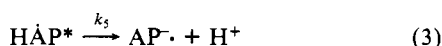
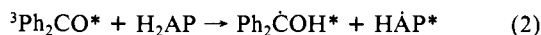
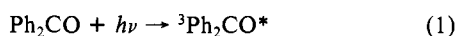


Figure 1. CW ESR spectra observed during the photolysis of benzophenone and ascorbyl palmitate (a) in IPA/toluene at room temperature and (b) in IPA/toluene solution containing 5% v/v  $\text{H}_2\text{SO}_4$ .

the largest intensity variation occurring in the latter case. Time-resolved CIDEP experiments (using technique described previously<sup>12</sup>) showed strong emissive polarization with a  $T_1$  of 4  $\mu\text{s}$  for the high-field component of  $\text{AP}^-$  only and no polarization for the low-field component. Emissive polarization with a considerably longer  $T_1$  of 14  $\mu\text{s}$  was noted for  $\text{Ph}_2\dot{\text{C}}\text{OH}$ . Lowering the temperature of substituting ethanol as the solvent did not alter the pattern of the polarization.

Addition of base (10% v/v NaOH) to the solution of  $\text{H}_2\text{AP}$  and benzophenone resulted in a "normal" CW ESR spectrum having hyperfine lines of equal intensity for  $\text{AP}^-$ . For this system time-resolved CIDEP experiments showed weak emissive polarization for both hyperfine lines. However, photolysis of a solution of  $\text{H}_2\text{AP}$  and benzophenone containing 5% v/v  $\text{H}_2\text{SO}_4$  resulted in a single-line ESR spectrum (Figure 1b) having  $g$  factor 2.0048. In time-resolved experiments strong emissive polarization with  $T_1$  of 6  $\mu\text{s}$  was noted for this single line. These unusual CIDEP observations can be accounted for by considering some of the chemical reactions involved in such a system.

The relative proportions and pH dependence of the dissociated forms of  $\text{H}_2\text{A}$  in solution, i.e.,  $\text{HA}^-$  and  $\text{A}^{2-}$ , can be estimated spectrophotometrically.<sup>13</sup> Both  $\text{H}_2\text{A}$  and  $\text{H}_2\text{AP}$  are predominantly unionized in ethanol solution. ESR studies on radicals derived from ascorbic acid have demonstrated that  $\text{A}^-$  is the most stable species formed over the pH range 0-9. However, Laroff, Fessenden, and Schuler<sup>10</sup> have observed the neutral radical  $\text{H}\dot{\text{A}}$  with an estimated  $g$  factor of 2.00482 in very acidic solution (4 M  $\text{HClO}_4$ ). The  $\text{p}K_a$  of  $\text{H}\dot{\text{A}}$  is thought to be  $\sim 0.4$ ,<sup>10</sup> thus rapid deprotonation to  $\text{A}^-$  is expected in nonacidic media. However, in organic solvents  $\text{H}\dot{\text{A}}\text{P}$  may dissociate to a lesser extent. The following reactions may explain the CW and CIDEP observations of the  $\text{H}_2\text{AP}$ /benzophenone system in neutral, basic, and acidic solution:



The well-established phototriplet mechanism of CIDEP explains the formation of the emissively polarized benzophenone ketyl radical and  $\text{H}\dot{\text{A}}\text{P}^*$  by hydrogen abstraction from  $\text{H}_2\text{AP}$  by the polarized triplet benzophenone (eq 2). In neutral solution the

radical anion  $\text{AP}^-$ , resulting from dissociation of  $\text{H}\dot{\text{A}}\text{P}^*$  is unpolarized indicating that the first-order rate constant for deprotonation ( $k_5$ ) is less than  $1/T_1$  for  $\text{H}\dot{\text{A}}\text{P}^*$  (i.e.,  $k_5 < 0.2 \times 10^6 \text{ s}^{-1}$ ). The anomalous emissive polarization on the high-field line of  $\text{AP}^-$  is in fact a result of the presence of  $\text{H}\dot{\text{A}}\text{P}^*$  which only partially overlaps the  $\text{AP}^-$  spectrum due to the difference in their  $g$  values. This spectral overlap also accounts for the distortion of line intensities in the CW ESR spectrum (Figure 1a) since the  $\text{H}\dot{\text{A}}\text{P}^*$  radical underlies only the high-field component of  $\text{AP}^-$ . Upon addition of NaOH the deprotonation rate was greatly enhanced and the equilibrium was shifted entirely to the right, giving a "normal" CW ESR spectrum of  $\text{AP}^-$ . If  $k_5$  is comparable to or greater than  $1/T_1$  of  $\text{H}\dot{\text{A}}\text{P}^*$ , the resulting radical anion  $\text{AP}^-$  will exhibit emissive polarization which will be observed on both hyperfine components; the magnitude of polarization retained will be dependent upon the relative magnitude of  $k_5$  to  $1/T_1$ . Conversely, addition of a strong acid may well shift the deprotonation equilibrium to the left, resulting in observation of the neutral radical  $\text{H}\dot{\text{A}}\text{P}^*$  only in the CW spectrum. This radical exhibited strong emissive polarization in the time-resolved experiment as predicted by theory.

The results demonstrate the usefulness of the CIDEP technique in mechanistic studies. In the present case, the combination of the physical technique and chemical information led to a significant finding of the "elusive" neutral ascorbate radical as well as the nature of the primary photoreaction of benzophenone with ascorbates.

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#### Aggregation of a Bacteriochlorophyllide $d$ : Direct Evidence for a Nonsymmetric Aggregate in Solution

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Despite intense interest and activity, the molecular organization of the chlorophylls (Chls) and bacteriochlorophylls (BChls) in vivo remains open to question. A considerable body of spectroscopic data has provided evidence for dimerization, aggregation, and chlorophyll-protein interactions to account for the various BChl forms observed in vivo.<sup>3</sup> One may arbitrarily distinguish between the symmetric<sup>4</sup> and nonsymmetric models;<sup>5</sup> the latter include the Fong,<sup>6</sup> Shipman,<sup>7</sup> and synthetic<sup>8</sup> models for Chl and BChl reaction centers. We describe here the first direct experimental evidence for the nonsymmetric nature of a methyl bacteriochlorophyllide (BChlide; generically, a pyrochlorophyllide) dimer in solution and derive the detailed geometry of the dimer.

When BChlide  $d$  [ $\text{Et}, \text{Et}$ ]<sup>9,10</sup> (1) is dissolved in  $\text{CDCl}_3$ , an ex-

(1) University of Liverpool.

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(3) (a) Govindjee, Ed. "Bioenergetics of Photosynthesis"; Academic Press: New York, 1975. (b) Katz, J. J.; Norris, J. R.; Shipman, L. L. *Brookhaven Symp. Biol.* 1976, 28, 15-66.

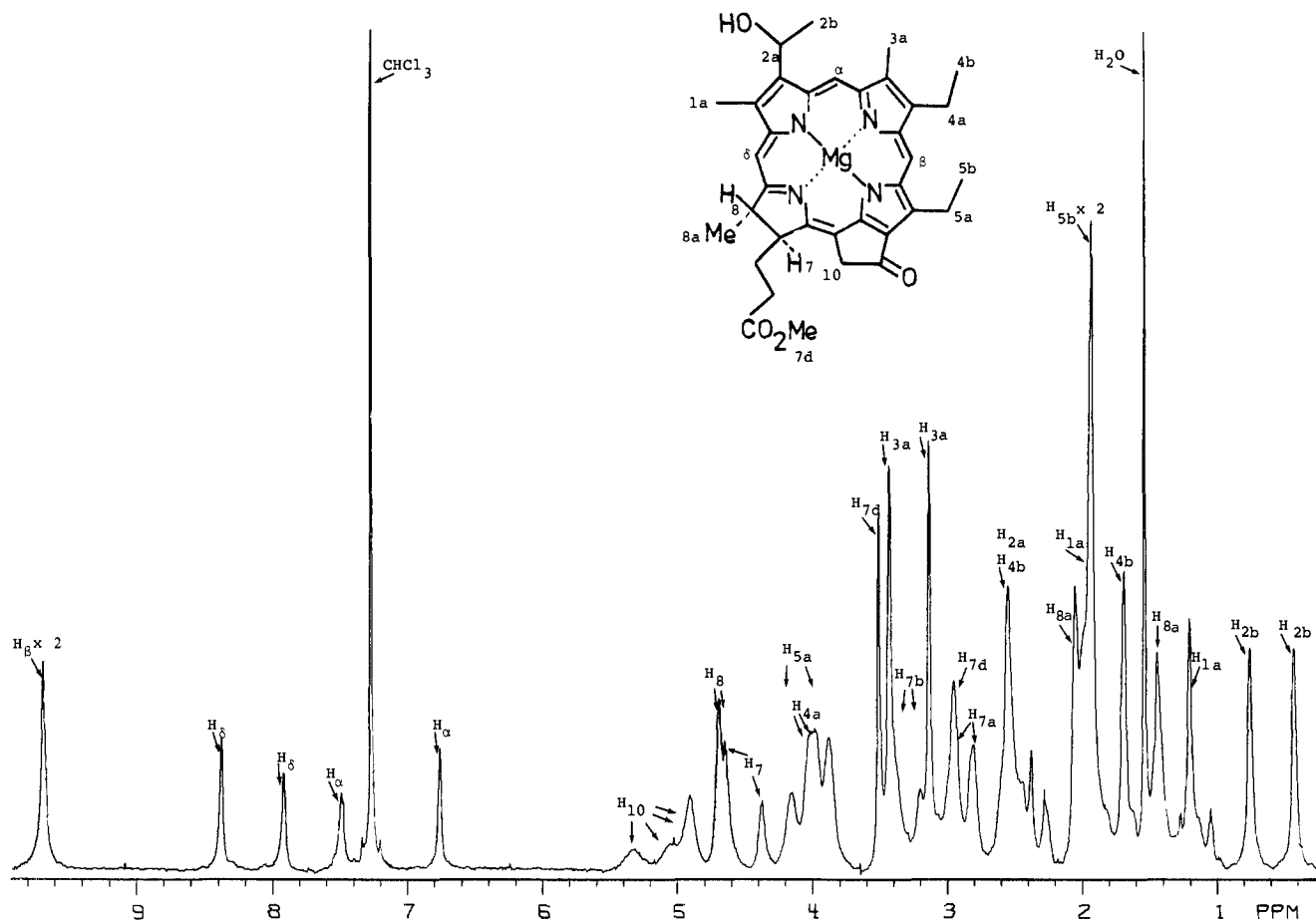
(4) By "symmetric" is meant a dimer or aggregate in which all the molecules are chemically identical.

(5) Katz, J. J.; Brown, C. E. *Bull. Magn. Reson.* 1983, 5, 3-49.

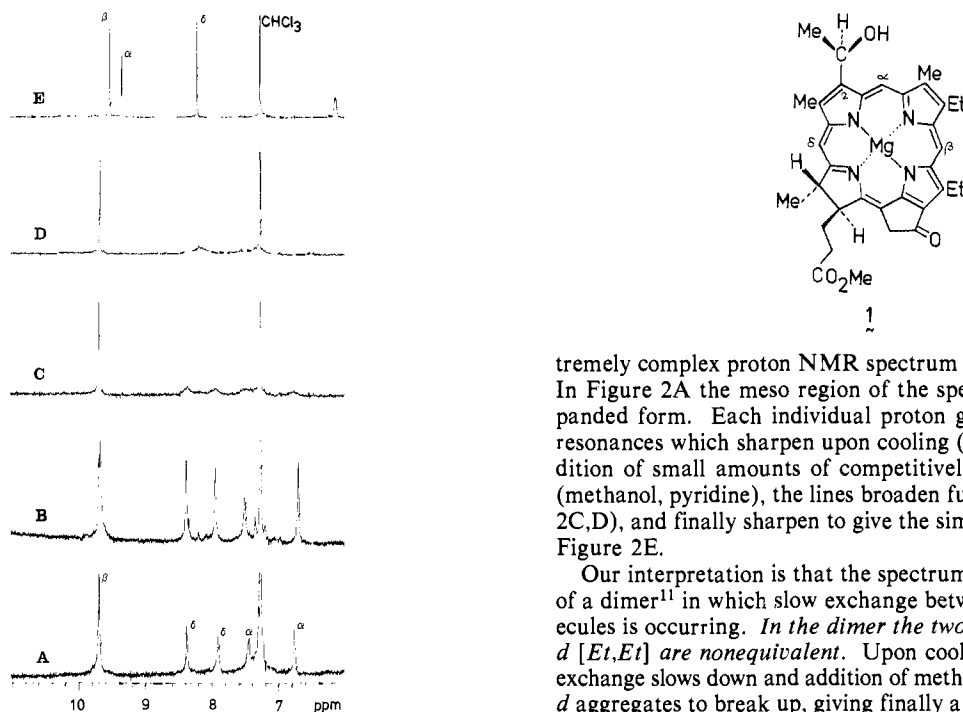
(6) Fong, F. K.; Koester, V. J. *J. Am. Chem. Soc.* 1975, 97, 6888-6890. Fong, F. K. *J. Am. Chem. Soc.* 1975, 97, 6890-6892.

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**Figure 1.** Proton NMR spectrum, 360 MHz, of Bchlride *d* [Et,Et] (**1**) (4.7 mM in  $\text{CDCl}_3$ ). Assignments shown are based on NOE, saturation transfer, and integration, as well as spectra of certain regioselectively deuterated derivatives of **1**.<sup>15</sup> The 2a and 7a,b assignments, mainly based on saturation transfer and integration experiments, are tentative; conformation of the 7a,b assignments awaits further deuteration experiments.



**Figure 2.** Low-field (meso proton) region in the 360-MHz proton NMR spectra of Bchlride *d* [Et,Et] (**1**) (4.7 mM in  $\text{CDCl}_3$ ). (A) At room temperature, (B) at  $-50^\circ\text{C}$ , (C) at room temperature with ca. 2 mol equiv of  $\text{CD}_3\text{OD}$ , (D) at room temperature with ca. 8 mol equiv of  $\text{CD}_3\text{OD}$  (E) at room temperature with a large excess of pure  $\text{CD}_3\text{OD}$ .

tremely complex proton NMR spectrum is observed (Figure 1). In Figure 2A the meso region of the spectrum is shown in expanded form. Each individual proton gives rise to two broad resonances which sharpen upon cooling (Figure 2B). Upon addition of small amounts of competitively coordinating ligands (methanol, pyridine), the lines broaden further, coalesce (Figure 2C,D), and finally sharpen to give the simple spectrum shown in Figure 2E.

Our interpretation is that the spectrum in pure  $\text{CDCl}_3$  is that of a dimer<sup>11</sup> in which slow exchange between the different molecules is occurring. *In the dimer the two molecules of Bchlride *d* [Et,Et] are nonequivalent.* Upon cooling the intermolecular exchange slows down and addition of methanol causes the Bchlride *d* aggregates to break up, giving finally a monomeric Bchlride *d*,

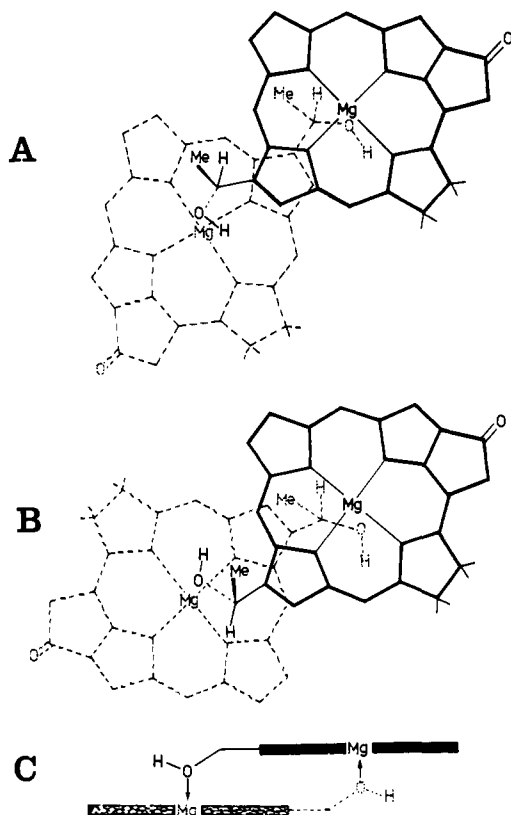
(9) The [Et,Et] nomenclature refers to the substituents at the 4- and 5-positions, respectively. The Bchlride was isolated from *Chlorobium vibriiforme* by using standard procedures.<sup>10</sup>

(10) E.g.: Goff, D. A. Ph.D. Dissertation, University of California, Davis, 1984. Smith, K. M.; Goff, D. A. *J. Chem. Soc., Perkin Trans. 1*, in press.

**Table I.** Observed Proton Chemical Shifts ( $\delta$ ) and Observed and Calculated Complexation Shifts ( $\Delta\delta$ ) for Methyl Bacteriochlorophyllide *d* [Et,Et] (1)

proton	monomer <sup>a</sup>	aggregate <sup>b</sup>	obsd	complexation shifts <sup>c</sup>			
				calcd (Figure 3A)		calcd (Figure 3B)	
				mol. 1	mol. 2	mol. 1	mol. 2
meso							
$\beta$	9.59	9.68	0.1	0.2	0.2	0.1	0.1
$\alpha$	9.43	7.47, 6.75	-2.0, -2.7	-2.6	-2.1	-2.5	-2.0
$\delta$	8.25	8.36, 7.91	0.1, -0.3	-0.1	-0.3	-0.1	-0.4
2b-Me	2.07	0.73, 0.41	-1.3, -1.7	-1.8	-1.9	-1.3	-1.7

<sup>a</sup> +25  $\mu$ L of methanol-*d*<sub>4</sub>. <sup>b</sup> 4.7 mM in CDCl<sub>3</sub>. <sup>c</sup>  $\delta_{\text{aggregate}} - \delta_{\text{monomer}}$ .



**Figure 3.** Proposed dimer structure of Bchl *d* [Et,Et] (1). (A) Face-to-face, (B) "piggy-back",<sup>12</sup> (C) end-on projection.

presumably with methanol coordinated to the magnesium atom.

The monomer spectrum may be completely interpreted and assigned by using previous chemical shift data. Using a combination of regioselective deuterium labeling, integration, nuclear Overhauser enhancement (NOE), and saturation transfer experiments between the components, the dimer/aggregate spectrum

(11) We note that in a layered aggregate, ring current effects are such that a molecule inside the sandwich will have very different chemical shifts from an end molecule (see ref 12 for a full discussion). Thus, simple symmetry arguments alone show that there are only three aggregates that will reproduce the observed spectrum. These are the dimer (AB), a tetramer (ABBA), and a polymer [(AB)<sub>n</sub>] in which *n* is so large that end units are not observed (i.e. *n* > 10). Of these, the dimer (which we favor) has a simple chemical interpretation, the tetramer requires two different types of chlorophyll/chlorophyll interaction, and the polymer would give broad unresolved peaks (see ref 13, Figure 9C) and is excluded on the basis of the optical spectra.<sup>14</sup>

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(14) The long-wavelength band of the Bchl *d* in CDCl<sub>3</sub> absorbs at 672 nm, shifting to 656 nm ( $\Delta\lambda = 16$  nm) upon addition of pyridine; the 672-nm absorption appeared to be independent of concentration, at least over the range from 4.0 mM to about 40  $\mu$ M. In contrast, the long-wavelength band of Bchl *d* in hexane<sup>17</sup> (for the proposed oligomer) appears at 728 nm and suffers a hypsochromic shift to 656 nm ( $\Delta\lambda = 72$  nm) upon disaggregation with methanol.

(Figure 1), consisting of two slightly broadened and overlapping BChlide *d* spectra, has been assigned.<sup>15</sup>

The chemical shifts of the meso and 8-methyl peaks in the aggregate are recorded in Table I, together with the corresponding values for the monomer and the resulting complexation shifts ( $\delta_{\text{aggregate}} - \delta_{\text{monomer}}$ ). These shifts, along with further refinement using other peaks in the remainder of the spectrum, were then used to deduce the dimer geometry, using the ring current model of the Chl ring described<sup>16</sup> and applied<sup>12</sup> previously. Following an earlier optical study of these systems in which aggregates of Bchl *c* and *d* were shown to form in hexane solution,<sup>14,17</sup> two possible aggregates were considered; one was a dimer, while the other was a larger oligomer. The spectrophotometric studies in hexane indicated<sup>17</sup> that the higher oligomer was more likely. In the present work, both models of the aggregate were again considered. Unlike the aggregate seen in hexane,<sup>17</sup> the head-to-head (oligomeric) model is clearly incompatible with the observed shifts (cf. the Chl *b* complexation shifts<sup>12</sup>), but the head-to-tail model proposed for the dimer gave sufficiently good agreement for the positional coordinates of the dimer to be refined on the basis of the observed shifts. Two different head-to-tail models were compatible with the observed shifts for the dimer, a face-to-face model (Figure 3A) and a "piggy-back"<sup>12</sup> model (Figure 3B); the calculated shifts for each are given in Table I. In the dimer both magnesium atoms are coordinated to the C-2 hydroxyl of the adjacent molecule, and the separation between the parallel macrocyclic planes is ca. 3.5 Å, with Mg-O distances of ca. 2.6 Å. In both models (Figure 3A,B) the observed nonequivalence in the proton spectra is accurately reproduced in the calculated complexation shifts (e.g., Table I).

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(15) Full details of these extensive experiments will be described elsewhere.

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### Photoreactivities of *o*-Alkoxy- and *o*-*tert*-Butylphenyl Ketones: A Dramatic Example of Conformational Inversion of Selectivity

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Alkoxy radicals abstract hydrogen atoms from ethers far more rapidly than from alkanes because the resulting  $\alpha$ -alkoxy radicals

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