to explore the cyclization of other unnatural substrates by this technique are in progress.

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# On the Red Shift of the Bacteriochlorophyll-*b* Dimer Spectra

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The UV-vis spectroscopy of chlorophylls often differs greatly from in vitro to in vivo. In particular, the long wavelength transition of bacteriochlorophyll-*b* (BChlb) in reaction centers of the photosynthetic bacterium *Rhodopseudomonas viridis* exhibits a large red shift (790 nm in vitro, 960 nm in vivo). The 960-nm absorption maxinum has been assigned to a BChlb dimer, "special pair", which was recently shown to exist in the X-ray crystal structure of *R. viridis*.[1,2] The origin of this red shift has been a subject of intense interest, and a number of reasons have been suggested to explain it including the following: solvent effects, electrostatic effects of amino acid side chains, dimer formation, and exciton interactions.[3-7]

We present here the results of the calculated UV-vis spectra, employing the quantum chemical INDO method,[8-10] of the BChlb dimer based on the X-ray coordinates seen in *R. viridis*. We observe a large red shift and intensification of the long wavelength transition that agrees well with experiment. While there may be many contributing factors to the spectral shift of BChlb dimers in vivo, the formation of the dimer alone appears to be sufficient to induce a large red shift.

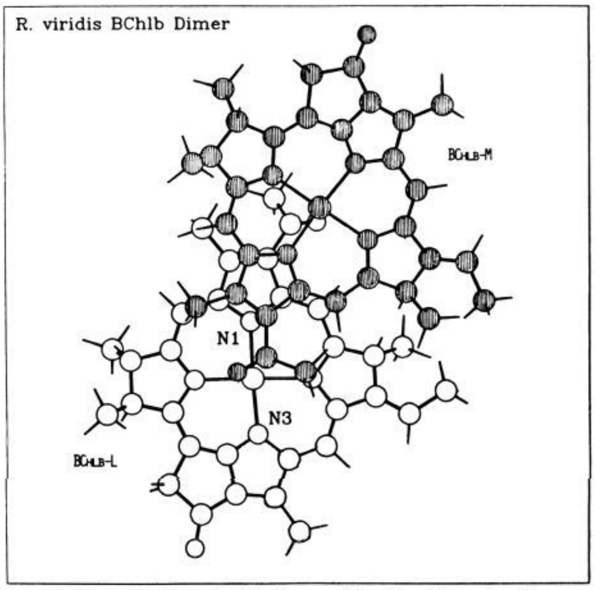

**Figure 1.** Bacteriochlorophyll-*b* dimer utilized in this study. The macrocycles are labeled BChlb-L or BChlb-M corresponding to their association with the L or M subunits of the photosynthetic membrane protein (ref 2 and 3).

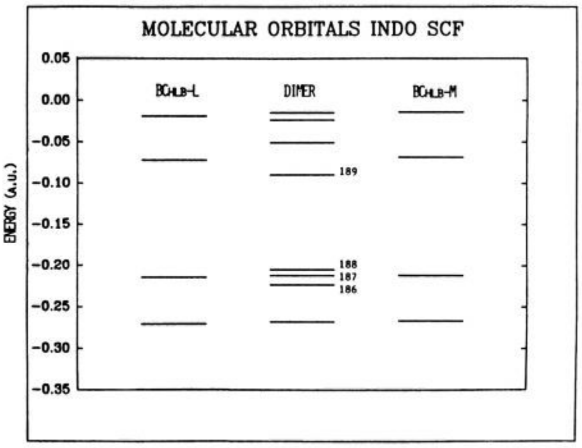

**Figure 2.** The molecular orbitals of the BChlb dimer and its constituent monomers were calculated separately. All calculations were closed shell restricted and converged to $10^{-6}$ in energy.

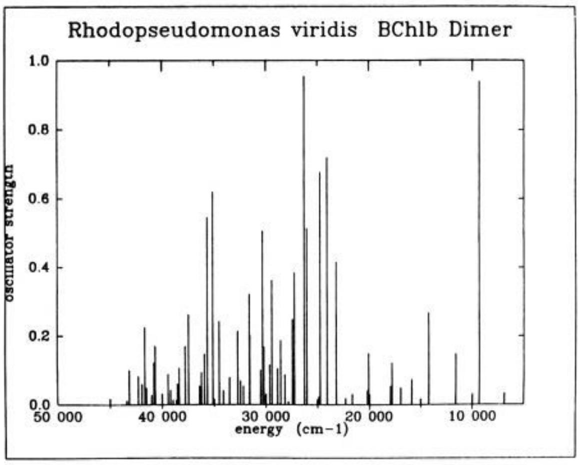

**Figure 3.** The calculated INDO/CI spectrum for bacteriochlorophyll-*b* dimer. The calculation includes the lowest 120 singly excited configurations from the self-consistent field ground state.

Figure 1 shows the structure of the BChlb dimer we employed which is based on the X-ray crystal coordinates.[1] The monomers are labeled as to their major association with either the L or M subunits of the membrane protein in which they are embedded.[1,2] The average distance between atomic centers of the two overlapping pyrrole rings is roughly 3 Å, and the Mg-Mg distance is about 7 Å. The macrocycles are skewed in the plane of the figure about an axis which is roughly perpendicular to the figure and passes through the two overlapping rings and are tilted nearly 15° relative to one another. The monomer MOs shown in Figure 2 are those that would constitute the four-orbital model as described by Gouterman.[11] The monomers, while not geometrically identical, have similar MOs. As well, their Qy absorptions (and oscillator strengths) are similar with BChlb-L and BChlb-M at 12 993 $\mathrm{cm}^{-1}$ (0.555) and 12 864 $\mathrm{cm}^{-1}$ (0.590), respectively.[12] The MOs of the BChlb dimer are split significantly and, except for dimer MOs 189 and 190, do not exhibit obvious monomer par-

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entage. We observe significant mixing of the four highest occupied MOs with those lying lower in energy. At this intermolecular separation it is apparent that a simple extension of the monomeric four-orbital model to the dimer is not justified. The strong overlaps of the monomer wave functions at this distance constitute a large perturbation that is inconsistent with a simple coupled chromophore model.

In Figure 3 we present the INDO calculated UV-vis spectra of the BChlb dimer. What is most striking is the appearance of a strong absorption at 9339 $\text{cm}^{-1}$ with an oscillator strength of 0.939. This represents a 3590-$\text{cm}^{-1}$ red shift relative to the average of the BChlb monomers. This absorption is composed of 90% dimer HOMO → LUMO (MOs 188 → 189) and has a strong *y* polarization. Note in Figure 1 that the *y* axis runs from N3 to N1 of BChlb-L. The Qy transition for BChlb monomers exhibit a major shift of charge density from the ring III side to the ring I side of the macrocycle.[13] In the dimer this shift in electron density is also observed, and, as the monomer *y* axes are roughly antiparallel, there is a net electron density shift toward the center of the dimer structure in the HOMO-LUMO transition. The configurations 186 → 189 and 187 → 189 mix in the configuration interaction (CI) to give a pair of transitions that bracket the 9339-$\text{cm}^{-1}$ transition at 6880 $\text{cm}^{-1}$ (0.032) and 11 616 $\text{cm}^{-1}$ (0.147), respectively. It is interesting to speculate on the possible role that the calculated transition at 6880 $\text{cm}^{-1}$ may play in electron transfer. Although there were no unacceptable steric hinderances in the crystal structure, slight geometric relaxation of some elements of the dimer may affect the MO splitting and hence this absorption. As well, the degree of the red shift is sensitive to the interplanar distance with the monomer spectrum being regenerated at large enough separation.[16] An analysis of these effects in addition to the charge-transfer characteristics of the remaining low-energy transitions and their modulation by electric fields is under investigation.

Although other mechanisms may be contributory and important, we have demonstrated that dimer formation within van der Waals radii for BChlb results, by itself, in a significant red shift with roughly a doubling in the oscillator strength of the long wavelength transition relative to the respective monomers. That a large red shift appears to be a consequence of this particular dimer formation should not be surprising. Large red shifts of the long wavelength transition in crystals of methylbacteriopheophorbide-*a* have been observed experimentally and attributed to $\pi$-$\pi$ interactions between the staggered macrocycle rings.[5] The BChlb macrocycles in the X-ray structure are quite close and appear to behave as a true supermolecule rather than two interacting monomers. Petke and Maggiora showed in theoretical calculations that Mg porphyrin-porphyrin dimers which were within van der Waals distances behaved as a true dimer.[14,15] Also our initial results appear to suggest some charge-transfer characteristics may be inherent in the dimer itself and be quite low lying.[16] It should be noted that the calculated effects of charges upon the UV-vis spectrum of chlorophylls and bacteriochlorophylls are known to be significant.[6,13] Thus the possibility exists that the presence of the proper electric field created by nearby polar substituents or secondary protein structures ($\alpha$-helices) could have a strong effect on the charge-transfer characteristics of the BChlb dimer in vivo. Furthermore, the Qy transition dipole moments for the isolated BChlb monomers are roughly antiparallel and displaced with an overlapping of ring I for both monomers. Although unable to account for the proper magnitude in the red shift, classical exciton theory shows that this relative configuration will result in a larger red shift than were the transition dipoles at right angles or were the macrocycles fully overlapping.[17,18]

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# On the Existence of Alkyl Carbanions in the Gas Phase

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Recently, we introduced a new method for the regiospecific generation of gas-phase carbanions by means of collision-induced decarboxylation of organic carboxylate anions in an FT-ICR (eq 1).[1] We have now adapted this method for use in our flowing afterglow-triple quadrupole instrument[2] and have explored the scope of the method with respect to the kinds of carbanions that can be produced. We describe here an experimental evaluation of the absolute stabilities of alkyl carbanions, as well as the observation of several new species synthesized by reaction 1.

$$RCO_2^- \rightarrow R^- + CO_2 \tag{1}$$

The procedure involves generation of the carboxylate anion in the flow tube by means of fluorodesilylation of the appropriate trimethylsilyl ester.[3] The carboxylate ion is extracted from the flow tube and mass-selected with the first quadrupole. Decarboxylation is effected by means of collision-induced dissociation (CID) in the second quadrupole and the resulting fragment ions are mass-analyzed with the third quadrupole. By monitoring the intensity of $R^-$ as a function of the carboxylate ion axial kinetic energy, we can also obtain an experimental threshold energy for reaction 1.[4]

We have conducted a general survey of the low-energy CID of carboxylate anions and conclude that decarboxylation is a universal fragmentation pathway for such ions.[5] A key observation is that the acetate anion can be decarboxylated to produce a low yield of the methyl anion (eq 2).[6] The fact that we can observe such a "fragile", weakly bound species as $CH_3^-$ with our

$$CH_3CO_2^- \xrightarrow{CID} CH_3^- + CO_2 \tag{2}$$

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