trans-DDP or [(dien)PtCl]Cl,[18] neither of which has antitumor activity.

An experiment was performed in which platinated DNA was treated with cyanide before exonuclease III digestion to see whether irreversible lesions were induced in the DNA by *cis*-DDP (Figure 1, lanes 6 and 7). Most of the major bands seen in control digests of unplatinated DNA were restored by the cyanide pretreatment. The bands near the $(dG)_5{\cdot}(dC)_5$ and the $(dG)_3{\cdot}(dC)_3$ sites (bands 1, 3 and 4) were still present, however, even when most of the platinum was removed before exonuclease III digestion. This result is reminiscent of previous observations[14] of a fraction of *cis*-DDP bound to DNA that could not be removed by cyanide treatment.

In summary, *cis*-DDP bound to $(dG)_n{\cdot}(dC)_n$ sequences, $n \geq 2$, modifies in a characteristic way the digestion of DNA by exonuclease III. This is the most direct demonstration to date of sequence specificity of the mode of binding of *cis*-DDP to DNA. The results are consistent with models that postulate binding of *cis*-DDP to adjacent deoxyquanosines or deoxycytidines as the effective lesion in platinum chemotherapy. Oligo(dG)·oligo(dC) sequences should be a major focus of attention for chemists engaged in modeling the interactions of *cis*-DDP with DNA.

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Stereoelectronic Properties of Photosynthetic and Related Systems. 10. Quantum Mechanical Characterization of the Excited States of Ethyl Chlorophyllide *a* Enol

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The idea that enolic tautomers of chlorophyll *a* (Chl *a*) might participate as intermediates in the primary events of photosynthesis in photosystem I of green plants has been postulated[1,2] but has received little or no experimental verification. Indeed, there has been no experimental characterization of Chl *a* enols until recently, when the optical and NMR spectra of Chl *a* silyl enol ethers[3] and related systems[4] were reported. More significantly, however, Wasielewski et al.[5] have examined the redox properties of Chl enols II and III (see Figure 1) as well as the magnetic resonance (ESR, ENDOR) spectra of the cation radicals of these systems. On the basis of their data they concluded that the π-cation radical of monomeric Chl *a* enol may be a more plausible alternative as a model for P700$^+$, the oxidized phototrap of photosystem I, than is the Chl *a* "special pair" dimer model proposed earlier.[6-8]

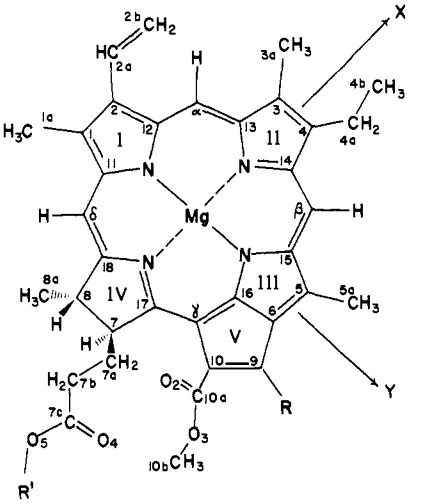

Figure 1. Molecular structure of (I) ethyl chlorophyllide *a* enol (R = OH, R' = C_2H_5); (II) chlorophyll *a* *tert*-butyldimethylsilyl enol ether (R = OSi-*t*-BuMe$_2$, R' = $C_{20}H_{39}$); (III) 9-deoxo-10-dehydro-9-hydrochlorophyll *a* (R = H, R' = $C_{20}H_{39}$). EtChl *a* (keto form) is obtained from I by reduction of the C_9–C_{10} double bond, addition of H at position 10, and substitution of a carbonyl oxygen for R at position 9.

Table I. Estimated Transition Energies, ΔE^{est}, Magnitudes of the Electric Dipole Moment, $|\mu|$, and Vector Components of the Dipole Moment for Low-Lying States of EtChl *a* Enol and EtChl *a*

state	ΔE^{est}, cm^{-1} [a]	$\lvert\mu\rvert$, D	μ_x,[b] D	μ_y,[b] D	μ_z,[b] D
		EtChl *a* Enol			
S_0	0.0	5.46	−3.86	2.35	3.06
S_1	9 922	9.68	−6.67	6.38	2.91
S_2	15 285	8.17	−5.80	4.87	3.05
S_3	18 109	9.30	−6.02	6.42	2.99
T_1	8 111	7.79	−5.11	5.07	2.98
T_2	12 733	8.28	−5.78	5.11	3.03
T_3	14 968	9.23	−7.13	5.02	3.03
		EtChl *a*[c]			
S_0	0.0	3.43	−1.62	−0.353	3.00
S_1	15 810	3.56	−1.79	0.811	2.97
T_1	10 740	3.31	−1.17	0.995	2.93

[a] Obtained from the equation given in ref 16. [b] A positive vector component points along the indicated axis from the origin of Figure 1 toward a region of positive charge. [c] Data computed from wave functions reported in ref 12.

The present communication deals with the interpretation of several important features of the electronic absorption spectra of Chl *a* enols. For this purpose, ab initio configuration interaction (CI) calculations were performed on ethyl chlorophyllide *a* enol (EtChl *a* enol, compound I in Figure 1), to obtain a theoretical description of the ground and low-lying singlet and triplet excited states. The computations performed include a self-consistent-field (SCF) calculation on the molecular ground state[9] using a basis set of floating spherical Gaussian orbitals (FSGO),[10] followed by the calculation of ground- and excited-state CI wave functions utilizing the CI procedure of Whitten and Hackmeyer.[11] Com-

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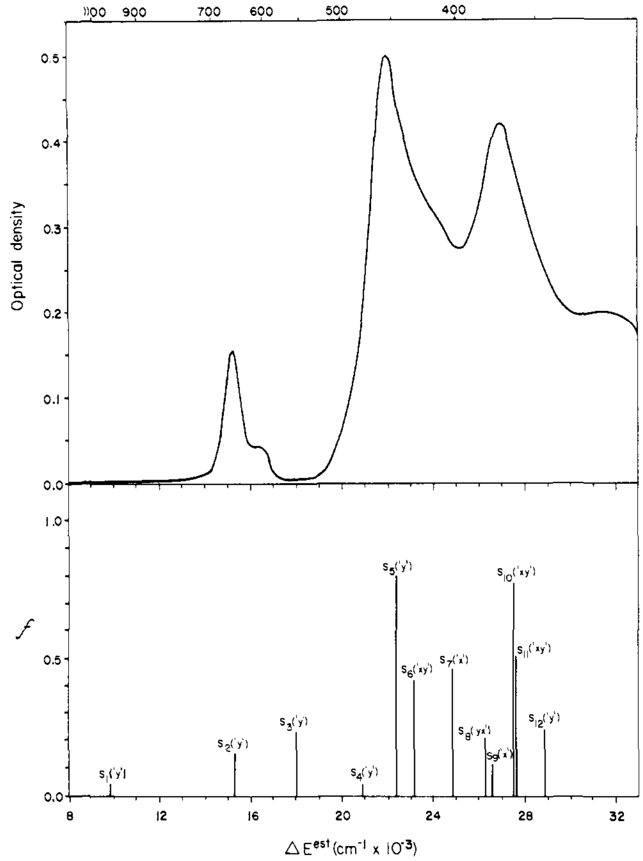

Figure 2. Comparison of the experimental spectrum of III (see Figure 1) in acetone (top) with calculated transition energies, oscillator strengths, and polarizations of EtChl *a* enol (bottom). Transition energies are estimates from the equation given in footnote 16; *f* represents the oscillator strength; approximate polarization directions are given in parentheses. "x" and "y" indicate transitions polarized predominately along the *x* and *y* axes, respectively, of Figure I. "xy" and "yx" refer to transitions of intermediate polarization which exhibit slightly more *x*- or *y*-polarized character, respectively. The experimental spectrum was obtained from M. Wasielewski of Argonne National Laboratory.

putational details have been described previously in studies of EtChl *a* (keto form)[12] and related systems.[13-16]

A number of molecules possess the same characteristic π-electron system as Chl *a* enol, including those in Figure 1 as well as "peripheral" magnesium complexes of pheophorbide *a*[17] and cyclopheophorbide *a* enols.[18] The electronic absorption spectra of III shown in Figure 2 is generally typical of these systems, as is the absence of observed fluorescence. The moderately low intensity absorption at about 15 200 cm^{-1} appears to be analogous to the more intense Q_y absorption at about the same energy in Chl *a*, but this is not the case. In Chl *a*, Q_y is firmly established as the $S_1 \leftarrow S_0$ absorption. In EtChl *a* enol, however, the calculated results shown in Figure 2 place $S_1 \leftarrow S_0$ at 9922 cm^{-1}, with an oscillator strength $f = 0.04$, while the 15 200 cm^{-1} absorption is due to $S_2 \leftarrow S_0$ ($f = 0.15$).[19] Therefore, the $S_1 \leftarrow S_0$ transition in II and III is apparently not observed due to the near-forbidden character of the transition. However, there is evidence of weak absorption near 750 nm observed in pheophorbide *a* enols.[3] The absence of observed fluorescence in these systems is also consistent with the predicted low $S_1 \leftarrow S_0$ emission probability and would be observed in the 9000–12 000 cm^{-1} region, not at ca. 15000 cm^{-1} as in Chl *a*.

Examination of the ground- and excited-state electronic charge distributions reveals several other relevant points. First, the electronic states of EtChl *a* enol are much more polar than those of EtChl *a*, as shown by the data in Table I. In particular, there is extensive charge reorganization associated with the $S_1 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions, which likely results in broad absorption bands. In this regard, we feel that the $S_3 \leftarrow S_0$ transition, which appears somewhat out of place in Figure 2, most likely appears as a broad band at the onset of the Soret absorption. The high intensity and split profile of the Soret band appears well represented by intense transitions to states S_5–S_7 and S_{10}–S_{11}. The polar nature of the computed electronic states of the enol (particularly, S_1 and S_3) also suggests that the absorption spectrum should be more easily influenced by solvent and environmental effects than in EtChl *a*, and there is some experimental evidence to support this.[3]

The estimated locations of the three lowest lying triplet states, T_1–T_3, are given in Table I. Unlike EtChl *a*, where S_1 and T_3 were predicted to be degenerate,[12] there is no low-lying triplet state in EtChl *a* enol within 2000 cm^{-1} of S_1, a feature which suggests that intersystem crossing might be more difficult in EtChl *a* enol than in EtChl *a*, and this is no doubt related to the difficulty of forming triplet states in these molecules.[5]

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A Primary Carbon-13 Equilibrium Isotope Effect. ^{13}C NMR Spectrum of 2,3-Dimethyl-2-[2-^{13}C]butylium Ion

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Among the many ^{13}C and ^{14}C kinetic isotope effects reported, few have involved formation of carbonium ions.[1] One might expect that solvolysis of isotopic carbon compounds would be slower since bonds are broken. However, the remaining bonds to the cationic carbon would be expected to become *stiffer*, producing an opposing effect and making the result difficult to predict. *Equilibrium* isotope effects would give a clearer indication, since they are independent of the transition state. The difficulty with coventional methods for measuring these isotope effects is that they are expected to be extremely small. We have recently reported a new NMR technique capable for measuring small isotope effects on equilibria with high accuracy.[2]

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