The Crystal and Molecular Structure of Triclinic Tetraphenylporphyrin

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Abstract: The crystal and molecular structure of triclinic tetraphenylporphyrin (TPP) has been solved using X-ray crystallographic techniques. The molecule is centrosymmetrical with two independent pyrrole and phenyl groups. Although the individual pyrrole and phenyl groups are planar within the error of their determination (<0.005 A), the porphyrin ring is nonplanar. One pair of centrosymmetrical pyrroles is essentially coplanar with the nuclear least-squares (NLS) plane of the porphyrin ring; the other pair, carrying the central hydrogen atoms, is inclined ±6.6° to this plane. The tilt of the latter is such that the distance between the central hydrogens is increased by 0.2 A, to 2.36 A. Both phenyl groups of TPP are rotated out of the NLS plane by about 60°; one phenyl is additionally inclined to this plane by ±9.1°. Although the porphyrin ring is nonplanar, the atoms of the inner 16-membered ring are individually planar, and the bond distances of this ring resemble those of a heterocyclic aromatic system. The 1,2 and 3,4 bond lengths of the independent pyrroles correspond closely to isolated double bonds and to this extent appear isolated from the inner ring; the phenyl groups also appear to be electronically isolated from the ring through shortened single bonds. The structure described herein corresponds closely with the hybrid of the two classical resonance forms of the porphyrin molecule. Finally, the fine points of the structure are discussed in terms of the molecular packing in the crystal.

Tetraphenylporphyrin (α, β, γ, δ) ($C_{44}H_{30}N_4$, see Figure 2), hereinafter referred to as TPP, is a synthetic nonmetallophorphyrin derivative. TPP is related to naturally occurring porphyrins by having the same macrocylic skeletal structure, which consists of four pyrrole groups alternately linked through methene carbon bridges.

The metalloporphyrin ring is found in a variety of important biological systems where it is either the active component of the system or in some way intimately connected with the activity of the system. Many of these biological porphyrin systems differ markedly in their behavior and it appears that this is due in large part to: (a) the effects of a central metal ion on the π-bonding system of the porphyrin ring, (b) the ease with which the porphyrin ring can assume various nonplanar conformations, (c) the chemistry and the stereochemistry of side chains of the porphyrin ring, and (d) the general molecular environment of the porphyrin in the biological system.

Porphyrins also possess an intrinsic interest in that they are examples of an extremely stable heteromacrocyclic π-bonding system with the ability to complex readily with many different metal ions. Although there are other ligands that behave similarly, the porphyrins are unusual in that they, as the ligand, act as the host to the metal ion. In the case of free-base porphyrins, additional interest centers about the exact nature of the central acidic hydrogen atoms. If the porphyrin skeleton were planar or nearly so, the two central hydrogens bound to opposite pyrrole groups would approach one another within about 2.0 A. This is indeed a close van der Waals contact and at the onset of this work, it seemed unlikely. Therefore, in the beginning, the nature of the central hydrogen atoms and their environment were of most concern to this structure determination. However, it has resulted since that other structural characteristics of the molecule are of at least equal interest.[2,3]

Experimental Section

Single crystals of TPP were grown by slowly evaporating solutions of TPP in benzene, chloroform, and dioxane.[4] All the crystals were elongated purple prisms, but those grown from benzene and chloroform were soft and did not diffract X-rays well. The crystals from dioxane, grown under a nitrogen atmosphere, were hard, slightly translucent, and good X-ray scatterers. One of these crystals, with approximate dimensions of 0.75 × 0.20 × 0.05 mm and with well-developed end faces, was used for X-ray examination because of its size and apparent crystal quality.

All the X-ray work was carried out with Cu Kα radiation and a General Electric XRD-5 equipped with a single-crystal orienter and a scintillation counter assembly. A survey of the diffraction pattern indicated that the crystal system was triclinic. By convention, the unit cell was chosen to be primitive and reduced with the three axes forming a right-handed coordinate system. The unit cell so chosen has the dimensions: $a = 6.44 \pm 0.01$, $b = 10.42 \pm 0.01$, $c = 12.41 \pm 0.01$ A, $\alpha = 96.06 \pm 0.05$, $\beta = 99.14 \pm 0.05$, $\gamma = 101.12 \pm 0.05°$, $V = 801.9 \pm 1.2$ A^3. The crystal density calculated on the basis of these dimensions and one molecule of TPP per unit cell is 1.273 g/cm^3. The density of several single crystals was measured to be 1.27 ± 0.01 g/cm^3 by suspending the crystals in a solution of silver nitrate and water. Thus, the number of molecules per unit cell was taken to be one.

In the triclinic case the required intensity data are confined within half of the limiting sphere. Since the single-crystal orienter used in this work was a quarter-circle model, once the crystal was mounted the segment of the sphere to be collected was fixed. Mosaic spreads of several reflections were therefore measured only to ensure that the crystal quality was sufficient for intensity data collection purposes. The spreads proved to be symmetrical and ranged from 0.3 to 0.6° in width, from background to background.

The intensities of the reflections were measured by the stationary crystal–stationary counter technique. In order to avoid $K\alpha_1$ and $K\alpha_2$ splitting effects, the data collection was confined to reflections with scattering angles (2θ) less than 110°, which corresponds to 0.94-A resolution. Of the 2007 independent reflections possible to this limit, the intensities of 1726 (86%) were large enough to be observed. During the intensity measurements the crystal was exposed to X-rays for about 33 hr, but its reflecting power was

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(2) For extensive reviews of structural studies of porphyrins, see T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Am. Chem. Soc.*, 87, 2305 (1965); L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, 43, 3100 (1965), and references contained therein.

(3) For a preliminary report of this work, see S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, 86, 927 (1964).

(4) A highly purified sample of TPP was kindly provided by Dr. Henry E. Rosenberg.

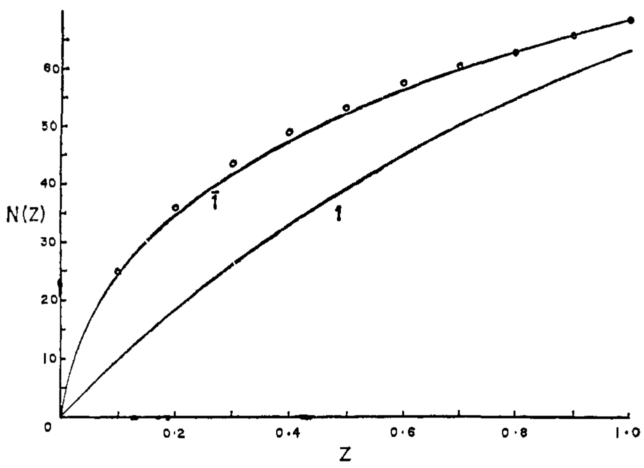

Figure 1. The observed intensity distribution of TPP, O, and theoretical distributions for P1 and $P\bar{1}$, ———.

not thereby altered; the intensities of four reflections which were monitored throughout the measurement period remained constant.

The intensities were corrected for absorption with a correction obtained by averaging intensity *vs.* ϕ curves (azimuthal orientation) of two reflections with χ values of 90°; the average curve had a maximum:minimum ratio of 1.10. The intensities so corrected were converted to structure amplitudes, and the latter were then scaled with the results of Wilson's method to approximate an absolute scale.

Structure Determination

The Center of Symmetry. The observed reflections were divided according to scattering angle into five groups. These were: (1) $2\theta < 30.00$, (2) $30.00 \leqslant 2\theta < 56.16$, (3) $56.16 \leqslant 2\theta < 75.00$, (4) $75.00 \leqslant 2\theta < 92.99$, and (5) $92.99 \leqslant 2\theta \leqslant 110.00°$. The first group, containing 50 reflections, was ignored in further considerations for theoretical reasons.[5] For each of the other four, the percentage, $N(z)$, of reflections with $|F|^2$ less than or equal to a fraction, z, of the group average was plotted as a function of z. The unobserved reflections were included with zero structure amplitudes. In Figure 1, the average of these plots is indicated by open circles and the two theoretical distributions for P1 and $P\bar{1}$ are shown by solid curves. Clearly, the observed $|F|^2$ distribution is centrosymmetric and the space group of the crystal is therefore $P\bar{1}$.

The Patterson Function and the Orientation of TPP. Since there is only one TPP molecule per unit cell and the space group is $P\bar{1}$, the molecule itself must be centrosymmetric. By taking the molecular center of symmetry as the unit cell origin, the translational parameters of TPP are fixed. Since the gross structure of the molecule was known, the determination of a trial structure reduced simply to the determination of an approximate angular orientation for the molecule.

In order to determine the angular orientation of the TPP molecule, a three-dimensional Patterson function was computed using the squares of the observed amplitudes as coefficients. The significant positive regions of this function were confined to the region of the plane which is parallel to the $(1\bar{2}1)$ planes and passes through the origin. If the vectors between atoms lie close to a plane, the atoms themselves also must lie close to that plane. Therefore, the $(1\bar{2}1)$ plane was concluded to be the approximate mean plane of the molecule. In support of this conclusion, the structure amplitudes of the $(1\bar{2}1)$, $(1\bar{3}1)$, and $(1\bar{2}0)$ reflections were, in that order, the largest reflections of all those observed and significantly so.

At this stage, the molecule was assumed to be strictly planar except for undertermined rotations of the four phenyl groups about the bonds joining them to the bridge carbon atoms between the pyrroles. The mean plane of the molecule, in accordance with the Patterson function, was taken to pass through the origin and lie parallel to the $(1\bar{2}1)$ planes. Thus, there remained to be determined only the orientation of the model molecule within this plane. As a further simplification, this planar model of TPP was assigned a fourfold rotation axis so as to fix its orientation within 90°.

The model was then systematically rotated about its fourfold axis 12 times (7.5° each time). In this way, the "correct" orientation would approach within 3.75° of one of these 12 positions (since a 90° rotation superimposes the model upon itself). For each orientation the coordinates of the model molecule (excluding the four atoms of each phenyl group which were expected for steric reasons to lie rotated out of the plane) were determined and a set of structure factors was computed. An over-all isotropic thermal parameter of 2.0 A^2, estimated from Wilson's method, was used in each calculation. The *R* value for each set of structure factors was then examined as a function of the orientation of the model. The *R* values fluctuated about the value of 0.73 ± 0.03 but one was considerably smaller than all the others (0.68). The point Patterson function of the model in the orientation corresponding to this minimum *R* was then compared with the observed Patterson in the $(1\bar{2}1)$ plane. Since the principal features of the two were in good agreement the orientation of the TPP molecule was taken to correspond with the minimum *R* value.

The phases of this set of structure factors were assigned to the observed amplitudes and an electron density (ρ_1) was computed. The carbon and nitrogen atoms of the porphyrin nucleus all appeared in ρ_1 at peak heights of approximately 6 eA^{-3} or more. However, the positions of these peaks were in some cases noticeably different from those of the model structure. This was expected, since the deduced orientation of the model was not exact and its planarity and fourfold symmetry were approximations.

The eight next-to-the-largest peaks in ρ_1 (average peak height of 3.7 eA^{-3}) besides those of the 16 model atoms were recognized to be the phenyl carbon atoms not included in the model. The terminal atom of one phenyl group in the model appeared in ρ_1 as an atom adjacent to the true terminal position. This phenyl group, as observed in ρ_1, was thus bent out of the plane of the model as well as rotated about the bond from its proximal atom to the porphyrin ring. The other phenyl group was not bent out of the plane but only rotated and its terminal atom corresponded to that of the model. Thus, although the phases employed to obtain ρ_1 were determined by a model which was a considerable oversimplification of the true structure, nevertheless, they were able to reveal a structure that was neither planar nor fourfold symmetrical, which corresponded in most of its essentials to that of the final structure.

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(5) A. J. C. Wilson, *Acta Cryst.*, 2, 318 (1949).

Table I. Final Atomic Parameters, Carbon and Nitrogen[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Peak height, eA^{-3}
C-1	0.1447	0.9597	0.6741	0.0254	0.0101	0.0072	0.0011	0.0037	−0.0002	6.3
C-2	0.3195	0.0528	0.7251	0.0278	0.0096	0.0065	0.0010	0.0034	0.0002	6.3
C-3	0.4046	0.7191	0.8866	0.0255	0.0100	0.0072	−0.0005	0.0016	0.0005	6.5
C-4	0.4799	0.7166	0.7913	0.0244	0.0094	0.0070	−0.0007	0.0019	0.0005	6.3
C-5	0.0216	0.9194	0.7558	0.0214	0.0075	0.0063	0.0012	0.0020	−0.0002	6.8
C-6	0.3128	0.0721	0.8397	0.0214	0.0071	0.0061	0.0008	0.0021	0.0004	7.0
C-7	0.4327	0.1904	0.0308	0.0204	0.0073	0.0059	0.0007	0.0013	0.0002	7.2
C-8	0.3110	0.1929	0.1852	0.0217	0.0068	0.0059	0.0008	0.0002	0.0000	6.9
C-α	0.4535	0.1661	0.9204	0.0218	0.0075	0.0069	0.0018	0.0023	0.0009	7.1
C-β	0.1790	0.1685	0.2634	0.0218	0.0072	0.0062	0.0010	0.0009	0.0002	7.0
N-1	0.1300	0.9885	0.8554	0.0204	0.0070	0.0062	0.0018	0.0012	0.0001	8.6
N-2	0.2641	0.1371	0.0769	0.0214	0.0068	0.0061	0.0006	0.0017	0.0002	8.7
ϕ_α-1	0.3634	0.7481	0.1171	0.0202	0.0084	0.0065	0.0018	0.0028	0.0009	7.2
ϕ_α-2	0.2087	0.7995	0.1608	0.0255	0.0106	0.0093	0.0040	0.0037	0.0016	6.3
ϕ_α-3	0.0428	0.7191	0.1968	0.0245	0.0127	0.0096	0.0015	0.0038	0.0023	5.7
ϕ_α-4	0.0315	0.5849	0.1885	0.0279	0.0116	0.0085	−0.0016	0.0029	0.0017	6.3
ϕ_α-5	0.1842	0.5318	0.1438	0.0338	0.0089	0.0086	0.0008	0.0044	0.0015	5.8
ϕ_α-6	0.3505	0.6128	0.1096	0.0292	0.0080	0.0082	0.0013	0.0024	0.0003	6.3
ϕ_β-1	0.2579	0.2393	0.3788	0.0295	0.0079	0.0062	0.0009	0.0019	0.0005	6.5
ϕ_β-2	0.4446	0.2222	0.4422	0.0286	0.0140	0.0063	0.0012	−0.0011	0.0018	5.8
ϕ_β-3	0.4859	0.7101	0.4509	0.0376	0.0168	0.0069	−0.0003	−0.0014	0.0023	5.1
ϕ_β-4	0.3981	0.3729	0.5913	0.0557	0.0151	0.0081	0.0011	0.0018	0.0001	4.7
ϕ_β-5	0.2136	0.3893	0.5297	0.0514	0.0133	0.0069	0.0039	0.0014	−0.0025	5.1
ϕ_β-6	0.1422	0.3232	0.4236	0.0406	0.0112	0.0073	0.0040	0.0030	−0.0014	5.7
$\sigma \times 10^4$	6–10	4–5	3–4	15–30	5–10	4–7	6–14	5–11	3–7	

[a] Anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Refinement of the Structure

The Fourier Refinement. New atomic coordinates were obtained from ρ_1 for all the carbon (22) and nitrogen (2) atoms; they were used to compute a new set of structure factors and the new phases were used to compute ρ_2. The phenyl groups in ρ_2 were all of the order of 5–6 eA^{-3} at peak height and their positions indicated considerable shifts from their ρ_1 coordinates. Coordinates from ρ_2 were used to begin a series of four structure-factor and related electron- and difference-density computations. Individual isotropic temperature factors were introduced after one cycle and the R factor went 0.46, 0.33, 0.19, and 0.16 for the four cycles of refinement. The last difference density showed clearly positive and negative regions in the vicinity of atomic positions, indicating anisotropic thermal motion. At this state it was decided to introduce anisotropic thermal parameters and to continue the refinement by the method of least squares.

The Least-Squares Refinement. A weighting scheme similar to that of Hughes was chosen for the least-squares refinement. For $|F_o| \leqslant 6.0$, the assigned weight was $1/(0.6)^2$, and for $|F_o| > 6.0$, it was $1/(0.1|F_o|)^2$. The initial parameters for least-squares refinement were those of the last Fourier cycle. These included isotropic temperatures factors which, before conversion to anisotropic, were varied with scale factor for two cycles of least-squares refinement. The shifts from the second cycle were small and isotropic refinement was terminated at $R = 0.122$.

Refinement including anisotropic thermal parameters proceeded by varying the thermal parameters of only six atoms per cycle. The four groups of six atoms chosen were the two phenyl and the two pyrrole plus methene bridge atom groups. The groups were chosen to be physically distinct, since only the temperature parameters of atoms adjacent to one another are likely to have interdependent shifts. Each group of thermal parameters (6 per atom, 36 total) was varied for one cycle. At the end of these four cycles, the R factor was 0.091.

A difference density was then computed based on the last structure-factor computation. The 15 largest peaks in this density, varying from 0.3 to 0.6 eA^{-3}, were located in the vicinity expected for the 15 hydrogen atoms of the asymmetric unit. They included the peak of the central hydrogen atom whose location was of particular interest. The hydrogen atoms, each with coordinates taken from the difference density and anisotropic thermal parameters identical with the atoms to which they were bonded, were included in the structure factors computed for the next least-squares cycle. This cycle varied the positions of all carbon and nitrogen atoms and the position and thermal parameters of the central hydrogen atom. The adjusted thermal parameters of the central hydrogen were not positive definite; consequently, the changes were ignored. A new set of structure factors was computed and these were used to compute a final difference density. The regions of all the atomic positions in this density were close to zero and, except for hydrogen atoms, no significant parameter shifts were indicated. The largest positive regions were of the order of 0.2 eA^{-3}. A final structure factor computation included all 39 atoms. The hydrogen atom coordinates for this computation incorporated shifts from the final difference density; all other atomic parameters were those of the last least-squares cycle. The final value of R was 0.056.

Results

The final coordinates and anisotropic thermal parameters of the carbon and nitrogen atoms are listed in Table I, the atoms therein labeled according to Figure 2. Hydrogen atom coordinates are given in Table II; their thermal parameters are the same as the atoms to which they bond. In Table III are listed the three

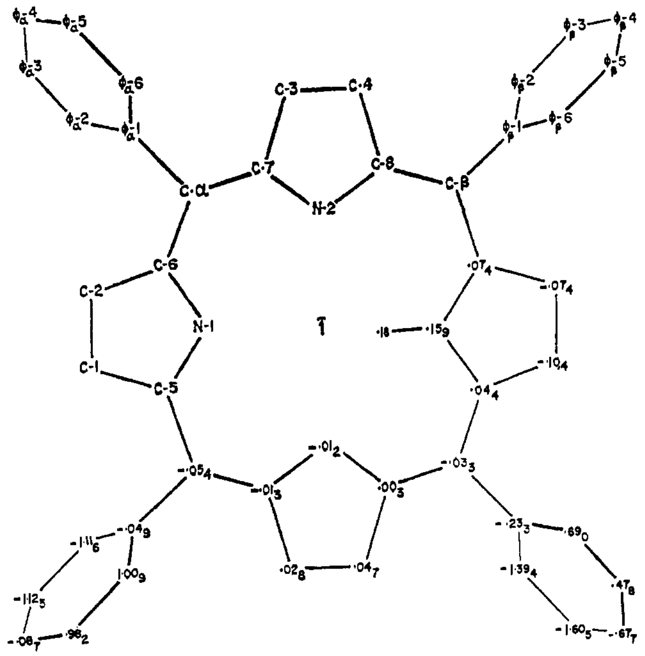

Figure 2. Deviations (in A) of the atoms of TPP from the nuclear least-squares plane (NLS). The labeling system of the atoms is also shown.

principal axes of the thermal ellipsoid of each atom, the direction cosines of each principal axis with respect to the direct cell axes, and the mean-square atomic displacement along each principal axis.

Table II. Final Hydrogen Atom Coordinates

Atom	x	y	z	Peak height, eA^{-3}
H(C-1)	0.109	0.922	0.592	0.6
H(C-2)	0.433	0.098	0.685	0.5
H(C-3)	0.263	0.671	0.903	0.5
H(C-4)	0.417	0.653	0.719	0.5
H(N-1)	0.082	0.988	0.922	0.4
H(ϕ_α-2)	0.229	0.900	0.179	0.4
H(ϕ_α-3)	0.079	0.239	0.780	0.5
H(ϕ_α-4)	0.076	0.468	0.774	0.5
H(ϕ_α-5)	0.180	0.426	0.136	0.5
H(ϕ_α-6)	0.466	0.577	0.075	0.6
H(ϕ_β-2)	0.467	0.844	0.587	0.6
H(ϕ_β-3)	0.361	0.731	0.422	0.5
H(ϕ_β-4)	0.453	0.423	0.669	0.4
H(ϕ_β-5)	0.123	0.449	0.557	0.3
H(ϕ_β-6)	0.017	0.665	0.621	0.5

A plane was fitted to the 24 carbon and nitrogen atoms of the porphyrin nucleus by the method of least squares.[6] The determined plane, which necessarily passes through the center of symmetry of the molecule, has the equation of $(3.799)x - (9.112)y + (3.042)z = 0$. In Figure 2, the perpendicular distances of the atoms from this plane are given. Least-squares planes were determined similarly for the individual phenyl and pyrrole groups of TPP. For comparison, the distances of the respective atoms from these planes are given in Table IV.

Table III. The Principal Axes of the Anisotropic Thermal Ellipsoids for the Carbon and Nitrogen Atoms of TPP. Direction Cosines of the Principal Axes Are with Respect to the Unit Cell Axes $\vec{a}, \vec{b}, \vec{c}$

Atom	cos $(\vec{a}, \vec{p})$	cos $(\vec{b}, \vec{p})$	cos $(\vec{c}, \vec{p})$	$8\overline{\pi^2\mu^2}$, A^2
C-1	0.4745	−0.7374	0.5873	5.42
	0.7050	0.5330	−0.0156	3.55
	−0.5268	0.4151	0.8092	3.63
C-2	0.7077	−0.6987	0.3710	5.16
	0.0680	0.6124	0.6510	3.50
	−0.7030	−0.3698	0.6626	3.69
C-3	0.7285	−0.8097	0.0415	5.29
	0.6173	0.5622	0.1673	3.18
	−0.2892	−0.1756	0.9856	4.40
C-4	0.7243	−0.8022	0.1150	5.10
	0.6231	0.5939	0.0801	3.00
	−0.2940	−0.0623	0.9903	4.20
C-5	0.2661	−0.6294	0.7853	4.21
	0.3121	0.7263	0.3378	2.75
	−0.9120	0.2764	0.5189	3.45
C-6	−0.5856	−0.6109	0.5952	3.87
	0.4390	0.7534	0.0845	2.69
	−0.6812	0.2432	0.7993	3.51
C-7	0.4290	−0.7237	0.6324	3.76
	0.4931	0.6389	0.2521	2.61
	−0.7567	0.2606	0.7327	3.61
C-8	−0.7412	0.0432	0.7804	4.11
	0.3816	0.6617	0.3644	2.44
	0.5520	−0.7485	0.5083	3.56
C-α	−0.0014	−0.1288	0.9875	4.08
	0.4266	0.7974	−0.0752	3.00
	−0.9044	0.5896	0.1388	3.56
C-β	−0.6024	−0.0410	0.8822	3.99
	0.4045	0.6906	0.2885	2.67
	0.6878	−0.7221	0.3724	3.71
N-1	−0.2540	−0.3605	0.9512	3.94
	0.3007	0.7499	0.3084	2.71
	0.9192	−0.5547	−0.0108	3.30
N-2	0.5104	−0.6098	0.6599	3.85
	0.3836	0.7600	0.1743	2.55
	−0.7693	0.2247	0.7311	3.63
ϕ_α-1	0.3411	−0.4745	0.8274	3.94
	−0.8669	−0.3098	0.3132	2.95
	−0.3636	0.8238	0.4664	3.57
ϕ_α-2	0.0660	0.0063	0.9620	5.48
	−0.9961	0.2509	0.2132	3.80
	−0.0585	−0.9685	0.1705	4.35
ϕ_α-3	−0.2448	0.6416	0.6949	5.91
	−0.8774	−0.2925	0.2954	3.49
	0.4124	−0.7088	0.6559	5.34
ϕ_α-4	−0.7162	0.8144	0.1251	6.34
	−0.6907	−0.5757	0.2375	3.30
	0.0977	−0.0726	0.9634	4.99
ϕ_α-5	0.8563	−0.4294	0.3322	5.83
	−0.3444	−0.8497	0.2807	3.38
	−0.3846	0.3060	0.9005	4.90
ϕ_α-6	0.2063	−0.3838	0.9089	5.02
	0.2111	0.8694	0.1392	3.17
	−0.9553	0.3109	0.3938	4.80
ϕ_β-1	0.9633	−0.4482	−0.0969	4.97
	0.2334	0.8106	0.2626	3.08
	−0.1320	−0.3769	0.9600	3.78
ϕ_β-2	−0.6285	0.8122	0.3250	6.63
	0.4940	−0.0626	0.7662	3.08
	−0.6008	−0.5800	0.5544	4.83
ϕ_β-3	−0.7124	0.7683	0.2988	8.71
	0.3712	−0.0566	0.8480	3.54
	−0.5955	−0.6366	0.4378	5.51
ϕ_β-4	−0.9589	0.4631	0.1200	9.60
	0.1116	0.3255	0.8410	4.50
	−0.2607	−0.8244	0.5275	6.43
ϕ_β-5	−0.9958	0.1088	0.2009	8.23
	−0.0162	0.5051	0.7713	2.98
	0.0888	−0.8561	0.6039	7.12
ϕ_β-6	0.9655	−0.2828	0.0958	6.34
	−0.1357	0.6141	0.7097	3.24
	−0.2227	−0.7366	0.6979	5.99

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[6] V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 12, 600 (1959).

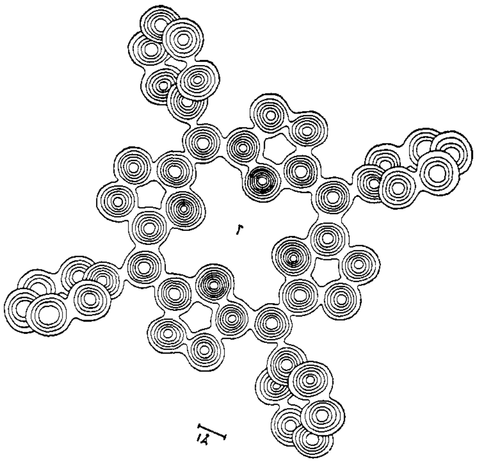

Figure 3. Final electron density for TPP viewed perpendicular to the NLS plane. Contours at 1-eA^{-3} intervals, starting at 1 eA^{-3}.

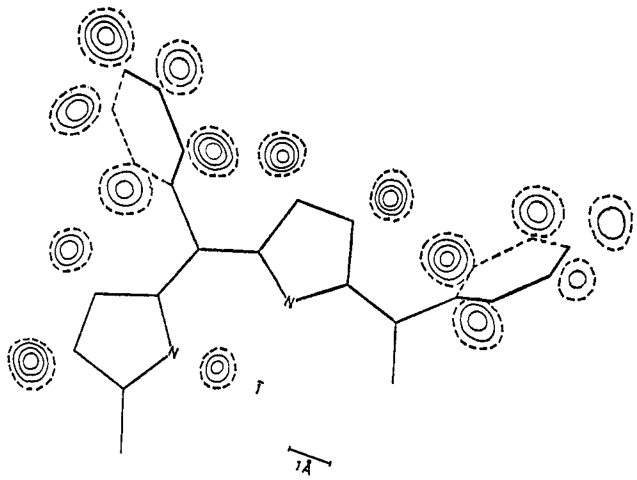

Figure 4. Hydrogen atom regions for TPP viewed perpendicular to the NLS plane. Contours at 0.1-eA^{-3} intervals, starting at 0.2 eA^{-3}, - - - -.

Figure 3 views the final electron density along the perpendicular to the least-squares plane of the porphyrin nucleus. The hydrogen atoms, obtained from the difference density preceding the final one, are seen in the same manner in Figure 4. In Figure 5, intramolecular distances and angles are given.

Table IV. The Atomic Deviations from the Least-Squares Planes of the Individual Pyrrole and Phenyl Rings

Atom	d, A	Atom	d, A
Pyrrole N-1		Pyrrole N-2	
N-1	0.006	N-2	0.008
C-1	0.006	C-3	0.006
C-2	−0.003	C-4	−0.001
C-5	−0.007	C-7	−0.008
C-6	−0.002	C-8	−0.004
σ =	0.005	σ =	0.006
Phenyl α		Phenyl β	
ϕ_α-1	0.001	ϕ_β-1	0.003
ϕ_α-2	0.003	ϕ_β-2	−0.002
ϕ_α-3	−0.002	ϕ_β-3	−0.001
ϕ_α-4	−0.004	ϕ_β-4	0.003
ϕ_α-5	0.008	ϕ_β-5	−0.002
ϕ_α-6	−0.006	ϕ_β-6	−0.002
σ =	0.004	σ =	0.003

Standard deviations of the carbon and nitrogen atom coordinates and the thermal parameters were obtained from the least-squares refinement. Their range is indicated at the end of Table I. The atomic parameters are determined most accurately in the porphyrin nucleus, less accurately in phenyl α, and least accurately in phenyl β. The standard deviation of the final electron and difference densities is estimated at 0.15–0.20 eA^{-3}. The standard deviations of the lengths and angles of the carbon–carbon and carbon–nitrogen bonds are approximately 0.005–0.01 A and 0.5–0.8°, respectively; those of the carbon–hydrogen and nitrogen–hydrogen bond distances are of the order of 0.05 A. Again, the accuracy is better for the bonds and angles of the porphyrin nucleus than for those of the phenyl groups.

Discussion of the Results

From Figure 2, it can be seen that the TPP molecule in the triclinic crystal form is significantly nonplanar in several respects: the phenyl and pyrrole rings are separately planar within the error of their determinations (see Table IV) but they are rotated and inclined with respect to the nuclear least-squares (NLS) plane of the molecule.

The N-1 pyrrole groups are tilted out of the NLS plane about an axis lying in the plane and passing through the C-2–C-6 and C-1–C-5 bonds. The perpendicular to the N-1 pyrrole plane makes a 6.6° angle with that of the NLS plane. The N-2 pyrrole groups are only tilted 1.4° with respect to the NLS plane about an axis through C-7 and the C-4–C-8 bond. The former and larger tilt causes the central hydrogen atom of one N-1 pyrrole group to lie 0.18 A above the NLS plane and that of the centrosymmetrically related group to lie the same distance below. Consequently, the distance between the two central hydrogen atoms (2.36 A) is about 0.2 A greater than it would be for a planar conformation.

As the relationships of the two types of pyrrole group to the NLS plane differ, so do those of the two types of phenyl group. The 1–4 axis of phenyl α is tilted much more with respect to the NLS plane than is the same axis of phenyl β, and in a different manner. The phenyl α 1–4 axis makes a 9.1° angle with its projection onto the NLS plane and intercepts the plane near C-α; the corresponding angle for the phenyl β axis is only 0.8°. If the phenyl groups were coplanar with the NLS plane, then to transform them to their true positions, they must be first tilted along their 1–4 axis so that atoms 1 and 4 are in their correct positions, and then the phenyl groups must be rotated about these axes. The required angles of tilt are given above; the rotation angles are 61.0° for phenyl α and 63.1° for phenyl β.

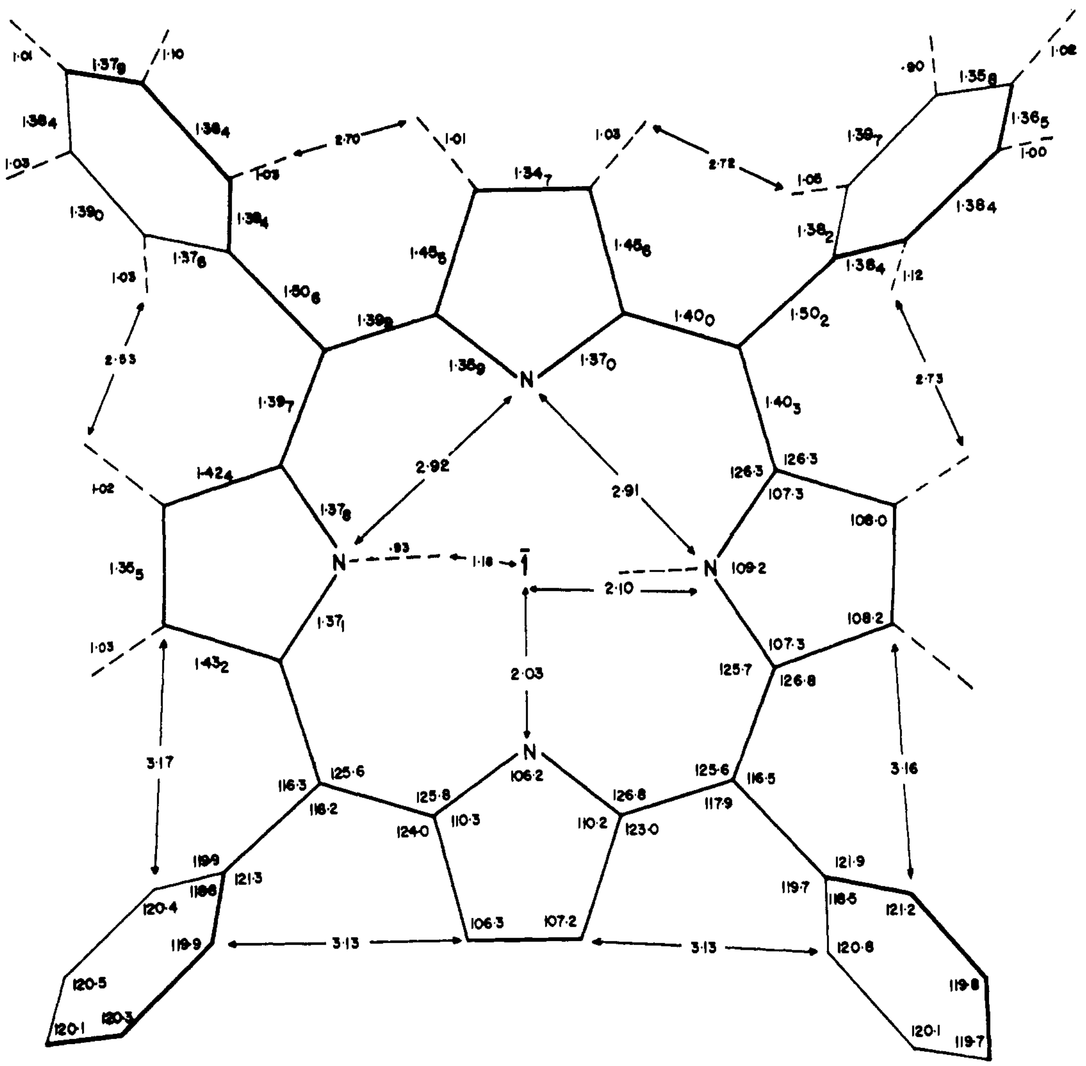

Figure 5. Distances (in A) and bond angles (in degrees) for TPP. Bonds to hydrogen atoms are broken.

The phenyl groups are thus rotated more than 60° out of the NLS plane and, furthermore, the α groups are tilted so the ϕ_α-4 lies 0.68 A from the plane. The phenyl rotation is as expected, since otherwise the phenyl hydrogen atoms proximal to the porphyrin ring would interfere with the pyrrole hydrogen atoms. The tilt, however, is unexpected. Conceivably, it could result from bond angle requirements of the central π-bonding system (preserving individual planar atoms, as is observed). However, it is more likely due to the manner in which the molecules pack. The closest intermolecular contact (3.40 A, see Figure 6) occurs between N-1 of one molecule and ϕ_α-2 of the neighboring molecule along the $\vec{a}$ direction.

Also of note is the packing mode of the pyrrole groups of molecules adjacent along the $\vec{a}$ direction. If the molecules are viewed along the perpendicular to the NLS plane, it is seen that an N-1 and an N-2 pyrrole group of one molecule lie, respectively, perpendicularly above an N-2 and N-1 group of the molecule below. The pyrrole pair in the upper molecule is related by a center of symmetry and an $\vec{a}$ translation to the lower pair. The closest intermolecular contact between these pyrrole groups is 3.63 A, from C-3 in one molecule to N-1 of the other. This contact and the way in which phenyl groups of neighboring molecules are related are shown in Figure 6.

Temperature-factor anisotropy (see Table III) is least for atoms of the porphyrin ring; it increases for the phenyl α atoms and is largest for the phenyl β atoms. The mean-square atomic displacements vary from atom to atom in the same manner as do the standard deviations of the atomic parameters. The mean-square displacement of a particular atom in the radial direction (toward or away from the molecular center) is usually less than in its tangential directions. The above properties of the thermal motion may probably be partly attributed to quasi-rigid angular oscillations about the molecular center. The larger mean-square displacements of phenyl β relative to phenyl α are probably a consequence of the closer packing of phenyl α.

From Figure 5, it appears that the atoms of the *interior ring* of the porphyrin skeleton form a heterocyclic aromatic system (C-5, N-1, C-6, C-α, C-7, N-2, C-8, C-β). The carbon–carbon bond distances of this system average 1.400 ± 0.002 A and the carbon–nitrogen distances average 1.370 ± 0.007. Furthermore, although the atoms of this system do not lie in a plane, the bonding about C-5, C-6, C-α, C-7, C-8, C-β is in

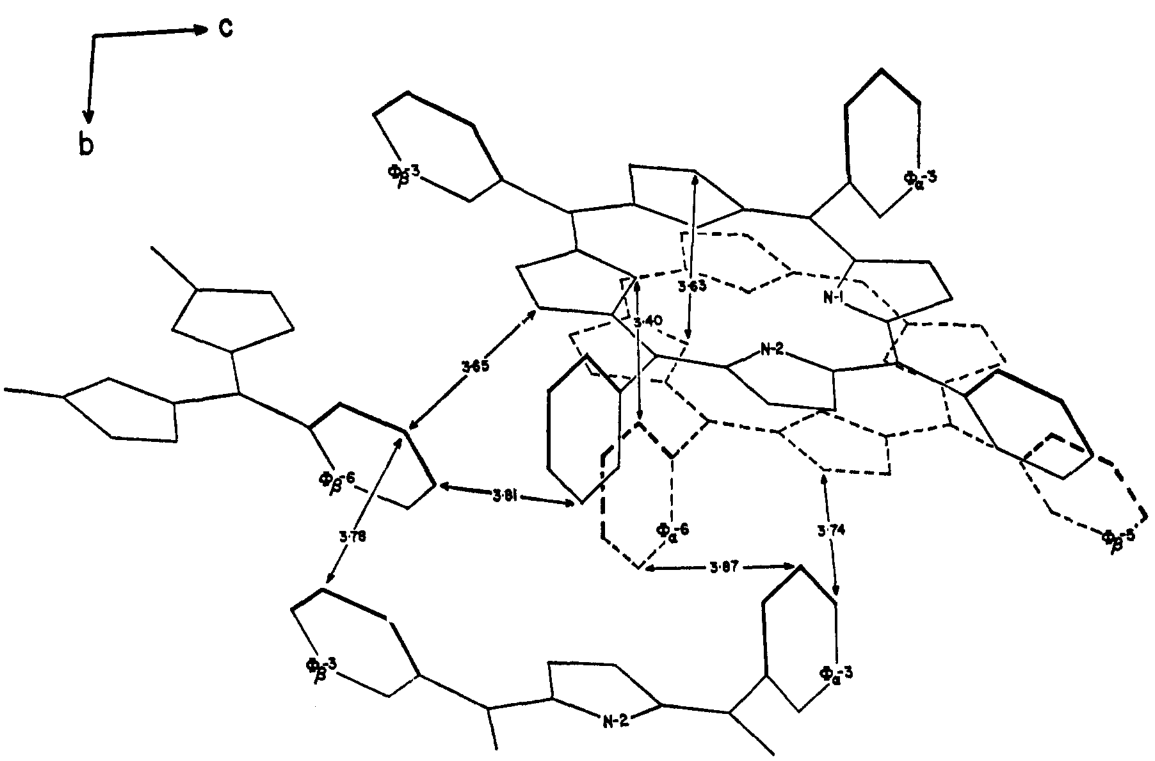

Figure 6. Packing of TPP molecules of neighboring unit cells viewed in the $-a^*$ direction. In relation to the molecule shown completely, the broken molecule is translated along $-a$, the molecule on the left is translated along $-c$, and the molecule in the foreground is translated along b and a. Close intermolecular contacts are given (in A).

each case planar (sum of the bond angles equals 360°). The C-1–C-2 and C-3–C-4 bonds of the pyrroles correspond closely in length to double bonds and to this extent these atoms appear to be isolated from the inner aromatic system with the bonds joining these four atoms to the interior ring being shorter than normal single bonds. Finally, the phenyl groups appear to be electronically isolated from the inner ring system; the phenyls are bound to the bridge positions through apparently shortened single bonds.

Concluding Remarks

In closing, it should be interesting to note that the porphyrin structure herein described corresponds closely with the structure expected of a hybrid of the two predominant classical resonance forms of the porphyrin molecule. These two forms are shown in Figure 7a and b; Figure 7c is an attempt at representing the expected nature of the hybrid. Also given in Figure 7c are the carbon–carbon and carbon–nitrogen distances of the independent pyrrole groups (observed mean distances), the carbon–carbon distance involving all four methene bridges (an observed average with a standard deviation of ±0.002 A) and the differences between the average distances of the independent pyrroles. Clearly, *in each case*, corresponding distances differ in the manner expected of the hybrid. The C-1–C-2 and the C-3–C-4 bond lengths of the pyrroles differ only by about the expected error but the other differences average about three times the standard error. Since a corresponding trend can also be detected in considering the bond angles, the behavior is probably significant.

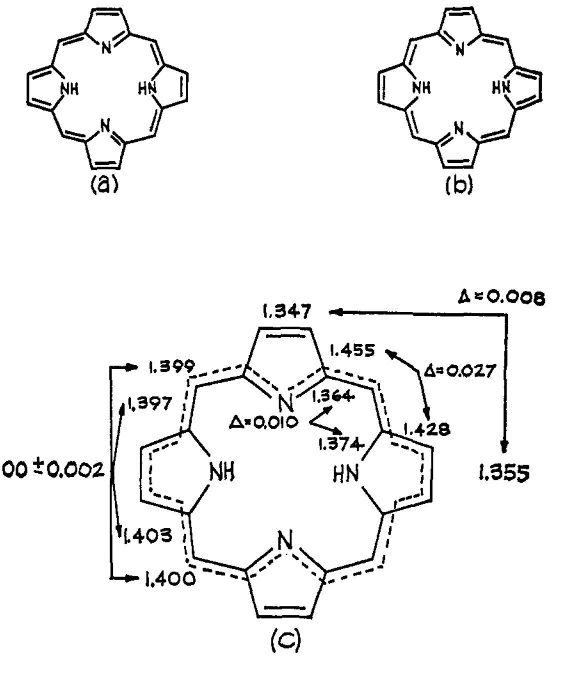

Figure 7. (a and b) Two dominant resonance structures of TPP. (c) Expected nature of the hybrid; the mean observed distances of independent pyrroles and differences (Δ) between corresponding bonds are also shown.

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