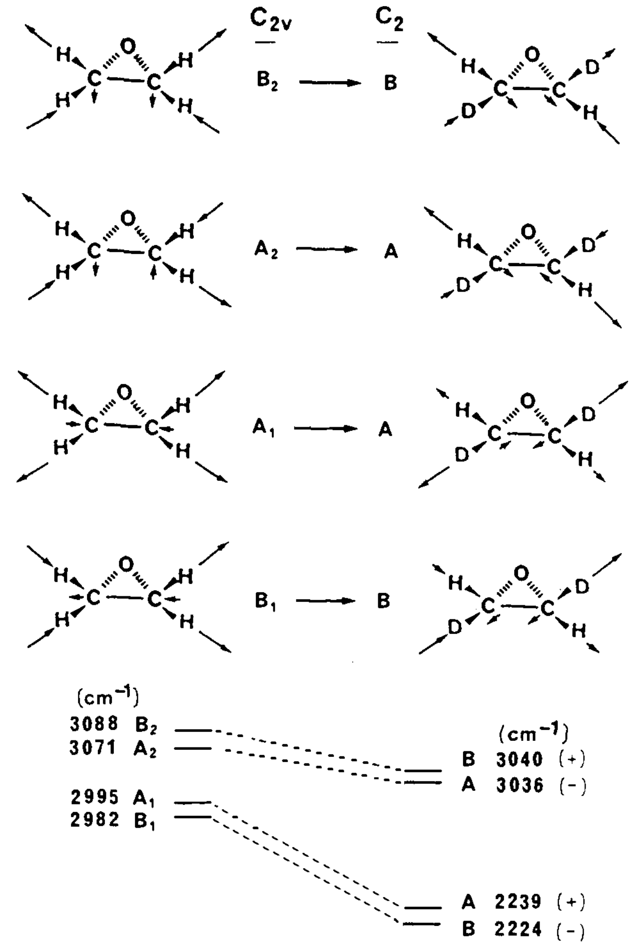


Figure 2. Correlation of calculated hydrogen stretching modes of oxirane (C_{2v} symmetry) and (*S*,*S*)-[2,3-$^2H_2$]oxirane (C_2 symmetry). Long arrows indicate directions of predominant atomic displacements. The minor displacements (small arrows) have been exaggerated for clarity.

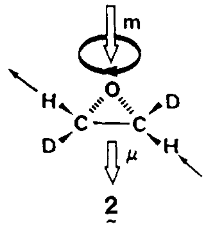
removed by spectral subtraction, since the impurity and benzene were present at unequal concentration for the two enantiomers. No interfering bands were observed in the CD-stretching region. For the spectra shown in Figure 1, the maximum absorbance in the CH stretching region due to impurity bands was less than 20% of the sample absorbance.

The VCD spectra consist of a CH-stretching couplet (3026 (+), 3004 cm^{-1} (−)), corresponding to the intense absorption band at 3022 cm^{-1} and a weak, unresolved band, and a CD-stretching couplet (2254 (+), 2228 cm^{-1} (−)) associated with the weak 2254-cm^{-1} and intense 2237-cm^{-1} absorption bands. The CH-stretching couplet is distinctly biased to positive intensity, whereas a smaller, but significant negative VCD bias is present in the CD-stretching region. Similar VCD biases were observed for all three synthetic batches.

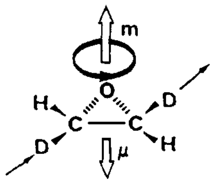
Normal coordinate analyses for both the tetraprotiooxirane and **1** were carried out with the ab initio force field of Lowe et al.[22] Calculated frequencies, mode symmetries, and schematic mode descriptions are shown in Figure 2. The mode correlation in Figure 2 shows that, although the relative magnitudes of the atomic displacements in the four modes change upon deuteriation, the relative phasings of the displacements do not change. The four modes maintain the symmetry order B, A, A, B from high to low frequency for both isotopomers.

From purely geometric considerations for the CH and CD oscillators in **1**, the A modes are predicted to be weak and the B modes intense. On the basis of the coupled oscillator model for the two chirally oriented CH or CD oscillators,[8] the four modes of **1** depicted in Figure 2 should give rise to a conservative (+,−) couplet, with the positive lobe at higher frequency, in each spectral region. The overall absorption and VCD patterns agree with these predictions.

The bias in the two couplets can arise from the ring current mechanism for VCD.[9] On the basis of the empirical rule 1 for an oscillator external to a ring but adjacent to a heteroatom in the ring,[1a,9b] contraction of a CH (or CD) bond injects electronic charge into the ring preferentially toward the oxygen, whereas elongation of the bond preferentially withdraws electronic charge from the oxygen. Positive ring current at constant electron density is initiated around the oxirane ring as shown in **2** and **3** for the B-symmetry stretches. The electric dipole transition moments μ and ring current magnetic dipole transition moment m for the B modes thus result in positive VCD bias in the CH-stretching region and negative VCD bias in the CD-stretching region, since the A modes are not enhanced. The smaller bias observed for the CD-stretching bands may be due partly to overlapping positive VCD intensity at $\sim$2220 due to an A mode in Fermi resonance with the A fundamental.



2



3

Recent VCD intensity calculations in our laboratory using a vibronic coupling formulation with floating basis functions[10] have also predicted VCD couplets for these modes with the observed sense and bias. Investigation of the other chiral deuteriated isotopomers of oxirane and extension to the mid-infrared region are in progress.

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Electrochromic Effects of Charge Separation in Bacterial Photosynthesis: Theoretical Models

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The primary charge separation in photosynthetic bacteria generates a dimeric bacteriochlorophyll (BChl) cation and a bacteriopheophytin (BPheo) anion[1-5] which lie within close proximity of each other ($\sim$10 Å).[6,7] The two radicals also lie

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Table I. Effect of Point Charges on the Q_y (red) Band of BChl *b*

point charge	position[a]	frequency shift of Q_y,[b] cm^{-1}	
+1	N(I) (*y*-axis)	-1440	red
-1	N(I)	2297	blue
+1	N(II) (*x*-axis)	-239	red
-1	N(II)	109	blue
+1	N(III) (*y*-axis)	1329	blue
-1	N(III)	-895	red
+1	N(IV) (*x*-axis)	-564	red
-1	N(IV)	440	blue
+1	C20	-1272	red
-1	C20	1993	blue
+1	C2	-1603	red
-1	C2	2872	blue
+1	O6	-1256	red
-1	O6	1886	blue
+1	C8a	1060	blue
-1	C8a	-1411	red
+1	C12	2579	blue
-1	C12	-1160	red
+1	O1	1796	blue
-1	O1	-1000	red

[a] Charge is 3.5 Å above the atom. [b] Relative to no charge; increasing the dielectric constant from 1 (vacuum) to 2 to simulate the hydrophobic environment of the chromophores in the RC[6] roughly halves the values shown.

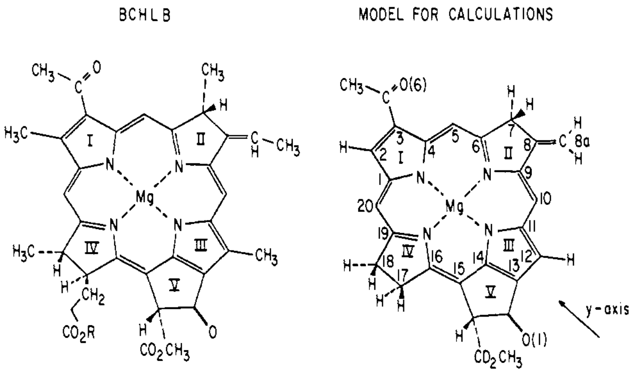

Figure 1. Structures of BChl *b*, the chromophore found in *R. viridis*, and of the model used in the calculations.

within van der Waals contact on opposite sides of a lone BChl "bridging" molecule.[6,7] Spectral changes in the red (Q_y) band of the bridge BChls have been observed on picosecond time scales following excitation of the reaction center (RC)[1-5,8] and have been variously attributed to the formation of a BChl anion,[8] to a charge-transfer state,[9] or to electrochromic effects.[2-5,10] We present calculations here which suggest that electrochromic effects caused by the photogenerated cation and/or anion can rationalize the optical changes observed in the flash photolyses as well as in trapping experiments.

INDO calculations[11] predict that point charges placed within 3-4 Å of BChls can induce significant shifts of the red (Q_y) band.[12]

Table II. Effect of Donor and Acceptor Charges on the Q_y (Red) Band of the Bridging BChl *b* of *R. viridis* Reaction Centers

charge	position	freq shift of Q_y,[a] cm^{-1}
+1	center of the (BChl $b)_2^+$; 3.94, -9.93, 2.54 Å[b]	1063
-1	center of the BPheo *b*; -1.41, 5.54, 8.46 Å[b]	653
+1, -1	cation and anion located as above	1857
10 charges of +0.1 au distributed over the 2Mg and 8N of (BChl $b)_2^+$		924
4 charges of -0.25 au distributed over the 4N of BPheo b^-		664
+, - cation and anion distributed as above		1709

[a] Relative to no charge; all blue shifts. [b] *x*, *y*, and *z* coordinates of the radicals $(BChl)_2^+$ or $BPheo^-$ relative to the center of the bridging BChl.

Table I lists values calculated for BChl *b*, the chromophore of *Rhodopseudomonas viridis*[6] (see Figure 1). (Similar results are obtained for the BChls *a* and *g* found in other photosynthetic bacteria.) The magnitude and sign of the optical shifts depend upon the placement and sign of the point charge: positive charges placed near ring I or negative charges situated near ring III cause large red shifts whereas reversing the charges results in large blue shifts.[13]

The primary charge separation in a RC should therefore induce a significant electrochromic effect on the optical spectrum of the BChl that bridges the primary donor and the BPheo. Table II lists the shifts calculated by using the *R. viridis* X-ray coordinates[6] for the bridging BChl *b* of the photochemically active L subunit with a positive charge placed at the donor (BChl $b)_2$ centroid and a negative charge at the center of the acceptor BPheo *b*. Also presented are the results of distributing the point charges over the cores of the donor and acceptor. Individually or together, these charges induce sizeable blue shifts for the bridging BChl *b*. The calculations do not reflect shielding effects by the protein and ring substituents which would further minimize the predicted shifts. The electrochromic effects would also be susceptible to additional modulation if changes in distances or orientations between the chromophores follow electron transfer.[14]

At the present level of refinement, the X-ray structure of *R. sphaeroides*, which contains BChl *a*, reveals a molecular architecture analogous to that of *R. viridis*.[7] Similar electrochromic shifts are thus predicted for the two species.

Experimentally, blue shifts of a few hundred wavenumbers in the spectra of the bridging BChls (*a* or *b*) have indeed been observed on picosecond time scales,[3-5,8] and they have been variously attributed to the formation of a BChl anion,[8] to a charge-transfer state,[9] or to electrochromic effects.[3-5,10] As suggested by the calculations presented above, such effects should certainly be induced by the generation of the $(BChl)_2$ cation donor and the BPheo anion acceptor. Subpicosecond changes observed[3,5] in the BChl spectra may also be electrochromic and caused by the electron as it traverses the gap[6] between donor and acceptor.

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(13) A point charge affects the optical spectrum principally through differential interactions with the dipole moments of the ground and excited states. The larger the initial difference between the ground- and excited-state values, the larger the perturbation. The ground state has a considerable dipole moment along the *y*-axis, which runs through rings I and III, whereas the transition to the Q_y state nearly cancels this moment. Therefore, for a charge at a given distance from the Mg, the calculated optical shifts for the Q_y band are largest near the *y*-axis and fall off toward the *x*-axis.

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The duplication of chromophores, four BChls and two BPheos, combined with the ground-state bleaching and the formation of cation and anion radicals, obviously complicates unambiguous assignments of some of the optical changes that reflect the rapid electron transfer carried out by the RC. However, in further support of the trends predicted by the calculations (Table II), BChl blue shifts are also observed when only the donor is oxidized or the acceptor is reduced under steady-state conditions.[4,10]

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Linear Free Energy Relationship between Keto ⇌ Enol Equilibrium Constants of Stable β,β-Dimesityl and Unstable β,β-Unsubstituted α-Substituted Enols[1]

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There has been a revival in this decade in the study of keto ⇌ enol equilibrium constants (K_{enol}) of simple enols.[2,3] Two types of enols have been studied. Simple unstable aliphatic or α-aryl-substituted enols, such as those of acetaldehyde,[4] acetone,[5] acetophenone,[6] or isobutyraldehyde,[7] were prepared by Capon's,[4a,b] Kresge's,[4c,5,6c,7] and Toullec's[6a,b] groups as short-lived intermediates, and their ketonization rates are recorded. When these are combined with the enolization rates of the ketones, accurate K_{enol} values in water are obtained. In parallel, K_{enol} values for sterically crowded polyaryl-substituted enols (Fuson-type enols[8]) that are kinetically and sometimes thermodynamically rather stable, such as β,β-dimesityl α-substituted ethenols[9] or acenaphthenols,[10] were determined accurately by us[9] and by Miller[10] in nonaqueous solvents, starting from both the ketones and the enols.

Table I. pK_{enol} Values for the Equilibria

$$R_2'CHC({=}O)R \xrightleftharpoons{k_{\text{enol}}} R_2'C{=}C(OH)R$$

R	R′ = H (H$_2$O, 25 °C)	ref	R′ = Mes (hexane, 94.6 °C)	ref
Mes	(5.5)[a]		−1.90[b]	9b
H	6.23	4c	−1.30[b]	9a
m-ClC$_6$H$_4$	7.57	6b	−0.34	9c
Ph	7.96	6b,6d	−0.01	9c
Me	8.22	5	0.19[b]	9b
p-MeOC$_6$H$_4$	8.64	6b	0.49	9c
t-Bu	(10.95)[a]		2.23[b]	9b

[a] Value predicted from the linear regression. [b] At 80.6 °C.

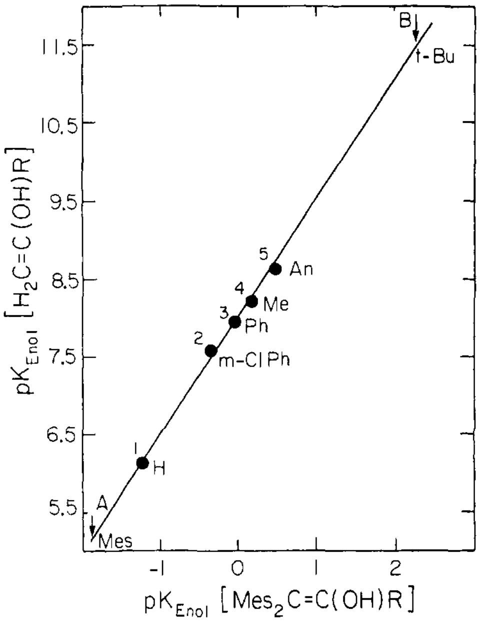

Figure 1. Correlation between pK_{enol} values for H$_2$C=C(OH)R in water and pK_{enol} values for Mes$_2$C=C(OH)R in hexane.

Are substituent effects correlated in the two types of systems? The question is of interest for three reasons. First, since K_{enol} values are sometimes determined more easily in one of the systems, coorrelation will permit the estimation of values which are not otherwise available in the other system. Second, K_{enol} values for the β,β-dimesityl (Mes)-α-alkyl and α-H systems **1** (R = H, Me, Et, *i*-Pr, *t*-Bu) are correlated with Taft's steric parameters,[9b] with the rotational barriers of the correlated two-ring flip in these systems,[11] and with the R—C=C bond angles or the C=C—Mes (cis to R) dihedral angles for **1**.[12] Consequently, a correlation between substituent effects in **1** and in the β,β-unsubstituted α-substituted systems **2** could suggest that a correlation may exist between K_{enol} values for **2** and steric and structural parameters for this system. Third, the two systems differ in the bulk and the conjugative ability of the β-substituents and probably in the conformation of the OH group.[13] The solvent is also different. Could a correlation be found in spite of these differences?

$$\underset{\mathbf{1}}{Mes_2C{=}C(OH)R} \qquad \underset{\mathbf{2}}{H_2C{=}C(OH)R}$$

Data for correlation of the K_{enol} values for **1** in hexane and of **2** in water are available for R = H, Me, Ph, *p*-ClC$_6$H$_4$, and *p*-MeOC$_6$H$_4$ (Table I). Data for other substituents in one series have at present no parallel in the other series and are not given, except for the values for R = Mes and *t*-Bu in system **1**. The data are plotted in Figure 1 as a LFER of pK_{enol}(**2**) vs. pK_{enol}(**1**), where p$K_{\text{enol}} = -\log K_{\text{enol}}$. A linear correlation is obtained with a slope of 1.33 ($r = 0.9991$).

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