5–10% of $5^{15}$ cannot be redissolved in pentane).

Mass spectra and UV–vis spectra of each polyene are what might be expected on the basis of what is known for isoprenoids[1] and synthetic polyenes.[4] For example, the parent ion is the most intense with peaks for the doubly charged ions becoming significant for the longer polyenes, while the lowest energy transition[4c] ($^1B_u \leftarrow {}^1A_g$) in the UV–vis spectra is solvent dependent and red shifts with increasing chain length.[8]

$^{13}$C NMR spectra of samples of $5^7$, $5^9$, and $5^{11}$ show them to consist of ~75% of a single relatively symmetric isomer ($C_{2h}$ or $C_{2v}$) having 7, 9, or 11 olefinic resonances, respectively. The chemical shifts for $5^7\mathbf{a}$, $5^9\mathbf{a}$, and $5^{11}\mathbf{a}$ (**a** implies this major isomer) are listed in Table I. It should be noted that the chemical shift of the innermost carbon atoms in the chain in this isomer appear to be converging upon 130 ppm, a chemical shift close to that observed in *cis*-polyacetylene (128 ppm in the solid state).[11] Preliminary heteronuclear and homonuclear (H/H) correlation experiments suggest that the first olefinic carbon atom in the chain in the **a** isomer gives rise to the resonance at ~140 ppm, while the second gives rise to that at ~120 ppm.[13] Irradiation into the formally all-trans forbidden transition (the so-called cis band 140 nm above the origin of the $^1B_u \leftarrow {}^1A_g$ transition) in $5^7$ yields a material whose $^{13}$C NMR spectrum shows it to consist of >90% of another isomer ($5^7\mathbf{b}$, Table I). On the basis of the observation that $5^7\mathbf{b}$ appears to be significantly less soluble and more crystalline than $5^7\mathbf{a}$ and on the basis of a characteristic strong, well-resolved, red-shifted UV–vis spectrum, we propose that $5^7\mathbf{b}$ is the all-trans isomer.

Several pieces of evidence suggest that the di(*tert*-butyl)-capped polyenes containing 17 or more double bonds are relatively unstable under the experimental conditions we have employed so far. First, significant amounts of $5^{17}$ and $5^{19}$ should be formed.[10] Second, attempts to prepare a distribution of longer polyenes by using 10 equiv of **1** gave only a reduced yield of qualitatively the same distribution of polyenes as that obtained employing 5 equiv of **1**. Third, from qualitative observations the longer the polyene the more extensively it decomposes to give pentane-insoluble material. We speculate that insoluble material results from cross-linking and that higher polyenes cross-link more readily. We hope to prepare longer polyenes by employing the parent tricyclo[4.2.0]deca-3,7,9-triene, since the retro Diels–Alder reaction in the polymer prepared by ring opening proceeds under relatively mild conditions.[5]

We believe that polyenes prepared by controlled ring-opening metathesis polymerization will help fill a significant gap in our knowledge of this important class of molecules. A valuable feature of the method is the ability to control the nature of at least one end group in the Wittig-like capping reaction. Extensions of such studies may allow us to prepare molecules with unusual nonlinear optical properties.[12]

**Supplementary Material Available:** Full details of the preparation and isolation of the polyenes and partial spectroscopic data (1 page). Ordering information is given on any current masthead page.

(11) (a) Maricq, M. M.; Waugh, J. S.; MacDiarmid, A. G.; Shirakawa, H.; Heeger, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7729. (b) Gibson, H. W.; Pochan, J. M.; Kaplan, S. *J. Am. Chem. Soc.* **1981**, *103*, 4619. (c) Mehring, M.; Weber, H.; Miller, W.; Wegner, G. *Solid State Commun.* **1983**, *45*, 1079.

(12) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S.; Zyss, J., Eds. Academic Press, Inc.: New York, 1987; Vol. 1 and 2.

(13) **Note Added in Proof.** Homo- and heteronuclear correlation experiments suggest that the **a** isomer has a *trans*(*cis*,*trans*)$_n$ configuration ($n = 7$, 9, 11) as a result of stereoselective initiation, propagation, and capping reactions.

# Phosphorescence Spectra of Bacteriochlorophylls

Larry Takiff and Steven G. Boxer*

*Department of Chemistry, Stanford University
Stanford, California 94305*

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We wish to report phosphorescence spectra of the lowest triplet state of a number of bacteriochlorophylls (BChls) which provide the first accurate values for the triplet state energies of these chromophores. There have been many previous attempts to estimate the triplet state energies of bacteriochlorins motivated by the possible importance of triplet states in photosynthesis, the utility of these chromophores as sensitizers and quenchers of singlet oxygen, model studies of electron transfer, and intrinsic theoretical interest in the excited state energies of extended conjugated macrocycles.[1]

These observations were made possible by the recent development of liquid nitrogen cooled germanium photodiode detectors which are highly sensitive in the 800–1800 nm region. We recently reported phosphorescence spectra of photosynthetic reaction centers (RCs)[2] and have used identical methods in the present study. The absorbance, fluorescence, and phosphorescence spectra of BChl *a* are shown in Figure 1 and are typical of the spectra we obtain. Table I summarizes the results for several compounds. Luminescence decay kinetics were compared with the triplet lifetimes measured by transient absorption spectroscopy and were found to be the same within the experimental error.[3] The high sample concentrations and excitation light intensities required to observe this weak phosphorescence preclude the measurement of excitation spectra, as the luminescence intensity is not proportional to the sample absorbance under these conditions. The fluorescence quantum yield of BChl *a* is about 0.21;[4] we estimate that the phosphorescence quantum yield is roughly $10^{-7}$ by comparison of the integrated intensities of the emission bands, and this is typical of the bacteriochlorins.

It is seen that the singlet–triplet splittings of BChls are about the same as those measured for chlorophylls. The widths and shapes of the phosphorescence bands are about the same as their lowest energy absorbance and fluorescence bands. We find very little difference in the phosphorescence maxima of 5- and 6-coordinate BChl *a*, in contrast to those reported for Chl *a* (Table I, footnote i).[5]

These triplet energies may have important implications for triplet energy transfer from the BChl dimer to carotenoids in the

(1) Connolly and co-workers (Connolly, J. S.; Gorman, D. S.; Seely, G. R. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 649–669) estimated a $^3$BChl *a* energy of 5300–6100 cm$^{-1}$. Krasnovskii concluded that the energy of $^3$BChl *a* might be slightly higher than that of oxygen in its $^1\Delta_g$ state (7882 cm$^{-1}$) (Krasnovskii, A. A., Jr. *Photochem. Photobiol.* **1979**, *29*, 29–36). Song (Song, P. S. *Am. Chem. Soc. Symp. Adv. Chem. Plant Pigments*; Academic Press: New York, 1970; pp 33–74) calculated the energy of $^3$BChl *a* to be 7100 cm$^{-1}$. Weiss (Weiss, C. *J. Mol. Spectrosc.* **1972**, *44*, 37–80) predicted a value of 5600 cm$^{-1}$ for bacteriochlorin. Petke et al. (Petke, J. D.; Maggiora, G. M.; Shipman, L. L.; Christoffersen, R. E. *Photochem. Photobiol.* **1980**, *32*, 399–414) calculated a value of 9752 cm$^{-1}$ for ethylbacteriopheophorbide *a* and 7880 cm$^{-1}$ for ethylbacteriochlorophyll *a*. Sekino and Kobayashi (Sekino, H.; Kobayashi, H. *J. Chem. Phys.* **1987**, *86*, 5045–5052) estimated a triplet energy of 5200 cm$^{-1}$ for metallobacteriochlorin.

(2) Takiff, L.; Boxer, S. G. *Biochim. Biophys. Acta* **1988**, *932*, 325–334.

(3) For example, the $^3$BChl *a* lifetime at 77 K measured by transient absorption is 132 ± 1 $\mu$s and the phosphorescence lifetime is 124 ± 7 $\mu$s. Chlorin impurities absorbing around 680 nm are common contaminants of bacteriochlorins, but phosphoresce at much shorter wavelength with much longer lifetimes than the bacteriochlorins (Krasnovskii, A. A., Jr.; Romanyuk, V. A.; Litvin, F. F. *Dokl. Akad. Nauk SSSR* **1973**, *209*, 965).

(4) Tait, C. D.; Holten, D. *Photobiochem. Photobiophys.* **1983**, *6*, 201–209.

(5) It has been suggested that singlet fission may be important in the initial events of photosynthesis (Thurnauer, M. C.; Katz, J. J.; Norris, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3270–3274. Merrifield, R. E.; Avakian, P.; Groff, R. P. *Chem. Phys. Lett.* **1969**, *3*, 155–157). This mechanism requires, however, that the $^3$BChl energy be less than or equal to half the excited singlet energy, which is ruled out by the data in Table 1.

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**Table I.** Absorption ($Q_y$), Fluorescence, and Phosphorescence Maxima for Bacteriochlorins and Related Chromophores[a]

| molecule | $\bar{\nu}_{max}$ absorption | $\bar{\nu}_{max}$ fluorescence | $\bar{\nu}_{max}$ phosphorescence | $\bar{\nu}_{max}$(fluorescence) − $\bar{\nu}_{max}$(phosphorescence) |
|---|---|---|---|---|
| bacteriochlorophyll *a* 5-coordinate[c] | 12950 (772) | 12850 (778) | 8240 (1214) | 4610 |
| bacteriochlorophyll *a* 6-coordinate[d] | 12870 (777) | 12740 (785) | 8190 (1221) | 4550 |
| Zn-bacteriochlorophyll *a* 5-coordinate[e] | 12970 (771) | 12935 (773) | 8330 (1200) | 4600 |
| Zn-bacteriochlorophyll *a* 6-coordinate[f] | 12950 (772) | 12850 (778) | 8320 ± 50 (1202) | 4530 |
| bacteriopheophytin *a*[e] | 13300 (752) | 13180 (759) | 9110 (1097) | 4070 |
| bacteriochlorophyll *b* 6-coordinate[g] | 12320 (818) | 12180 (821) | 7970 ± 40 (1255) | 4210 |
| Zn-tetraphenyl-bacteriochlorin 5-coordinate[e] | 13290 (752.6) | 13250 (755) | 8640 (1157) | 4610 |
| H₂-tetraphenyl-bacteriochlorin[e] | 13510 (740) | 13510 (740) | 9500 ± 100 (1053) | 4010 |
| *Rb. sphaeroides* reaction centers[h] | 11520 (868) | 10880 (919) | 7590 (1318) | 3290 |
| *Rps. viridis* reaction centers[h] | 10000 (1000) | 9810 (1019) | 6680 (1497) | 3130 |
| chlorophyll *a* 6-coordinate[i] | | 14860 (673) | 10310 (970) | 4550 |
| chlorophyll *b* 6-coordinate[i] | | 15150 (660) | 10870 (920) | 4280 |

[a] Recorded at 77 K. Numbers in parentheses are in nanometers, all others are in wavenumbers. Uncertainties are ±20 cm⁻¹ unless otherwise indicated. The coordination number of central metal ions was determined from the absorption spectrum at 77 K, c.f.: Evans, T. A.; Katz, J. J. *Biochem. Biophys. Acta* **1975**, *39*, 414. [b] Equal to the singlet–triplet splitting, if the Stokes shifts in the singlet and triplet states are equal (see ref 2). [c] In triethylamine. [d] In 10% pyridine/2-methylTHF. [e] In 2-methylTHF. [f] In 30% pyridine/2-methylTHF. [g] In 16% pyridine/toluene. [h] In poly(vinyl alcohol) film (see ref 2). [i] From Dvornikov et al. (Dvornikov, S. S.; Knyukshto, V. N.; Solovev, K. N.; Tsvirko, M. P. *Opt. Spectrosc. (USSR)* **1979**, *46*, 385–388) in a mixture of diethyl ether, petroleum ether, isopropyl alcohol, and pyridine. We observed phosphorescence from chlorophyll *a* in 1% pyridine/2-methylTHF at 77 K with $\bar{\nu}_{max}$ at 10360 cm⁻¹.
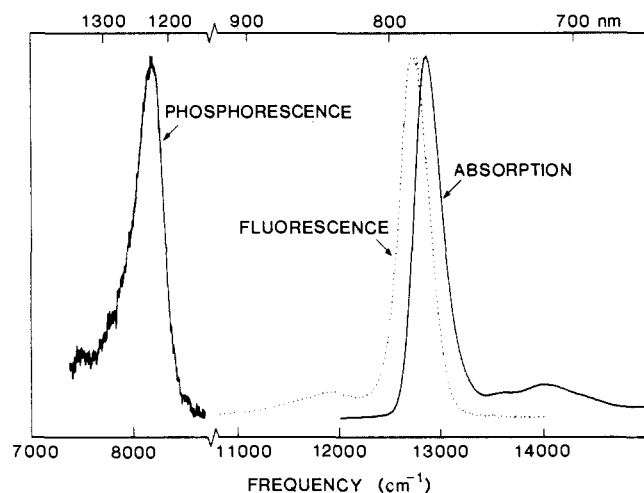


**Figure 1.** Absorption, fluorescence, and phosphorescence spectra of bacteriochlorophyll *a* in 10% pyridine/2-methyltetrahydrofuran (v:v) at 77 K (6-coordinate). The bacteriochlorophyll *a* concentrations were about 40, 2, and 100 μM, respectively. The spectra have been scaled for convenient presentation; the phosphorescence intensity is about 10⁶ times weaker than the fluorescence. Excitation wavelengths were 605 nm for phosphorescence and 610 nm for fluorescence ($Q_x$ excitation). The emission spectra are corrected for the spectral response of the detection system (note the break in the horizontal scale).

RC. A monomeric BChl is found very close to the dimer in the X-ray structure of RCs;[6] a carotenoid has been located adjacent to this monomeric BChl, roughly 10 Å from the dimer,[7] which

is too far for fast (ns) triplet energy transfer.[8] Combining the absorption maximum of monomeric BChl *a* in the RC (802 nm) with the Stokes shift and singlet–triplet splitting of BChl *a* (Table I), we calculate the triplet state of the monomeric BChl *a* in the *Rb. sphaeroides* RC to be less than 200 cm⁻¹ above that of the dimer. The temperature dependence of transient absorption signals in carotenoid-containing *Rb. sphaeroides* RCs can be interpreted in terms of energy transfer from the triplet state of the dimer to the carotenoid via a state which lies 200 ± 40 cm⁻¹ above the dimer triplet state.[9] Thus, we suggest that triplet energy transfers from the dimer to the carotenoid via the monomeric BChl *a*, explaining the long distance of transfer and the absence of transfer at low temperature.[9,10] By contrast, we estimate the triplet state of the monomeric BChl *b* in the *Rps. viridis* RC to be about 1000 cm⁻¹ above that of the dimer, which explains why no dimer to carotenoid triplet energy transfer is seen in this species at any temperature.[11]

(6) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385–398. Chang, C. H.; Tiede, D.; Tang, J.; Smith, U.; Norris, J. *FEBS Lett.* **1986**, *205*, 82–86. Allen, J. P.; Feher, G.; Yeates, T. O.; Komiya, H.; Rees, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 5730–5734.

(7) Deisenhofer, J.; Michel, H. In *The Photosynthetic Bacterial Reaction Center*; Breton, J., Vermeglio, A., Eds.; NATO ASI Series, Plenum: New York, 1988; p 1. Allen, J. P.; Feher, G.; Rees, D. C. *Biophys. J.* **1988**, *53*, 205a.

(8) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836–850.

(9) Schenck, C. C.; Mathis, P.; Lutz, M. *Photochem. Photobiol.* **1984**, *39*, 407–417. These authors also suggested that energy transfer occurs via a BChl but proposed that the intermediate state was a triplet charge transfer state (Shuvalov, V. A.; Parson, W. W. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 957–961), which is unlikely based upon EPR (Hoff, A. J.; Proskuryakov, I. I. *Chem. Phys. Lett.* **1985**, *115*, 303–310) and phosphorescence (Takiff and Boxer, op. cit.) spectroscopy of the RC.

(10) Frank, H. A.; Machnicki, J.; Friesner, R. *Photochem. Photobiol.* **1983**, *38*, 451–455. Our mechanism also explains the increase in the RC triplet zero field splitting with temperature (Hoff and Proskuryakov, op. cit.) as well as the temperature dependence of the RC phosphorescence line shape (the broadening of the band on the blue side at high temperature may be due in part to phosphorescence of the RC monomer BChls, which is not resolved from the dimer phosphorescence since the energy gap is only 200 cm⁻¹ or less).

(11) Holten, D.; Windsor, M. W.; Parson, W. W.; Thornber, J. P. *Biochim. Biophys. Acta* **1978**, *501*, 112–126.