

norbornadiene.^{12,28} A plausible alternative,²⁹ addition to the 5 and then to the 3 position of benzvalene, does not compete.

On photolysis through Pyrex, 0.8 *M* solutions of III in CD₂Cl₂ at ca. 30° or in CD₃CN at 78° give mainly benzene and some 1,2-diazacyclooctatetraene.⁵ There are small amounts of other products that have not yet been isolated and there is 4–6% prismane. Except for prismane, the products were identified only by pmr analysis and accounted for 70–80% of the starting azo compound, which was consumed.

Prismane was isolated in 1.8% yield after photolyzing 3.2 g of III as a 0.19 *M* solution in isobutane at 35° (sealed tubes), evaporating solvent, distilling at 10⁻⁶ Torr, and purifying by glpc.³⁰ It is an explosive colorless liquid: pmr (CCl₄) singlet at τ 7.72 ($J_{\text{1:3C-H}} = 180$ Hz);³² ¹³C nmr (in C₆D₆) δ +30.6 ppm (from TMS, d, $J_{\text{1:3C-H}} = 179.7 \pm 2$ Hz);³⁵ ir (CS₂, cm⁻¹) 3066 (s), 1765 (w), 1640 (w), 1223 (s), 950 (m), 881 (w), 798 (s), 733 (w), 670 (m); mass spectrum (75 eV) *m/e* 78 (100%, parent), 77 (20%), 52 (22%), 39 (13%), no others more than 10% of base; uv (isopentane), inadequately measured because of benzene contamination, but $\epsilon_{223\text{nm}} \leq 90$.³⁷

Prismane is stable at room temperature. At 90° in toluene-*d*₈ it decomposes with a half-life of 11 hr, giving 61 mol % of benzene and no other product detectable by pmr spectroscopy.³⁸ It is therefore unnecessary to cool the reaction mixture in which prismane is prepared. In fact it is essential for the success of the synthesis that during the photolysis the azo compound III be heated.^{39,40} Thus, in toluene-*d*₈ at -65° after 5 hr of photolysis, pmr analysis shows the consumed starting material converted 92% into 1,2-diazacyclooctatetraene, 14% into benzene, and 0% into prismane, while after similar photolysis at 30° these products are observed in 6, 47, and 8% yields. To mitigate prismane's assumed instability by cooling the reaction mix-

ture is therefore a mistake, for prismane is a stable molecule.

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Anion Radical of Bacteriochlorophyll

Sir:

Investigations on the redox chemistry of intact photosynthesizing systems, extracted photosynthetic units, and chlorophylls have led to a general recognition¹⁻⁷ that the primary photochemical step involves electron donation from chlorophyll (Chl) in green plants and algae and from bacteriochlorophyll (BChl) in purple bacteria. Those chlorophyll molecules undergoing photooxidation appear to be in a specialized environment, perhaps a bridged dimer configuration,¹ and following electron donation the π -cation radicals of Chl or BChl are observed.^{1-3,7-10} In contrast, the identity of the primary electron acceptor is unknown,^{6,11} and its spectral and chemical properties only now are being elucidated.^{2,10-18} Among the suggested candidates in the case of bacterial photosynthesis are iron,^{6,15} ferridoxin,¹⁶ pteridines,¹⁹ flavines,¹⁸ and ubiquinone.^{6,15,17} Due to the expected similarity in optical and epr characteristics of its anion and cation, BChl itself could not be ruled out as a primary acceptor,^{3,6} and thus a source for the observed light-induced signals. However, we have prepared the anion radical of BChl

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(30) Chromosorb G (5 ft \times 1/4 in.) with 5% didecyl phthalate and 1.25% triethanolamine.³¹

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(32) As expected,³³ this is larger than the 160 Hz in a cubane derivative.³⁴

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(35) Cf. cuneane's carbon shared between three- and four-membered rings: δ +31.8 ($J = 175$ Hz).³⁶

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(37) In hexamethylprismane the corresponding extinction is ca. 1000.^{14,e} If the uv of prismane is similar in shape¹⁶ to that of its hexamethyl derivative, the spectrum is hypsochromically shifted by at least 35 nm.

(38) There was an initial short burst of decomposition at twice this rate yielding a full mole of benzene. This may be due to catalysis by impurities that are then consumed.

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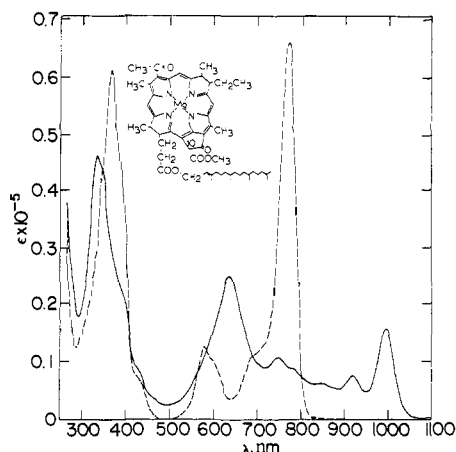


Figure 1. Optical absorption spectra in DMF at 25°: dashed line, BChl; solid line, BChl \cdot^- .

and report here spectral and redox properties which are *incompatible* with those presently attributed to the reduced species appearing in bacterial photosynthesis.

Polarographic studies of Chl or BChl have demonstrated^{20,21} that the anion radical is formed at the first reduction wave ($E_{1/2} = -1.08$ V vs. sce in butyronitrile). Stable dimethylformamide or butyronitrile solutions of BChl \cdot^- were prepared under vacuum by electrolysis in an apparatus which allowed continuous optical monitoring of the catholyte. Simultaneous coulometry confirmed reduction by one electron, and BChl was regenerated quantitatively by electrooxidation. The optical spectrum of BChl \cdot^- is shown in Figure 1.

The epr spectrum of BChl \cdot^- in butyronitrile ($g = 2.0028 \pm 0.0002$) (Figure 2a) resembles the spectrum of the cation radical¹⁰ in overall line width, but only the

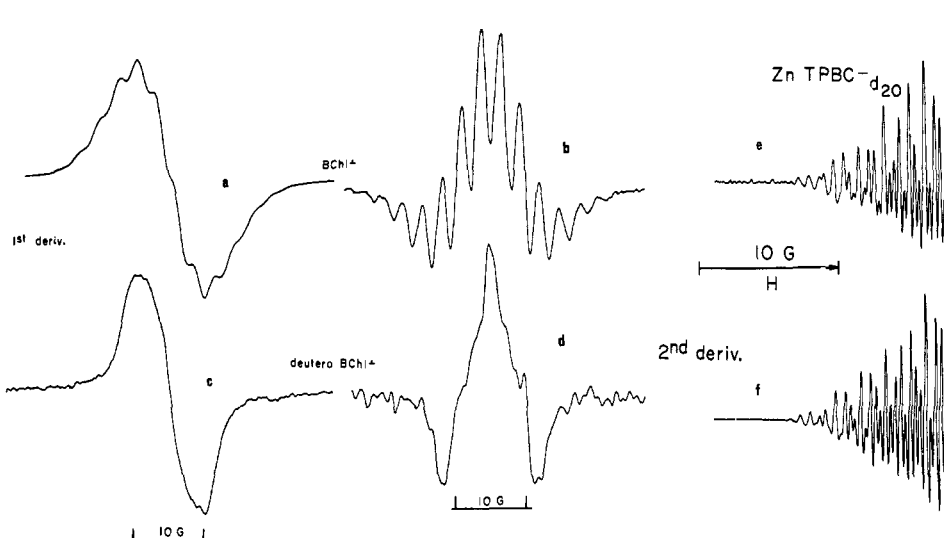


Figure 2. (a) First- and (b) second-derivative epr spectra of BChl \cdot^- ; (c) first- and (d) second-derivative spectra of deuterio-bacteriochlorophyll \cdot^- ; (e) half of second-derivative spectrum of ZnTPBC- d_{20} \cdot^- (deuterated phenyl groups); (f) computer simulation of e. All spectra at -20° in butyronitrile.

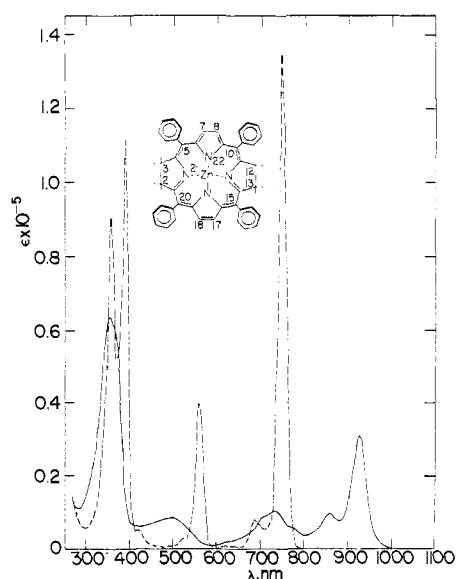


Figure 3. Optical absorption spectra in DMF at 25°: dashed line, ZnTPBC; solid line, ZnTPBC \cdot^- .

anion displays the partially resolved, 12-line hyperfine spectrum (seen to better advantage in the second derivative spectrum, Figure 2b). Collapse of the hyperfine splitting (hfs) and narrowing of the spectrum upon deuteration (Figure 2c,d) establishes the presence of hydrogen splittings, but the line-width decrease of ca. 1.5 is less than that predicted (3.99) by assuming only proton interactions which are replaced by deuterium interactions.²² It is likely that residual ^{14}N hfs is the cause of the slight line-width decrease, an assumption strengthened by observation of ^{14}N hfs in the epr spectrum of zinc tetraphenylbacteriochlorin (ZnTPBC) anion radical.

That ZnTPBC \cdot^- is a good model for BChl \cdot^- is

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(22) BChl obtained from *R. rubrum* was more than 99% deuterated except for the C-10 proton. The difference in BChl ester side chains between samples isolated from *R. rubrum* and *Chromatium* does not affect the spin density distribution. Although hfs from the C-10 proton cannot be ruled out, its contribution to the line width in the deuterated sample is expected to be minor.

demonstrated by comparison of its electronic spectrum (Figure 3) with that of BChl \cdot^- . Noteworthy similarities are bleaching of the intense ir band, uv band(s) shifting to higher energies, and appearance of an absorption with vibrational structure in the region 800–1100 nm. Furthermore, both spectra agree well with the general features of metallo-tetrahydroporphyrin anion radical spectra calculated with π -electron closed-shell²³ or open-shell SCF theories.⁸ For example, open-shell computations give the following transition energies (dipole oscillator strengths) to compare with experimental findings: 1020 nm (0.17), 710 (0.09), 565 (0.002), 520 (0.15), 339 (0.85), 325 (0.87), 312 (2.09).

The hfs observed in the epr spectrum of ZnTPBC \cdot^- and selectively deuterated compounds (Figure 2e) permits the following assignments (see Figure 3 for numbering): four β -pyrrole protons, $a_{\text{H}_7} = 1.80$ G; eight CH₂ protons, $a_{\text{H}_2} = 0.70$ G; two nitrogen nuclei, $a_{\text{N}} = 2.88$ G, and an additional splitting of $a_{\text{H}} \sim 0.1$ G due to phenyl protons. Hyperfine constants calculated from SCF-MO spin densities and McConnell relationships are $a_{\text{H}_7} = 1.62$ G, $a_{\text{H}_2} = 0.62$, $a_{\text{N}_{21}} = 2.72$, and $a_{\text{N}_{22}} = 0.42$. On this basis the experimental nitrogen splitting is assigned to N₂₁.

Although its identity remains uncertain, some properties presently attributed to the primary acceptor are readily distinguished from those found for BChl \cdot^- . Thus, the acceptor has an epr signal^{13,15} at $g = 2.005$ with a line width of 7–8 G, and no hfs (*vs.* $g = 2.0028$, 10-G line width, and 12 resolved lines); a possible optical absorption^{12,14,17} at *ca.* 430–455 nm with no significant absorption from 900 to 1100 nm (*vs.* no increase in absorption at 450 nm but characteristic ir absorption); and a midpoint potential^{13,24–26} of -0.05 to -0.20 V (*vs.* $E_{1/2} = -0.84$ V *vs.* SHE). In contrast to the favorable comparison of properties of oxidized Chl or BChl with photooxidized reaction centers^{4,6,7,27,28} which has led to the identification of Chl \cdot^+ and BChl \cdot^+ in photosynthesis, one must conclude on the basis of properties presently assigned to the primary acceptor that this species is not BChl.

However, the possibility of a reactive BChl \cdot^- serving as a precursor to the observed electron acceptors is not excluded. Our findings suggest that flash spectroscopy with rapid time resolution could well include the 900–1100-nm region where BChl \cdot^- has a characteristic absorption.

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Stereochemical Dependence of the Sign and Magnitude of Coupling Constants on Geometry in ¹⁵N (*E*)- and (*Z*)-Aldimines

Sir:

A growing body of evidence¹ has indicated that both the magnitude and the sign of nuclear spin coupling constants are affected by the relative stereochemistry of proximate lone pairs of electrons on atoms such as nitrogen and phosphorus. The particular spin system of interest here is that between hydrogen and nitrogen-15 across a carbon–nitrogen double bond (H–C= ¹⁵N—). Thus, hydrazones,² imines,^{3,4} oximes,^{5,6} and aza aromatic systems^{5b,6,7} show larger ²J(H–C= ¹⁵N—) couplings when the hydrogen is *cis* (~ 14 to 16 Hz) rather than *trans* (~ 2 to 5 Hz except for aza aromatic systems) to the nitrogen lone pair. Unfortunately, in each of these investigations either the stereochemistry of the molecule or the absolute sign of the coupling constant was not known with certainty, or only one of the two possible geometric isomers was examined. The most definitive study was that of Crepau and Lehn^{5a} on ¹⁵N-formaldoxime; in this case, the signs of ²K_(H–C=¹⁵N) (*K* defined in ref 14) for the two non-equivalent hydrogens attached to carbon were demonstrated to be opposite. The absolute sign of the larger ²K (lone pair *cis* to hydrogen) was assumed positive based on the sign determined for H–C= ¹⁵N in ¹⁵N-quinoline.^{5b} We now report the first unequivocal assignment of both the sign and magnitude of the ²J(H–C= ¹⁵N) coupling for an (*E*)- and (*Z*)-*N*-alkylaldimine.

N-Alkylaldimines were chosen for this study for several reasons: (i) systems with a heteroatom bearing a lone pair (*e.g.*, oximes) on the atom attached to nitrogen were avoided in view of possible complications due to the additional lone pair, (ii) the *Z* isomers of *N*-arylaldimines were known to have lifetimes so short⁸

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