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Crystal and Molecular Structure of Methyl Pheophorbide with Applications to the Chlorophyll Arrangement in Photosynthetic Lamellae[1]

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Abstract: The structure of methyl pheophorbide *a*, $C_{36}H_{38}N_4O_5$, a derivative of chlorophyll, has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1$, with a = 8.035 (4), b = 28.531 (20), and c = 7.320 (4) Å, β = 110.96 (6)°, and Z = 2. The structure was solved by trial-and-error methods and refined by block-matrix techniques to a conventional R of 0.051 for 1616 independent nonzero reflections measured with a manual diffractometer. Thirty-five of the 38 hydrogen atoms were included in these calculations. The hydrogen atoms bonded to nitrogen are disordered. There are no chlorin–chlorin intermolecular contacts less than 3.5 Å. A model for the arrangement of chlorophyll molecules in photosynthetic lamellae is proposed in which nonparallel chlorophyll molecules are related by a 2_1 screw axis and are linked by water molecules.

Lack of sufficiently large crystals has hindered X-ray diffraction studies of chlorophyll, but structures have been reported for several more or less related compounds including porphin,[2] two modifications of tetraphenylporphin,[3,4] a magnesium tetraphenylporphin hydrate,[5] phthalocyanin,[6] and a magnesium phthalocyaninpyridine hydrate.[7] More similar to chlorophyll are a phyllochlorin ester[8] which has the chlorin moiety of chlorophyll (*i.e.*, a saturated bond in ring IV) but which lacks the fifth isocyclic ring, and vanadyldeoxophylloerythroetioporphyrin[9] which has the isocyclic ring but is unsaturated in ring IV.[10]

We became interested in methyl pheophorbide *a* ($C_{36}H_{38}N_4O_5$, Figure 1) because of its structural similarity to chlorophyll and the availability of crystals. It differs from chlorophyll *a* only by having two hydrogen atoms rather than magnesium in the center and a methyl ester rather than a phytyl ($C_{20}H_{39}$) ester on the side chain off ring IV.[11] This paper reports our results concerning the crystal structure and molecular geometry of this substance, as well as a proposed model for the packing arrangement of chlorophyll in photosynthetic lamellae.

Experimental Section

Methyl pheophorbide *a* (MePPb) was obtained from R. B. Woodward in 1961. The red-violet flakes, too small for X-ray diffraction measurements, were recrystallized from a 1:1 benzene–methanol solution by slow evaporation to dryness in the dark. The resultant opaque crystals resembled soft lumps of coal with dimensions as great as 2 mm. A wedge-shaped fragment which measured 0.2 × 0.1 × 0.05 mm was detached with a razor blade and used for both the determination of cell dimensions and the collection of data.

Weissenberg photographs of this fragment indicated Laue symmetry 2/m. The intrinsic molecular noncentricity and the systematic absences on Weissenberg photographs (0*k*0, $k \neq 2n$) imply that the probable space group is $P2_1$. Both the cell dimensions and intensity data were measured with a General Electric XRD-5 X-ray diffractometer equipped with a copper tube, a manual quarter-circle Eulerian-cradle goniostat, and a 0.003-in. thick nickel filter at the receiving slit. The distances from the crystal to the X-ray source and to the receiving slit are 14.5 and 17.8 cm, respectively. The crystal was aligned with (101) normal to the instrumental φ axis. The χ, φ, and 2θ values of 25 reflections, for each of which the α doublet was resolved (λ = 1.5405 Å for Cu Kα_1), were used in a least-squares refinement of the unit cell parameters and crystal orientation. The unit cell dimensions (at room temperature, ~23°) are a = 8.035 ± 0.004, b = 28.531 ± 0.020, and c = 7.320 ± 0.004 Å, and β = 110.96 ± 0.06°. A density of 1.25 ± 0.01 g/cm³ was obtained from flotation in aqueous solutions of $ZnBr_2$, KBr, and NaI. The calculated density is 1.285 for a formula weight of 606.7, Z = 2, and V = 1567 Å³.

Each reflection in half a sphere in reciprocal space corresponding to spacing ≧1.006 Å ($2\theta \leqq 100°$) was counted for 10 sec with crystal and counter stationary and at a takeoff angle of 4°. Individual backgrounds were measured for reflections seriously affected by streaking from lower orders; for the rest, backgrounds were taken from a plot of background as a function of Bragg angle. Of the 3214 reflections measured, the intensities of 3103 were above background. The rms difference between $I(hkl)$ and $I(h\bar{k}l)$ was 6.2% of $I(hkl)$. The intensities of the Bijvoet pairs were averaged to produce 1662 independent reflections of which 1616 had net intensities greater than zero. The intensities of three standard reflections, measured periodically, varied by less than ±2%. No correction was made for absorption (μ = 6.9 cm⁻¹).

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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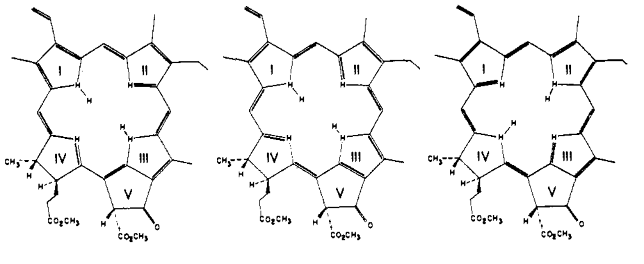

1a 1b II

Figure 1. Three resonance structures of two tautomers of methyl pheophorbide *a*.

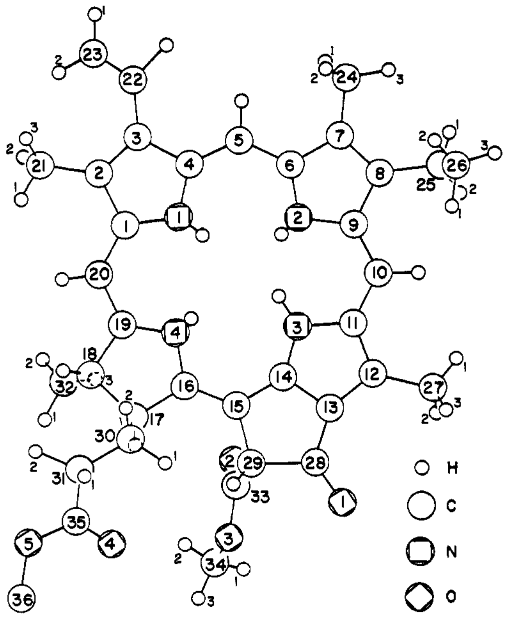

Figure 2. Numbering scheme for methyl pheophorbide *a*. Hydrogen atoms are numbered by the atoms to which they are bonded.

Scattering factors of Stewart, Davidson, and Simpson[12] were used for hydrogen and of Cromer and Mann[13] for other atoms. The function minimized by least squares was $(R_2)^2 = \Sigma w(\Delta F)^2/\Sigma w|F_o|^2$. The weight w was zero if $I = 0$. Otherwise it was calculated from the larger of the counting statistics and the difference between duplicate measurements.[14]

Computer programs used on the CDC-6600 computer include: WILSON, an unpublished Wilson-plot program by Maddox and Maddox; R. E. Long's phase determination program;[15] LS200, our unpublished least-squares program; and Johnson's ORTEP.[16]

The structure was found by a trial-and-error method. The Patterson function indicated the orientation of the plane of the molecule. A predicted model of the central part of the molecular structure was systematically translated and rotated in this orientation in search of the best agreement of observed and calculated structure factors for 147 low-angle reflections. The best agreement found was $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.64$. One of the two models which gave this value eventually refined, by a combination of Fourier and least-squares methods, to the structure presented below. All 45 heavy atoms were found in this way, and with isotropic temperature factors, R was reduced to 0.128.

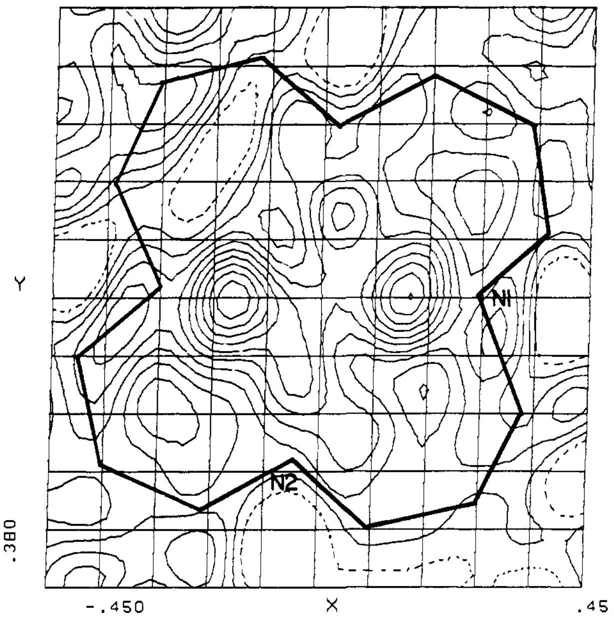

Figure 3. Section of ΔF Fourier in the chlorin plane. The contour interval is 0.0243 e/Å^3, with zero contour broken and negative contours omitted. The heavy lines indicate the bonds connecting the pyrrole nitrogen and methine carbon atoms.

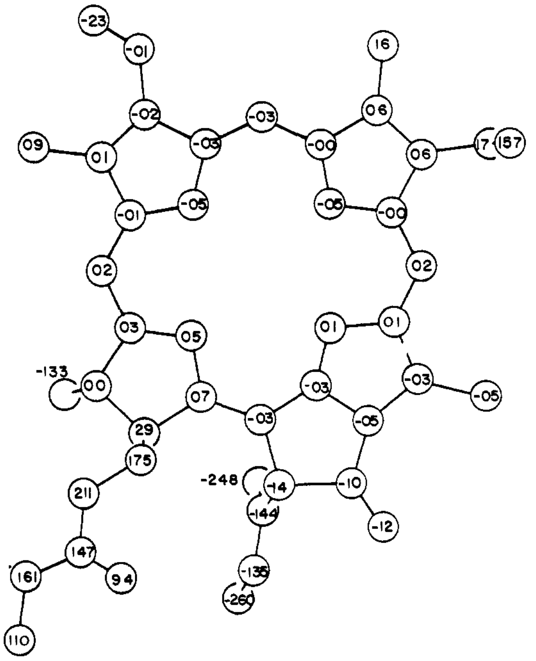

Figure 4. Deviations (×100 in Å) from the least-squares plane through atoms N-1–N-4, C-1–C-16, C-19 and C-20.

With ΔF Fourier maps, 31 of the 38 hydrogen atoms were recognized, and four other small peaks appeared in the center near the four nitrogen atoms. Anisotropic temperature factors were assigned to the 45 heavy atoms, and the 31 hydrogen atoms were included with $B = 6$ (but not refined); R dropped to 0.069. The two hydrogen atoms on C-23 (Figure 2) were not observed but were inserted at calculated positions. The three hydrogen atoms on C-36 were not located and were not included in the calculations. Half-hydrogen atoms were inserted on the four nitrogen atoms. Attempts to refine all the coordinates of the hydrogen atoms were unsuccessful. In the final calculations, 15 of the hydrogen atoms were held at fixed positions (1.0 Å from their respective carbon atoms), and common thermal parameters were assigned to nine groups of hydrogen atoms.

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Table I. Coordinates and Thermal Parameters for Atoms Other than Hydrogen[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N-1	0.2659 (6)	0.5000	0.7105 (7)	3.1 (2)	5.0 (2)	6.2 (2)	0.6 (2)	1.7 (2)	0.6 (2)
N-2	−0.0450 (8)	0.4385 (2)	0.4893 (8)	5.5 (3)	3.5 (3)	7.2 (3)	0.0 (3)	2.2 (2)	−0.3 (2)
N-3	−0.2717 (7)	0.5119 (2)	0.4655 (6)	3.1 (2)	5.6 (3)	5.6 (2)	−0.2 (2)	0.8 (2)	−0.4 (2)
N-4	0.0265 (8)	0.5785 (2)	0.6912 (9)	3.5 (2)	4.6 (3)	5.8 (3)	0.1 (3)	1.4 (2)	−0.3 (2)
C-1	0.3873 (7)	0.5327 (2)	0.8123 (8)	3.4 (3)	5.2 (3)	5.5 (3)	0.5 (2)	1.4 (2)	0.8 (2)
C-2	0.5617 (7)	0.5109 (2)	0.8787 (8)	3.7 (3)	5.6 (3)	5.4 (3)	0.8 (2)	1.7 (2)	1.2 (2)
C-3	0.5381 (7)	0.4661 (2)	0.8143 (8)	4.1 (3)	5.3 (3)	6.5 (3)	1.2 (2)	2.1 (2)	1.4 (2)
C-4	0.3486 (7)	0.4580 (2)	0.7087 (7)	3.9 (3)	5.7 (3)	5.6 (3)	0.5 (2)	1.6 (2)	1.1 (2)
C-5	0.2703 (7)	0.4168 (2)	0.6244 (9)	4.6 (3)	4.7 (3)	7.1 (3)	0.2 (2)	2.2 (2)	0.3 (2)
C-6	0.0875 (8)	0.4068 (2)	0.5278 (9)	5.9 (3)	4.6 (3)	6.6 (3)	−0.1 (3)	2.8 (3)	0.1 (2)
C-7	0.0205 (10)	0.3615 (2)	0.4543 (10)	6.6 (4)	5.0 (3)	8.0 (4)	0.1 (3)	2.8 (3)	−0.2 (3)
C-8	−0.1594 (10)	0.3661 (2)	0.3689 (11)	7.1 (4)	4.9 (3)	8.1 (4)	−0.8 (3)	2.4 (3)	−1.0 (2)
C-9	−0.2003 (8)	0.4148 (2)	0.3928 (9)	5.1 (3)	4.8 (3)	6.4 (3)	−0.9 (2)	1.6 (2)	−0.5 (2)
C-10	−0.3683 (8)	0.4340 (2)	0.3340 (9)	4.8 (3)	5.5 (3)	6.2 (3)	−0.9 (2)	1.8 (2)	−0.3 (2)
C-11	−0.4068 (7)	0.4807 (2)	0.3640 (8)	4.0 (3)	5.5 (3)	5.8 (3)	−0.4 (3)	1.0 (2)	0.0 (2)
C-12	−0.5675 (7)	0.5051 (2)	0.3050 (8)	4.1 (3)	6.2 (3)	5.7 (3)	−0.3 (3)	1.8 (2)	0.7 (2)
C-13	−0.5284 (6)	0.5511 (2)	0.3719 (7)	3.2 (3)	6.0 (3)	4.7 (2)	−0.1 (2)	0.6 (2)	0.2 (2)
C-14	−0.3430 (7)	0.5537 (2)	0.4688 (7)	3.5 (3)	5.2 (3)	5.0 (3)	−0.1 (2)	1.1 (2)	0.0 (2)
C-15	−0.2812 (6)	0.5974 (2)	0.5470 (7)	3.5 (2)	5.5 (3)	5.1 (2)	1.0 (2)	1.0 (2)	0.1 (2)
C-16	−0.1075 (7)	0.6094 (2)	0.6618 (8)	3.9 (2)	4.3 (2)	5.4 (3)	0.3 (2)	1.4 (2)	0.0 (2)
C-17	−0.0474 (7)	0.6541 (2)	0.7714 (8)	3.2 (2)	5.4 (3)	6.0 (3)	0.6 (2)	1.4 (2)	0.0 (2)
C-18	0.1576 (7)	0.6508 (2)	0.8282 (9)	3.3 (2)	5.9 (3)	5.5 (3)	−0.2 (2)	1.1 (2)	−0.4 (2)
C-19	0.1802 (7)	0.6004 (2)	0.7889 (8)	3.5 (3)	3.8 (2)	5.9 (3)	0.1 (2)	1.4 (2)	0.1 (2)
C-20	0.3476 (7)	0.5782 (2)	0.8467 (8)	3.2 (2)	5.3 (3)	5.9 (3)	−0.2 (2)	1.6 (2)	0.0 (2)
C-21	0.7292 (8)	0.5345 (3)	0.9996 (11)	3.5 (3)	6.9 (4)	7.5 (4)	−0.5 (3)	1.4 (3)	0.8 (3)
C-22	0.6729 (9)	0.4292 (3)	0.8426 (11)	3.6 (3)	8.4 (4)	9.2 (4)	1.3 (3)	1.6 (3)	1.4 (3)
C-23	0.8346 (14)	0.4349 (4)	0.8980 (17)	8.9 (6)	10.7 (6)	15.8 (9)	2.1 (5)	1.5 (6)	−2.4 (6)
C-24	0.1260 (11)	0.3174 (2)	0.4722 (14)	8.5 (5)	5.6 (4)	11.8 (6)	0.3 (3)	4.1 (4)	−0.7 (3)
C-25	−0.2969 (10)	0.3287 (2)	0.2756 (13)	7.9 (4)	5.2 (3)	11.4 (5)	−1.0 (3)	2.9 (4)	−1.3 (3)
C-26	−0.3578 (13)	0.3056 (3)	0.4197 (18)	10.4 (6)	7.9 (5)	15.3 (8)	−3.3 (5)	5.7 (6)	−2.3 (5)
C-27	−0.7511 (7)	0.4849 (3)	0.1883 (10)	3.8 (3)	8.8 (4)	7.4 (3)	−1.8 (3)	0.2 (3)	0.6 (3)
C-28	−0.6044 (8)	0.5963 (2)	0.3759 (8)	4.2 (3)	6.6 (3)	5.3 (3)	0.7 (2)	1.3 (2)	0.8 (2)
C-29	−0.4432 (6)	0.6298 (2)	0.4868 (8)	3.7 (3)	5.8 (3)	5.5 (3)	0.5 (2)	1.1 (2)	0.2 (2)
C-30	−0.1023 (8)	0.6560 (2)	0.9537 (9)	4.2 (3)	5.6 (3)	6.3 (3)	0.0 (2)	1.8 (2)	−0.3 (2)
C-31	−0.0409 (10)	0.6985 (3)	1.0813 (10)	5.3 (4)	7.1 (4)	7.0 (4)	0.3 (3)	2.3 (3)	−1.0 (3)
C-32	0.2272 (11)	0.6834 (3)	0.7085 (13)	5.6 (4)	5.6 (3)	10.1 (5)	−0.4 (3)	4.2 (4)	0.0 (3)
C-33	−0.4347 (7)	0.6664 (2)	0.3453 (10)	3.3 (3)	6.1 (3)	8.0 (4)	1.0 (2)	1.1 (3)	0.9 (3)
C-34	−0.5272 (12)	0.7416 (3)	0.2155 (15)	9.1 (5)	4.9 (3)	13.0 (6)	−0.1 (3)	3.2 (4)	1.7 (4)
C-35	−0.1337 (11)	0.7419 (3)	0.9924 (12)	6.8 (4)	7.1 (4)	8.2 (4)	−1.2 (4)	2.5 (3)	−2.2 (4)
C-36	−0.1471 (21)	0.8255 (3)	1.0239 (19)	25.5 (14)	5.8 (4)	14.4 (8)	0.4 (6)	8.6 (9)	−0.1 (5)
O-1	−0.7581 (5)	0.6092 (2)	0.3103 (7)	3.5 (2)	8.6 (2)	8.0 (2)	1.5 (2)	1.0 (2)	1.0 (2)
O-2	−0.3617 (7)	0.6620 (2)	0.2286 (9)	9.2 (3)	9.3 (3)	12.0 (4)	2.9 (2)	6.8 (3)	3.6 (3)
O-3	−0.5272 (6)	0.7040 (2)	0.3527 (7)	7.6 (3)	5.8 (2)	9.2 (3)	1.8 (2)	3.0 (2)	0.4 (2)
O-4	−0.2666 (10)	0.7448 (2)	0.8529 (11)	10.6 (4)	8.8 (3)	11.1 (4)	2.5 (3)	0.9 (3)	0.1 (3)
O-5	−0.0574 (9)	0.7796 (2)	1.0903 (10)	13.8 (5)	8.1 (3)	12.8 (4)	−2.3 (3)	3.8 (4)	−3.6 (3)

[a] The anisotropic temperature factor is $\exp(-\Sigma_i\Sigma_j h_i h_j b_i b_j B_{ij}/4)$, where b_i is the length of the ith reciprocal axis. The numbers in parentheses here and in the other tables are the estimated standard deviations of the least significant digit(s).

Half the atoms were refined in each cycle. On the last two cycles, no parameter shifted as much as 0.1σ. With the parameters listed in Tables I and II, $R = 0.051$ for 1616 nonzero structure factors and $R = 0.053$ for all 1662 data; $R_2 = 0.063$. The standard deviation of an observation of unit weight is 2.14. This high value is believed to reflect a combination of effects: an inadequate description of the thermal motion, the incomplete treatment of the hydrogen atoms, and probably an underestimation of systematic errors in the data. Average values of $w(\Delta F)^2$ are not correlated with intensity or Bragg angle. The highest peak in the final ΔF map is 0.15 e/Å^3.[17]

Extensive calculations were made to establish the positions of the two hydrogen atoms at the center of the molecule. Following the technique of La Placa and Ibers[18] we found the positions of the four peaks to be insensitive to the number of terms in the ΔF synthesis, and in the best case the ratio of peak height to estimated standard deviation averaged 6.0. A final ΔF map based on data for which $\sin\theta/\lambda < 0.47$ and shown in Figure 3 agrees closely with results earlier in the analysis. It shows the four peaks and suggests somewhat greater occupancy adjacent to rings I and III than at II and IV, perhaps in the ratio 0.6/0.4.

An attempt was made to check the absolute configuration using the anomalous dispersion effect,[19] using the 3214 unaveraged data, but the result was not decisive. The configuration proposed by Fleming[20] is used in all tables and figures.

In retrospect, we examined the trial structure which led to the final result. In the refinement the center of the molecule shifted 0.21 Å and the molecule rotated about 10°. Shifts of atoms range from 0.17 to 0.74 Å.

Discussion

Bond distances and angles are listed in Tables III and IV, according to the numbering shown in Figure 2. The chlorin ring is nearly flat, but the departures from planarity are statistically significant. The deviations from the least-squares plane through atoms N-1–N-4, C-1–C-16, and C-19 and C-20 are presented in Figure 4. Rings I, II, and III are each planar to within 0.01 Å and ring V is planar to within 0.02 Å. Ring IV is not

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(17) A table of observed and calculated structure factor amplitudes 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-72-3613. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(18) S. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

(19) Dispersion corrections, estimated from absorption coefficients, were $\Delta f'' = 0.011$, 0.022, and 0.037 for C, N, and O, respectively.

(20) I. Fleming, *Nature (London)*, **216**, 151 (1967).

Table II. Coordinates and Isotropic Thermal Parameters for Hydrogen Atoms[a]

Atom	x	y	z	B, A^2
H-1–N-1	0.163 (12)	0.499 (3)	0.680 (12)	2.4 (11)
H-1–N-2	−0.038 (15)	0.458 (3)	0.528 (15)	2.4
H-1–N-3	−0.159 (12)	0.502 (3)	0.499 (11)	2.4
H-1–N-4	0.016 (19)	0.562 (4)	0.667 (18)	2.4
H-1–C-5	0.350	0.389	0.639	4.8 (4)
H-1–C-10	−0.471 (7)	0.414 (2)	0.252 (7)	4.8
H-1–C-17	−0.101 (7)	0.677 (2)	0.697 (8)	4.8
H-1–C-18	0.229 (7)	0.655 (2)	0.961 (8)	4.8
H-1–C-20	0.432 (7)	0.601 (2)	0.903 (7)	4.8
H-1–C-21	0.702 (8)	0.565 (3)	1.052 (9)	7.2 (8)
H-2–C-21	0.799 (9)	0.545 (2)	0.946 (9)	7.2
H-3–C-21	0.811 (9)	0.517 (2)	1.122 (9)	7.2
H-1–C-22	0.659 (6)	0.386 (2)	0.835 (7)	4.8
H-1–C-23	0.913	0.407	0.914	10.4 (8)
H-2–C-23	0.884	0.467	0.930	10.4
H-1–C-24	0.224	0.326	0.425	13.5 (17)
H-2–C-24	0.193	0.314	0.615	13.5
H-3–C-24	0.038 (12)	0.291 (4)	0.398 (14)	13.5
H-1–C-25	−0.247	0.306	0.206	10.4
H-2–C-25	−0.403	0.342	0.168	10.4
H-1–C-26	−0.438 (11)	0.331 (3)	0.471 (14)	12.7 (15)
H-2–C-26	−0.257	0.295	0.538	12.7
H-3–C-26	−0.431	0.277	0.366	12.7
H-1–C-27	−0.746	0.454	0.126	15.8 (20)
H-2–C-27	−0.802	0.508	0.078	15.8
H-3–C-27	−0.838	0.485	0.258	15.8
H-1–C-29	−0.450	0.646	0.605	4.8
H-1–C-30	−0.244 (12)	0.652 (3)	0.901 (12)	10.4
H-2–C-30	−0.033 (11)	0.633 (3)	1.034 (12)	10.4
H-1–C-31	−0.074 (12)	0.694 (3)	1.155 (14)	10.4
H-2–C-31	0.113 (12)	0.712 (3)	1.137 (11)	10.4
H-1–C-32	0.196 (7)	0.718 (2)	0.738 (7)	5.6 (7)
H-2–C-32	0.329 (8)	0.681 (2)	0.735 (9)	5.6
H-3–C-32	0.162 (7)	0.673 (2)	0.563 (9)	5.6
H-1–C-34	−0.610 (15)	0.738 (4)	0.083 (19)	16.7 (22)
H-2–C-34	−0.408	0.749	0.209	16.7
H-3–C-34	−0.565	0.770	0.271	16.7

[a] Coordinates listed without standard deviations were not refined. Thermal parameters listed without standard deviations were constrained to be the same as one of the preceding ones.

Table III. Bond Distances (Å) in Methyl Pheophorbide

Atoms	Distance	Atoms	Distance
N-1–C-1	1.364 (8)	C-19–C-20	1.408 (7)
N-1–C-4	1.372 (8)	C-22–C-23	1.225 (13)
N-2–C-6	1.348 (8)	C-25–C-26	1.469 (14)
N-2–C-9	1.373 (8)	C-28–C-29	1.580 (8)
N-3–C-11	1.394 (8)	C-28–O-1	1.211 (7)
N-3–C-14	1.328 (7)	C-29–C-33	1.490 (9)
N-4–C-16	1.347 (8)	C-30–C-31	1.503 (10)
N-4–C-19	1.340 (8)	C-31–C-35	1.471 (11)
C-1–C-2	1.448 (7)	C-33–O-2	1.203 (9)
C-1–C-20	1.381 (8)	C-33–O-3	1.318 (8)
C-2–C-3	1.353 (8)	C-34–O-3	1.469 (10)
C-2–C-21	1.482 (9)	C-35–O-4	1.187 (11)
C-3–C-4	1.459 (7)	C-35–O-5	1.315 (10)
C-3–C-22	1.472 (9)	C-36–O-5	1.491 (12)
C-4–C-5	1.371 (8)	N-1–H-1–N-1	0.78 (9)
C-5–C-6	1.412 (8)	N-2–H-1–N-2	0.62 (10)
C-6–C-7	1.429 (9)	N-3–H-1–N-3	0.90 (9)
C-7–C-8	1.361 (10)	N-4–H-1–N-4	0.51 (11)
C-7–C-24	1.496 (10)	C-10–H-1–C-10	1.01 (5)
C-8–C-9	1.453 (9)	C-17–H-1–C-17	0.87 (5)
C-8–C-25	1.511 (10)	C-18–H-1–C-18	0.94 (5)
C-9–C-10	1.376 (8)	C-20–H-1–C-20	0.93 (5)
C-10–C-11	1.404 (9)	C-21–H-1–C-21	1.01 (7)
C-11–C-12	1.392 (8)	C-21–H-2–C-21	0.85 (7)
C-12–C-13	1.398 (8)	C-21–H-3–C-21	1.04 (6)
C-12–C-27	1.528 (8)	C-22–H-1–C-22	1.24 (5)
C-13–C-14	1.404 (7)	C-24–H-3–C-24	1.05 (10)
C-13–C-28	1.431 (8)	C-26–H-1–C-26	1.12 (9)
C-14–C-15	1.388 (8)	C-30–H-1–C-30	1.07 (9)
C-15–C-16	1.390 (7)	C-30–H-2–C-30	0.93 (8)
C-15–C-29	1.526 (7)	C-31–H-1–C-31	0.69 (9)
C-16–C-17	1.492 (8)	C-31–H-2–C-31	1.21 (9)
C-17–C-18	1.551 (7)	C-32–H-1–C-32	1.05 (6)
C-17–C-30	1.550 (8)	C-32–H-2–C-32	0.77 (6)
C-18–C-19	1.490 (8)	C-32–H-3–C-32	1.05 (6)
C-18–C-32	1.515 (10)	C-34–H-1–C-34	0.97 (13)

planar. Atoms C-17 and C-18 are, respectively, 0.22 Å above and 0.04 Å below the plane of atoms N-4, C-16, and C-19. This chlorin conformation is similar to that found in the phyllochlorin ester.[8]

The inner hydrogen atoms of the triclinic modification of tetraphenylporphine[3] (tri-TPP) are on diagonally opposite pyrrole rings. The diagonal N···N distance of 4.20 Å for these nitrogen atoms is 0.14 Å larger than the N···N distance for the other nitrogen atoms as if the hydrogen atoms repel each other. In MePPb, the electron density at sites H-1-N-1 and H-1-N-3 is greater than at sites H-1-N-2 and H-1-N-4, and the N-1···N-3 distance of 4.06 Å is considerably shorter than the N-2···N-4 distance of 4.23 Å. We conclude that the distortion is due to some other factors, such as the fifth isocyclic ring and the saturation in ring IV. In the VO-DPEP structure,[9] the analogous distances are 3.96 and 4.08 Å.

The C-17–C-18 bond length of 1.551 ± 0.007 Å in MePPb, compared with 1.34 ± 0.02 Å in the porphyrin VO-DPEP,[9] exhibits the single-bond character which distinguishes a chlorin from a porphyrin. Correspondingly, the C-16–C-17–C-18 and C-17–C-18–C-19 angles are decreased from an average of 107 ± 3° in VO-DPEP to an average of 101.5 ± 0.5° in MePPb. The C-16–C-17 and C-18–C-19 bond distances are increased from 1.43 and 1.46 Å, each ±0.02, to, respectively, 1.492 and 1.490, each ±0.008. Since ring V contains a β-keto ester, we examined the ring V bond distances to determine the amount of keto–enol tautomerism. The short C–O distance (1.211 ± 0.007 Å) and the long C–C distance (1.580 ± 0.008 Å) exclude much tautomerism, in agreement with the results obtained from infrared absorption.[21]

The C-13–C-28 bond distance of 1.431 ± 0.008 Å is smaller than the 1.526 ± 0.007-Å distance for bond C-15–C-29. We conclude that the ketone carbonyl is in conjugation with the chlorin ring system.

The vinyl group on ring I is also in conjugation with the main chlorin ring. The C-3–C-22 bond length of 1.472 ± 0.009 Å in MePPb is considerably shorter than the 1.56 ± 0.02 Å distance for a similar bond in VO-DPEP,[9] which links an ethyl group to ring I. There is considerable steric hindrance between that vinyl group in MePPb and the methyl group also attached to ring I. Not only is the vinyl group shifted out of the chlorin plane by 14°, but the three angles C-3–C-2–C-21, C-2–C-3–C-22 and C-3–C-22–C-23 are also increased in such a way as to increase the distance between C-21 and C-23.

Bond parameters of MePPb and of tri-TPP,[3] averaged in accordance with C_{4v} (4 mm) symmetry, are listed in Table V. With the exclusion of the saturated bond C-17–C-18, the two average geometries are the same within the experimental precisions. However, the spread of values in MePPb is greater than the estimated accuracy, and we believe the variability at least

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Table IV. Bond Angles (Degrees) of Methyl Pheophorbide[a]

Atoms	Angle	Atoms	Angle
C-1–N-1–C-4	110.5	C-14–C-13–C-28	109.0
C-6–N-2–C-9	106.3	N-3–C-14–C-13	109.3
C-11–N-3–C-14	108.9	N-3–C-14–C-15	136.2
C-16–N-4–C-19	108.2	C-13–C-14–C-15	114.5
N-1–C-1–C-2	107.8	C-14–C-15–C-16	127.2
N-1–C-1–C-20	125.2	C-14–C-15–C-29	106.4
C-2–C-1–C-20	127.0	C-16–C-15–C-29	126.5
C-1–C-2–C-3	106.9	N-4–C-16–C-15	120.5
C-1–C-2–C-21	124.7	N-4–C-16–C-17	112.7
C-3–C-2–C-21	128.4	C-15–C-16–C-17	126.7
C-2–C-3–C-4	108.9	C-16–C-17–C-18	101.6
C-2–C-3–C-22	128.6	C-16–C-17–C-30	110.8
C-4–C-3–C-22	122.5	C-18–C-17–C-30	111.9
N-1–C-4–C-3	105.9	C-17–C-18–C-19	101.4
N-1–C-4–C-5	127.4	C-17–C-18–C-32	112.6
C-3–C-4–C-5	126.7	C-19–C-18–C-32	112.6
C-4–C-5–C-6	128.8	N-4–C-19–C-18	113.6
N-2–C-6–C-5	124.8	N-4–C-19–C-20	123.3
N-2–C-6–C-7	111.4	C-18–C-19–C-20	123.1
C-5–C-6–C-7	123.7	C-1–C-20–C-19	128.8
C-6–C-7–C-8	106.4	C-3–C-22–C-23	126.2
C-6–C-7–C-24	127.0	C-8–C-25–C-26	111.7
C-8–C-7–C-24	126.6	C-13–C-28–C-29	106.1
C-7–C-8–C-9	106.6	C-13–C-28–O-1	130.4
C-7–C-8–C-25	128.7	C-29–C-28–O-1	123.5
C-9–C-8–C-25	124.7	C-15–C-29–C-28	103.9
N-2–C-9–C-8	109.3	C-15–C-29–C-33	112.2
N-2–C-9–C-10	125.0	C-28–C-29–C-33	107.4
C-8–C-9–C-10	125.7	C-17–C-30–C-31	115.6
C-9–C-10–C-11	125.2	C-30–C-31–C-35	113.8
N-3–C-11–C-10	121.1	C-29–C-33–O-2	125.2
N-3–C-11–C-12	107.8	C-29–C-33–O-3	112.1
C–10-C-11–C-12	131.1	O-2–C-33–O-3	122.6
C-11–C-12–C-13	107.0	C-31–C-35–O-4	126.6
C-11–C-12–C-27	126.1	C-31–C-35–O-5	112.5
C-13–C-12–C-27	126.9	O-4–C-35–O-5	120.9
C-12–C-13–C-14	107.0	C-33–O-3–C-34	115.3
C-12–C-13–C-28	144.0	C-35–O-5–C-36	117.6

[a] Standard deviations are 0.7–0.9° for angles involving atoms C-23, C-26, O-4, or O-5; for other angles they are 0.4–0.6°.

Table V. Average Bond Distances and Angles

Bond or angle	Methyl pheophorbide	Tetraphenylporphin[a]
N–C(α)[b]	1.36 (2) A	1.37 (1) A
C(α)–C(β)	1.45 (3)	1.44 (2)
C(β)–C(β)	1.37 (2)[c]	1.35 (1)
C(α)–C(m)	1.39 (2)	1.40 (1)
C(α)–N–C(α)	108 (2)°	108 (2)°
N–C(α)–C(β)	110 (3)	109 (1)
N–C(α)–C(m)	125 (5)	126 (1)
C(β)–C(α)–C(m)	125 (5)	125 (2)
C(α)–C(β)–C(β)	107 (1)[c]	107 (1)
C(α)–C(m)–C(α)	128 (2)	126 (1)

[a] Derived from ref 3. [b] The α- and β-pyrrole carbon atoms and the methine carbon atoms are designated by α, β, and m, respectively. [c] Does not include bond C-17–C-18.

in part reflects real differences in bond order. We have not attempted a detailed interpretation of these distances. Our electron density results correspond to partial hydrogen atoms on all four rings, but with an excess on rings I and III (Figure 1). Examples already exist for both ordered and disordered hydrogen atoms. Among porphyrin and phthalocyanin structures tri-TPP[3] has inner hydrogen atoms localized on just two diagonally opposite nitrogen atoms while phthalocyanin,[22] tetragonal TPP,[4] and porphin[2] have disordered hydrogen atoms. Nuclear magnetic resonance studies of several symmetrical porphyrins[23] have shown that the ring currents and presumably the shapes of all four pyrrole groups are identical. This implies that the hydrogen atoms are not localized when the porphyrins are in solution. Katz and coworkers, in their nmr study[24] of chlorophyll and its derivatives, found two distinct peaks for the two inner hydrogen atoms of methyl pheophorbide. Since no two pyrrole groups are chemically equivalent, this fact suggests localization on two nitrogen atoms. The molecular orbital calculations of Weiss, Kobayashi, and Gouterman[25] have predicted that they will lie on pyrrole rings I and III.

A view of the molecular packing is shown in Figure 5. Parallel molecules, tipped 16° from the *b* axis and related by *a* and *c* translations, are packed in a pseudohexagonal array. Such layers, related by the screw axes, are stacked in the *b* direction. Within the layer, the plane of each molecule is 3.49 and 3.52 Å from the planes of its nearest neighbors. Similar distances are 3.43 and 3.39 Å in porphin[2] and methoxyiron(III) mesoporphyrin IX dimethyl ester.[26]

Packing of Chlorophyll in Photosynthetic Lamellae. Steinman,[27] Frey-Wyssling,[28] and Park[29] have demonstrated that the chloroplast membranes are composed of 200-Å units which exist in highly ordered arrays. These particles, called quantasomes, may be the morphological photosynthetic unit.[30] Each quantasome contains approximately 230 chlorophyll molecules.[29] It is generally accepted that the number of energy traps is much less than the number of chlorophyll molecules. Therefore, a mechanism for the transfer of energy from one chlorophyll molecule to another is required.

Chlorophyll is very hygroscopic[21] and water is necessary to form microcrystalline chlorophyll.[31] What is biologically interesting is that chlorophyll–water complexes have a similar electron paramagnetic resonance spectrum to photosynthesizing chloroplasts, whereas anhydrous chlorophyll does not.[31] Previous structural determinations of the molecules of $MgTPP \cdot H_2O$[5] and $MgPc \cdot H_2O \cdot 2C_5H_5N$[7] lead us to believe that the water molecules are coordinated as a fifth ligand to the central magnesium atom which is 0.3–0.5 Å out of the molecular plane.[32] An infrared absorption study of chlorophyll–water aggregates[21] indicates that the water is hydrogen bonded both to the ring V ketone carbonyl and to the O-2 ester carbonyl oxygen atoms of the ad-

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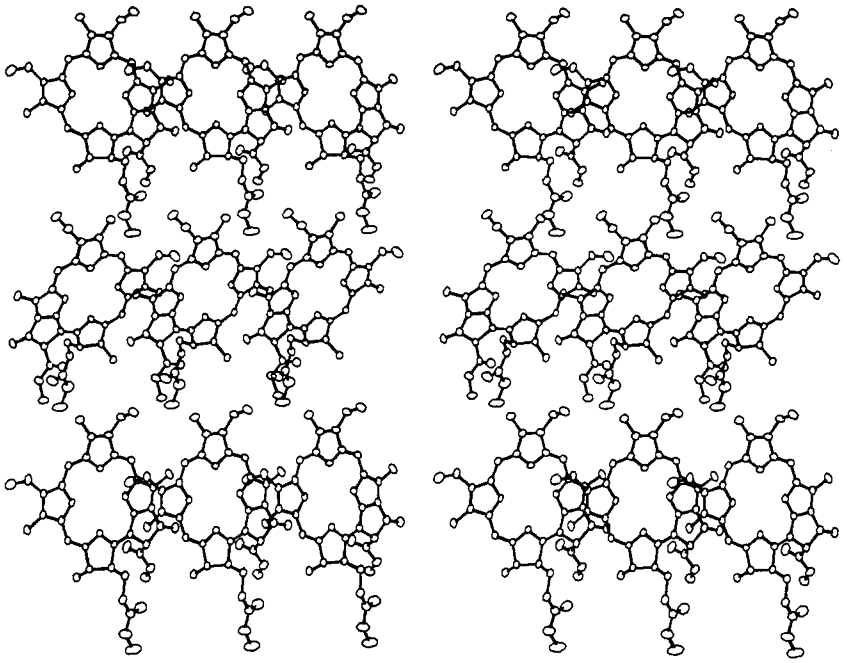

Figure 5. Stereoscopic view of the crystal structure of methyl pheophorbide *a*, viewed down the reciprocal *c* axis; *a* axis horizontal, *b* axis vertical.

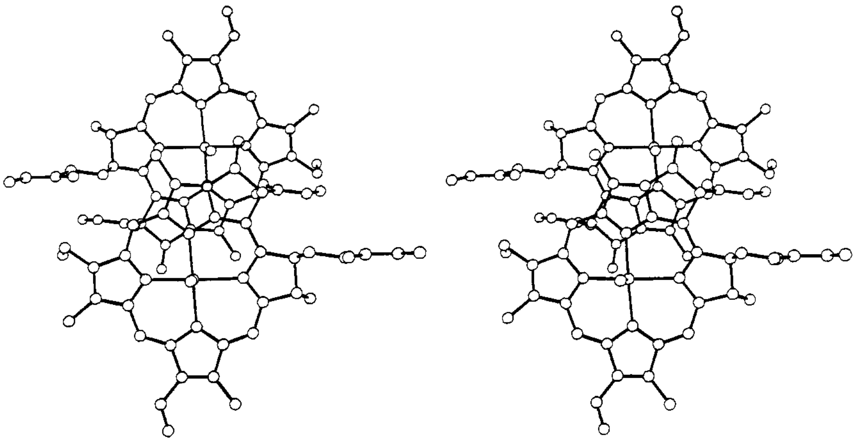

Figure 6. Stereoscopic view of proposed dimer of water and chlorophyll; only the first carbon of each phytyl group is shown.

jacent molecule. The OH stretch absorption frequencies for the hydrogen atoms of the water molecule are at 3240 cm^{-1} for the hydrogen bond involving O-1 and 3460 cm^{-1} for O-2. We have used a correlation[33] between O–H stretch absorption frequencies and the corresponding O···O distances to estimate that the O-water···O-1 and O-water···O-2 distances are 2.78 and 2.89 Å, respectively.

We propose a model of chlorophyll which has dimensions similar to MePPb with the magnesium atom 0.50 Å out of the plane and a water molecule 2.02 Å above the magnesium atom. Hydrogen bonds connect the water molecule to the next chlorophyll. Repetition by simple translations leads to molecular crowding, but repetition by a 2_1 screw axis permits a satisfactory fit, as shown for two molecules in Figure 6. Rings III and V of one molecule overlap with rings V and III of an adjacent molecule. We have several conclusions about such a dimer. (1) The magnesium atom must be substantially out of the chlorin plane to maximize intermolecular spacings between the ring V carboxyl group and the chlorin ring. (2) The molecules must be nonparallel to increase the distance between the ring V carboxyl group and the atoms of ring II. In our model the interplanar angle is 14°, but orientations with larger interplanar angles cannot be excluded *a priori*. (3) If the molecules are separated by their maximum possible distance, atom C-27 of one molecule collides with atom C-30 of the adjacent one. This particular intermolecular distance is increased as the intermolecular distance is decreased, subject to the hydrogen-bonding constraints. The decrease in intermolecular distance is limited, however, by possible contacts between the ring V carboxyl group of one molecule and ring II of the other. We have used an interplanar spacing of 5.49 Å, which is 0.22 Å less than the maximum possible interplanar spacing subject to these constraints. (4) The ring IV alkyl chain and the ethyl group of ring II must be rotated

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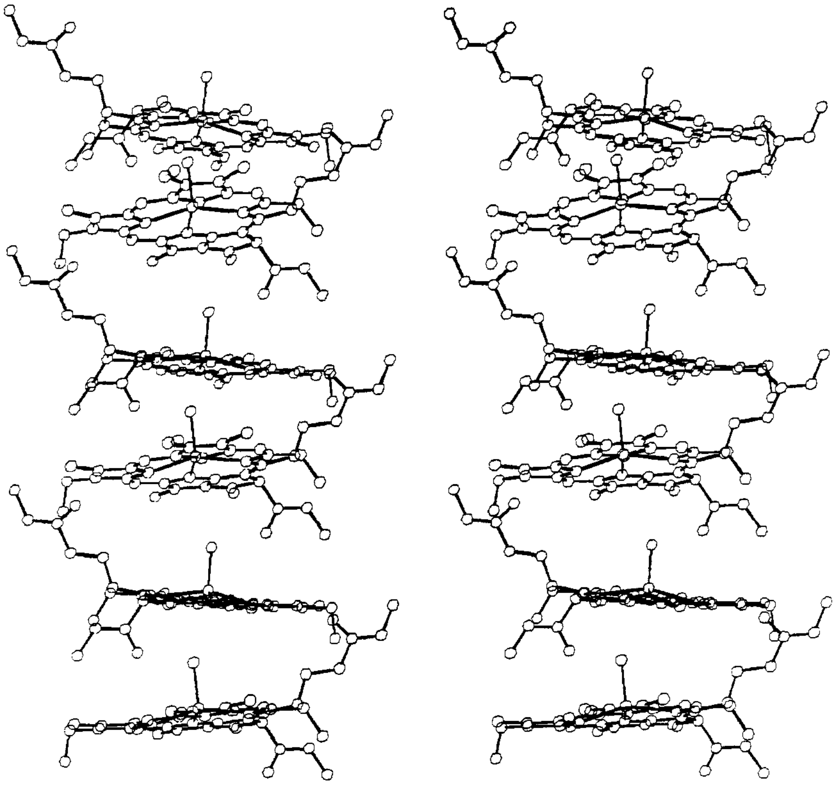

Figure 7. Stereoscopic view of proposed model of a chlorophyll–water polymer which might exist in photosynthetic lamellae. Only the first carbon atom of each phytyl group is shown. The region on each side of the depicted polymer contains phytyl chains, lipids, and, farther out, proteins.

from the positions in the crystal structure of methyl pheophorbide to avoid intermolecular collisions.

Nuclear magnetic resonance studies of chlorophyll aggregates[24] have indicated that the major area of overlap involves rings III and V, although the chemical shift caused by aggregation is very small. This feature of our postulated model agrees with the nmr data.

Plant lamellae, when stained with $KMnO_4$ and viewed under the electron microscope, exhibit a banded structure.[34] The bands appear to be layers of protein and lipid, and at least the phytyl chain of the chlorophyll molecules may be in the lipid fraction. In their study of the permeability of thin films, Danielli and Davson[35] suggested that membranes are composed of protein molecules which adsorbed onto a lipid layer. We propose a model (Figure 7) for the aggregation of hydrated chlorophyll molecules within the lipid layer. In this figure, only the first carbon of the phytyl group is shown. The phytyl groups, which radiate out opposite sides of the chlorophyll–water polymer, extend toward the protein bands on each side and are necessary to firmly orient the chlorophyll heads which are in the center.

As a variation of the model, the chlorophyll–water polymer could be bent enough to form a circular cover for the quantasome. The phytyl chains would be in one of two possible configurations. In the first, half the phytyl chains would project out from the quantasome and half would project in. In the other possibility, all phytyl chains and some of the lipids would be on the surface of the quantasome. In any of these linear and nonlinear models, the chlorin groups are oriented in such a way that any molecule can absorb a photon and transmit the energy to an adjacent molecule *via* the water molecule. Energy can be transmitted to the O-1 carbonyl, which is in resonance with the rest of the chlorin group. In this way, energy can be shuttled until it is trapped in some unique chlorophyll–protein complex.

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