15.95%, and GOF = 2.916 for 3067 reflections and $R_F = 8.65\%$, $R_{wF} =$ 15.76%, and GOF = 3.310 for 2652 reflections with $F_o \geq \sigma(F_o)$; the data-to-parameter ratios were 8.50:1 for all included data and 7.35:1 for $F_o \geq \sigma(F_o)$ reflections. The final difference Fourier map showed peaks of approximate density 0.85 e Å^{-3} within 1.25 Å of the sulfur atoms in the cyclopentadienide anion. Since no suitable disorder model could be included in the refinement to account for the contribution of the methyl hydrogens, the analysis was declared complete.

Final positional and thermal parameters are given in the supplementary material.

Crystal and Molecular Structure of Methyl Bacteriopheophorbide a. A Model for a Primary Electron Acceptor in Bacterial Photosynthesis

K. M. Barkigia,[*1a] **J. Fajer,**[1a] **K. M. Smith,**[1c] **and G. J. B. Williams**[1b]

Contribution from the Department of Energy and Environment and the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, and the Department of Chemistry, University of California, Davis, California 95616. Received February 23, 1981

Abstract: Bacteriopheophytin is a key component in the mechanism by which photosynthetic bacteria transduce solar energy into chemical form. The structure of methyl bacteriopheophorbide a, a bacteriopheophytin derivative, has been determined by three-dimensional X-ray diffraction. The compound crystallizes in space group $P\bar{1}$ in a unit cell containing a molecule of methyl bacteriopheophorbide and a benzene molecule of crystallization, with lattice constants $a = 7.2502$ (8) Å, $b = 8.1070$ (9) Å, $c = 17.224$ (5) Å, $\alpha = 90.80$ (2)°, $\beta = 94.17$ (2)°, and $\gamma = 110.38$ (1)°. The structure has been refined with isotropic thermal parameters on F by full-matrix least squares to $R_F = 0.110$, based on 860 reflections. The molecules associate in chains via π–π interactions with ring I of one molecule overlapping ring III of its neighbor with a vertical separation of 3.6 Å. The one-dimensional chains form two-dimensional layers *without* the intervention of the hydrogen bonding by water molecules previously reported for chlorophyllides. This work represents the first crystallographic determination of a bacteriochlorin and confirms the canonical structures and relative orientations of the five chiral centers of bacteriochlorophyll a derivatives.

Photosynthetic bacteria, plants, and algae harvest light via an antenna network comprised of bacteriochlorophylls or chlorophylls and funnel the incident light into reaction centers. In these special environments, an array of (bacterio)chlorophylls transduces the gathered photons into oxidants and reductants that drive the biochemistry of the organisms.[2–4] Reaction centers of purple bacteria[5] contain four bacteriochlorophylls (BChl), two bacteriopheophytins (BPheo, metal-free BChls) and other components of the electron transport chain. A "special pair" of the BChls[6,7] acts as electron donor and transfers an electron to BPheo[7–9] within

4 ps of excitation,[10] possibly via one or more of the remaining BChls.[11] The BPheo anion in turn reduces a quinone in ~200 ps.[9] The rapid translocation of the electron away from the primary donor, via BPheo, thus stabilizes the charge separation and minimizes wasteful back reactions.

Although several crystallographic determinations of chlorophyll derivatives have been reported,[12–15] no corresponding data exist for bacteriochlorophylls, except for the structure of a BChl protein at 2.8 Å resolution.[16] We report here the crystal and molecular structure of methyl bacteriopheophorbide a (MeBPheo), a bacteriopheophytin in which the esterifying fatty alcohol side chain found in vivo has been replaced by a methyl group (I). Although the precision of this study is limited by the extremely small size of the sole crystal obtained, the results (1) confirm the structures

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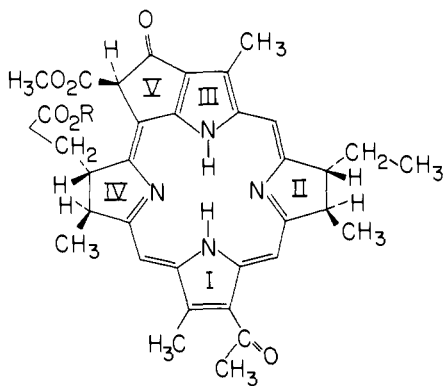
R = phytyl or geranylgeranyl in BPheo
R = methyl in MeBPheo

of BPheo and BChl, and the relative orientations of their substituent groups, previously deduced by spectroscopic and degradation studies,[17-19] (2) provide the stereochemical parameters for molecular orbital calculations that describe the unpaired spin density profiles of the light-induced radicals in the reaction center, profiles which are significantly affected by the orientations of the substituents,[7,20] (3) establish that the molecules associate in one-dimensional chains that form two-dimensional layers without the hydrogen bonding by water molecules previously found in chlorophylls,[14] and (4) offer possible packing models for the BPheos in the reaction center.

Experimental Section

Bacteriochlorophyll a was extracted from *Rhodospirillum rubrum*, demetallated and transesterified using 3% sulfuric acid in methanol,[21] and then chromatographed on neutral alumina (Merck, Brockmann Grade V). Elution with 5% methylene chloride in toluene yielded methyl bacteriopheophorbide a (MeBPheo). A final purification was carried out by preparative thin layer chromatography on silica gel G (elution with 1% tetrahydrofuran in methylene chloride). The NMR spectrum of the compound matched that reported in the literature.[22]

A sole, small crystal of MeBPheo was grown by evaporation in the dark from a sample of material dissolved in methylene chloride to which benzene had been added. This crystal was examined by preliminary precession photography with use of Mo Kα radiation; it diffracted X-rays poorly, as has been the precedent with chlorophyll derivatives. It was mounted on a CAD4 diffractometer and aligned. An autoindexing routine yielded a triclinic unit cell, and a computerized examination of the Niggli matrix of the Buerger reduced cell indicated no higher lattice symmetry.[23] All independent reflections with a $2\theta \leq 110°$ were measured, giving 2371 unique data points, of which 860 had $F_o \geq 3\sigma(F_o)$. Throughout the six weeks of data collection, the intensities of three monitor reflections were measured periodically. No statistically significant fluctuations or trends in these monitors were found.

The structure was solved with use of MULTAN 78[24] which produced 20 of the atoms in the bacteriochlorin framework. The remaining nonhydrogen atoms and a benzene molecule of crystallization were located from multitudinous difference density syntheses. The structure was refined

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Table I. Crystallographic Details for $C_{36}N_4O_6H_{40} \cdot C_6H_6$

unit cell, space group, triclinic, *P*1, *Z* = 1, *M* = 702.82,
$V = 946.41$ Å
$a = 7.2502 (8)$ Å^a	$\alpha = 90.80 (2)°$
$b = 8.1070 (9)$ Å	$\beta = 94.17 (2)°$
$c = 17.224 (5)$ Å	$\gamma = 110.38 (1)°$

density calcd, 1.23 g/cm³
crystal description, tiny platelet
  $d(110) = 0.14$ mm
  $d(1\bar{1}0) = 0.05$ mm
  $d(001) = 0.015$ mm
data collection
  diffractometer, Enraf–Nonius, CAD4
  radiation, Cu Kα, λ = 1.5418 Å, graphite monochromated
  linear absorption coefficient, 6.76 cm⁻¹ (analytical absorption
    corrections were calculated by using the program, ABSOR[26])
  2θ range $0 \leqslant 2\theta \leqslant 110°$
  no. of reflections, 4552 measured, 2371 unique,
    860 with $F_o \geqslant 3\sigma(F_o)$
scattering factors, Cromer and Mann;[25a] Stewart, Davidson, and Simpson[25b]
refinement, isotropic model using full-matrix least-squares against
  data having $F_o \geqslant 3\sigma(F_o)^b$
  $R_F = 0.110$ $R_F = \Sigma |F_o - F_c|/\Sigma |F_o|$
  $R_{wF} = 0.101$ $R_{wF} = (\Sigma(wF_o - F_c)^2/\Sigma wF_o^2)^{1/2}$

a The figures in parentheses are the standard deviations of the least significant figure here and throughout this paper. *b* The quantities F_o and F_c are the observed and calculated structure factor amplitudes, *w* is the experimental weight where $w^{-1} = \sigma^2_c + (0.03F_o)^2$ and σ^2_c is the variance from counting statistics. All programs, except MULTAN 78, are described in the CRYSNET manual of Brookhaven National Laboratory.[26]

Table II. Final Positional and Thermal Parameters for MeBPheo^a

	x	y	z	B, Å²
O1	-358(4)	-735(4)	120(2)	47(5)
O2	-434(5)	-349(4)	207(2)	57(6)
O3	-268(5)	-475(4)	279(2)	74(7)
O4	365(7)	-4(6)	398(3)	180(17)
O5	245(6)	-256(5)	338(2)	119(10)
O6	120(4)	607(3)	-249(2)	50(6)
N1	4(5)	268(4)	-60(2)	21(6)
N2	-236(5)	-54(4)	-168(2)	36(7)
N3	-241(5)	-266(4)	-43(2)	39(8)
N4	8(5)	34(4)	70(2)	43(7)
C1	112(5)	382(4)	-2(2)	19(7)
C2	176(6)	553(4)	-33(2)	36(8)
C3	115(6)	536(4)	-105(2)	40(9)
C4	-8(5)	332(4)	-130(2)	23(7)
C5	-103(5)	259(4)	-204(2)	30(8)
C6	-214(5)	76(4)	-226(2)	27(8)
C7	-308(6)	11(5)	-305(2)	41(9)
C8	-386(6)	-194(5)	-290(2)	40(9)
C9	-346	-209	-206	35(9)
C10	-398(6)	-383(4)	-172(2)	24(7)
C11	-357(6)	-402(5)	-93(2)	29(8)
C12	-392(5)	-553(4)	-47(2)	15(6)
C13	-322(5)	-518(4)	31(2)	12(6)
C14	-214(6)	-323(5)	29(3)	55(11)
C15	-139(5)	-269(4)	97(2)	16(7)
C16	-11(6)	-91(5)	120(2)	35(9)
C17	113(5)	-28(4)	192(2)	27(7)
C18	160(6)	183(5)	191(2)	40(10)
C19	99(5)	194(4)	110(2)	38(9)
C20	158(6)	35(4)	70(2)	33(8)
C21	309(6)	722(5)	5(2)	43(9)
C22	129(5)	649(4)	-180(2)	30(7)
C23	187(6)	844(5)	-157(2)	51(9)
C24	-455(6)	89(5)	-323(2)	50(9)
C25	-276(6)	-288(5)	-346(2)	62(11)
C26	-332(6)	-272(5)	-430(3)	78(11)
C27	-507(5)	-744(4)	-83(2)	24(7)
C28	-297(6)	-575(5)	95(3)	67(11)
C29	-18(5)	-418(4)	162(2)	23(6)
C30	295(6)	-73(4)	202(2)	44(8)
C31	435(6)	-20(4)	264(2)	36(7)
C32	76(6)	248(5)	249(2)	41(8)
C33	-305(5)	-409(4)	215(2)	32(7)
C34	-382(7)	-470(6)	340(3)	95(13)
C35	372(8)	-68(7)	338(3)	113(16)
C36	183(9)	-330(7)	414(3)	145(20)
C37	134(7)	-659(6)	-417(3)	89(13)
C38	-28(8)	-622(6)	-426(3)	89(13)
C39	-157(10)	-674(8)	-476(4)	134(20)
C40	-108(10)	-785(8)	-521(3)	127(18)
C41	20(10)	-844(7)	-535(4)	144(21)
C42	183(8)	-786(8)	-469(4)	122(17)

a Positional parameters have been multiplied by 10³ and thermal parameters by 10. The form of the Debye–Waller factor is $\exp[-B(\sin^2\theta)/\lambda^2]$.

by full-matrix least-squares methods against the 860 data having $F_o \geq 3\sigma(F_o)$. Due to the relatively small number of reliably estimated data,
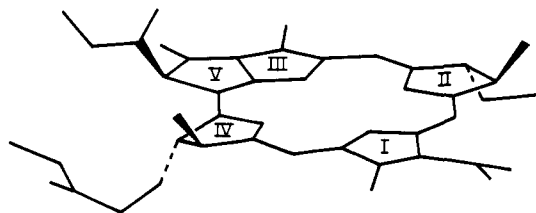
Figure 1. A view of MeBPheo illustrating the relative orientations of the side chains.
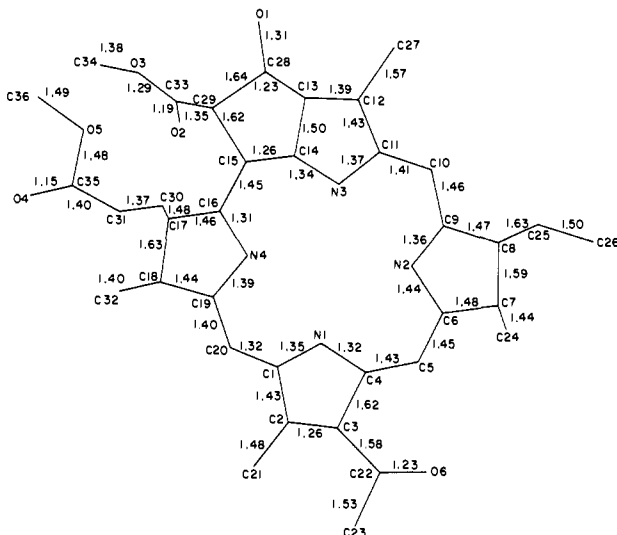
Table III. Comparison of Average Bond Distances (Å) in MeBPheo and Similar Molecules

	EtChl a[14,15]	EtChl b[14,15]	MePheo[13]	MeBPheo[a]
$C_\alpha-C_\beta$ (sat.)	1.524 (8)	1.532 (10)	1.491 (6)	1.46 (2)
$C_\beta-C_\beta$ (sat.)	1.555 (9)	1.566 (12)	1.551 (7)	1.61 (3)
$C_\alpha-C_\beta$ (unsat.)	1.448 (4)	1.441 (5)	1.431 (3)	1.50 (2)
$C_\beta-C_\beta$ (unsat.)	1.370 (5)	1.365 (8)	1.371 (5)	1.33 (2)
C28–C29	1.568 (9)	1.570 (13)	1.580 (8)	1.64 (4)

[a] The esd of the mean was estimated as $\sigma = (1/\Sigma(1/\sigma_i^2))^{1/2}$.

Figure 2. Nomenclature and bond distances[27] for MeBPheo. The average esd on a typical C–C bond is 0.04 Å.
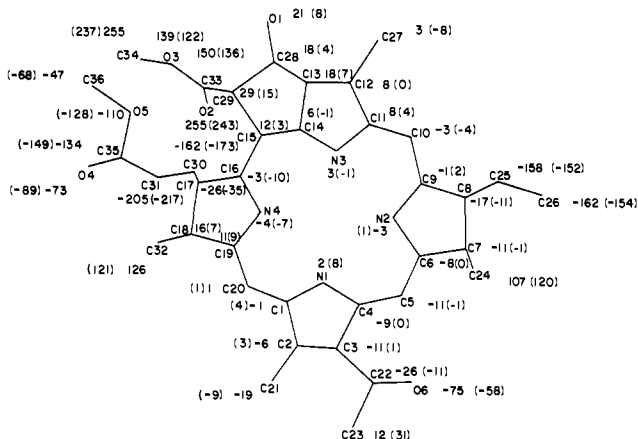

Figure 3. Deviations (Å × 10^2) from the least-squares plane of the four nitrogens. The figures in parentheses are the deviations from the plane of the macrocycle.

the atoms were permitted only isotropic expression of their thermal motion. After refinement conclusively showed that the molecule was a bacteriochlorin, the hydrogen atoms were placed in calculated positions 0.95 Å away from their respective carbon atoms and each was assigned a *B* of 6.0 Å². The electron density from the hydrogens was treated as a fixed contribution to the total density. The region in the center of the molecule was examined very carefully, in an attempt to locate the two central hydrogen atoms. Since it was not possible to select any two sites as being dominant, they were positioned with half occupancy at each of the four possible sites. The several tautomers which can be envisioned for MeBPheo are therefore not distinguished by this analysis.

The isotropic thermal parameters for some of the peripheral atoms are high, but no disordered model for their positions could be determined from these data. An attempt to "correct" some of the unusual bond distances in the macrocycle by manually repositioning some atoms, C3 and C28, for example, and then allowing these atoms to refine along with the others, always resulted in the deviant atoms returning to their original location. A final difference map revealed a few peaks of approximately 0.4 e/Å³ near ring 4 and one near C21. A summary of the crystallographic details is given in Table I. The final positional and thermal parameters for all nonhydrogen atoms are presented in Table II. The coordinates of the hydrogen atoms as well as the observed and calculated structure factor amplitudes have been deposited as Supplementary Material.

Discussion

This work represents the first crystallographic determination of a bacteriochlorophyll structure; it clearly confirms the accepted molecular connectivity and the relative configuration of the five chiral centers as consistent with the work of Brockmann[17] (Figure 1). The absolute configuration of these centers is not determined by this analysis, however. Atom names, according to the scheme developed for methyl pheophorbide[13] (MePheo) and the chlorophyllides,[14,15] are given in Figure 2 which presents selected bond distances.[27] Bond angles are included with the Supplementary Material, as are distances and angles for the benzene of crystallization.

In accord with the comparable determinations in the chlorophyllides,[13-15] the $C_\beta-C_\beta$ distances in the saturated rings are somewhat longer than those expected for normal single bonds because of the bulky substituents on the β-carbon atoms. They are also significantly longer than the $C_\beta-C_\beta$ bonds of 1.533 (8) and 1.556 (9) Å in the reduced rings of dimethyloctaethylisobacteriochlorin which bear a similar pattern of side chains.[28] However, this elongation is accompanied by a concomitant shortening of the $C_\alpha-C_\beta$ bonds of rings II and IV. Some average distances from this work and similar molecules with known crystal structures[13-15] (ethyl chlorophyllide a (EtChl a), ethyl chlorophyllide b (EtChl b) and MePheo) are compared in Table III. As previously observed in the chlorophylls, the C28–C29 bond is long, presumably due to strain in ring V,[13] and to possible errors in the model.

Rings I, II, and III are essentially planar, while ring IV is distorted. The fragment composed of rings III and V is also planar with the exception of C29. Geometric details of these planes have been included as Supplementary Material. The deviations of the atoms from the plane of the four nitrogen atoms and the plane of the macrocycle are shown in Figure 3. Most noteworthy are the very large displacements of C24, C25, C30, C32, and C33 which clearly designate C7, C8, C29, C17, and C18 as tetrahedrally coordinated. The tetrahedral nature of C29 implies that the molecule exists in the keto form in the crystal since the enol tautomer requires sp² hybridization of C29.

Although Ibers and co-workers[29] suggested that the puckering of nickel(II) *meso*-tetramethylchlorin relative to the corresponding porphyrin may be of biological significance, examination of the structures of free base, magnesium or zinc chlorins,[12-15,30] bacteriochlorins, and isobacteriochlorins[28,31] reveals no major ste-

(27) The sparcity of data for such a large molecule obviously accounts for some of the deviant bond distances.

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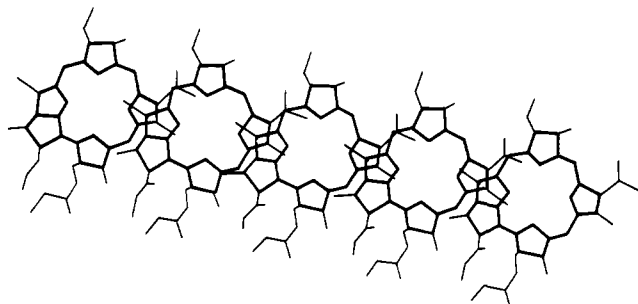
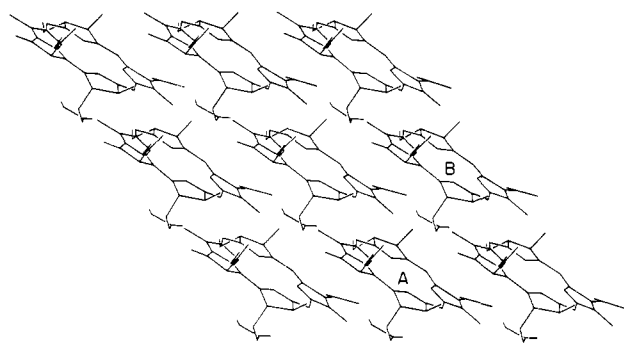**Figure 4.** Stacking of the MeBPheo molecules to form one-dimensional chains.

Figure 5. Aggregation of MeBPheo molecules into two-dimensional networks. The distance between the centroids of molecules A and B is 7.25 Å.

reochemical variations on progressive saturation of the porphyrin macrocycle.[32] The biological role of the reduced porphyrins may perhaps be better ascribed to their electronic configurations, where the migration of the HOMOs and LUMOs upon successive reduction controls both their redox and optical properties.[33] Nonetheless, the flexibility of the reduced rings of MeBPheo, as evidenced by the different conformations of rings II and IV, may be relevant to comparisons of the paramagnetic resonance features of BChl radicals in vivo and in vitro. For example, Davis et al.[7] invoked a flattening of ring IV in the BChl b cation of *Rhodopseudomonas viridis*, in order to rationalize the disparate ESR and ENDOR parameters of the radicals in solution and in the reaction center.

An important associative mode, exemplified by this structure and exhibited in all other known crystal structures[12-15] of chlorophyll–like species (MePheo, EtChl a, EtChl b, methyl chlorophyllide a, pyrochlorophyllide a, and phyllochlorin ester (PE)), is that of chain formation, presumably via π–π interactions. Figure 4 illustrates these one-dimensional chains. The perpendicular separation of the overlapping rings I and III which form this linkage is 3.6 Å. As in MePheo[13] and PE,[12] this association occurs in MeBPheo without the intervention of water molecules which link adjacent molecules through hydrogen bonding in the magnesium complexes.[14,15] This determination demonstrates that this

specific aggregation of molecules into one-dimensional chains is independent of the peripheral substituents and further shows that the steric effects of the bacteriochlorin framework do not differ from those of a chlorin.

In MeBPheo, the one-dimensional chains associate to form two-dimensional layers, as illustrated in Figure 5. Similar nets have been reported for chlorophyll derivatives[14,15] with one lattice water and one water molecule coordinated to the magnesium. In these species (EtChl a, EtChl b, MeChl a), active participation by the waters of solvation and crystallization was though to be important in the formation of the nets.[14,15] The present structure indicates, however, that this association may be spontaneous for these macrocycles.

The stacking pattern of MeBPheo and its relatively low oxidation potential[34] ($E_{1/2}$ = +0.7 V vs. SCE) suggest that partial oxidation of the compound with bromine may lead to conducting molecular crystals similar to the nickel(II) tetrabenzporphyrin-iodine complexes recently reported.[35]

A puzzling spectral feature of BChl in reaction centers and antennae is the significant red shift of the 775 nm absorption band in vitro[34] to as much as 890 nm in vivo. In purple bacteria, antenna BChl-proteins containing as few as two BChls absorb at 890 nm,[36] while the special pair of BChls, which acts as primary donor in the reaction center, peaks at 870 nm.[5,6] The protein complex extracted from the green bacterium, *Prosthecochloris aestuarii*, whose structure has been determined, absorbs at 809 nm, and is comprised of 3 subunits of seven BChls each, in fairly irregular orientation.[16] Whether the red shifts are caused by complexation at the magnesium atom and/or at the periphery, or are simply induced by the close aggregation of the pigments, as described here, may be resolved by optical studies of single crystals of MeBPheo. Such studies may also provide an indication of the interaction between the two BPheos found in reaction centers where their first absorption band does not differ from that in vitro. The two chromophores are believed to exist in different environments, and their Q_y transitions are not parallel.[37] The arrangement of the BPheos in vivo may thus be more analogous to the displacement of ~7 Å between layers observed here, which would result in more rotational freedom and less exciton coupling, than to the close packing of 3.6 Å between nearest neighbors found in the crystal.

Supplementary Material Available: A listing of structure amplitudes, bond angles, distances, and angles for the benzene of crystallization, least-squares planes, and fractional coordinates for the hydrogen atoms (10 pages). Ordering information is given on any current masthead page.

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