of  $0.010 \text{ \AA}$ ., while not objectively significant in terms of the accuracy of either datum, does reinforce an impression gained from inspection of Table II, namely, that the apparent positions of phenyl carbon atoms probably are affected by libratory motion of the phenyl group. If, however, corrections for libratory motion should amount to only  $0.010 \text{ \AA}$ . on the average for C–C distances in the phenyl group, they would seem to become quite negligible for bond distances within the porphine skeleton.

TABLE III  
BOND LENGTHS

Bond	Length, $\text{\AA}$ .	$\sigma, \text{\AA}$ .	Bond	Length, $\text{\AA}$ .	$\sigma, \text{\AA}$ .
N–C <sub>1</sub>	1.351	0.007	C <sub>5</sub> –C <sub>6</sub>	1.514	0.007
N–C <sub>4</sub>	1.349	.007	C <sub>6</sub> –C <sub>8</sub>	1.376	.008
C <sub>1</sub> –C <sub>2</sub>	1.444	.008	C <sub>8</sub> –C <sub>9</sub>	1.389	.010
C <sub>2</sub> –C <sub>3</sub>	1.362	.009	C <sub>9</sub> –C <sub>7</sub>	1.394	.011
C <sub>3</sub> –C <sub>4</sub>	1.432	.008	C <sub>7</sub> –C <sub>11</sub>	1.378	.011
C <sub>4</sub> –C <sub>5</sub>	1.411	.007	C <sub>10</sub> –C <sub>11</sub>	1.377	.010
C <sub>5</sub> –C <sub>1</sub> *	1.394	.007	C <sub>10</sub> –C <sub>8</sub>	1.396	.009

The difference between any pair of chemically quasi-equivalent bond distances within the porphine skeleton (Table III) is in no case large enough relative to the estimated standard deviation to achieve objective significance. For the pyrrole ring, we write then  $N-C_\alpha = 1.350 \pm 0.007$ ,  $C_\alpha-C_\beta = 1.438 \pm 0.008$ ,  $C_\beta-C_\beta = 1.362 \pm 0.009 \text{ \AA}$ ., and for the bonds to methine carbon ( $C_5$ ),  $C_\alpha-C_5 = 1.403 \pm 0.007$ ,  $C_5-C_5 = 1.514 \pm 0.007 \text{ \AA}$ .. The contribution of  $\pi$ -bonding to  $C_5-C_5$  must be very small (*cf.* Fig. 1 and the subsequent discussion of angular parameters), and  $1.51 \text{ \AA}$ . is a reasonable value for a pure  $\sigma$ -bond between trigonally hybridized carbon atoms.

(13) *Cf.* J. M. Robertson, "Organic Molecules and Crystals," Cornell University Press, Ithaca, N. Y., 1953, p. 226.

(14) Chemical Society Special Publication No. 11, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

Bond orders for the C-C and C-N bonds in the porphine skeleton, as read from the bond order *vs.* bond length curves given by Lofthus<sup>15</sup> are: N-C<sub>α</sub>, 1.56; C<sub>α</sub>-C<sub>β</sub>, 1.45; C<sub>α</sub>-C<sub>5</sub>, 1.63; C<sub>β</sub>-C<sub>β</sub>, 1.83. In constructing his curves, Lofthus utilized molecular orbital theory along with essentially standard<sup>14</sup> values for certain reference bond lengths; the one assumed value,<sup>15</sup> 1.274 Å. for the C=N bond of order two, agrees with our own estimate of 1.27-1.28 Å. The bond orders thus obtained are larger, of course, than those provided by the valence bond approach. From the curve given by Pauling<sup>16</sup> for the latter case, one obtains bond orders of 1.25 for C<sub>α</sub>-C<sub>β</sub>, 1.46 for C<sub>α</sub>-C<sub>5</sub>, and 1.75 for C<sub>β</sub>-C<sub>β</sub>, whereas the crude approximation obtained by counting formulations of Kekulé type only suggest bond orders of  $\frac{5}{4}$ ,  $\frac{3}{2}$ , and  $\frac{7}{4}$ , respectively. It will be interesting to see what the MO treatment<sup>8</sup> of the porphine skeleton gives for both the C-C and the C-N bond lengths.

Table IV lists bond angles (*cf.* Fig. 1) with associated standard deviations for the molecule, and Table V displays the departures from planarity of a number of key groupings of atoms. One sees that, besides the

TABLE IV  
BOND ANGLES

Angle	Value	$\sigma$	Angle	Value	$\sigma$
C <sub>1</sub> NC <sub>4</sub>	108.9°	0.4°	C <sub>1</sub> <sup>a</sup> C <sub>5</sub> C <sub>4</sub>	125.2°	0.5°
NC <sub>1</sub> C <sub>2</sub>	108.2	.4	C <sub>1</sub> <sup>a</sup> C <sub>5</sub> C <sub>6</sub>	118.2	.4
C <sub>5</sub> C <sub>1</sub> <sup>a</sup> N <sup>a</sup>	126.3	.5	C <sub>5</sub> C <sub>6</sub> C <sub>16</sub>	121.4	.5
C <sub>5</sub> C <sub>1</sub> <sup>a</sup> C <sub>2</sub> <sup>a</sup>	125.5	.5	C <sub>5</sub> C <sub>6</sub> C <sub>3</sub>	119.2	.5
C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	107.2	.5	C <sub>10</sub> C <sub>6</sub> C <sub>8</sub>	119.4	.5
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	106.5	.5	C <sub>9</sub> C <sub>7</sub> C <sub>11</sub>	119.1	.7
NC <sub>1</sub> C <sub>5</sub>	109.2	.5	C <sub>8</sub> C <sub>3</sub> C <sub>9</sub>	121.9	.6
NC <sub>1</sub> C <sub>5</sub>	125.8	.5	C <sub>8</sub> C <sub>9</sub> C <sub>7</sub>	118.5	.7
C <sub>5</sub> C <sub>1</sub> C <sub>3</sub>	124.6	.5	C <sub>11</sub> C <sub>10</sub> C <sub>6</sub>	118.4	.6
C <sub>4</sub> C <sub>5</sub> C <sub>6</sub>	116.6	.5	C <sub>7</sub> C <sub>11</sub> C <sub>10</sub>	122.5	.7

TABLE V

QUANTITATIVE DATA FOR QUASI-PLANAR GROUPINGS OF ATOMS

Grouping (see Fig. 1)	Distance (Å.) of atom from mean plane of grouping	Inclination to (001)
Pyrrole ring, NC <sub>1</sub> C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	N, -0.008; C <sub>1</sub> , 0.008; C <sub>2</sub> , -0.008 C <sub>3</sub> , 0.006; C <sub>4</sub> , -0.001	12.0°
Benzene ring, C <sub>6</sub> C <sub>7</sub> C <sub>8</sub> C <sub>9</sub> C <sub>10</sub> C <sub>11</sub>	C <sub>6</sub> , -0.014; C <sub>7</sub> , 0.001; C <sub>8</sub> , 0.006 C <sub>9</sub> , 0.001; C <sub>10</sub> , 0.017; C <sub>11</sub> , -0.010	81.7°
C <sub>5</sub> C <sub>4</sub> C <sub>1</sub> <sup>a</sup> C <sub>6</sub> (bonds to C <sub>5</sub> )	C <sub>5</sub> , -0.011; C <sub>4</sub> , 0.004; C <sub>1</sub> <sup>a</sup> , 0.004 C <sub>6</sub> , 0.004	13.8°
C <sub>1</sub> <sup>a</sup> C <sub>5</sub> N <sup>a</sup> C <sub>2</sub> <sup>a</sup> (bonds to C <sub>1</sub> <sup>a</sup> )	C <sub>1</sub> <sup>a</sup> , -0.011; C <sub>5</sub> , 0.004; N <sup>a</sup> , 0.002 C <sub>2</sub> <sup>a</sup> , 0.004	10.3°
C <sub>4</sub> C <sub>5</sub> C <sub>3</sub> N (bonds to C <sub>4</sub> )	C <sub>4</sub> , 0.032; C <sub>5</sub> , -0.015; C <sub>3</sub> , 0.003 N, -0.033	8.7°
MN <sup>a</sup> C <sub>1</sub> <sup>a</sup> C <sub>5</sub> C <sub>4</sub> N "chelate ring"	M, -0.113; N <sup>a</sup> , 0.069; C <sub>1</sub> <sup>a</sup> , -0.010 C <sub>5</sub> , -0.071; C <sub>4</sub> , 0.048; N, 0.066	7.3°
N <sup>a</sup> C <sub>1</sub> <sup>a</sup> C <sub>5</sub> C <sub>4</sub> N	N <sup>a</sup> , -0.002; C <sub>1</sub> <sup>a</sup> , 0.006; C <sub>5</sub> , -0.024 C <sub>4</sub> , 0.041; N, -0.032	11.0°

benzene and the pyrrole rings, the groupings of four atoms (or three bonds), C<sub>5</sub>C<sub>4</sub>C<sub>1</sub><sup>a</sup>C<sub>6</sub> and C<sub>1</sub><sup>a</sup>C<sub>5</sub>N<sup>a</sup>C<sub>2</sub><sup>a</sup>, show insignificant departures from planarity; this is not quite true of the similar grouping C<sub>4</sub>C<sub>5</sub>C<sub>3</sub>N. The planes of a pyrrole ring and of the grouping C<sub>5</sub>C<sub>4</sub>C<sub>1</sub><sup>a</sup>C<sub>6</sub> centered at methine carbon are inclined 12.0 and 13.8°, respectively, to (001). The similarity of these angles, however, does not imply a similarly close approach to coincidence of the respective planes. A rotation of

C<sub>5</sub>C<sub>4</sub>C<sub>1</sub><sup>a</sup>C<sub>6</sub> of 6.5° around the C<sub>5</sub>-C<sub>1</sub><sup>a</sup> bond would achieve effective coplanarity of this group with the pyrrole ring in the second quadrant (Fig. 1), but a rotation of 13.6° around the C<sub>5</sub>-C<sub>4</sub> bond would be required for coplanarity with the pyrrole ring in the first quadrant.

The dihedral angle between the planes of C<sub>5</sub>C<sub>4</sub>C<sub>1</sub><sup>a</sup>C<sub>6</sub> and the phenyl group is 81.5°; also the line of intersection of these planes passes very nearly through the atomic centers of C<sub>5</sub>, C<sub>6</sub>, and C<sub>7</sub>, and is inclined 14.2° to (001). The C<sub>5</sub>-C<sub>6</sub> distance of 1.514 ± 0.007 Å. corresponds to a pure  $\sigma$ -bond between trigonally hybridized carbon atoms. It is clear (1) that interaction between the  $\pi$ -bonding systems of the porphine skeleton and the phenyl group is feeble, and (2) that the configurational geometry meets all requirements for  $\sigma$ -bonding of the several carbon atoms in trigonal hybridization. This latter conclusion, with no significant reservation, applies to the carbon-nitrogen framework of the molecule as a whole (*vide infra*).

A particularly interesting question is whether the metalloporphine skeleton within an externally unconstrained metalloporphyrin should be planar. The metal derivative is specified in order to eliminate the asymmetric repulsions between pairs of hydrogen atoms attached to nitrogen and to allow choice of a central atom known to favor a planar array of the four nitrogen ligands.

That the porphine skeleton is a resonating system, *i.e.*, that  $\pi$ -bonding contributes materially to stabilization of the framework, is quite insufficient to assure planarity for the equilibrium configuration. The (negative) energy from  $\pi$ -bonding is a mathematical minimum for a planar configuration, and, consequently, the associated restoring force is zero for initial deformation.<sup>16a</sup>

Recalling that trigonal hybridization of carbon (and nitrogen) calls for three coplanar bonds directed 120° apart, the essential planarity displayed by each of the pertinent bond groupings (Table V) is to be re-emphasized. Considerable strain in the bond angles is unavoidable, but is in some measure dependent upon the degree of ruffling of the skeleton. One then asks whether, in a free molecule of the metallo derivative, the most favorable pattern of  $\sigma$ -bonding corresponds to a general coplanarity of the several flat subgroupings of Table V (excluding, of course, the phenyl group).

It is plausible in any case to postulate retention of a fourfold axis, either 4 or  $\bar{4}$ , to require equivalence among the four six-membered rings (Fig. 1) having the common junction M. In a planar skeleton of D<sub>4h</sub>-4/m symmetry each six-membered ring is fully characterized by the three bond lengths, M-N, N-C, and C-C, and two of the three bond angles at nitrogen, pyrrole carbon, and methine carbon. This fully extended configuration requires the sum of the five angles at carbon and nitrogen to be 630°, which is 30° in excess of that (5 × 120 = 600°) corresponding to ideal  $\sigma$ -bonding. A ruffling of the skeleton in agreement with D<sub>2d</sub>-42m, which retains the M-N bond directions as the twofold axes while allowing movement of methine carbon in the

(16a) NOTE ADDED IN PROOF.—Part of the subsequent discussion, namely that which deals with a possible energy barrier to reflection of configuration through the mean plane, derives from the mistaken premise that  $\sigma$ -bonding, by itself, can ensure the presence of such a barrier. Consequently the discussion covers a possible, but not the most probable, case.

(15) A. Lofthus, *Mol. Phys.*, **2**, 367 (1959).

(16) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 236.

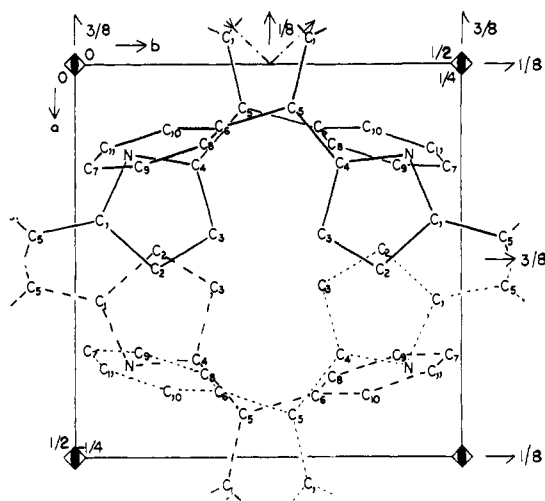


Fig. 2.—Diagram to illustrate the packing relations in crystalline tetraphenylporphine. Symmetry equivalent portions of the molecular skeleton are shown for molecules centered at 000,  $0 \frac{1}{2} \frac{1}{4}$ ,  $\frac{1}{2} 0 \frac{1}{4}$ ,  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ ; these are distinguished from one another in the drawing by using different line characters and weights.

vertical symmetry planes, can reduce the angular strain without affecting either the planarity of the trigonally hybridized bond systems or the number of independent bond lengths. Inasmuch as the bond angles at pyrrole carbon and nitrogen are constrained to a narrow range of values, *ca.*  $125$ – $126^\circ$ , the bond angle at methine carbon is the obvious beneficiary of most of the over-all reduction produced by such ruffling, and whereas variations of a degree or two from the ideal  $120^\circ$  angle have little energetic significance, similar variations from a highly strained angle of  $126$  or  $127^\circ$  surely are energetically consequential. Some redistribution of angular strain, but no change in the qualitative pattern, is produced by varying the M–N distance within reasonable limits, say  $1.90$ – $2.10$  Å. It is unnecessary to consider either the more general ruffling permitted by  $S_4$  or any other mode of deformation from a planar skeleton in order to reach the following conclusions.

Nothing in the analysis appears to justify the belief that a planar configuration of the skeleton can minimize the energy contributed by  $\sigma$ -bonding; it is highly probable, on the contrary, that a ruffled (or alternative nonplanar) configuration is required to this end. The departure from planarity in the equilibrium configuration, of course, is determined by minimization of the total ( $\sigma + \pi$ )-bonding energy.

Although a small energy difference associated with deformation is consistent with what may seem to be a disproportionately large ruffling, direct experimental proof of ruffling in an unconstrained molecule may be difficult to obtain. The energy barrier to reflection of configuration through the mean plane must be small, and the probability of such reflection must increase rapidly with rising temperature. At a sufficiently high temperature, perhaps even at  $300^\circ\text{K}$ ., the skeleton should behave as if the potential energy associated with reflection of configuration had a single, very broad minimum. Those experimental techniques which determine only the averaged configuration then would find a planar skeleton in a free molecule, albeit in a

state of highly anisotropic, strongly excited, thermal vibration.

Kendrew's observation<sup>17</sup> that in the myoglobin structure the iron atom lies more than  $0.25$  Å. out of the mean plane of the heme group perhaps indicates that the easy deformability of the porphine skeleton is one of its useful biological characteristics. Of greater importance, we surmise, are the overly large effective sizes of the high spin  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions and their tractability in accepting unorthodox coordination groups determined by external constraints on the ligands.<sup>18</sup> The porphine skeleton, nonetheless, may be expected to conform to whatever effective symmetry, *e.g.*,  $C_4$ , that may be demanded by the special circumstances.

The parallel stacking of apparently flat phthalocyanine molecules at essentially the graphite layer separation of  $3.40$  Å. is evidently conducive to unusually large energetic stabilization in the crystal; it is, consequently, fully compatible with the type of naturally ruffled, but readily deformable, molecule described above. Parallel stacking of approximately flat molecules is observed also in the crystalline nickel derivative of 2,4-diacetyldeuterioporphyryl-IX-dimethyl ester.<sup>19</sup> The packing relations in crystalline tetraphenylporphine are very different, as Fig. 2 and the data of Table VI demonstrate. There is just one intermolecular contact between the heavy atoms,  $\text{C}_{10}$ – $\text{N} = 3.43$  Å., which is

TABLE VI

## PACKING DISTANCES IN THE CRYSTALLINE ARRANGEMENT

Type <sup>a</sup>	Dist., Å.	Type <sup>a</sup>	Dist., Å.	Type <sup>a</sup>	Dist., Å.
$\text{C}_{10}$ – $\text{N}^b$	3.43	$\text{C}_{11}$ – $\text{C}_4^b$	4.24	$\text{C}_1$ – $\text{C}_2^c$	4.11
$\text{C}_{10}$ – $\text{C}_4^b$	3.57	$\text{C}_3$ – $\text{C}_3^c$	3.51	$\text{C}_2$ – $\text{N}^c$	4.14
$\text{C}_{11}$ – $\text{C}_1^b$	3.66	$\text{C}_7$ – $\text{C}_7^c$	3.65	$\text{C}_{11}$ – $\text{C}_9^c$	4.14
$\text{C}_{11}$ – $\text{N}^b$	3.69	$\text{C}_7$ – $\text{C}_9^c$	3.79	$\text{C}_1$ – $\text{C}_1^c$	4.21
$\text{C}_{10}$ – $\text{C}_1^b$	3.76	$\text{C}_3$ – $\text{C}_2^c$	3.83	$\text{C}_8$ – $\text{C}_9^d$	3.83
$\text{C}_{10}$ – $\text{C}_5^b$	3.93	$\text{C}_3$ – $\text{C}_8^c$	3.83	$\text{C}_9$ – $\text{C}_7^d$	3.91
$\text{C}_{10}$ – $\text{C}_3^b$	4.00	$\text{C}_9$ – $\text{C}_9^c$	3.91	$\text{C}_9$ – $\text{C}_9^d$	3.93
$\text{C}_{10}$ – $\text{C}_2^b$	4.09	$\text{C}_2$ – $\text{C}_2^c$	3.94	$\text{C}_8$ – $\text{C}_7^d$	3.99
$\text{C}_3$ – $\text{C}_3^b$	4.18	$\text{C}_2$ – $\text{C}_4^c$	3.96	$\text{C}_2$ – $\text{C}_7^e$	4.08
$\text{C}_{11}$ – $\text{C}_2^b$	4.23	$\text{C}_3$ – $\text{C}_4^c$	4.01	$\text{C}_2$ – $\text{C}_{11}^e$	4.20

<sup>a</sup> From an atom (no superscript) in the asymmetric unit (Fig. 1) of a molecule centered at the origin to an atom (with identifying superscript) in a molecule centered in <sup>b</sup>  $0 \frac{1}{2} \frac{1}{4}$ , <sup>c</sup>  $\frac{1}{2} 0 \frac{1}{4}$ , <sup>d</sup>  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ , or <sup>e</sup> 010.

very near the graphite layer separation, and there are only three such contacts which are below  $3.65$  Å. The hydrogen atoms in tetraphenylporphine evidently play a more prominent role in determining the packing relations than is the case in the phthalocyanines. The colinearity of the axis ( $\text{C}_6$ – $\text{C}_7$ ) of the phenyl group with methine carbon ( $\text{C}_3$ ) and the pattern of thermal vibrations for phenyl carbon atoms (Table II) carry no suggestion of any special strain in the packing relations. Thus the crystalline arrangement is compatible either with a naturally ruffled porphine skeleton or with a planar skeleton of extraordinarily low rigidity.

(17) J. C. Kendrew, *Science*, **139**, 1259 (1963), who mentions also that D. Koenig, the Johns Hopkins University, has observed a similar phenomenon by structure analysis of hemin.

(18) Such effects are strikingly illustrated in the seven-coordinate ethylenediaminetetraacetato anionic complexes of  $\text{Mn}^{+2}$  and  $\text{Fe}^{+3}$  and in the octahedrally coordinated acid complex of  $\text{Fe}^{+3}$ . The Fe–N distance (involving nitrogen of a tertiary amine) is never less than  $2.22$  Å. and is always  $0.20$  Å. or more longer than the longest Fe–O bond in the same complex. Cf. S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964); M. Lind and J. L. Hoard, *ibid.*, **3**, 34 (1964); M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **3**, 34 (1964); J. L. Hoard, C. H. L. Kennard, and G. S. Smith, *ibid.*, **2**, 1316 (1963).

(19) T. A. Hamor and J. L. Hoard, study in progress.