pyrophosphate oxygens during the closely related enzymatic isomerization of farnesyl to nerolidyl pyrophosphate, a result that has been interpreted in terms of an allylic cation–pyrophosphate anion pair.[16] While an equilibrium between geranyl and linalyl pyrophosphate may exist at the active site of bornyl pyrophosphate synthetase, the initial cyclization step involving formation of a new C–C bond is most likely irreversible. The absence of observable isotope scrambling in either *d*- or *l*-bornyl pyrophosphate implies that the cyclization step is fast compared to positional isotope exchange during the initial isomerization step, without giving any information as to the relative rates of ring closure compared to either forward or reverse isomerization.

Poulter has recently reported that [1-^{18}O]geranyl pyrophosphate reisolated from incubations with prenyl transferase has not undergone detectible scrambling, in spite of strong evidence for the generation of allylic cations at the enzyme active site.[21] In the bornyl pyrophosphate synthetase reaction, the observed lack of positional isotope exchange is all the more remarkable when one considers the transient generation of an α-terpinyl cation—pyrophosphate anion pair in which the charge separation is at least 3 Å. Further studies that address the stereochemical implications of Scheme I are in progress, and the results will be reported in due course.

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On the Electronic Excited States of Model Chlorophyll

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The interaction of light with chlorophyll is one of the most important chemical reactions, for nearly all of life centers on photosynthesis. At the heart of this reaction is a magnesium chlorin complex, and it is the interaction of this complex with light that is the first step in photosynthesis. Since this molecular system is so widely used, it follows that the electronic structure of this molecule in its ground and excited states must possess some unique properties. In this paper we report on a preliminary investigation of the electronic structure of magnesium porphine in its ground and excited states as a first step in order to shed some light on these properties.

Methods. All calculations were of the restricted Hartree–Fock (RHF) type and were performed at the INDO level.

Closed-shell calculations were done by conventional RHF methods; open-shell calculations were performed by using an open-shell RHF procedure described elsewhere.[1]

Two types of parameter schemes were used: Pople type[2] for geometry optimization (INDO/1), and spectroscopic type[3] for spectra (INDO/S). The initial coordinates were taken from crystal X-ray data[4] subsequently symmetrized[5] and then optimized by using the INDO/1 method. The electronic spectra were calculated at the X-ray geometry and at the optimized geometry by performing selected singles-only configuration interaction calculations.

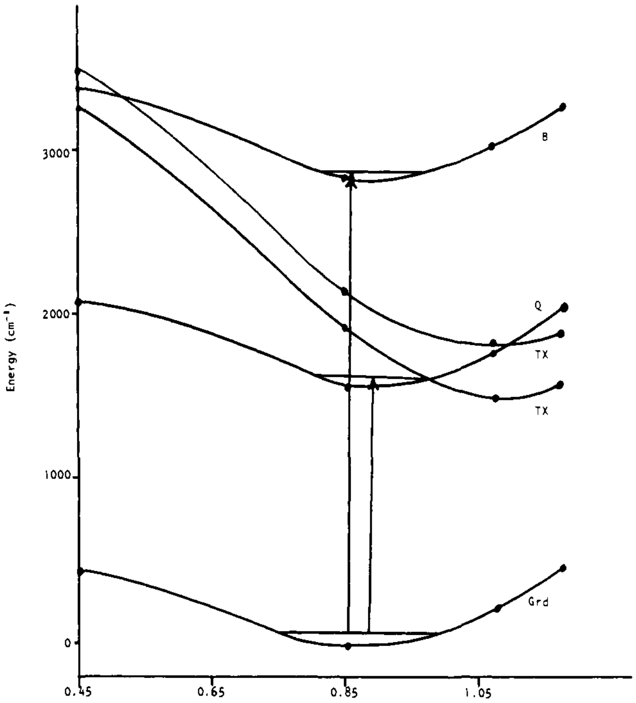

Figure 1. Lowest lying potential energy curves as a function of the Mg distance from the mean plane of the four chelating nitrogen atoms of porphin. Q is the state responsible for the visible band; B, for the Soret; and TX, the two porphin-to-Mg charge-transfer states.

Table I. Transition Energies Relative to Ground State[a] (cm^{-1})

band		geometry X (0.451)[b]	geometry G (0.848)	geometry * (1.08)	exptl[c]	ab initio[d]
Q	$^1E_1$	17424	15940	15524	17500	17100
CT	$^1A_2$	30745	19357	13042	forbidden	
Soret B	$^1E_1$	31099	28411	27884	24000	26200
CT	$^1B_1$	34871	21598	16231	forbidden	

[a] Singles-only CI relative to ground state at indicated geometry. [b] Numbers in parentheses are Mg distance from plane of nitrogen (Å). [c] Mg etioporphyrin (see ref 9). [d] Linearly fit to spectrum (see ref 8).

Excited states of interest were chosen from these CI calculations and calculated with the open-shell RHF formalism[1] by using both sets of parameters.

Starting coordinates for the excited-state geometry optimizations were chosen to be the optimized ground-state coordinates. All coordinates are optimized by using a gradient technique and the Murtagh–Sargent method of function optimization.[6]

Results. It is felt that the important photochemically excited state is most likely a singlet.[7] We therefore report here the singlet spectrum of magnesium porphine at three different geometries by using singles-only CI and spectroscopic parameters. The geometries are X-ray crystal coordinates (X), optimized ground state (G), and optimized excited state (*). The spectra obtained are shown in Table I along with experimental values. Symmetry

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assignments are based on the point group C_{4v}. Also included are results from ab initio calculations.[8]

It is clear from this table that optimizing the X-ray crystal coordinates results in only minor changes in the allowed transitions. However, this change has a marked effect on the forbidden charge-transfer bands. The first of these bands now lies near the visible Q band and well below the intense Soret or B band.

Since charge separation plays an important role in photosynthesis, the geometry of the first charge-transfer state was optimized and the electronic spectrum calculated at this geometry. The results of these calculations are given in Table I. At this geometry, the lowest excited state is now the charge-transfer state.

Using the results listed in Table I along with the respective ground-state energies, we constructed a series of potential energy curves, and these are shown in Figure 1. (It should be noted that the energies plotted correspond to fully optimized geometries, while the reaction coordinate plotted is the nitrogen–magnesium distance. As expected, the Q, B, and ground-state curves parallel each other but not the charge-transfer curves. The most notable features of the figure is the crossing of the charge-transfer curves and the Q-state curve. This crossing makes the spectroscopically forbidden charge-transfer state accessible from the first excited state upon relaxation.

These results have prompted us to propose the following possibility: Upon absorption of light, the ground-state molecule is converted to its first excited state. Under the right geometric conditions this excited molecule can then undergo internal conversion to the $^1A_2$ charge-transfer state. The geometry relaxes, causing the magnesium to move from 0.79 to nearly 1.01 Å out of the plane of the ring. (The change in Mg charge is from 0.54 to −0.02.) Since this state is of A_2 symmetry, the excited state will not decay rapidly into the A_1 ground state. At this point, the magnesium could interact with a neighboring molecule or directly with an electron-acceptor molecule, initiating the charge separation necessary for photosynthesis.

We stress the following points that these calculations have suggested. Magnesium is formally Mg^{2+}, and porphine, Por^{2-}. Somewhere in the spectrum there *must* exist a charge-transfer excitation from Por^{2-} to Mg^{2+}. The magnesium ion Mg^+ is considerably larger than Mg^{2+}, the latter with a rare gas electronic configuration. Since Mg^{2+} is out of the plane, Mg^+ must be further out of the plane, suggesting a strong energy dependence of this state upon Mg atom out-of-plane motion. Mg^+, removed from the porphine plane, is a strong electron donor. These features are general and are independent of the calculation performed. The transition energies and the crossing of the curves in Figure 1 are *not* independent of the calculation. In addition, transition energies calculated are also found to depend on the molecules involved and their environments, and thus the crossings, if they are to occur, are extremely sensitive. Mg porphine is not photosynthetically active; chlorophylls in the right in vivo environments are. For this charge-transfer mechanism to play an important role we must speculate that the in vivo conditions are just those required to cause population of the charge-transfer state and curve crossings such as suggested in Figure 1. The reduced double bonds to form chlorins, the presence of ring V, and fifth and possibly sixth position ligands that set the Mg-to-porphine out-of-plane distance are probably all crucial. Furthermore, we do not insist upon the importance of this state in photosynthesis. This state does, however, assign a rather unique role to chlorophyll molecules and might explain the appearance of Mg in nearly all photosynthetic molecules.

Before concluding, we point out that Dupuis et al. have suggested that the $a_{1u}(\pi) \rightarrow 3s$ or $a_{1u}(\pi) \rightarrow 3s$ Rydberg transitions may play a role in photosynthesis.[10] These nearly degenerate states were estimated to lie at about 26 000 cm^{-1} from ionization information, or near the Soret band. Such transitions might be appealing, as they throw the electron into a diffuse orbital with an average radius of perhaps 6 Å, where the electron might be picked up by an acceptor. These transitions have the same symmetry as do the charge-transfer excitations suggested here. Their consideration into the configuration interaction calculation might be expected to further lower the energy of the predicted charge-transfer excitations, increasing further the potential of these states for being photochemically active.

This work is of course only preliminary. Additional calculations on magnesium chlorin as well as other Mg-containing systems are currently under way.

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Reinvestigation of NADH Analogue Redox Reactions in Acetonitrile: Consequences of Isotope Scrambling on Kinetic and Product Isotope Effects

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Of continuing interest and debate is the reaction mechanism for hydride-equivalent transfer from dihydronicotinamides.[1-6] The direct hydride transfer (H^-) mechanism was generally accepted until Chipman and Steffens reported, in what appeared to be evidence for a stepwise mechanism, a discrepancy between the kinetic (k_H/k_D) and product (Y_H/Y_D) isotope effects for reduction of trifluoroacetophenone by a dihydronicotinamide.[2] They later retracted their earlier conclusions,[7] when they realized hydration and reversible adduct formation could account for their observed difference in k_H/k_D and Y_H/Y_D values. Others, however, using dihydronicotinamide reductions in "dry" aprotic solvents[8-10] or employing the nonhydratable nicotinamide analogue *N*-benzyl-3-carbamoyl-1,4-dihydroquinoline,[9] have reported disparities between k_H/k_D and Y_H/Y_D that they considered to be consistent with a multistep mechanism for hydride-equivalent transfer. Of particular mention are the k_H/k_D and Y_H/Y_D values for the reaction (in acetonitrile) of *N*-methylacridinium ion (**1**) with *N*-benzyl-1,4-dihydronicotinamide[8] (**2**), *N*-benzyl-3-carbamoyl-1,4-dihydroquinoline[9] (**3**), and *N*-aryl-1,4-dihydronicotinamides.[10] We show herein that these reactions (although originally thought to provide good evidence for a multistep mechanism, in as much as hydration and adduct formation could not occur) can no longer be considered in support of a step-wise mechanism.

Reaction of **1** with hydride donors **2** and **3** was followed by observing the decrease in [**1**] at λ 415 nm by UV spectrophotometry (eq 1). The reactions were carried out in dry (<0.010% H_2O) acetonitrile solution ([**1**] = 3 × 10^{-5} M, [**2** or **3**] = 3.30

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