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Radicals of Isobacteriochlorins: Models of Siroheme and Sirohydrochlorin

Sir:

The biological assimilation of sulfite and nitrite is enzymatically mediated by sulfite and nitrite reductases which catalyze the six-electron reductions of sulfite to hydrogen sulfide and of nitrite to ammonia:

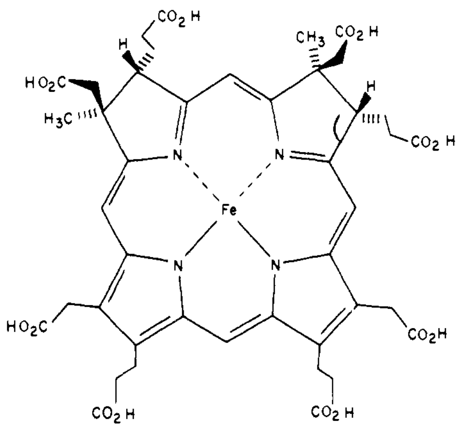
$$SO_3^{2-} + 8H^+ + 6e^- \rightarrow H_2S + 3H_2O,$$
$$\text{and } NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$$

In green plants, the latter reaction is light driven. Photosynthetically reduced pyridine dinucleotide serves as an electron source for the reduction of the enzyme:

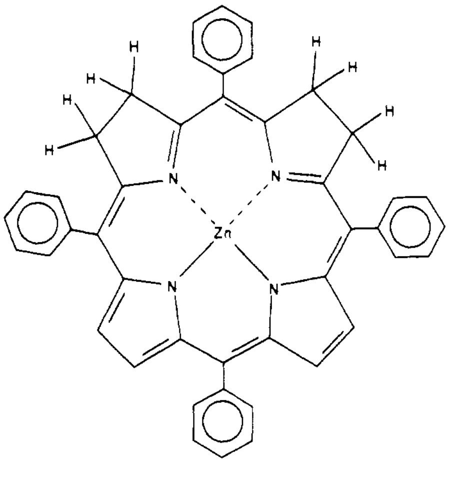
$$\text{chlorophyll} \xrightarrow{h\nu} \text{NADH} \rightarrow \text{flavoprotein} \rightarrow \text{ferrodoxin} \rightarrow \text{nitrite reductase}$$

The prosthetic group of the enzymes has recently been shown[1] to contain siroheme, an iron isobacteriochlorin with eight carboxylic acid side chains (I). A further biological role for isobacteriochlorins has also been invoked[2] with the identification of sirohydrochlorin, a demetalated siroheme, as an intermediate in the biosynthesis of vitamin B_{12}.

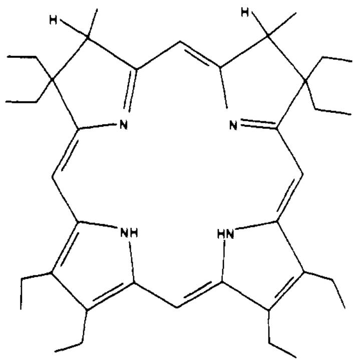
A salient feature of the isobacteriochlorin skeleton is its ease of oxidation and difficulty of reduction compared with those of porphyrins or chlorins.[3] In particular, the facile oxidation (vide infra), raises the intriguing possibility that the ligand itself may undergo redox reactions in the multielectron reductions of the substrates to ammonia and hydrogen sulfide. (Examples of biological two-electron transfers which involve several oxidation states of iron and electron abstraction from the porphyrin are found[4] in catalase and horse radish peroxidase, enzymes which contain heme prosthetic groups.)



I



II



III

To probe the magnetic, optical, and redox characteristics of the isobacteriochlorin class, we describe here MO calculations and ESR, ENDOR, optical, and electrochemical results for two model compounds: zinc tetraphenyl isobacteriochlorin (ZnTPiBC, II), whose recently determined[3b] X-ray structure verifies that two adjacent pyrrole rings are reduced in isobacteriochlorins, and dimethyloctaethyl isobacteriochlorin (H_2DMeOEiBC, III), a compound[3d] which is a close analogue, structurally and spectrally, to sirohydrochlorin.

Electrochemical oxidation[5] of H_2DMeOEiBC in CH_2Cl_2 at +0.5 V (vs. SCE) requires 1 (±0.1) electron to yield the optical spectrum shown in Figure 1. One-electron reduction at 0.0 V regenerates better than 95% of the original H_2DMeOEiBC spectrum. Oxidation to the cation induces a bleaching of the 600-nm band, the appearance of a weak broad

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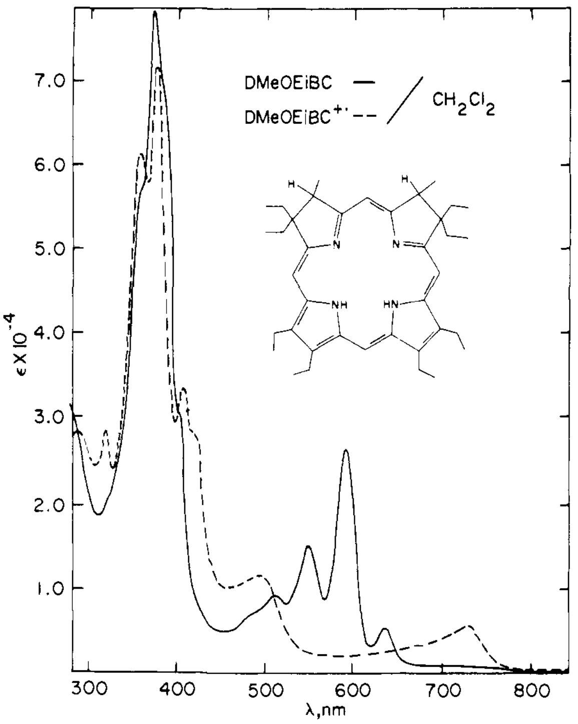

Figure 1. Optical absorption spectra, in CH_2Cl_2, of $H_2DMeOEiBC$ (—) and its cation radical (- - -).

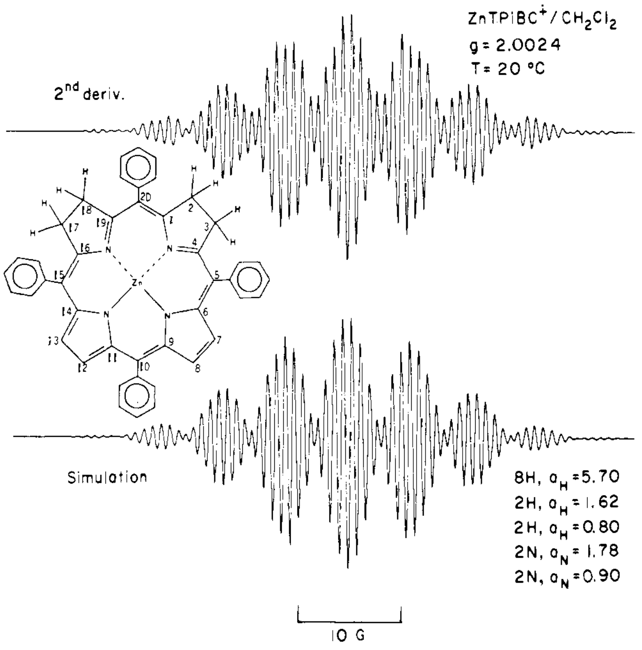

Figure 2. Second derivative ESR spectra of $ZnTPiBC^{+} \cdot ClO_4^{-}$ in CH_2Cl_2 at 20 °C and a simulation which assumes the splitting constants shown.

absorption stretching into the near-infrared region, and a diminution of the Soret band. Similar spectral changes characterize the oxidation of ZnTPiBC.[3e]

Chemical oxidation[6] of ZnTPiBC yields the ESR spectrum displayed in Figure 2. The nine major packets and the smaller hyperfine splittings are assigned to eight equivalent protons, a_H = 5.7 G, two sets of two protons, a_H = 1.6 and 0.8 G, and two sets of two nitrogens, a_N = 1.8 and 0.9 G, on the basis of selective deuterations, ENDOR experiments, and molecular orbital calculations. Self-consistent field Pariser-Parr-Pople calculations[5] (Figure 3) predict that abstraction of an electron from an isobacteriochlorin results in an $^2A_2$ state (for an idealized C_{2v} symmetry) and places significant unpaired spin density at the α carbons of the reduced rings (C-1, C-4, C-16, C-19) with smaller densities at the β positions of the unsaturated rings (C-7, C-8, C-12, C-13).[7] The interaction of the protons on the reduced rings with the unpaired spin density ρ at C-1, C-4, C-16, C-19 is defined by the McConnell relationship $a_H = \rho_{C\text{-}1}(-9 + 97 \cos^2\theta)$ where θ is the dihedral angle between the $2p_z$ orbital of the α carbon and the plane defined by the α and β carbons and the proton.[8] In chlorins, θ ranges[9] between 30 and 45°; therefore the calculations clearly suggest that the 8β protons of the reduced rings should exhibit large hyperfine splittings and the observed splittings of 5.7 G are thus assigned to these positions.[10] For protons adjacent to the π system, $a_H = 27\ \rho_C$, and the calculations yield a_H values of 1.4 G for the two protons on C-7 and C-13 and 0.6 G for the protons on C-8 and C-12.

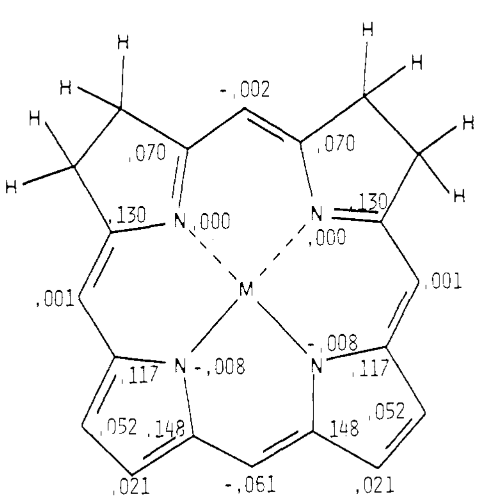

Figure 3. Unpaired spin densities calculated by SCF Pariser Parr Pople theory for a metallo isobacteriochlorin cation radical.

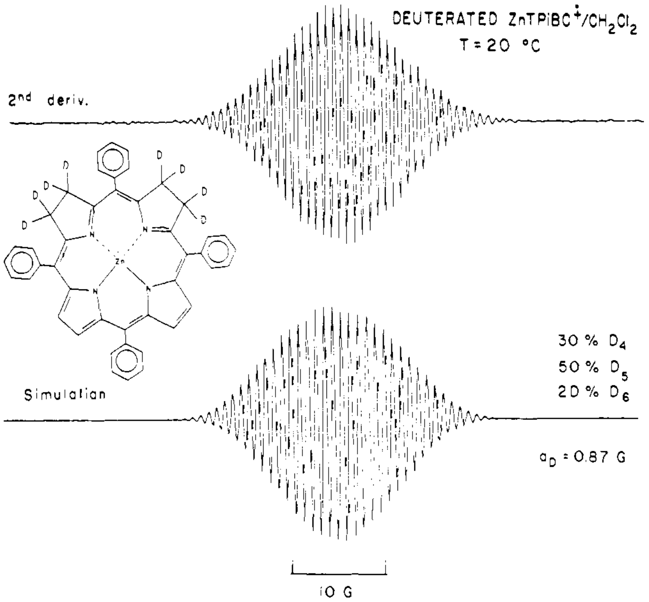

Figure 4. Second derivative ESR spectra, in CH_2Cl_2 at 20 °C, of $ZnTPiBC^{+}\cdot$ partially deuterated at the reduced pyrrole rings. The simulation assumes that the sample contains 30% d_4-h_4, 50% d_5-h_3, and 20% d_6-h_2. All other splitting constants are those shown in Figure 2.

ENDOR measurements[11] on $ZnTPiBC^{+}\cdot$ in CH_2Cl_2-mineral oil at −20 °C reveal two proton splittings of 1.7 and 0.8 G. The simulation shown in Figure 2 incorporates these assignments: eight protons (saturated rings), a_H = 5.7 G; two protons (at C-7 and C-13), a_H = 1.6 G; and two protons, a_H = 0.8 G (C-8 and C-12). An accurate fit to the experimental

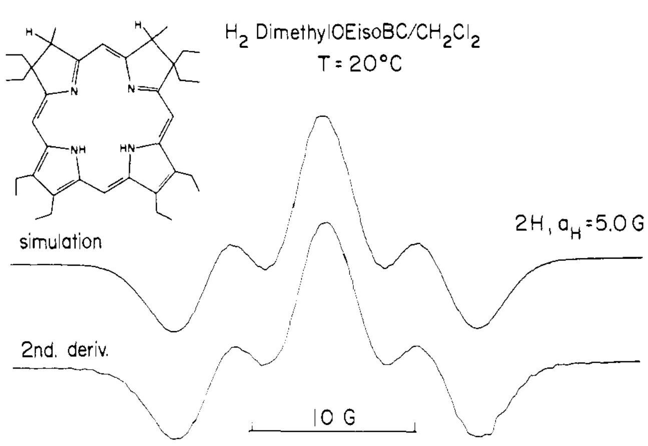

Figure 5. Second derivative ESR spectra, in CH_2Cl_2, of $H_2DMeOEiBC^{+}\cdot ClO_4^-$. The simulation demonstrates that two equivalent protons determine the spectral pattern observed. The peak-to-peak line width of the first derivative signal is ~10 G.

spectrum requires two additional sets of two nitrogens with a_N = 1.8 and 0.9 G. (Nitrogen hyperfine constants reflect[8] the spin density at the adjacent carbons as well as at the nitrogen itself.)

Confirmation of these assignments is obtained by partial exchange of the protons on the reduced rings with deuterons, by treatment of ZnTPiBC with potassium in *tert*-butyl alcohol-d_1 according to Whitlock and Oester.[12] The ESR spectrum of the resulting deuterated species is shown in Figure 4. The spectrum has collapsed significantly compared with that of $ZnTPiBC^{+}\cdot$ (Figure 2) as expected from the difference in gyromagnetic ratios and nuclear spins of hydrogen and deuterium ($I = {}^1/_2$ and 1, $a_D = 0.1535a_H$). The spectrum of Figure 4 can be fitted by a simulation which maintains the nitrogen and small proton splittings and assumes the indicated distribution of partial deuteration at the reduced rings. These results clearly confirm the assignments of the eight large proton splittings as arising from the reduced rings. Further support of these conclusions derives from the cation of $H_2DMeOEiBC$, which contains only two protons on the reduced rings and whose three-line ESR spectrum (Figure 5) of intensities 1:2:1 is unambiguously attributable to two equivalent protons of a_H = 5 G. Although the multitude of smaller splittings expected from the nitrogens, meso protons, and methylene amd methyl groups is not resolved, spin densities at these positions, comparable with those found in $ZnTPiBC^{+}\cdot$, can readily be accommodated within the envelope of the $H_2DMeOEiBC^{+}\cdot$ spectrum.

Half-wave potentials for isobacteriochlorins, measured by cyclic voltammetry, are listed in Table I and contrasted there with those of analogous chlorins and porphyrins. The notable features of these results are the significant cathodic shifts of the redox potentials: the isobacteriochlorins are considerably easier to oxidize and harder to reduce than the corresponding chlorins and porphyrins. (Note that the redox span between the first ring oxidation and reduction potentials ($\Delta E_{\pm}$) remains insensitive to hydrogenation of the pyrrole rings.)

Table I. Redox Potentials of Isobacteriochlorins[a] ($E_{1/2}$ vs. SCE)

compound	oxidation 2	oxidation 1	reduction 1	reduction 2	$\lvert\Delta E_{\pm}\rvert$[b]
H_2TPiBC	0.95	0.57	−1.52		2.09
ZnTPiBC	0.69	0.28	−1.73		2.01
CuTPiBC	0.75	0.40			
$H_2DMeOEiBC$	0.96	0.37	−1.72		2.09
ZnDMeOEiBC	0.66	0.08	−1.95		2.03
H_2TPP[c]	1.28	0.95	−1.05	−1.47	2.00
ZnTPP[c]	1.03	0.71	−1.35	−1.80	2.06
CuTPP[c]	1.16	0.90	−1.20	−1.68	2.10
H_2OEP[c]	1.32	0.83	−1.45	−1.87	2.28
H_2 etiochlorin I	1.16	0.65	−1.42	−1.86	2.07
Zn etiochlorin I	0.84	0.35	−1.60		1.95

[a] Oxidations in CH_2Cl_2 or butyronitrile, reductions in butyronitrile (0.1 M tetra-*n*-butylammonium perchlorate). [b] E_1(oxidn) − E_1(redn). [c] Literature values from ref 13.

These properties may dictate the choice of the isobacteriochlorin framework for the multielectron transfers in nitrite and sulfite reductases and suggest that siroheme may function via π cation radicals. Such radicals should display the optical and ESR properties described here (Figures 1 and 5). Furthermore, the peripheral unpaired spin density distribution calculated and found in the model compounds indicates that NMR spectra of these radicals should exhibit significant contact shifts and line broadening.

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Iridium Complexes in Alkane Dehydrogenation

Sir:

The functionalization of alkanes under mild conditions by soluble transition-metal compounds is a challenging problem.[1]

In this connection, we have been studying, in noncoordi-

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