



Figure 3. Linear display of the skeletal deviations from the plane defined by the four nitrogens of Zn tetraphenylporphyrin, 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 tetraphenylporphyrin¹⁰ (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 $\sim \pm 1$ Å relative to the plane of the four nitrogens. NMR data¹¹ 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 ZnTPP¹⁴ 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 observed⁸ 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, $\lambda_{\text{max}} = 807$ 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, $\lambda_{\text{max}} = 762$ 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 triplet¹⁷ and

oxidized donor¹⁸ of *Rps. viridis* and the vectorial electron flow¹⁶ 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* ($\lambda_{\text{max}} = 793\text{--}825$ nm).^{19,20}

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(20) Tronrud et al.⁶ note that the seven BChls that comprise the BChl *a* antenna protein of *P. aestuarii* fall into two distinct conformational classes. Calculations for the seven individual BChls, based on these crystallographic data, indeed yield low-energy absorption maxima that parallel the conformational variations (Gudowska-Nowak, E.; Fajer, J., unpublished results). Obviously, these calculations, by themselves, do not account entirely for the experimental spectrum of *P. aestuarii* because excitonic interactions between close neighbors in the protein are not included.

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) triads¹⁻¹⁰ and a carotenoid-porphyrin-diquinone

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fluorescence measurements²⁷ on **1-5** reveals that singlet energy transfer between porphyrins is faster than or roughly comparable to the rates of the other processes which depopulate the excited singlet states. The C-P_A-P_B-Q singlet state also decays by other photophysical processes (step 2 in Scheme I) with $k_2 = 2.5 \times 10^8 \text{ s}^{-1}$ (based on the 4.0 ns fluorescence lifetime for **5**). C-P_A-P_B-Q decays by photophysical processes ($k_4 = 1.0 \times 10^8 \text{ s}^{-1}$ based on a fluorescence lifetime of 9.9 ns for **2**) and by electron transfer (step 7) to yield C-P_A-P_B^{•+}-Q^{•-}. Photoinitiated electron transfer between the porphyrins is thermodynamically unfavorable in this molecule. In the limit of rapid singlet energy transfer, the porphyrin fluorescence decay of **1** would be a single exponential with a lifetime τ , where $1/\tau = (k_2 + k_4 + k_7)/2$. On this basis, an electron transfer rate constant of $k_7 = 2.4 \times 10^8 \text{ s}^{-1}$ was calculated from the measured fluorescence lifetime of 3.4 ns and the values of k_2 and k_4 mentioned above. Given the experimental errors involved ($\pm 25\%$ for rate constants) and the use of model compounds to estimate rate constants for k_2 and k_4 , this rate constant is in good agreement with the photoinitiated electron transfer rate constant of 2.4×10^8 calculated for **4** in the manner described above from its fluorescence lifetime of 4.5 ns.

Competing with charge recombination in C-P_A-P_B^{•+}-Q^{•-} is electron transfer which ultimately yields C^{•+}-P_A-P_B-Q^{•-} with an overall quantum yield of ca. 0.25 based upon total light absorbed. In Scheme I, this is shown as a two-step process (steps 8 and 10) involving a C-P_A^{•+}-P_B-Q^{•-} intermediate. Cyclic voltammetric measurements on model compounds, which ignore coulombic stabilization, suggest that C-P_A^{•+}-P_B-Q^{•-} would be more stable than C-P_A-P_B^{•+}-Q^{•-} by roughly 0.1 eV, and this would be consistent with a discrete intermediate. On the other hand, coulombic stabilization of C-P_A-P_B^{•+}-Q^{•-} might lower the energy of this state below that of C-P_A^{•+}-P_B-Q^{•-}. In this case, conversion of C-P_A-P_B^{•+}-Q^{•-} to C^{•+}-P_A-P_B-Q^{•-} could involve a single process aided by superexchange interactions of P_A. The long²⁶ lifetime of the final state is the result of the large spatial separation of the cation and anion and the fact that endergonic electron transfers⁷ would be needed to place the charges on adjacent chromophores.

Excitation of **1-5** yields porphyrin triplet states, and in **1** and **3** both of these triplets are rapidly (≤ 20 ns) quenched by the carotenoid via triplet energy transfer; P_A is evidently serving as a triplet energy relay. In addition, the carotenoid moiety of **5** and therefore presumably that of **1** and **3** transfers singlet energy to the attached porphyrin with ca. 10% overall efficiency. Thus, tetrad **1** mimics not only multistep photoinitiated electron transfer (which is characteristic of natural photosynthesis) but also chlorophyll antenna function (singlet energy transfer between chlorophylls), carotenoid antenna function (singlet energy transfer from carotenoids to chlorophylls), and carotenoid photoprotection from singlet oxygen damage (carotenoid quenching of chlorophyll triplet states).

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2,5,7,7-Tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene: The First Isolation and Characterization of a Boratanorcaradiene

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The perturbation of electronic and structural properties caused by replacement of a carbon by a boron atom is a topic of expanding theoretical¹ and experimental² interest. In most of the previously examined cases, electrically neutral trivalent boron atoms are used to simulate isoelectronic and nearly isosteric carbocations. Likewise, tetravalent anionic boron groups (borates) can be thought of as negatively charged analogues of neutral carbon atoms. We report herein the first isolation and characterization of a boratanorcaradiene: 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (**1**) is a blood-red, reactive solid formed from UV irradiation of (*p*-biphenyl)triphenyl borate (**2**).

Borate **2** (Me₄N⁺ salt, ¹¹B NMR: δ -6.76, BF₃·OEt₂ = 0.00) is easily prepared by reaction of biphenyllithium with triphenylborane.³ Its absorption spectrum in acetonitrile solution shows a band at 272 nm ($\epsilon_{\text{max}} = 22600 \text{ M}^{-1} \text{ cm}^{-1}$) characteristic of biphenyl derivatives. Irradiation of **2** in a degassed acetonitrile solution at 254 nm ($1.2 \times 10^{-2} \text{ M}$, Rayonet Reactor, 0 °C, 2 h) leads to formation of a deeply red reaction mixture and appearance of new ¹¹B NMR resonances at δ -26.6 and -27.2. Integration of the product peaks immediately after irradiation shows them to be present in a ratio of 1:1; after 2 h at 30 °C this ratio becomes 5:1. Additional heating causes no further change.

The major product from photolysis of **2** can be isolated in 30% yield by repeated fractional crystallization from CH₃CN/ether. The air and water sensitive red solid has an ¹¹B NMR absorption at δ -26.6. Its elemental analysis gives the formula C₃₄H₃₆BN,³ the same as that of starting borate. The product's UV-vis spectrum in CH₃CN shows two bands: 294 nm ($\epsilon_{\text{max}} = 19000 \text{ M}^{-1} \text{ cm}^{-1}$) and 510 nm ($\epsilon_{\text{max}} = 2700 \text{ M}^{-1} \text{ cm}^{-1}$).⁴

The ¹H and ¹³C NMR spectra of the photoproduct are particularly revealing. Its 500 MHz ¹H NMR spectrum in THF-*d*₈ at room temperature is shown in Figure 1. The two singlets (δ 1.39, 5.55), the triplets at δ 7.17 and 7.02, and the doublet at 7.69 are unaffected when the solution is cooled to -10 °C, but the triplets at δ 6.81 and 6.68 and the doublet at δ 7.10 begin to broaden. Further cooling results in additional broadening until at -80 °C the broadened peaks split into sharpened multiplets. The ¹³C NMR spectrum of the photoproduct shows detectable peaks for only nine carbons, two (δ 37.1 and 135.5) broadened

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(4) The red color of **1** persists, apparently undiminished, even at liquid N₂ temperature. This observation rules out the possibility that it is due to the presence of a minor isomer in equilibrium with **1**.