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Supplementary Material Available: Tables of atomic positional and thermal parameters for **2** (2 pages). Ordering information is given on any current masthead page.

Structural and Theoretical Models of Photosynthetic Chromophores. Implications for Redox, Light Absorption Properties and Vectorial Electron Flow

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Recent structural data for (bacterio)chlorophylls and chlorins as isolated molecules[2-5] and in proteins[6-8] demonstrate the skeletal flexibility of the chromophores that can be imposed by crystal packing and/or protein constraints. We present here single-crystal X-ray data for a homologous series of methyl bacteriopheophorbides *d*, derived from the antenna chlorophylls of the green photosynthetic bacterium *Chlorobium vibrioforme*.[5] The results illustrate the crystallographically significant conformational variations possible for the same chlorophyll skeleton. Comparable variations have also been noted, albeit at lower resolution, for the bacteriochlorophylls *a* (BChl) in the BChl antenna protein of *Prosthecochloris aestuarii*[6] and the BChls *b* that comprise the primary donor (special pair) of the *Rhodopseudomonas viridis* reaction center protein.[7,8]

We thus consider theoretically the possibility that such conformational variations can affect the highest occupied (HOMOS) and lowest unoccupied (LUMOS) molecular orbital levels of the chromophores and thereby modulate their redox potentials and light absorption properties. We test the concept by demonstrating that a sterically distorted porphyrin of known structure exhibits experimental optical and redox properties in solution consonant with theory and extend the calculations, using crystallographic data for the *Rps. viridis* primary donor,[8] to show that a redox asymmetry is possible in the BChl subunits that comprise the special pair of that bacterium.

Smith and Bobe[9] have demonstrated that green bacteria *light-adapt* by sequential alkylation of the antenna chlorophylls to yield a series of homologues with different substituents at position 4 of ring II (see structure in Figure 1). Single-crystal X-ray diffraction of metal-free derivatives (pheophorbides) from *Chlorobium vibrioforme* yield the following results:[5] (a) The substituents range from ethyl to *n*-propyl, isobutyl, and neopentyl. (b) Removal of the magnesium affords a series of dimeric and higher aggregates that are hydrogen bonded via the 2-(1-hydroxyethyl) group to the 9-keto group or to the carbonyl group of the propionic acid side chain of ring IV, depending on the method of crystallization. (c) Significant conformational variations are found for the same pheophorbide skeleton, depending on the

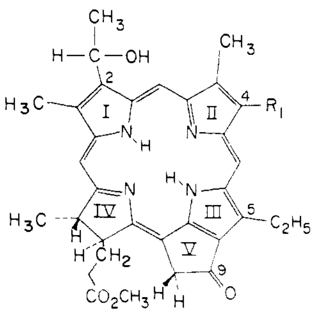

Figure 1. Structural formula of methylbacteriopheophorbide *d*. R_1 can be ethyl, *n*-propyl, isobutyl, or neopentyl.

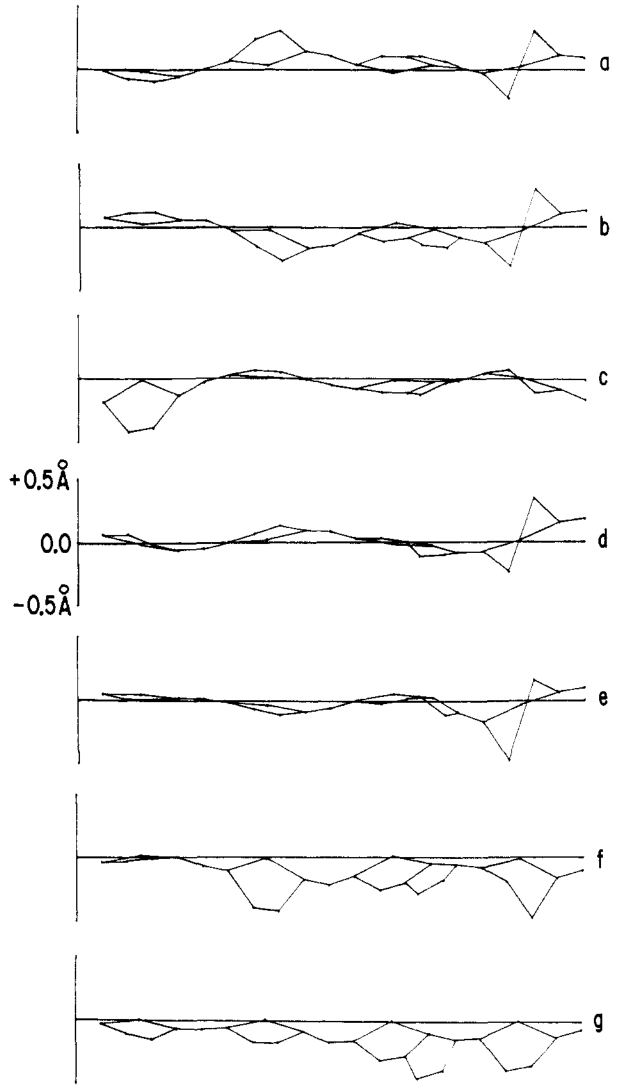

Figure 2. Linear display of the skeletal deviations from the plane defined by the four nitrogens of the bacteriopheophorbides *d*, in Å. Substituents are not shown. Illustrated are: (a) and (b) the two crystallographically independent molecules in the unit cell of 4,5-diethyl-methylbacteriopheophorbide *d*; (c) 4-propyl, 5-ethyl-meBPheo *d*; (d) and (e) the two crystallographically independent molecules in the unit cell of 4-isobutyl,5-ethyl-meBPheo *d*; (f) a different aggregate of 4-isobutyl,5-ethyl-meBPheo *d*; (g) 4-neopentyl,5-ethyl-meBPheo *d*. The order of the rings is I, II, III, V, and IV from left to right. Esd's for the deviations from planarity ≤0.01 Å.

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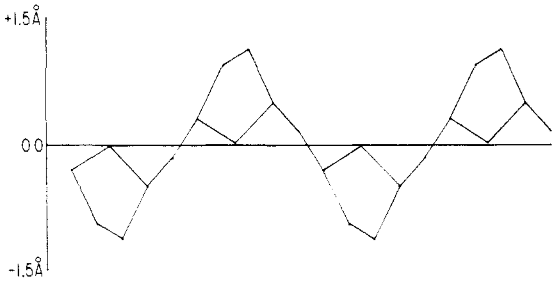

Figure 3. Linear display of the skeletal deviations from the plane defined by the four nitrogens of Zn tetraphenyloctaethylporphyrin, in Å. Substituents are not shown. Esd's for the deviations from planarity ≤0.02 Å.

aggregation. The deviations of the pyrrole rings from the plane defined by the four nitrogens range between ±0.5 Å and are illustrated in Figure 2.

Preliminary single-crystal X-ray data show zinc tetraphenyloctaethylporphyrin[10] (ZnTPOEP, (5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18-octaethylporphinato)zinc(II)) to be severely saddle shaped (Figure 3) with the β protons of adjacent pyrrole rings displaced by ~±1 Å relative to the plane of the four nitrogens. NMR data[11] establish that the puckered conformation is retained in CH_2Cl_2 solution. Remarkably, the first absorption band of the compound is shifted to 637 nm compared with λ_{max} of 586 nm for Zn tetraphenyl porphyrin (ZnTPP) or 569 nm for Zn octaethylporphyrin (ZnOEP). Also noteworthy, the oxidation halfwave potential of ZnTPOEP in CH_2Cl_2 has decreased to +0.47 V (versus SCE) compared to those of ZnTPP and ZnOEP, $E_{1/2}$ = 0.75 and 0.63 V, respectively, while the reduction potentials in tetrahydrofuran are as follows: $E_{1/2} = -1.54, -1.35$, and -1.63 V, for ZnTPOEP, ZnTPP, and ZnOEP, respectively.

Quantum mechanical ZINDO calculations[12,13] predict the experimental trends with calculated red shifts of 1900 cm^{-1} for a conformational change from a planar Zn porphyrin to one with the saddle structure of ZnTPOEP to be compared with observed shifts of 1370 and 1880 cm^{-1} relative to ZnTPP[14] and ZnOEP,[14] respectively. The calculations also predict that the puckered porphyrin will be easier to oxidize by 0.12 eV, whereas reduction is insensitive to the distortion. Similar calculations for puckered chlorins and bacteriochlorins predict red shifts of 1200 and 820 cm^{-1}, respectively.

Extension of the calculations to the different conformations observed[8] for the BChls *b* that comprise the special pair of *Rps. viridis* also predicts different optical and redox properties. For the BChl *b* associated with the L protein subunit, λ_{max} = 807 nm with calculated energies of −2.030 and −5.850 eV for the LUMO and HOMO, respectively, and for the BChl associated with the M subunit, λ_{max} = 762 nm with energies of −1.920 and −5.880 eV for the LUMO and HOMO.[15]

The above combination of experimental and theoretical results clearly suggests that the conformational variations observed in vitro and in vivo can provide a mechanism for altering optical and redox properties. Such effects, in conjunction with additional modulations induced by neighboring protein residues,[7,16] may thus combine to cause the observed asymmetry in the triplet[17] and oxidized donor[18] of *Rps. viridis* and the vectorial electron flow[16] that occurs in the reaction center. The same considerations also offer an attractively simple rationale for the optical features of the BChl *a* antenna of *Prosthecochloris aestuarii* (λ_{max} = 793–825 nm).[19,20]

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A Carotenoid–Diporphyrin–Quinone Model for Photosynthetic Multistep Electron and Energy Transfer

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Photosynthetic reaction centers use light to generate energetic, long-lived charge-separated states by employing a series of short-range electron-transfer steps to achieve overall long-range charge separation across a lipid bilayer membrane. We have previously shown that covalently linked carotenoid–porphyrin–quinone (C–P–Q) triads[1-10] and a carotenoid–porphyrin–diquinone

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