Structure of Octaethylporphyrin. A Comparison with Other Free Base Porphyrins

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Abstract: The structure of 1,2,3,4,5,6,7,8-octaethylporphyrin has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions $a = 9.791$ (2) Å, $b = 10.771$ (2) Å, $c = 7.483$ (2) Å, $\alpha = 97.43$ (1)°, $\beta = 106.85$ (1)°, and $\gamma = 93.25$ (1)°. The observed and calculated densities are 1.19 (1) and 1.191 g cm^{-3}, respectively. The structure was solved by the determination of the best orientation of a calculated porphyrin ring in an origin removed sharpened Patterson map. Least-squares refinement has led to a final value of the conventional R factor (on F) of 0.039 for the 2518 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of well separated molecules, each with a crystallographically imposed center of symmetry. The porphyrin macrocycle is essentially planar with two independent pyrrole rings which are significantly different from each other. The amino hydrogen atoms are located on one pair of nitrogen atoms. A comparison of this structure with those of meso-substituted porphyrins and porphine indicates that the structures are similar but that substituent groups on the macrocycle cause changes in geometry closest to the point of substitution.

Complete X-ray crystallographic structure determinations have been reported for three free base porphyrins. Two of these determinations have been of meso-substituted porphyrins, $\alpha,\beta,\gamma,\delta$-tetra-$n$-propylporphyrin (TPrP)[1] and $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin (TPP),[2] and the third that of porphine,[3] the parent compound of the porphyrin series. Codding and Tulinsky[1] have proposed a common structure for the free base porphyrin macrocycle by averaging the results of these three determinations.

Naturally occurring porphyrins have aliphatic substituents, not at the meso positions but at the eight pyrrole positions. Therefore, it is of interest to determine the structure of a free base porphyrin with pyrrole substituents and to compare it with the common structure proposed by Codding and Tulinsky.[1] For this reason we have undertaken the structure determination of 1,2,3,4,5,6,7,8-octaethylporphyrin (OEP), a synthetic porphyrin with ethyl groups substituted at the eight pyrrole positions.

Experimental Section

A sample of OEP was kindly supplied by Professor H. H. Inhoffen. Suitable crystals, deep purple in color, were obtained by slow evaporation from dichloromethane solution. Preliminary precession photographs taken with Cu Kα radiation showed only the required center of symmetry and hence the space group is either $P1$ or $P\bar{1}$.

A crystal with approximate dimensions of 0.35 × 0.40 × 0.60 mm was selected for data collection and mounted on a Picker four-circle automatic diffractometer. The lattice parameters obtained as previously described,[4,5] by careful hand centering of 18 reflections with Cu Kα_1 radiation (λ 1.5405 62 Å) in the range $40 \leq 2\theta \leq 80°$, are $a = 9.791$ (2), $b = 10.771$ (2), $c = 7.483$ (2) Å; and $\alpha = 97.43$ (1), $\beta = 106.85$ (1), $\gamma = 93.25$ (1)°. The calculated density based on one molecule per unit cell is 1.191 g/cm^3 and agrees well with an observed value of 1.19 (1) g/cm^3, as measured by flotation in aqueous zinc chloride solution.

Data were collected in shells of 2θ by the θ–2θ scan method using Cu Kα radiation prefiltered with Ni foil. The first block of data was measured with the diffractometer in the bisecting mode. The scan range in 2θ was from 1° below the Cu Kα_1 peak to 1° above the Cu Kα_2 peak. The takeoff angle was 3.3° and the receiving counter was positioned 31 cm from the crystal with an aperture 5.2 mm high and 5.7 mm wide. The pulse height analyzer was set to admit about 90% of the Cu Kα peak. Background counts were taken for 10 sec at each end of the scan range and a scan rate of 2° in 2θ per minute was used. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts per second during a scan. The attenuators were of Cu foil and gave attenuator factors of about 2.3. Data were collected in the range $5 < 2\theta \leq 124°$. To collect data at an angle in 2θ greater than 124° it was required that the diffractometer be placed in the parallel position. With this change a second block of data was collected. The scan range in 2θ was from 1.5° below the Cu Kα_1 peak to 1° above the Cu Kα_2 peak. The background counts were increased to 20 sec each. All other parameters remained the same. Data were collected in the range $120 < 2\theta \leq 160°$. The geometry of the diffractometer allowed measurement of only 40% of the possible reflections and required the termination of data collection at 160° in 2θ. During the course of data collection standard reflections from diverse regions of reciprocal space were measured every 75 reflections. For the first block of data six standards were chosen and for the second block three different high-angle reflections were chosen. The deviations of these standards were all within counting statistics.

The data were processed as previously described [4,5] using a value of 0.04 for p. Of the 2999 reflections measured, 2736 were unique and of these 2518 have $F^2 > 3\sigma(F^2)$ and were used in subsequent refinements. Both blocks of data collected contain reflections from the range $120 < 2\theta \leq 124°$. Those reflections measured twice in this range deviated an average of 1.1% from their average values. Data were collected with $l \geq 0$, so Friedel pairs of the type $hk0$ were measured. These pairs of reflections deviate an average of 0.6% from their average values. Sample calculations for an absorption correction were made using a linear absorption coefficient of 4.99 cm^{-1}. The transmission factors calculated ranged from 0.85 to 0.88 indicating that an absorption correction was not necessary.

Solution and Refinement of Structure. Normalized structure factors ($|E|$'s) scaled such that $\langle E^2 \rangle = 1.0$ were calculated from the measured structure amplitudes.[6] The statistical distribution of the

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[1] P. W. Codding and A. Tulinsky, *J. Amer. Chem. Soc.*, **94**, 4151 (1972).

[2] S. J. Silvers and A. Tulinsky, *ibid.*, **89**, 3331 (1967).

[3] B. M. L. Chen and A. Tulinsky, *ibid.*, **94**, 4144 (1972).

[4] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[5] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[6] In addition to local programs for the CDC 6400, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, Cahen's AGNOST absorption program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, Dewar's program FAME for Wilson statistics and generation of normalized structure factors. Our least-squares program, NUCLS, in its nongroup form closely resembles the Busing and Levy ORFLS program.

Table II. Atomic Parameters for Octaethylporphyrin

Atom	x	y	z	B, A^2, or β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N1	−0.0977 (1)[b]	−0.1693 (1)	0.0077 (2)	0.0093 (1)	0.0061 (1)	0.0140 (3)	0.0004 (1)	0.0013 (1)	0.0021 (1)
N2	−0.1235 (1)	−0.0081 (1)	−0.2826 (2)	0.0089 (1)	0.0063 (1)	0.0129 (3)	0.0004 (1)	0.0005 (1)	0.0021 (1)
C1	−0.2054 (1)	−0.2400 (1)	−0.1333 (2)	0.0085 (1)	0.0058 (1)	0.0156 (3)	0.0052 (1)	0.0021 (2)	0.0015 (1)
C2	−0.2543 (1)	−0.3523 (1)	−0.0698 (2)	0.0088 (1)	0.0062 (1)	0.0168 (3)	0.0002 (1)	0.0029 (2)	0.0017 (1)
C3	−0.1723 (1)	−0.3486 (1)	0.1112 (2)	0.0089 (1)	0.0062 (1)	0.0176 (3)	0.0002 (1)	0.0031 (2)	0.0027 (1)
C4	−0.0752 (1)	−0.2328 (1)	0.1583 (2)	0.0087 (1)	0.0059 (1)	0.0161 (3)	0.0005 (1)	0.0023 (2)	0.0024 (1)
C5	0.1132 (1)	−0.0805 (1)	0.3946 (2)	0.0087 (1)	0.0066 (1)	0.0135 (3)	0.0012 (1)	0.0018 (2)	0.0020 (1)
C6	0.2121 (1)	−0.0375 (1)	0.5792 (2)	0.0094 (1)	0.0071 (1)	0.0127 (3)	0.0017 (1)	0.0021 (2)	0.0018 (1)
C7	0.2811 (1)	0.0756 (1)	0.5726 (2)	0.0089 (1)	0.0069 (1)	0.0128 (3)	0.0015 (1)	0.0015 (2)	0.0008 (1)
C8	0.2240 (1)	0.1044 (1)	0.3844 (2)	0.0084 (1)	0.0063 (1)	0.0138 (3)	0.0010 (1)	0.0010 (2)	0.0011 (1)
CA	0.0224 (1)	−0.1918 (1)	0.3361 (2)	0.0095 (1)	0.0068 (1)	0.0149 (3)	0.0008 (1)	0.0023 (2)	0.0029 (1)
CB	0.2623 (1)	0.2098 (1)	0.3140 (2)	0.0091 (1)	0.0062 (1)	0.0155 (3)	0.0003 (1)	0.0009 (2)	0.0012 (1)
C21	−0.3747 (1)	−0.4490 (1)	−0.1842 (2)	0.0095 (1)	0.0082 (1)	0.0223 (4)	−0.0015 (1)	0.0023 (2)	0.0025 (2)
C22	−0.3340 (2)	−0.5454 (2)	−0.3210 (3)	0.0154 (2)	0.0082 (1)	0.0289 (5)	−0.0018 (1)	0.0036 (3)	−0.0014 (2)
C31	−0.1769 (2)	−0.4426 (1)	0.2403 (2)	0.0114 (2)	0.0086 (1)	0.0218 (4)	−0.0008 (1)	0.0032 (2)	0.0054 (2)
C32	−0.0747 (2)	−0.5431 (2)	0.2310 (4)	0.0174 (3)	0.0116 (2)	0.0400 (7)	0.0037 (2)	0.0073 (4)	0.0122 (3)
C61	0.2344 (2)	−0.1074 (2)	0.7444 (2)	0.0127 (2)	0.0084 (1)	0.0128 (3)	0.0019 (1)	0.0024 (2)	0.0028 (2)
C62	0.3403 (2)	−0.2057 (2)	0.7453 (2)	0.0155 (2)	0.0101 (1)	0.0213 (4)	0.0041 (1)	0.0035 (2)	0.0059 (2)
C71	0.3978 (1)	0.1548 (1)	0.7272 (2)	0.0105 (2)	0.0080 (1)	0.0133 (3)	0.0009 (1)	0.0006 (2)	0.0000 (2)
C72	0.5473 (2)	0.1233 (2)	0.7271 (3)	0.0098 (2)	0.0116 (2)	0.0214 (4)	0.0006 (1)	0.0008 (2)	−0.0012 (2)
N2-H	−0.0736 (22)	−0.0015 (18)	−0.1568 (29)	2.87 (43)					
CA-H	0.0316 (18)	−0.2489 (16)	0.4334 (25)	1.91 (34)					
CB-H	0.3390 (18)	0.2678 (16)	0.3969 (25)	1.72 (33)					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures.

$|E|$'s was examined and compared with the theoretical distributions for acentric and centric cases. The distribution found for OEP closely resembled the values for a centric crystal, thus suggesting that the correct space group is $P\bar{1}$.

Using the quantities $|E^2 - 1|$ a sharpened, origin-removed Patterson was constructed. A careful examination of the map revealed a plane of high vector density. A plot of this plane showed pseudo-fourfold symmetry and suggested what proved to be the correct orientation of the porphyrin molecule in the cell. Based on the appearance of the Patterson map, trial positional parameters for each of the 12 independent nonhydrogen atoms of the porphyrin macrocycle were calculated assuming a planar molecule and using the interatomic distances of porphine given by Chen and Tulinsky.[3] A structure factor calculation using these positional parameters was followed by a Fourier synthesis which clearly displayed the four independent ethyl groups as well as the porphyrin macrocycle, indicating that the assumed model was correct.

The structure was refined by full-matrix least-squares techniques. The quantity minimized is $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. Values of the atomic scattering factors[7] and the anomalous terms[8] were taken from the usual sources.

Least-squares refinement for three cycles of the positional parameters of each nonhydrogen atom and the isotropic temperature factors assigned to each led to values of R and R_w of 0.134 and 0.211. Two subsequent cycles in which each atom was allowed anisotropic vibrations reduced the values of R and R_w to 0.095 and 0.154. At this point a difference Fourier map was calculated clearly revealing as the 23 highest peaks the positions of the 23 independent H atoms. The H atoms of the ethyl groups were idealized (C–H = 1.0 Å, ∠'s = 109.5°, B(H) = B(C)) and added as fixed contributions in subsequent refinements. The three independent H atoms bonded directly to the porphyrin macrocycle were assigned isotropic temperature factors and were allowed to vary in further refinements. A subsequent refinement varying parameters for all nonhydrogen atoms and for the three macrocycle H atoms resulted in values of 0.046 and 0.074 for R and R_w. An examination of the values for F_o and F_c for the most intense reflections indicated that a correction for extinction should be made. A refinement including an isotropic extinction parameter in addition to the other parameters gave agreement values of 0.040 and 0.072 for R and R_w. (The extinction parameter converged to a final value of 3.3 (3) $\times$ 10^{-3} e^{-2}.) A final cycle of refinement which included terms for anomalous scattering resulted in values for R and R_w of 0.039 and 0.072. Refinement was terminated at this point since the last cycle led to only a small decrease in the agreement values and the parameters shifted by less than 0.1 σ.

An analysis of $|F_o|$ and $|F_c|$ as a function of setting angles, magnitude of $|F_o|$, and Miller indices showed no unusual trends. The standard deviation of an observation of unit weight is 3.09.

A final difference Fourier synthesis was essentially featureless with no peaks greater than 0.2 e/Å^3. A structure factor calculation for the 218 reflections having $F_o^2 < 3\sigma(F_o^2)$, which were omitted from the refinement, showed only nine reflections having $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. These 218 reflections were omitted from Table I[9] where the values of $10|F_o|$ and $10|F_c|$ are given.

The final atomic parameters and their errors are listed in Table II. The calculated atomic parameters for the ethyl hydrogen atoms are given in Table III.

Results and Discussion

The crystal structure consists of discrete molecules of OEP. The shortest intermolecular distances are hydrogen–hydrogen contacts of 2.4 Å. The four independent ethyl groups are normal. All the methyl and methylene hydrogen atoms are staggered, as expected. The average $C_{E\alpha}$–$C_{E\beta}$ bond distance is 1.520 (6) Å.

The molecular structure of OEP is quite similar to those structures found for previously determined porphyrins.[1-3] Figure 1 displays the numbering scheme chosen for the molecule and a perspective view is shown in Figure 2. Important distances and angles are listed in Table IV and are shown in Figure 3. The root-mean-square amplitudes of vibration are normal and are listed in Table V along with the angle between the axis of maximum amplitude of each atom and the normal to the plane defined by the N atoms.

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(7) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, in press, Table 2.2A.

(8) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(9) Table I will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-5148. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

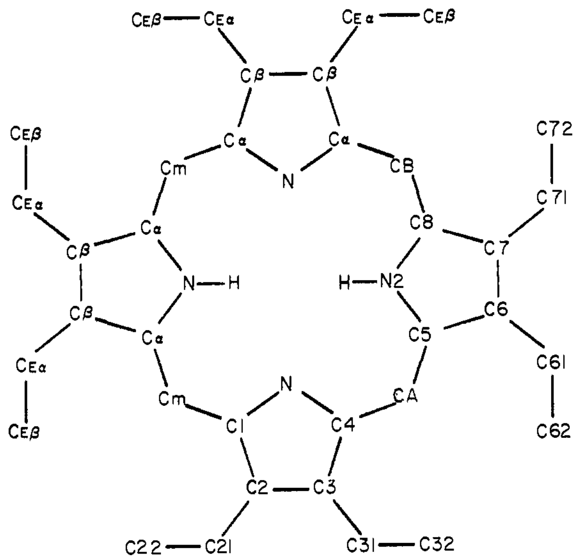

Figure 1. A sketch of the centrosymmetric OEP molecule showing the two labeling schemes. The upper left portion of the figure shows the labeling scheme used when referring to general positions. The lower right shows the numbering scheme for specific atoms.

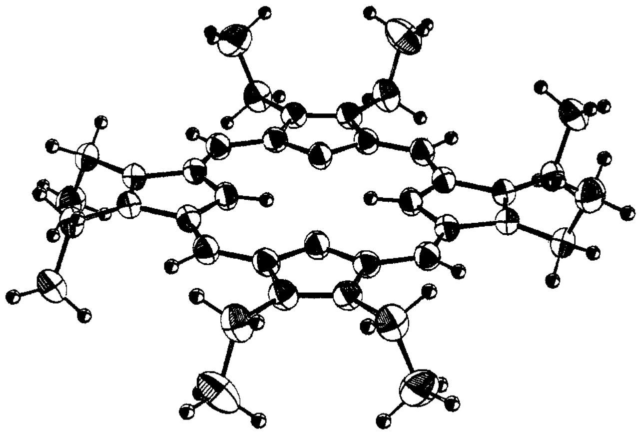

Figure 2. A perspective drawing of the OEP molecule. Nonhydrogen atoms are drawn at their 50% probability ellipsoids. The hydrogen atoms have been drawn artificially small.

Table III. Idealized Positions for the Ethyl Hydrogen Atoms

	x	y	z
C21-H1	−0.4544	−0.4045	−0.2583
C21-H2	−0.4103	−0.4945	−0.0954
C31-H1	−0.2767	−0.4840	0.2078
C31-H2	−0.1483	−0.3972	0.3740
C61-H1	0.2717	−0.0454	0.8632
C61-H2	0.1399	−0.1500	0.7399
C71-H1	0.3835	0.1432	0.8515
C71-H2	0.3887	0.2454	0.7100
C22-H1	−0.2597	−0.5961	−0.2497
C22-H2	−0.4206	−0.6035	−0.3984
C22-H3	−0.2936	−0.5017	−0.4082
C32-H1	−0.0814	−0.6046	0.3178
C32-H2	−0.1027	−0.5905	0.0966
C32-H3	0.0258	−0.5078	0.2639
C62-H1	0.4366	−0.1642	0.7549
C62-H2	0.3484	−0.2518	0.8557
C62-H3	0.3053	−0.2677	0.6253
C72-H1	0.6216	0.1836	0.8264
C72-H2	0.5609	0.0353	0.7568
C72-H3	0.5605	0.1286	0.6009

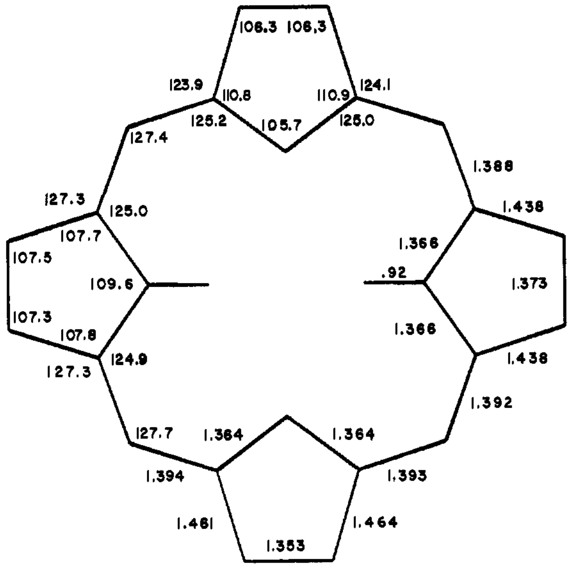

Figure 3. Important bond distances (in angstroms) and bond angles (in degrees).

Table IV. Selected Bond Distances (Å) and Angles (deg)

		Ring 1	
N1-C1	1.3639 (18)	C1-N1-C4	105.7 (1)
N1-C4	1.3635 (18)	N1-C1-C2	110.9 (1)
C1-C2	1.4614 (18)	N1-C4-C3	110.8 (1)
C3-C4	1.4638 (17)	C1-C2-C3	106.3 (1)
C2-C3	1.3535 (21)	C4-C3-C2	106.3 (1)
C1-CB′	1.3936 (21)	N1-C1-CB′	125.0 (1)
C4-CA	1.3930 (21)	N1-C4-CA	125.2 (1)
C2-C21	1.5006 (19)	C3-C4-CA	123.9 (1)
C3-C31	1.4940 (19)	C2-C1-CB′	124.1 (1)
C21-C22	1.5143 (25)	C1-C2-C21	125.7 (1)
C31-C32	1.5231 (25)	C4-C3-C31	125.7 (1)
		C3-C2-C21	127.9 (1)
		C2-C3-C31	128.0 (1)
		C2-C21-C22	114.4 (1)
		C3-C31-C33	112.8 (1)
		Ring 2	
N2-C5	1.3660 (17)	C5-N2-C8	109.6 (1)
N2-C8	1.3679 (17)	C5-N2-(N2-H)	124.8 (12)
N2-(N2-H)	0.918 (21)	C8-N2-(N2-H)	125.5 (12)
C5-C6	1.4383 (19)	N2-C5-C6	107.7 (1)
C7-C8	1.4380 (20)	N2-C8-C7	107.8 (1)
C6-C7	1.3729 (19)	C5-C6-C7	107.5 (1)
C5-CA	1.3919 (19)	C8-C7-C6	107.3 (1)
C8-CB	1.3884 (19)	N2-C5-CA	125.0 (1)
C6-C61	1.4987 (19)	N2-C8-CB	124.5 (1)
C7-C71	1.4964 (18)	C6-C5-CA	127.3 (1)
C61-C62	1.5221 (21)	C7-C8-CB	127.3 (1)
C71-C72	1.5216 (21)	C5-C6-C61	124.9 (1)
		C8-C7-C71	125.0 (1)
		C7-C6-C61	127.6 (1)
		C6-C7-C71	127.7 (1)
		C6-C61-C62	112.9 (1)
		C7-C71-C72	113.1 (1)
CA-(CA-H)	1.000 (18)	C4-CA-C5	127.4 (1)
CB-(CB-H)	0.956 (18)	C1-CB′-C8	127.7 (1)
		(CA-H)-CA-C4	117.4 (10)
		(CA-H)-CA-C5	115.1 (10)
		(CB-H)-CB-C1	116.9 (10)
		(CB-H)-CB-C8	115.3 (10)

The stereochemistry of the OEP molecule is dominated by a delocalization of π-electron density throughout the porphyrin macrocycle. This results in C–C and C–N bond distances which are intermediate between those expected for single and double bonds and

Table V. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Int	Max	Angle[a]
N1	0.177 (2)	0.186 (2)	0.223 (2)	17 (1)
N2	0.167 (2)	0.188 (2)	0.224 (2)	18 (1)
C1	0.183 (2)	0.187 (2)	0.213 (2)	33 (3)
C2	0.185 (2)	0.198 (2)	0.213 (2)	147 (5)
C3	0.180 (2)	0.198 (2)	0.221 (2)	147 (4)
C4	0.178 (2)	0.191 (2)	0.217 (2)	27 (3)
C5	0.174 (2)	0.197 (2)	0.209 (2)	38 (5)
C6	0.174 (2)	0.196 (2)	0.218 (2)	60 (3)
C7	0.175 (2)	0.190 (2)	0.222 (2)	60 (2)
C8	0.174 (2)	0.189 (2)	0.218 (2)	43 (2)
CA	0.178 (2)	0.202 (2)	0.219 (2)	14 (2)
CB	0.180 (2)	0.190 (2)	0.229 (2)	31 (2)
C21	0.183 (2)	0.227 (2)	0.253 (2)	25 (2)
C22	0.195 (2)	0.278 (2)	0.291 (2)	
C31	0.185 (2)	0.220 (2)	0.271 (2)	156 (2)
C32	0.196 (2)	0.280 (2)	0.334 (3)	
C61	0.173 (2)	0.219 (2)	0.246 (2)	46 (3)
C62	0.186 (2)	0.257 (2)	0.279 (2)	
C71	0.173 (2)	0.214 (2)	0.241 (2)	53 (3)
C72	0.193 (2)	0.239 (2)	0.284 (2)	

[a] Angle in degrees between the axis of maximum amplitude and the normal to the plane defined by the N atoms.

comparable to values found for similar bonds in other aromatic systems. If the OEP molecule were deprotonated, the resulting doubly charged anion would be expected to show pseudo-fourfold symmetry. The presence of the amino protons prevents the molecule from achieving fourfold symmetry, but the deviations from such high symmetry are small.

The two independent pairs of pyrrole rings possess small but significant differences. As Tulinsky and his coworkers[1-3] have shown, these differences are expected for a hybrid of the two major resonance forms of the porphyrin macrocycle and may be viewed as perturbations on a model of totally delocalized π-bonding. Figure 4 shows these two resonance structures and also the average carbon–carbon and carbon–nitrogen bond distances found for chemically equivalent bonds within each pyrrole ring. The differences (Δ's) between corresponding bonds of the two different pyrrole rings are also given. These differences are similar to those found in previous porphyrin structures.[1-3]

A least-squares plane was calculated for the atoms of the porphyrin macrocycle, and the distances of the atoms from this plane are listed in Table VI. This

Table VI. Deviations (Å) from Weighted Least-Squares Planes

Atom	Porphyrin macrocycle[a]	Ring 1[b]	Ring 2[c]
N1	0.039 (2)	−0.001 (2)	
C1	−0.006 (2)	0.004 (2)	
C2	−0.049 (2)	−0.005 (2)	
C3	−0.007 (2)	0.005 (2)	
C4	0.038 (2)	−0.002 (2)	
N2	−0.014 (2)		−0.005 (2)
C5	0.003 (2)		0.018 (2)
C6	−0.031 (2)		−0.015 (2)
C7	−0.022 (2)		−0.007 (2)
C8	0.000 (2)		0.014 (2)
N2-H	−0.066 (25)		−0.055 (22)
CA	0.027 (2)		
CB	0.015 (2)		

[a] Plane equation: $8.336x - 5.199y - 3.443z = 0$ (triclinic coordinates). [b] Plane equation: $8.135x - 5.450y - 3.520z = -0.102$. [c] Plane equation: $8.335x - 5.207y - 3.436z = 0.017$.

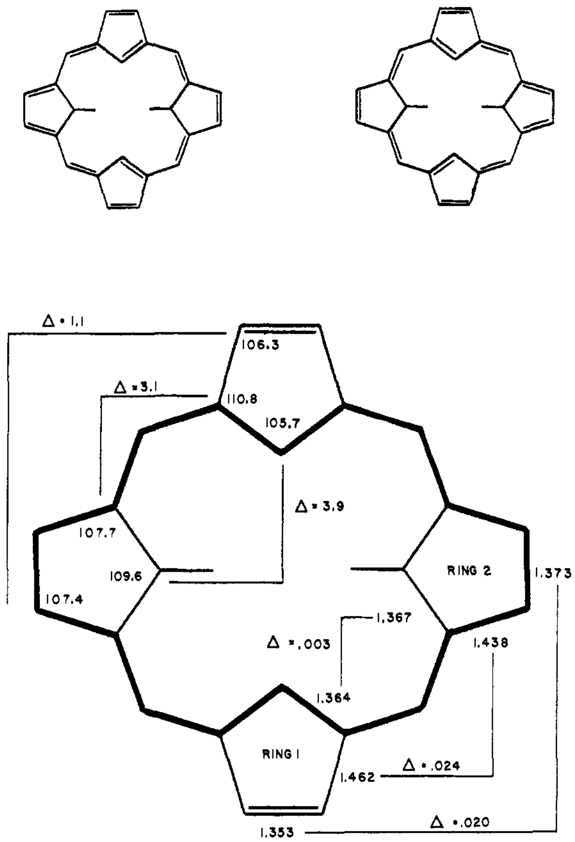

Figure 4. The two upper figures show the dominant resonance forms of the porphyrin macrocycle. The lower figure shows the expected nature of a hybrid of the dominant resonance forms by heavy lines and double bonds. Average observed bond distances (in Å) and angles (in deg) for chemically equivalent bonds within each pyrrole ring are shown. Differences (Δ's) between corresponding bonds and angles of the two independent pyrrole rings are also shown.

Table VII. Average Bond Distances and Bond Lengths for Several Porphyrins[a]

	TPP	TPrP	Meso Porphyrin[b]	Porphine	OEP	Common structure[b]
			Ring 1			
$N-C_\alpha$	1.364	1.372	1.367	1.374	1.364	1.372 (10)
$C_\alpha-C_\beta$	1.455	1.443	1.448	1.452	1.462	1.451 (9)
$C_\beta-C_\beta$	1.347	1.341	1.345	1.345	1.353	1.345 (3)
$C_\alpha-N-C_\alpha'$	106.2	106.6	106.2	106.1	105.7	106.3
$N-C_\alpha-C_\beta$	110.3	109.5	109.4	109.8	110.8	109.8
$C_\alpha-C_\beta-C_\beta'$	106.8	107.3	107.0	107.1	106.3	107.1
$N-C_\alpha-C_m$	126.3	126.4	126.4	125.0	125.1	
$C_\beta-C_\alpha-C_m$	123.5	124.5	123.8	125.1	124.0	
			Ring 2			
$N-C_\alpha$	1.374	1.376	1.375	1.380	1.367	1.378 (4)
$C_\alpha-C_\beta$	1.428	1.437	1.432	1.431	1.438	1.432 (6)
$C_\beta-C_\beta'$	1.355	1.352	1.354	1.365	1.373	1.360 (10)
$C_\alpha-N-C_\alpha'$	109.2	110.0	109.6	108.6	109.6	109.4
$N-C_\alpha-C_\beta$	107.3	106.7	107.0	107.9	107.7	107.5
$C_\alpha-C_\beta-C_\beta'$	108.1	108.3	108.2	107.9	107.4	108.0
$N-C_\alpha-C_m$	126.0	127.1	126.6	125.5	125.0	
$C_\beta-C_\alpha-C_m$	126.6	126.2	126.4	126.9	127.3	
$C_\alpha-C_m$	1.399	1.397	1.398	1.382	1.392	
$C_\alpha-C_m-C_\alpha'$	125.6	125.0	125.3	127.1	127.6	
Ref	*c*	*d*	*c, d*	*e*	*f*	*d*

[a] Bond lengths are in Å and bond angles in degrees. [b] Defined in text. [c] Reference 2. Errors were estimated by original authors as 0.005–0.010 Å for individual bond lengths and 0.5–0.8° for individual bond angles. [d] Reference 1. Errors: 0.004 Å and 0.2–0.4°. [e] Reference 3. Errors: 0.004–0.007 Å and 0.3–0.5°. [f] This work. Errors: 0.002 Å and 0.1–0.2°.

portion of the OEP molecule is essentially planar with all atoms within 0.05 Å of the least-squares plane. Least-squares planes were also calculated for each of the independent pyrrole rings. The results are listed in Table VI and indicate that ring 1 has smaller deviations from planarity than does ring 2. The imino hydrogen atom is bound to the nitrogen atom of ring 2 at a distance of 0.92 (2) Å. It is 0.05 Å from the least-squares plane of ring 2. The distance between the two imino hydrogen atoms across the center of the molecule is 2.36 (4) Å.

Table VII lists average bond distances and bond angles for those porphyrins whose structures have been determined completely. The values for TPP and TPrP are quite similar and have been averaged to give values representative of meso-substituted porphyrins. Also listed are the values for the common structure of free base porphyrins proposed by Codding and Tulinsky.[1] As previously indicated[1] the largest structural differences between the meso-substituted porphyrins and porphine involve the methine carbon atom. The meso porphyrins which are substituted at the methine carbon atom have C_α–C_m bond lengths which are about 0.018 Å longer than the C_α–C_m bond length found in porphine. In a similar manner, the C_α–C_m–C_α' bond angle is 1.8° smaller than the value for porphine.

OEP is substituted at the pyrrole positions and it would be expected that the largest structural difference between porphine and OEP would involve the pyrrole atoms. This appears to be the case, as the parameters in Table VII indicate. Both the C_α–C_β and the C_β–C_β' bond distances in each of the pyrrole rings are about 0.01 Å longer in OEP than in the unsubstituted porphine molecule.

The result of substitution is the same in the meso porphyrins and in OEP. Those carbon–carbon bonds closest to the site of substitution are lengthened. This lengthening of bonds is not unexpected in aromatic systems and indicates a reduction in the π-electron density at the substituted carbon atom and a subsequent transfer of π-electron density to the substituent atoms. This is supported by the observed short bond distance of 1.498 (4) Å for the average C_β–$C_{E\alpha}$ bond length.

A comparison of all the results shown in Table VII indicates that the common structure for the porphyrin macrocycle proposed by Codding and Tulinsky[1] is a good model but that substituent groups can be expected to cause significant changes in bond parameters. The naturally occurring porphyrins have pyrrole substituents and can be expected to have bond lengths and angles similar to those observed for OEP. It should be noted, however, that certain natural prophyrins have substituent groups such as vinyl groups which can conjugate with the porphyrin macrocycle and may cause additional changes in bond parameters.

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Synthesis and Reversible Ligation Studies of New Low-Spin Iron(II) Complexes Containing a Planar Cyclic Tetradentate Ligand and Other Donor Molecules Including Carbon Monoxide

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Abstract: The synthesis and characterization of three hexacoordinate low-spin Fe(II) complexes are described. All the complexes contain TIM, a 14-membered tetraimine macrocyclic ligand derived from 2,3-butanedione and 1,3-diaminopropane and all are isolated as PF_6^- salts: $[Fe(TIM)(CH_3CN)_2](PF_6)_2$, $[Fe(TIM)(imid)_2](PF_6)_2$, and $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$. Preparative difficulties encountered in the synthesis of $[Fe(TIM)X_2](PF_6)_2$ (which are not encountered with the Ni(II) and Co(III) TIM complexes) are alleviated through the addition of stannous chloride to the reaction mixtures. In acetonitrile solutions $[Fe(TIM)(CH_3CN)_2]^{2+}$ undergoes reversible substitution reactions with both imidazole and carbon monoxide. In the case of imidazole one or more of the following three complexes are present in solution depending on the concentration of imidazole: $[Fe(TIM)(CH_3CN)_2]^{2+}$, $[Fe(TIM)(CH_3CN)(imid)]^{2+}$, and $[Fe(TIM)(imid)_2]^{2+}$. Estimates of the equilibrium constants involved in the substitution reactions show that the $[Fe(TIM)(CH_3CN)(imid)]^{2+}$ is the favored species but that the formation constant for $[Fe(TIM)(imid)_2]^{2+}$ is large enough such that no free imidazole is detectable by pmr spectroscopy when the imidazole:Fe(TIM) ratio in the system is 2. With carbon monoxide the two species present in solution are $[Fe(TIM)(CH_3CN)_2]^{2+}$ and the mixed complex $[Fe(TIM)(CH_3CN)(CO)]^{2+}$ (when $P_{CO} \leq 1$ atm).

In recent years the chemistry of synthetic complexes containing macrocyclic ligands has commanded a great deal of attention.[1] A part of the motivation for expending considerable effort in the field has come from the continuing hope that a significantly more complete understanding of the chemistry of the naturally occurring macrocycles will be forthcoming from investigations of the synthetic ones.[2,3] Included among

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[1] D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius Alfred Werner*, 174 (1967).