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THE PI ELECTRON STRUCTURE AND ABSORPTION SPECTRA OF CHLOROPHYLLS IN SOLUTION

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Abstract

This paper reviews the spectra of and proposes new assignments for the electronic absorption spectra of protochlorophyll, chlorophyll a, bacteriochlorophyll a and their respective pheophytins. The assignments are based on a detailed comparison of absorption, fluorescence polarization, circular dichroism (CD), and magnetic circular dichroism (MCD) spectra in the visible and ultra-violet with the well understood spectra of the unsubstituted parent rings. Pariser-Parr self-consistent molecular orbital calculations are used for guidance.

Our assignments agree with earlier work on the Q_x and Q_y transitions in the visible region. Extensive configuration interaction calculations confirm that these can be treated within the limited CI framework of the Gouterman four-orbital model, as in porphin. The Soret band of chlorin and ADJ-tetrahydroporphin, but not that of OPP-tetrahydroporphin, can also be represented by the four-orbital model.

Newly available MCD spectra indicate that the B transitions of chlorophyll a and pheophytin a are accidentally degenerate and together produce the major Soret peak, in contrast to previous assignments. A new pi-pi* transition, which we name eta for convenience although it is of mixed parentage, produces the satellite on the major Soret peak previously assigned to the B_y. This new band becomes allowed from the combined perturbations of carbonyl substitution and ring distortion by the isocyclic ring. It disappears if the isocyclic ring is cleaved or if its carbonyl group is reduced.

The Soret band of bacteriochlorophyll displays dramatic solvent effects in which five bands interchange intensity. Our calculations and those of Song indicate that at least three allowed and two forbidden transitions lie in this region. The lowest triplet of bacteriochlorophyll is predicted to be only 5500-7100 cm^{-1} above the ground state.

Calculations of the spectroscopic effects of ring reduction and substitution agree fairly well with experiment. In particular, the "480 nm" band recently identified in free base porphins is predicted to occur in free base chlorins and pheophytins, and in fact can be found in their spectra. Predicted shifts in ground state charge density upon carbonyl substitution agree qualitatively with the limited available data. Transition monopoles are calculated for the visible transitions of chlorophyll a and bacteriochlorophyll a.

A longstanding aim of the molecular orbital theory of porphyrins has been wave functions for ground and excited states of chlorophyll good enough to support a definitive assignment of the absorption spectra. Such wave functions would supply the quantum chemist's answer to the old question of why grass is green. They would be valuable, among other things, in calculating the properties of chlorophylls in aggregated states related to their structure in vivo.

The self-consistent molecular orbital theory of Pariser, Parr and Pople (SCMO-PPP) (1,2) has made it relatively easy to perform approximate calculations on large π electron systems. These calculations depend on moderately severe assumptions and mildly arbitrary input parameters, and are best approached with some skepticism. One test is to start with a simpler relative whose properties are well understood, and to build up to the desired molecule by adding chemical perturbations one by one. The chlorophylls are suited to such an approach, as their parent rings, the porphyrins, have been subjected to extensive theoretical analysis, the results of which have been thoroughly compared with experiment.(3,4,5,6,7) Moreover, experimental data on a large number of substituted porphyrins and reduced porphyrins are available.

The present study began as an attempt to extend to carbonyl substituted porphyrins, among which are the chlorophylls, the extensive SCMO-PPP calculations we previously performed on porphyrins and larger macrocycles.(6,7) The effects of substitution are much subtler than those of ring reduction, and we found it necessary to gather many more

spectra than had been used in our previous comparisons between theory and experiment. Careful comparison of the absorption spectra of closely related molecules, plus qualitative interpretations of newly available magnetic circular dichroism (MCD) spectra, led us to revise a number of long accepted spectroscopic assignments and to propose several new ones. We then compared our calculated results with our newly expanded phenomenological interpretations of the data, and found that they agreed moderately well.

Introductory Survey

This paper will focus mainly on the spectra of protochlorophyll a, chlorophyll a, and bacteriochlorophyll a. These and some other photosynthetic pigments are shown in Fig. 1. They are substituted magnesium derivatives of the parent rings porphin, chlorin (dihydroporphin) and bacteriochlorin (OPP-tetrahydroporphin), respectively.

Information on the structure of these rings and their typical spectra will be found in ref. 4. Structures of some metal-free "free base" derivatives related to chlorophyll a are found in Table I.(8,9) All these molecules show an intense absorption in the blue or near ultraviolet region, the so-called Soret band, and bands of lower oscillator strength (though occasionally greater extinction coefficient) in the visible or near infra-red. These bands are due entirely to pi-pi* excitations within the conjugated macrocycle.

Spectra of photosynthetic porphyrins in solution at varying levels of oxidation are shown in Figs. 2 and 3. Fig. 2 shows the spectra of protochlorophyll a and chlorophyll a; Fig. 3, of bacteriochlorophyll a and 2-desvinyl-2-acetyl chlorophyll a. Each compound of each pair is

identical to the other except for the reduction of a double bond. The spectrum of the ADJ-THP analog of chlorophyll, called hypochlorophyll, is given in reference 8. (See Fig. 8.)

The solution spectra of the chlorophylls have been reviewed many times,(14) most recently by Goedheer (15) and by Gurinovitch, Sevchencko and Solov'ev.(16) The latter review includes a discussion of high resolution spectra of porphyrins and chlorins taken at low temperature, an area which we shall not consider here.

THEORETICAL METHODS

The approximations of the SCMO-PPP-CI theory are by now well known.(1,2,6) The parameters and geometries in most of these calculations were taken from our earlier work (6) to facilitate comparison. CO bond distances were taken as 1.215 Å from X-ray data of Hoard (17) on nickel diacetyl deuteroporphyrin. "Traditional" values were used for carbon and nitrogen parameters, rather than the "standard" parameters used for reduced porphyrins in reference 6. The valence state ionization potential and electron affinity of oxygen were taken from Miller.(18) Two values for the resonance integral β_{CO} were used. One, β_{CO} = -3.19 eV, equals the value of β_{CC} for the same internuclear distance. The other, β_{CO} = -2.36 eV, is from Leibovici and Deschamps.(19) These values span the highest and lowest values in the literature, up to 1967. Qualitative conclusions were independent of the choice of β_{CO}.

Alkyl and meso-aryl substituents and distortions of the ring due to the isocyclic ring of chlorophyll derivatives were ignored in most calculations. Each nitrogen was given 1.5 pi electrons; the central

metal was not considered explicitly. Toward the end of the research, we attempted to simulate effects of ring distortion by using the geometry of methyl pheophorbide a determined by Fischer et al.(20). In some calculations, the oxygen was brought into closer conjugation with the ring by use of the oxygen parameters of Tichý.(21). ASMO-CI calculations were performed using the "$\Delta\alpha$ = 5.5" parameters of McHugh et al.(7).

In extended configuration interaction (CI) calculations, the basis set was arbitrarily cut off at about 150 nm (60-75 configurations) to stay within the capacity of the computer. Whenever possible, the cutoff was made at a natural break in the density of electronic states. The programs used in these calculations were written by W. Donath, expanded by C. Weiss,(22) and further improved by P. Miller and J. Weeks.

Experimental oscillator strengths were estimated from unresolved published data by the formula

$$f = 4.61 \times 10^{-9} \, \varepsilon \, \delta$$

where ε is the molar extinction coefficient and δ the band width at half height, measured in wave numbers. This "triangle" formula is exact only for bands of perfect Gaussian shape.

Review of Porphin Theory

The basis for the interpretation of these spectra is the four orbital model of Gouterman,(3,4) who built on earlier work by Moffitt (23) and Platt.(24) An essentially equivalent interpretation, based on the free electron model, has been made by Kuhn (25). The early history of the theory of porphyrin spectra has been thoroughly reviewed by Gurinovitch.(16)

In the original Gouterman model,(3,4) the visible and near-ultraviolet absorption bands are interpreted phenomenologically as arising from

electronic excitation from the highest two filled orbitals to the lowest two empty orbitals (Fig. 4). The lowest empty e_{gx} and e_{gy} orbitals are degenerate by symmetry in metal porphins, while the highest filled a_{1u} and a_{2u} orbitals are almost degenerate (Fig. 4). The $(a_{1u}e_g)$ and $(a_{2u}e_g)$ configurations interact pairwise to give minus and plus states in which the equal transition dipoles cancel and reinforce each other, respectively. (Configurations are singlets unless otherwise indicated.) This gives rise to a weak Q transition and a very intense B transition (Fig. 5), corresponding to the visible and Soret bands, respectively. The major features of this model have been confirmed by extensive and careful experiments by the Russian school of spectroscopists.(16)

SCMO-PPP-CI calculations have placed the success of the four-orbital model in a larger theoretical context, and cleared up discrepancies between the spectroscopic data and the results of the Hückel theory.(5,26) The calculations gave good qualitative agreement with the porphin triplet-triplet absorption spectrum, as well as with the ordinary visible and near ultra-violet absorption spectra of a wide variety of porphyrin derivatives, including azaporphyrins, phlorins, reduced porphyrins, tetrabenzoporphyrins, and phthalocyanines. Felton has used much the same parameters in calculations on the porphyrin radical mono- and di--anion (27) and -cation,(28) as well as on isoporphyrin (29) and isophlorin.(30)

The main features of SCMO calculations of metal porphin are not affected by a large range of theoretical refinements.(22,31) McHugh et al.(7) have extended them to the far ultra-violet absorption and to MCD spectra in the visible and near ultra-violet. They improved their predicted oscillator strengths by using transition gradients instead of transition dipoles.

At the same time as the theory of porphyrin spectra has been advancing, data has become available on the absorption, fluorescence polarization, CD and MCD of families of porphyrins and chlorophyll derivatives.(9,10,11) In the visible spectrum of porphyrins, x- and y-polarized transitions have opposite signs in MCD and usually in CD spectra as well. The reasons for this are different in MCD and CD, and cannot be explained in a simple "physical" picture.(7,11) The MCD of an isolated doubly degenerate transition of a square molecule typically resembles the derivative of the absorption band. The cross-over, or zero point ideally should coincide with the absorption maximum.

The four main visible transitions in free base porphins are assigned to Q_x and Q_y daughters of the metal porphin Q bands and their (0-1) overtones. As in metal porphins, intensity of the vibrational overtones is borrowed from the Soret band and does not follow the Franck-Condon envelope.

The intrinsic (0-0) intensities of the Q_x and Q_y bands of the free base are very sensitive to substituents, while the borrowed intensity of the vibrational overtones is less sensitive to these perturbations, at least in porphins.(3,16) This is the theoretical basis for the widely used classification of substituted free base porphyrins into "spectral types" (etio, rhodo, chloro, etc.).(32)

The B_x and B_y transitions underlying the Soret band were initially assumed degenerate. This assignment could not be made to agree with the calculations without fudging. Sundbom suggested (33) that three electronic transitions underlie the Soret band of porphin free base: B_x, B_y and N_x, instead of two as in metal porphins. The B_y has about the same oscillator strength as in metal porphins, but the B_x and N_x each

have about half that amount. Experimental absorption and MCD spectra are consistent with this conclusion, if the N_x is much broader than the two B transitions.

McHugh et al.(7) agree that there are three transitions in the Soret region, but present evidence for a different assignment. Extending a proposal by F. Longo, they suggest that the extra transition appears as a band at 480 nm long known by porphyrin chemists to wax and wane in intensity according to substituent. This variation is thought to be caused by changes in intensity borrowing from the Soret band by a previously unsuspected x-polarized transition.

RESULTS

A. Unsubstituted Reduced Porphyrins: Theory and Experiment

When one or more of the porphin double bonds is reduced to form a chlorin or tetrahydroporphin, the energies of the molecular orbitals appear to shift in a manner that can be predicted from the orbital electron densities on the atoms involved in the double bond to be reduced (4,34a). Fig. 4 shows these energies as calculated in the present treatment.

These shifts in orbital energy destroy the near-degeneracy of the lowest excited configurations (Fig. 5). In the Hückel model, the x-configurations in chlorin are degenerate, and their transition dipoles cancel and reinforce each other, as in porphin, to produce the weak Q_x and the strong B_x, respectively.(5) The Q_y band is therefore predicted to be more intense in chlorin than it is in porphin. SCMO orbitals show a similar pattern.

In OPP-THP, where the relative shifts in orbital energies are more than doubled, the $\underline{Q}_y$ band is predicted to be further red-shifted and intensified, and the $\underline{B}_y$ is at higher energy than the $\underline{B}_x$. The x-polarized configurations, on the other hand, are more nearly degenerate, and again interact to give a weak $\underline{Q}_x$ band. (The high intensity normally associated with $\underline{B}_x$ is distributed among several interacting x-polarized transitions.) OPP-THP is a typical "long field" molecule , and absorbs at longer wavelengths than chlorin even though it is more reduced.(26). In both molecules, the longer wavelength transition is allowed in the direction with the longer path of conjugation, this time in keeping with a primitive "antenna" model.

Fig. 5 shows the energy level diagrams for the lower excited states of the reduced metal porphyrins given by SCMO-PPP-CI calculations from the present work. The result is displayed at each of three steps: a) pure configuration energies, corresponding to the length of the arrows in Fig. 4, less two-electron terms; b) minimum CI; c) extensive CI involving 60-75 configurations.

The first two columns agree with the four-orbital results of reference 6. Contrary to the hopes of the early theorists (5), however, the effects of the new terms introduced in this model vary from porphyrin to porphyrin. This probably dashes hopes for a simple phenomenological theory for reduced porphyrin spectra.

The configurational purity of the lowest excited state, calculated in the four-orbital model, rises from 52% in porphin to 68% in chlorin and 84% in OPP-THP. Adding more configurations has little effect, as all porphyrin $\underline{Q}$ states are derived at least 97% from four-orbital model configurations. In chlorin and ADJ-THP, the $\underline{B}$ bands are derived 87% and 95%

from four-orbital model states, respectively, compared to 84% in porphin. CI integrals between pairs of four-orbital configurations vary almost 100% from porphyrin to OPP-THP. The transition dipole of a particular transition, however, varies only about ±20%.

The most accurate way to compare these results to experiment is to consider quantitative spectra of a series of porphyrins with the same substituents, taken in the same solvent, but differing in the level of ring reduction. Fig. 6a-c shows the most suitable matched data in the literature for the visible and Soret regions of porphyrins with symmetrically disposed saturated or meso-aryl substituents; these sets of spectra are fuller than those used in previous tests of theoretical models, but none of the sequences is complete. Probably the most important gap is the ultra-violet and quantitative visible spectrum of a metal OPP-THP.

We do not know to which metal porphyrins our calculations correspond, and the ratio of Soret to visible intensities (especially in porphin) depends strongly on the central metal. The zinc porphyrin sequence of Fig. 6c may correspond most closely to the calculations, since its Q transition is almost forbidden.

The assignments of the visible spectrum are the same as in previous work, and the calculations agree about as well as before.(5,6) Experimentally and in the calculation, the Q_y band in the chlorin is much more intense than the doubly degenerate Q band in porphin. The Q_y is also shifted to lower energy. The Q_x band of chlorin is stronger than the porphin Q in three of the four series, but is not strong enough to stand out from the vibrational overtones of the Q_y. Its energy is about the same as that of the porphin Q. The calculations in Fig. 5 do not reproduce these trends very well.

The chlorin B bands are predicted to come at the same energy as those of porphin, and are in fact so found. The CI pattern of chlorin and hence its spectrum is somewhat similar to that of tetrabenzoporphin.(6,7,44) The calculation correctly predicts that B_x and B_y are accidentally almost degenerate in unsubstituted metal chlorins. The B_y is 260 cm^{-1} above the B_x in the four-orbital model, but 170 cm^{-1} below it in extended CI. (X-allowed states are not constrained by symmetry and will be lowered by CI more than y-allowed states.) The calculated energy order of B_x and B_y is not affected by extension of the CI basis set in substituted chlorins.

In chlorin, N_y is predicted to be the first moderately intense band above the Soret (Fig. 5). In addition, the calculated ultra-violet spectrum has many allowed bands, which are descended from forbidden bands of the porphin ring but which are now allowed because of the loss of a plane of symmetry. These bands usually have a predicted oscillator strength of at least 0.04, and often as much as 0.2. ASMO calculations on free base chlorin, using orbitals calculated for the metal derivative and the "$\Delta\alpha$ = 5.5" parameters of McHugh, indicate that the Soret band of this compound includes three major allowed electronic transitions, much as in free base porphin.(7,33)

For OPP-THP, we must rely mostly on the spectrum of bacteriochlorophyll in Figs. 3 and 7. (See also Table II.) Both bacteriochlorophyll and Mg tetraphenyl OPP-THP (Fig. 5) have the Q_y so red-shifted from the corresponding chlorins that the Q_x is easily identified by fluorescence polarization.(15) This shift is qualitatively reproduced in the calculations, although it is underestimated. There is a quantitative discrepancy in that the oscillator strength of the Q_y band of chlorophyll a is nearly that of bacteriochlorophyll a; the prediction is that it should be less.

$\underline{B}_x$ and $\underline{B}_y$ are predicted to split in OPP-THP and its substituted derivatives, a prediction in agreement with experiment. The $\underline{B}$-$\underline{Q}$ energy splitting is overestimated in both chlorin and OPP-THP, as in our previous calculations and those of all other workers.[3]

The Soret region of OPP-THP cannot be described by the four-orbital model. According to our calculation (Fig. 5), it includes three allowed and two forbidden bands, instead of the two allowed bands characteristic of the other unsubstituted metal porphyrins. The theoretical origin of the new allowed band is as follows. The $4e_{gy}$ orbitals[4] of porphyrin are raised sharply in energy on reduction to OPP-tetrahydroporphyrin (Fig. 4). This raises the energies of the $(1a_{1u}4e_{gy})$ and $(3a_{2u}4e_{gy})$ configurations so high that transitions to the $4e_{gy}$ from the new $\underline{a}$ orbital are only slightly higher in energy. The $\underline{a}$ orbital is a descendant of the $2a_{2u}$ and $2b_{2u}$ orbitals in porphin. Since the transitions $(2a_{2u}4e_g)$ and $(2b_{2u}4e_g)$ interact to form the $\underline{L}$ and $\underline{N}$ bands of porphin,(6) the $(\underline{a}e_{gx})$ bands of chlorin and OPP-THP have been named $\underline{N}$. The $\underline{N}_y$ bands of the reduced porphyrins are split to higher energies by interaction with $\underline{B}_y$. Thus only the $\underline{N}_x$ is important to the present discussion.

The $\underline{N}_x$ and $\underline{B}_x$ bands of OPP-THP and bacteriochlorophyll $\underline{a}$ are the only spectral features we have encountered in these calculations that are affected by expansion of the CI basis set beyond that of the four orbital model. Our calculations and those of Otten (46) show that the $\underline{N}_x$ band steadily loses predicted intensity (dipole formula) to the $\underline{B}_x$ as the number of configurations is increased. When all 99 singly excited configurations are included, the predicted $\underline{N}_x$ oscillator strength drops to an entirely reasonable 0.08.(46)

The ultra-violet spectrum of OPP-THP is thus predicted to have no electronically allowed transitions at all for 10 700 cm^{-1} above the energy of the Soret band. None of the allowed bands in this region of the porphin spectrum is predicted to be there in OPP-THP. The L band has been eliminated by the loss of a bonding orbital, the N_x band has been red-shifted below the Soret energy, and the N_y has been blue-shifted by the rise in $4e_{gy}$ orbital energy. This prediction is largely rooted in the symmetry of the molecule, and extends to bacteriochlorophyll and presumably to other substituted OPP-THP derivatives.

The orbital pattern for ADJ-THP is calculated by Hückel and SCMO methods to be similar to that of chlorin, a prediction borne out by the similarity of the available ADJ-THP spectra to those of the corresponding chlorins.(37,42,47) The Q bands are found at energies slightly higher than the corresponding bands in chlorin, a result also given by the calculation. The Soret band of ADJ-THP is predicted to be practically degenerate in the four-orbital model, both in the "standard" and in the "traditional" treatment.(6) Extended CI increases this splitting from 54 to 260 cm^{-1}, and predicts that the y band will be higher in energy (see Ref. 3 for axes). The experimental value of the B splitting is 420 cm^{-1}.(42,37) It would be interesting to confirm these assignments by fluorescence polarization and MCD.

We see, then, that the four-orbital model correctly accounts for intensity differences among reduced metalloporphyrin spectra in the visible and Soret regions, but does not do very well at predicting quantitative energy shifts. Except in the Soret band of OPP-THP, this result is largely unaffected by increased CI. This suggests that the four-orbital model is essentially correct, but that our quantitative representation by the SCMO-PPP-CI model is inadequate. The consistent overestimation of the B-Q splitting suggests

that the fault is in the treatment of electron correlation. In fact, the pure configuration energies of Fig. 5 reproduce the experimental energy shifts of the visible bands better than do the post-CI state energies.

B. Substituted Porphyrins

To help the reader through the subsequent discussion, we have summarized in Fig. 8 our interpretation of the experimental energy level diagrams for magnesium porphyrins related to chlorophyll a. Our assignments are deduced in the following sections by comparison of absorption and MCD spectra of related compounds, using the calculations judiciously as guides. The theory of MCD in molecules of low symmetry has not yet been worked out. This means that interpretations of MCD in substituted porphyrins must remain tentative.

a. Protochlorophyll: Theory and Phenomenology

The experimental absorption, CD and MCD spectra of protochlorophyll a (11) are shown in Fig. 9. Assignments shown for the visible and Soret regions are those made by Houssier and Sauer.(10,11) Assignments at higher energy are by analogy to metal etioporphyrins (7) and 2,4-diacetyl deuteroporphyrins.[5] (40) We call attention to the anomalous MCD ($A > 0$, $\theta_M < 0$) associated with the Q_y transition.(7)

Results of an extensive CI, SCMO-PPP calculation of monocarbonyl porphin, intended to represent protochlorophyll a, are shown in Fig. 10, along with experimental energies. Also shown are the results of a more recent calculation by Song,(51) who considered four different sets of semi-empirical parameters, and selected as the one most nearly in agreement with experiment

a set which represents the central magnesium ion as a point charge of +1.5 electrons that affects the ionization potentials and electron repulsion integrals of the nitrogens. This disagrees with Zerner and Gouterman,(52) who calculate by extended Hückel theory that the charge on the magnesium is +0.6, in magnesium porphin. Both calculations give accurate predictions of the Q energies, although Song's gives the better value for $E(Q_x) - E(Q_y)$.

Our calculation produces the curious result that both of the visible transitions are predicted to be almost parallel, i.e. $Q_{"x"} \parallel Q_{"y"}$. This result is contrary to the fluorescence polarization studies of Houssier and Sauer,(10) which show the bands to be roughly perpendicular, and may well be due to the neglect of saturated substituents which would raise the a_{1u} orbital energy relative to that of the a_{2u}. On the other hand, it may be related to the anomalous MCD measured by the same workers and shown in our Fig. 9.(11).[6] Further theoretical work on this spectrum would be useful. (The Song calculation gives $Q_x \perp Q_y$, the expected result.)

Both calculations greatly overestimate the B-Q energy splitting. Our calculations predict the next states above the Q band to be the closely spaced B_x and B_y states. The Song calculation predicts three intense transitions in the same region.

The experimental Soret band of protochlorophyll a is deceptively complex. The split into B_x and B_y is clearly indicated by fluorescence polarization,(10) and is consistent with the CD and dimer absorption. Yet the B_x transition shows only a very slight negative MCD - too small to show up on the figure - and the well shaped double MCD corresponds in wavelength to the B_y and to the small satellite band on the short wavelength

tail of the Soret.(11,53) In zinc deuteroporphyrin, a metal porphin whose Soret band should include only two degenerate transitions, there is a typical double MCD. This evidence suggests that the Song assignment could be correct, and that the double MCD could result from a near degeneracy between the B_y and a new transition just above it. Alternatively, the B_x and the B_y MCD may have different shapes and amplitudes. Neither of these explanations is completely satisfactory.

The main effect of carbonyl substitution in our predicted absorption spectrum of monocarbonyl and 2,4-dicarbonyl porphin at higher energies is to break down the symmetry and make forbidden bands allowed. In particular, $(1a_{1u}2b_{1u})$ and $(3a_{2u}2b_{1u})$ bands appear in the spectrum at energies above the Soret band, with predicted oscillator strengths of 0.13 in monocarbonyl and 0.55 in dicarbonyl porphin. Both these bands are forbidden in square symmetry. From their energies and their prominence in the spectrum of carbonyl porphins, they should correspond to the η bands identified in the experimental spectra of metal 2,4-diacetyl deuteroporphyrins.(40)

The absorption curve in Fig. 9 suggests that the η band is split into two components of opposite polarization, as indicated by two bumps on the absorption curve and a trough in the CD curve. The trough is much deeper in vinyl protochlorophyll,(10) a fact which may indicate a new pi-pi* state involving the vinyl group. Such states are predicted by SCMO calculations in which vinyl groups are introduced explicitly.

In place of the N and L bands of square porphyrin, the model predicts a cluster of bands of various parentages and polarizations. Experimentally, the N absorption band in protochlorophyll shows signs of three separate transitions. The first (N_1) corresponds to the 332 nm

peak called N by Caughey et al.(40) The second (N_2) is a slight inflection at about 325 nm, and the third (N_3) appears as a shoulder in the absorption and as a peak in the CD. The L band can no doubt be further resolved as well. A new band, the M band,(7) appears at 239 nm.

b. Pheophytins and Other Free Base Chlorins: Phenomenology

To facilitate comparison, we have constructed a graded series of substituted free base chlorins, each one differing only slightly from its predecessor. (MCD and quantitative absorption spectra for a comparable series of metal chlorins are not available.) The compounds used are listed in Table I; representative spectra are shown in Figs. 11 and 12.

Detailed comparison of the visible portions of these and other absorption spectra shows five regions whose appearance remains similar from molecule to molecule, a fact well documented by the early German spectroscopists.(56,57) The region at longest wavelengths includes a sharp, intense band, usually together with a satellite at slightly higher energy. The intense absorption band, which is associated with a small positive MCD peak, is assigned to the Q_y transition. The second and third regions contain low humps from 540-590 nm (550-615 nm in pyromethyl pheophorbide).

The fourth peak at 536 nm in pyromethyl pheophorbide is clearly assigned to the Q_x transition by the large negative peak in MCD (Fig. 11) and the small positive CD band. This confirms the earlier assignment, which was based on the well-resolved negative peak in the fluorescence polarization (58) of pheophytin a, whose absorption spectrum is practically the same as that of pyromethyl pheophorbide a. The same peak appears at 519 nm in the absorption spectrum of etiochlorin (Fig. 11).

Turning now to the spectrum of unsubstituted free base chlorin in Fig. 11, we see that this peak is absent. We interpret this to mean that the (0-0) band of the Q_x transition has no intensity - i.e., that the transition dipoles of the configurations making up the Q_x state have cancelled exactly. This proposal needs to be confirmed by MCD. If it is correct, this transition will be a convenient point to calibrate future calculations on free base chlorins and pheophytins.

All six of the spectra in figures 11-12 show a fifth band at 480 nm, which may correspond to the transition identified by McHugh et al. in free base porphins (7). The band does not show up clearly in the MCD (Fig. 13). It disappears in chlorophyll a and in Mg 9-oxy-desoxo methyl pheophorbide a,(59) lending weight to the suggestion that is is specifically a free base transition.

The spectra of tetraphenyl-, etio-, and unsubstituted chlorins are less clear-cut. The "480" band is present in free base tetraphenyl chlorin and absent in most of its metal derivatives, but is present in the copper, silver and tin complexes.(43) Free base chlorin and etiochlorin have a prominent double peak between 488-496 nm. The low temperature fluorescence polarization spectrum of free base chlorin shows that the twin peaks are of opposite polarization,(60) strongly suggesting that they are the (0-1) of the Q_x and the (0-0) of an x-polarized "480" band, respectively. On the other hand, the spectrum of Mg chlorin shows a similar band, although it is weaker and red shifted.(61) Low temperature fluorescence polarization studies of this molecule and of Mg etiochlorin might well settle the assignment in this region.

The Soret bands of the free base chlorins are complicated to interpret. The Soret band of unsubstituted free base chlorin can be resolved

into two components of nearly the same energy and intensity but of opposite polarization,(60) split by only 550 cm^{-1}. These are assigned to the B_y and B_x transitions, in order of increasing energy. Nearly all of the free base chlorins listed in Table Ia and Ic show the single, well-shaped absorption band exemplified by meso-phyllochlorin in Fig. 12. This is known as a chlorin-type spectrum. The Soret band of 9-desoxo-meso-pyromethyl pheophorbide is well-shaped but is broader than that of meso-phyllochlorin. B_x and B_y are apparently degenerate in these molecules within the resolution of the spectra. We cannot exclude the possibility of a broad N_y transition in the short wavelength tail of the Soret band of these spectra by analogy to the Sundbom assignment for free base porphin.(33) Low temperature and fluorescence polarization spectra would be useful here.

In meso-pyromethyl pheophorbide, the Soret band is less intense, and is split into two components of different energies and intensities. This is known as a phorbin-type spectrum. Most previous workers have assigned the main peak and the shoulder to B_x and B_y transitions, respectively,(6,15) an assignment based mostly on fluorescence polarization data.(62,65)

Newer, more highly resolved room temperature fluorescence polarization spectra of pheophytin a by Goedheer (63) show clearly that the red edge of the Soret band is y-polarized relative to the main peak and to the shoulders at 400 nm and 375 nm in castor oil. They do not reproduce the sharp rise in polarization at $\lambda<400$ nm shown in ref. 15. These results cast doubt on the traditional assignment. They indicate that $E(B_y) < E(B_x)$, as in unsubstituted free base chlorin.

Even this reassignment is insufficient to explain the MCD spectra shown in Fig. 13. In chlorin e_6, whose absorption resembles that of meso-phyllochlorin, a large positive MCD at the long wavelength side of the Soret at 420 nm is followed by a huge negative peak at 395 nm. The cross-over point of the MCD lies on the long wavelength side of the absorption maximum. A large positive peak corresponds to the satellite band in absorption at 364 nm. This spectrum is consistent with magnetic coupling between nearly degenerate B states and a vibrational overtone or (more likely) a new electronic transition at higher energy. It is likely that the polarization of some or all of these states are tilted off the major axes. More theoretical work is thus needed to explain these spectra; fluorescence polarization data for chlorin e_6 might also be useful.

In the phorbin-type Soret band of pyromethyl pheophorbide, on the other hand, the upward and downward excursions of the MCD are almost equal in magnitude, and the cross-over point comes at almost exactly the same wavelength as does the absorption peak. In other words, the main peak of the "split" Soret gives the typical MCD of a doubly degenerate transition - a pattern much simpler than that associated with a "well-shaped" Soret band. Moreover, the downward excursion shows a well-defined shoulder that corresponds nicely to the shoulder on the "split" Soret band.[7]

We tentatively conclude, then, that the main peak in both "split" and "well-shaped" Soret bands - i.e., both phorbin and chlorin-type spectra - comes from a doubly degenerate B transition, and to the shoulders on the "split" Soret band of pheophytins and pheophorbide is a third transition. In chlorin-type spectra, this newly identified transition is either forbidden or else buried under the intense B bands. This conclusion is implicit in the tabulated assignments of Houssier and Sauer.(11)

In the absence of reliable calculations for absorption and MCD intensities, it is difficult to assign this intensity to a particular forbidden electronic band. We shall tentatively call this new transition η by analogy to the spectra of carbonyl substituted porphyrins.(40) A positive MCD peak appears at wavelengths corresponding to the Soret tail.

The difference in structure between 9-desoxo-meso-pyromethyl pheophorbide a and meso-pyromethyl pheophorbide a is the carbonyl substituent on the cyclopentene ring - i.e., the conversion of the cyclopentene ring into a cyclopentenone ring. This seems to be the critical requirement for a phorbin-type spectrum. Chlorin e_6, for example, with an α-saturated substituent on the meso position and an α-carbonyl at the 6 position, has a chlorin-type Soret peak. Introduction of the cyclopentene ring broadens the Soret band, presumably due to the new unresolved transition, and the carbonyl group splits out the resolved shoulder, reducing the intensity of the main peak.[8]

This new assignment is consistent with the fact that the ratio of the heights of the main peak and the shoulder of the chlorophyll a Soret band (which we shall later assume to be analogous to that of pheophytin) varies from 0.54-0.95 depending on the solvent.(64) We assume that the CI giving rise to intensity stealing by η from B is solvent (or ligand) dependent. Another possibility is solvent dependent CI between B_x and B_y. Alternatively, the relative extinction coefficients of B and η may change depending on the energy split between them, without any change of oscillator strength.

c. The Chlorophylls: Phenomenology

The visible spectra of the chlorophylls and their derivatives are more poorly resolved than, and hence are best assigned by comparison to, those

of the pheophytins. The visible absorption spectrum of chlorophyll a (Figs. 2, 14, 15) shows four humps similar to, although not as well resolved as, the first four humps of the pheophytin a spectrum. Fluorescence polarization (58,62,65) (Fig. 14) and magnetic circular dichroism (11) (Fig. 15) have generally been interpreted to mean that the intense peak at longest wavelength is the Q_y, while the third hump at 578 nm is the Q_x. The second hump is appropriately spaced to be the (0-1) of the Q_y. The visible spectra of chlorophyll d, 2-desvinyl-2-acetyl chlorophyll a (12) (Fig. 3) and Mg-9-oxy-desoxy-methyl pheophorbide a (59) resemble the spectrum of chlorophyll a, as do those of a variety of allomerization intermediates.(66) We may assign the third hump in each to the Q_x. (This comes at 591 nm in 2-desvinyl-2-acetyl chlorophyll a.)

We have used this traditional assignment in Fig. 15 and in our comparisons with theory. However, new low temperature fluorescence polarization experiments have raised the possibility that the Q_x is actually the second hump in the spectrum, and that vibrational overtones of these bands interleave thereafter.

The first of these is the fluorescence polarization spectrum of zinc tetraphenyl chlorin and of chlorophyll a in frozen alcohol glass.(67) In these molecules, the third visible transition at about 575 nm, which we have identified as the Q_x band in the spectrum of chlorophyll a in ether, almost disappears. The nearest thing to an x-polarized transition that remains is a band at 639 nm in chlorophyll a (~600 nm in zinc tetraphenyl chlorin), which Sevchenko et al.(67) identify as a shifted Q_x.

Similar results have been obtained very recently by Song (50) from frozen ether solutions of chlorophyll a at 77°K. In Song's polarization

spectra, both the 639 nm and the 575 nm bands are clearly x-polarized, though the latter band is not clearly resolved in absorption. In other words, by the traditional assignment, the (0-1) of the Q_y is strongly x-polarized. This is surprising at first, but is entirely possible. CD and MCD spectra at low temperatures are needed, as are theoretical studies of possible vibronic interchange of intensity between Q_x and Q_y as a result of environmental change.

The visible spectrum of chlorophyll b beyond the Q_y is almost completely structureless; fluorescence polarization measurements taken in castor oil indicate that the Q_x band is a small shoulder that appears to the red of the hump at 594 nm when the spectrum is taken in ether solution.(15,62) MCD spectra for these compounds would be useful for testing these assignments.

The Soret region of chlorophyll a in ether (Fig. 15) shows an intense peak at 428 nm (in ether) accompanied by a satellite band at higher energy. It thus resembles the phorbin-type "split Soret" of the pheophytins. The main peak and its satellite have been assigned by previous workers to the B_x and B_y transitions from fluorescence polarization measurements.(10,15,65) At the time, this was thought to be the Soret assignment for both chlorophylls and pheophytins. The new polarization work on the Soret band of pheophytins discussed in the previous section now indicates that the order of B_x and B_y transitions may be reversed in the two sets of compounds.

The MCD spectrum of chlorophyll a in the Soret region (11) (Fig. 15) shows a clear double MCD with a cross-over precisely at the absorption maximum, much like that of the pheophytins. A shoulder on the MCD at 398 nm corresponds fairly well to the absorption shoulder at 409 nm.[7]

In contrast to previous workers but in agreement with our remarks on pheophytins, we assign the main peak to a doubly degenerate B and the hump at higher energies to a band, forbidden in unsubstituted chlorin, which steals intensity from the Soret because of the distortion of the chlorin pi system by the isocyclic ring and its conjugated carbonyl.

This intensity stealing is responsible for the observation that phorbin-type Soret bands are less intense than chlorin bands, both absolutely and relative to the intensity of the visible transitions. MO calculations suggest that both this shoulder and the second shoulder at 380 nm are derived from overlapping "mongrel" (mixed parentage) bands descended from eta, N and forbidden porphyrin transitions. It may well be related to the hypothetical state just above the Soret state that we invoked as a possible explanation for the MCD spectrum of protochlorophyll a. We shall, for convenience, label the two chlorophyll a shoulders η_1 and η_2 by analogy to the protochlorophyll a spectrum. The broad absorption between 325-380 nm may well conceal further structure and new electronic transitions made slightly allowed by the reduction of the ring. The shallow hump at 325 nm in the chlorophyll a spectrum corresponds nicely in energy and shape to the protochlorophyll N_1 band.[9]

As in pheophytin a, this assignment can be made consistent with the fluorescence polarization data of Fig. 14 if we assume that the B_y transition loses more of its intensity to the η_1 than does the B_x, or if the transitions are at an angle with respect to the major axes. This would account for the x-polarization of the red side of the main Soret peak. The first shoulder is practically unpolarized (Fig. 14). The second shoulder, which we have labeled η_2, has a slight y polarization at room temperature which is greatly increased at 77°K.(49) The third hump, which

we have called N, is an envelope of many bands. Our proposed assignments for the chlorophyll a spectrum are shown in Fig. 15.

Qualitative absorption spectra by Holt (59,66) make it possible to construct a graded series of magnesium chlorins parallel to the series of pheophytins discussed in the previous section. The Soret band of phyllin e_6,(66) the Mg derivative of chlorin e_6, is a narrow single "chlorin-type" peak with a vibrational shoulder much like that of chlorin e_6. So is that of Mg 10-oxy-desoxo-methyl pheophorbide.(59) The latter compound, in which the chlorophyll a isocyclic cyclopentenone ring has been reduced to a hydroxy-substituted cyclopentene ring, has a Soret band much narrower than that of its free base.

In the allomerization intermediate Mg purpurin-7-lactone methyl ether dimethyl ester, the five-membered isocyclic ring is converted into a substituted six-membered lactone ring (Table I(d)). The Soret band is broader than that of the above two compounds, but does not have a resolved η shoulder.(66) These spectra are consistent with the idea that the η shoulder is resolved only in the presence of a carbonyl substituted, five-membered isocyclic ring. In view of the solvent effects on the intensity ratio of B and η transitions of chlorophyll a,(66) it would be well to check for solvent effects in the Soret region of these spectra as well.

The addition of a second carbonyl group complicates the Soret region in ways that we cannot interpret in detail. Chlorophyll b and its pheophytin have chlorin type spectra.(15) The chlorophyll d and 2-desvinyl-2-acetyl chlorophyll a Soret spectra are probably related to the phorbin spectrum (Fig. 3). The first Soret shoulder (η_1) has moved closer to the main peak, giving a lumpy appearance to the band. The secondary peak at 382 nm is the η_2. (Chlorophyll c is a porphin, not a chlorin.(68a))

Mg purpurin 18 methyl ester,(66) in which the isocyclic ring is a six-membered anhydride ring, has a pronounced Soret shoulder. The Soret band of Mg purpurin 7 trimethyl ester (66) appears to contain three closely spaced peaks. (See Tables I(d) and I(a) for structures.) In this compound, there is no isocyclic ring. Apparently a carbonyl substituent conjugated to the γ-position suffices to complicate the Soret band.

Visible and Soret absorption spectra of the pheophytin a and b derivatives of zinc, copper (+2) and nickel (+2) are similar to those of chlorophyll a except for small shifts and changes in intensity.(69) Jones et al.(70) report a broad transition at higher energies than, and well resolved from, the Soret band of copper pheophytin a but not of zinc pheophytin a. The intensity of the η_1 band thus appears to be a function of the central metal. The manganous pheophytin a (71) spectrum resembles that of chlorophyll a.

It would be useful to have MCD spectra of these compounds, as well as absorption spectra of the free bases of the allomerization intermediates discussed in the last section. The near infra-red absorption spectra of monomeric manganic pheophytin a would also be of interest, since Baker (72) has recently identified crystal field transitions in the weak near IR absorption spectra of manganic hematoporphyrin.

The hypothesis that low-lying n-π* excited states may play a role in chlorophyll a spectroscopy has re-appeared from time to time, most recently in ref. 73. Early evidence presented in favor of n-π* absorption in the visible region is reviewed and rejected by Gurinovitch.(16) More recently, the observation of quasi-line spectra in ethyl chlorophyllide a (74) excludes such transitions at wavelengths longer than 667 nm. Further work along these lines would be very useful.

The bacteriochlorophyll a Soret band shown in Fig. 7 varies greatly with solvent and cannot be analyzed with a simple model. We believe that there are at least five transitions between 310-410 nm, although only three are indicated on the diagram in Fig. 8. MCD (45) and fluorescence polarization (15,75) spectra show clearly that the main peak at 357-373 nm and its major long wavelength shoulder at 390-400 nm are the B_x and B_y, respectively. There is a shoulder at 406 nm in the ether spectrum, which we shall call "B^-" and a definite inflection ("B^+") between the two B daughters which appears in all four solvents in absorption and/or MCD.

A fourth and fifth band at 339 and 317 nm in bacteriochlorophyll vary greatly in intensity from solvent to solvent. We shall call them η_1 and η_2, respectively. Some of these complications may be due to the simultaneous presence of several solvated species. The absorption of bacteriopheophytin a in ether generally resembles that of bacteriochlorophyll.(15)

d. Reduced Porphyrins: Theory

Weiss et al.(6) published four-orbital model SCMO calculations of metal chlorin, phlorin, OPP-THP, and ADJ-THP, and achieved qualitative agreement with experimental spectra. Their paper reviews earlier Hückel calculations on these unsubstituted rings. The Weiss treatment was extended by McHugh et al.(7) and by Otten (46) to include more CI. Otten (46) has done similar calculations on the bacteriochlorin radical cation and anion.

Table II compares our new theoretical results on reduced porphyrins and those of the Song "electrostatic" model described earlier (50,51) with the phenomenological assignments deduced in the last section. The calculations reproduce the visible energies and intensities of the chlorins rather well.

Song's calculated values of $E(Q_x) - E(Q_y)$ agree well with the traditional assignment of the Q_x. Ours are comparable to vibrational spacings and are in slightly better agreement with the notion that the Q_x overlaps with the (0-1) of the Q_y. The calculations on substituted porphyrins, like those on unsubstituted rings, overestimate the B-Q energy split and do not treat central metal or saturated substituents explicitly. This makes it difficult to see how well we have represented the effects of individual substituent perturbations.

For this reason, we selected pairs of chlorin free bases from the graded series described earlier and compared the experimental effects of simple substitutions with the results of calculations meant to simulate them (Table III). As the spectra in Figs. 11-12 show, both 2-vinyl and 6-carbonyl substitution produce a marked red shift in B and Q energies. Of the four possible quantitative comparisons of theory and experiment, two agree reasonably well, one disagrees, and one is moot for want of sufficient data. The experimental effects themselves are inconsistent from compound to compound.

The spectra of Fig. 12 and the experimental data in Table III show that the closing of the isocyclic ring dramatically increases the intensity of the Q_x but not that of the Q_y. Djerassi (9) has pointed out that the intensity of the Q_x band in a similar series of free base chlorins is especially sensitive to substituents. This behavior parallels that of the porphyrin Q band, and is characteristic of transitions which are forbidden because of a cancellation of transition dipoles by CI. A small perturbation can change the CI coefficients of the Q_x enough that the transition dipoles no longer cancel, and can thus produce large relative changes in intensity. The transition dipoles of the configurations

making up the chlorin $\underline{Q}_y$ are not near cancellation, with the result that this band is insensitive to the influence of substituents. Calculations of the effect of isocyclic ring closure (see below) predict a 2- to 3-fold increase in $\underline{Q}_x$ intensity, and little or no change in $\underline{Q}_y$.

The predicted Soret oscillator strength is greatly overestimated by the transition dipole formula; transition gradients (Fig. 5) do much better, at least on unsubstituted porphyrins.(7) Our calculations predict a very small splitting in the Soret region between $\underline{B}_x$ and $\underline{B}_y$ transitions, in agreement with our independently deduced assignments. The spectrum predicted by our regular parameters has only weak bands at energies higher than the Soret. This disagrees with our assignment of the Soret satellite to a new electronic transition.[10]

To explore the reasons for this latter disagreement, we increased the conjugation between the carbonyl and the ring, and simulated the distortion of the pi system by the isocyclic ring. (See Methods section.) Each of these changes increases the predicted intensity of a y-polarized transition just above the Soret band. Together they raise the oscillator strength of this transition and lower that of the $\underline{B}_y$ until their ratio reaches 0.45. This result would be consistent with the fluorescence polarization data shown in Fig. 14. It would be interesting to repeat these calculations with complete CI.

The Song model described earlier also predicts three separate electronic transitions in the Soret region. When the charge of the central metal is taken as +1.5, as in the results of Table II, the lowest of these three bands in energy is predicted to be polarized parallel to the emitting transition, in clear disagreement with experiment. More recent calculations with metallic charge = +1.7 again give

three bands. This time, however, the lowest of these is x-polarized, with only 1/5 the total oscillator strength of the system. The other two are mutually perpendicular, and roughly at 45° to the x and y axes. This result agrees with the phenomenology deduced earlier.

More theoretical work is clearly needed to explain the Soret region of chlorophyll. As matters now stand, a model can be found to justify almost any assignment. Vibronic interactions between $\underline{B}_x$, $\underline{B}_y$, η, $\underline{N}$ and $\underline{Q}$ are likely to be important.

The Song calculations with $\underline{Z}$ = +1.5 agree nicely with the absorption spectrum of chlorophyll d, predicting four allowed transitions underlying the Soret band, the highest in energy considerably to the blue of the chlorophyll a Soret band. MCD and fluorescence polarization data on chlorophyll d would be useful. On the other hand, the absence of an intense η shoulder in the chlorophyll b absorption is in disagreement with his model.

Our predicted energies for bacteriochlorophyll and bacteriochlorin visible bands agree reasonably well with experiment, as do those of Otten.(46) The predicted $\underline{Q}_y$ intensities from the transition dipole formula are 2-3 times too large; those from transition gradients (Fig. 5) are too small. The Song prediction of x-y splittings in $\underline{B}$ and $\underline{Q}$ bands is very good in both bacteriochlorophyll and chlorophyll a.

The Soret band of bacteriochlorophyll a resists definitive assignment. Our calculations and Otten's predict an x-polarized shoulder on the long wavelength edge, the predicted intensity of which decreases with increasing CI. There is also a forbidden band on either side of the $\underline{B}_x$. The calculation of Song predicts a very weak y-allowed band on the long wavelength shoulder of the $\underline{B}_x$, and an additional weak y-allowed

transition between B_x and B_y. Neither of these predictions corresponds exactly to the spectrum observed (Fig. 7), but either could be made to fit by ad hoc assumptions regarding solvent-dependent vibronic interactions. Both experimental and theoretical work are needed on the solvent effects.

The Soret band of bacteriochlorophyll should be a sensitive probe of its environment but will probably be too complicated to interpret in detail. Detailed information regarding dimer structure can in principle be extracted from the well-resolved Q_x and Q_y transitions.(79) Predicted polarizations of the B and Q bands are shown in Table II. The Q bands of protoporphyrin (not tabulated), chlorophyll a, and bacteriochlorophyll are nearly along the symmetry axes, in qualitative agreement with fluorescence polarization experiments.

C. Other Theoretical Results

a. Triplet States

Table IV shows the predicted energies of the four lowest triplet configurations relative to the ground singlet. Group theory dictates that these configurations not interact with each other in square porphins. An extensive CI calculation (6) indicates that interaction with higher states is not serious in these compounds.[10a] We assume that these properties carry over to the chlorophylls.

Predicted triplet energies change little from porphin to chlorin; the lowest two triplet configurations are much the same in ADJ-THP as well. In OPP-THP and bacteriochlorophyll, the lowest predicted triplet is only 5500-7100 cm^{-1} above the ground singlet. The habitual overestimation by the SCMO-PPP method of the two-electron terms that split singlet

and triplet configurations means that this prediction may be too low by a few thousand wave numbers. Even so, the low-lying triplet should provide a highly favorable route for radiationless loss of excitation energy that reaches the triplet manifold, and hence result in a very low phosphorescence yield.

Available data on the lowest triplet energies of porphyrins related to chlorophyll a are displayed in Fig. 8. To our knowledge, no phosphorescence data is available for protochlorophyll. The lowest triplet of chlorophyll a in polar glasses emits at 11 300 cm^{-1}, close to the predicted value.(80) The phosphorescence observed from chlorophyll a in dry non-polar glasses,(81) once attributed to an n-π* triplet, is probably due to an aggregate.(16)

The predicted triplet states of bacteriochlorophyll are at very low energies. The gap between the lowest triplet T_1 and the ground state is not much bigger than that between T_1 and T_2, and is much smaller than that between T_2 and T_3. This raises the possibility that observed short-lived triplet-triplet absorption spectra (82) may derive from a triplet state other than the lowest. If the longest lived triplet is actually T_3, as is suggested by the energy values, the observed T-T spectrum should depend on the wavelength of the pumping light. To the author's knowledge, no phosphorescence has ever been reported for bacteriochlorophyll.

Triplet-triplet absorption spectra of metal porphin have been calculated using "traditional" parameters, and were in excellent qualitative agreement with experiment.(6) The spectra are broad and relatively structureless because of the presence of many low-lying transitions. The electron in one of the closely packed anti-bonding orbitals can be further excited to higher levels, while the "hole" in the equally closely

packed bonding orbitals can be excited downward. A similar situation obtains in porphyrin radical anions and cations,(27,28,46) except that these species have either the hole or the anti-bonding electron, but not both. Experimental triplet-triplet absorption spectra have been measured for chlorophyll a,(83) and measurement of the absorption spectrum of the lowest excited singlet state of chlorophyll a should now be possible.(84) No calculations have been reported on the triplet-triplet or excited-singlet-to-doubly-excited-singlet spectrum of any reduced porphyrin.

b. Transition Monopoles

Transition monopoles are a quantitative expression of the fact that the oscillating charges ("transition density") associated with a quantum mechanical transition are inadequately represented as a point dipole, and really extend over the entire molecule.(85) The calculated transition monopoles for the Q bands of bacteriochlorophyll a are shown in Fig. 16, as derived from a calculation of 2,6-dicarbonyl-OPP-THP. These values have been normalized to agree with the experimental values of the transition dipoles for use in the calculation of intermolecular properties. The unusual solvent sensitivity of the Q_x (orange) band of bacteriochlorophyll is probably connected with the high value of the normalized transition monopole at the meso carbon and at the nitrogens of the reduced rings.

Transition monopoles from our calculations, together with certain assumptions about the conformation of ring substituents, have given reasonable values in coupled oscillator calculations of the rotatory power of the visible circular dichroism spectra of protochlorophyll a, chlorophyll a, and bacteriochlorophyll a.(86) Calculations using point transition dipoles greatly underestimated these quantities. This is not necessarily a tribute to the accuracy of our monopoles; it may be that

even the crudest representation of a transition density extended over the whole molecule suffices to greatly improve the calculated interaction. It would be worthwhile to develop theoretical treatments of this problem, and of the problem of the spectroscopy of dimers of particular mutual orientation, using transition gradients instead of monopoles, in view of their superior prediction of oscillator strength.[6]

c. Ground State Properties

Ground state charge densities and bond orders for unsubstituted reduced porphyrins are discussed in ref. 6. Knop and Fuhrhop (87) performed similar SCMO calculations and critically compared their calculated π-electron densities, free valences, and frontier orbital densities for porphin, chlorin, bacteriochlorin and phlorin, with the considerable chemical data that have only recently become available. Earlier, Katz *et al.*(88) reported ground state Hückel and SCMO calculations of chlorophyll *a*, and compared predicted charge densities and electrophilic and nucleophilic localization energies with rates of hydrogen exchange with solvent. Agreement was not good.

The molecular diagram of chlorophyll *a* in Fig. 17 shows a build-up of electron density on the *meso* carbon nearest the reduced ring, in agreement with experiment and with previous calculations.(6,51,89). This effect is intensified in bacteriochlorins, in which each *meso* carbon is adjacent to two reduced rings, again in agreement with experiment.(88,90) It is experimentally absent from free base pheophytins.(88) We also predict that the β-carbons on the half of the porphyrin ring towards the reduced pyrrole ring are strongly electrophilic, in agreement with other calculations.(6,51)

The major effect of carbonyl substitution is to shift electron density within the substituted pyrrole ring towards the carbon bearing the

substituent from the carbon adjacent to the substituted carbon. Other pyrrole rings are almost unaffected. This would predict that carbonyl substituents favor nucleophilic attack on the carbons adjacent to the substituted carbon, by analogy to the familiar directive effect of aromatic carbonyl substituents.

This effect is enormously greater in the Song calculations (51) than in ours, including calculations of ours intended to exaggerate the effect of the isocyclic ring. Song, moreover, finds a similar shift in electron density within the vinyl substituted ring, and a strongly electrophilic β-carbon in ring II (the ring opposite the reduced ring), both in contrast with our results.

Electron density is shifted in our calculations towards the carbonyl substituted ring from all four of the central nitrogens. This is consistent with the finding of Caughey that the CO stretching frequency of carbon monoxide ligated to carbonyl substituted hemes (ferrous porphyrins) increases with carbonyl substitution, while the binding constant of pyridine to nickel porphyrins decreases.(91) In each case, carbonyl substitution withdraws electrons from the center of the ring. In the first case, this makes the iron a poorer pi donor and weakens the metal-CO bond. This increases the triple bond character of the CO bond and increases the CO stretching frequency. In the latter case, electron withdrawal makes the nickel a better σ-acceptor and hence strengthens the binding between it and pyridine.

The isocyclic ring was predicted to induce a small increase in electron density at the δ-position at the expense of the γ. (See Table I for notation.) This distortion also produces a small increase in electron density at the center nitrogens, a fact which may explain the relative ease of protonation of chlorins containing an isocyclic ring.(16)

The bond orders of substituted reduced porphyrins predict substantial changes in bond lengths as compared to the parent porphyrin. Taking as a rule of thumb that a change of 0.1 units of bond order corresponds to a change of 0.02 Å in bond length,(2) we estimate that the CC bond linking the meso carbon to the alpha carbon of the reduced pyrrole ring will be 0.04 Å shorter than its mirror image adjacent to the unreduced ring, other things being equal. In methyl pheophorbide, the only reduced porphyrin whose structure has been determined by X-ray methods,(20) the distortions due to the isocyclic ring are much more important than those due to ring reduction.

The ground state pi dipole moment of unsubstituted chlorin is predicted to be 0.82 electron-Å in the direction towards the reduced ring. In chlorophyll a, (2-vinyl-6-carbonyl chlorin) the predicted dipole moment is 4 electron-Å toward the ring bearing the carbonyl with a slight tilt toward the reduced ring. This is the rough resultant of the dipole moment due to reduction and the moment due to displacement of electron density towards the carbonyl group. These values are expected to be too high.

The Q excited singlet state of chlorophyll a is predicted to have a dipole moment of 3.97 electron-Å, oriented at an angle of 5 degrees from the permanent ground state dipole. This is the lowest excited singlet band of chlorophyll a, and is presumably the photochemically active excited state in photosynthesis. Bacteriochlorophyll is predicted to have no pi dipole moment in either ground or excited states. None of these moments has been measured; experimental values would be very useful.

d. Highest Occupied and Lowest Empty Orbitals

Fig. 18 shows the coefficients of the highest occupied and lowest empty orbitals (HOMO and LEMO) of calculations representing chlorophyll a

and bacteriochlorophyll a. These and analogous data show that the vinyl and carbonyl groups play little role in the excitation corresponding to the Q bands of carbonyl substituted porphyrins. This means that these transitions have little "charge transfer character". Calculations using parameters that increase the conjugation of the oxygen with the ring confirm this conclusion.

The low electron density on the α-carbon of the vinyl group of chlorophyll a in the lowest empty molecular orbital raises the possibility that the chlorophyll a radical anion will have a negative spin density at this carbon.(2) The same might be true of complexes of pheophytin a with a paramagnetic metal whose odd electron can delocalize into a pi* orbital, such as Mn, Fe or Ni. Negative spin densities have already been reported for the α-carbon of the vinyl groups of cyanoprotoporphyrin IX iron (III).(92) In agreement with this observation, our calculations of the lowest antibonding orbital of divinyl porphin show coefficients on the α-carbons of the two vinyl groups of only ± 0.026.

e. Ionization Potentials and Electron Affinities

Relative ionization potentials (I.P.) and electron affinities (E.A.) in vacuum were estimated from the energies of the highest filled and lowest unfilled orbitals, respectively.

Chlorins are predicted to have I.P. within 0.05 eV of those of porphins, and 0.08-0.13 eV higher E.A. OPP-THP has 0.34 eV lower predicted I.P. than porphin and 0.35 eV higher predicted E.A.(6) ADJ-THP has 0.23 eV lower I.P. but 0.33 eV lower E.A. In other words, hypochlorophyll is predicted to be an inferior electron acceptor compared to bacteriochlorophyll. Each carbonyl substituent raises the predicted ionization potential of a porphyrin or reduced porphyrin by 0.10-0.16 eV. It raises the electron

affinity by 0.10-0.25 eV. 2,6- and 2,4- substitution have the same effect. Vinyl substitution has no effect.

Experimentally, the midpoint potentials for one-electron oxidation of a series of metal octaethyl chlorins are about 300 mv lower than those of the analogous metal porphins.(93) Similarly, bacteriochlorophyll has a midpoint potential about 300 mv lower than chlorophyll a.(94) No data is available for hypochlorophyll. Data on work functions of porphyrins (95) are insufficient for this kind of comparison.

DISCUSSION

The theory of porphyrin spectra emerges from this detailed review as a rather good qualitative guide to the spectroscopy of chlorophyll and related molecules. Starting from the thoroughly studied spectra of the unsubstituted porphin molecule, it is possible to follow systematically the spectroscopic changes to protochlorophyll a, chlorophyll a, and bacteriochlorophyll, using as intermediate steps a large number of known molecules with similar substituent patterns. These interpretations can be backed up with SCMO-PPPCI calculations.

One of the great conveniences of the porphyrin pi electron system has been that the results of such elaborate calculations can often be understood from a much simpler model, the limited CI picture known as the Gouterman four-orbital model. Except for some quantitative discrepancies, the visible spectra of the chlorophylls do respond well to this simplified approach. Since these are the spectra most often studied, the four-orbital model will certainly continue to merit wide use.

Our review shows that this is unfortunately not the general case. In the Soret region, the usefulness of the four-orbital model seems to be limited to unsubstituted metal porphin, chlorin, and tetrabenzporphin. More configurations must be included in theoretical treatments of metal phthalocyanines,(7) of free base porphyrins and pheophytins at all levels of reduction,(7,33) of bacteriochlorophyll and other OPP-tetrahydroporphyrins, and of chlorophyll derivatives with isocyclic cyclopentenone rings.

Close examination of the experimental data on which the four-orbital model is based reveals important second-order discrepancies. Neither the sum of the oscillator strengths of the B and Q transitions nor the B-Q energy splitting are accurately constant from molecule to molecule, contrary to the model. The effects of a given substituent are not constant from molecule to molecule. Finally, even the best SCMO treatments predict a porphyrin geometry inferior to that given by the simplest valence band treatment, badly overestimate two-electron repulsion integrals, and slightly overestimate the center of gravity of B and Q states.

On the experimental side, a good many molecules would have to be studied quantitatively before our knowledge of substituent effects on absorption spectra of chlorophyll-like molecules is complete. These include the metal derivatives (copper and magnesium would be most useful since they would best complement existing work) of most of the free base chlorins in Table I, and those of ADJ- and OPP-tetrahydroporphyrin, octamethyl OPP-THP (or its spectroscopic equivalent[11]), the free bases of compounds 9, 17 and 18 of Table I, and bacteriochlorophyll derivatives (with and without magnesium) analogous to the sequence constructed in that Table. Allomerized bacteriochlorophylls without the isocyclic ring would also be useful. (The synthesis of unsubstituted OPP-

tetrahydroporphyrin (96) raises the hope that the spectrum of this compound will soon be available.) It would also be useful to have the substituted porphins analogous to chlorophyll b ("protochlorophyll b") and to bacteriochlorophyll a. Solvent effects on the Soret region would be of great interest.

A more important experimental goal would be to apply newer spectroscopic techniques to a well-constructed sequence of these molecules. CD and MCD, especially at low temperatures, will provide new information on electronic and vibronic structures. Spectra of chlorophyll b, chlorophyll d, and the Chlorobium chlorophylls would be especially useful from the point of view of substituent effects. In fact, CD and especially MCD should be routinely used in the characterization of any new porphyrin derivative.

Triplet state energies of chlorophylls and bacteriochlorophylls need to be located, especially in view of the possible importance of these states in photosynthesis. Fig. 8 shows that chlorophyll a is the only photosynthetic pigment for which the position of even the lowest triplet is known, and even here there are unanswered experimental questions.

Excited state spectroscopy - both triplet-triplet and excited-singlet-to-excited-singlet - is lacking for most of the molecules considered in this review. The latter measurement will be an important aid to the differential absorption spectroscopy of in vivo photosynthetic intermediates in the nanosecond and subnanosecond time range.

Another useful measurement would be the direction and magnitude of the dipole moment of the excited state. This measurement would assist the theoretician in calibrating his models. High resolution photoelectron spectroscopy of a series of reduced porphyrins would make possible an important direct test of the one-electron orbital energy sequences (Fig. 4)

deduced from the spectra, and thus provide critical independent confirmation of the four-orbital model. Finally, Spallskii spectra of appropriate chlorophyll derivatives, along the lines of ref. 74, would assist in locating n-π* transitions hidden under the intense π-π* absorption.

On the theoretical side, it should ultimately be possible to construct a theory which repairs the quantitative failures of pi electron theory. Better treatment of electron correlation, perhaps along the lines of Gutfreund and Little,(97) should improve the estimate the B-Q splitting. Better parameters and explicit consideration of saturated substituents, of small changes in geometry,(98) and of sigma electrons should improve predictions of the effects of chemical perturbations like substituents and ring reduction.[12]

Existing pi electron theory should be able to provide an adequate explanation for excited state spectra. Doubly excited configurations will of course need to be included, so that new parameters will probably have to be chosen. Programs for this kind of calculation are now readily available, so that this work might well be undertaken by experimentalists.

An electronic theory of the MCD of unsymmetrical molecules is needed before much progress can be made on the MCD of the chlorophylls and pheophytins. The chlorophylls and bacteriochlorophylls require a theory of vibronic interactions in the Soret region in both absorption and MCD, including the effects of environment. The low temperature spectra of chlorophyll a - and no doubt of other molecules as they come to be studied - require a better model of vibronic interactions between Q_x and Q_y as well, one which will include the effects of ring reduction, substituent, and distortion due to the isocyclic ring. The origin of the solvent and temperature effects on these spectra is not at all clear. It would be

0 0 0 0 3 8 0 3 9 5 2

worthwhile to investigate theoretically the effects of small changes in equilibrium geometry, and of the small ligands attached to the magnesium.

The main theoretical challenges posed by chlorophyll spectroscopy lie in the area of sigma-pi, magnetic and vibronic interactions. We do not know the positions of n-π^* states originating from the unpaired electrons of either carbonyl oxygens of substituents or those of aza-nitrogens of the ring,(33) or of the charge transfer states from ring to metal or vice versa.(100)

Probably the most important use of these models of the chlorophyll and bacteriochlorophyll spectrum will be to calculate the intermolecular interactions that determine energy transfer in concentrated solutions and in the photosynthetic apparatus. These same interactions also determine the spectroscopic changes in absorption and circular dichroism in dimers and higher aggregates related to the structure of chlorophyll *in vivo*. One may hope that these and more sophisticated theories, once adequately calibrated, can be extended to larger aggregates, to monolayers, crystals, and to the antenna and reaction center chlorophylls of photosynthetic bacteria, algae and green plants, and to their interactions with primary electron donors and acceptors.

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FOOTNOTES

1. National Institutes of Health Postdoctoral Fellow, 1967-69.
2. Present Address: International Bank for Reconstruction and Development, 1818 H Street, N.W., Washington D.C. 20433.
3. A previous paper (34) concluded that SCMO-PPP calculations overestimated the B-Q splitting in 18-annulene, and that this presumed failure represented a general defect in the method. Subsequent measurements found a new state just where theory predicted it, so that the supposed overestimate was probably due to a misassignment of experimental spectra. (35) We must therefore look elsewhere for an explanation of the B-Q overestimate in porphyrins.
4. We have abandoned the b_1 b_2 c_1 c_2 orbital labeling used by Gouterman, (4) and refer to all orbitals by their group theoretical labels in the square symmetry of porphin whenever possible. Orbitals were traced from porphin to derivatives of lower symmetry by noting similarities in energy and nodal distribution.
5. Deuteroporphyrin IX is 1,3,5,8-tetramethyl, 6,7-dipropionic acid porphin.
6. We are grateful to M. Gouterman for this suggestion.
7. It should be pointed out that if two positive Gaussians with nearby peaks are added, their apparent maxima are pushed closer together. If a positive and a negative Gaussian are added, the maxima will appear to be further apart than they really are.

8. A phorbin molecule is a chlorophyll a derivative with a magnesium and an isocyclic ring.(8) By this definition, 9-desoxo-meso-pyromethyl pheophorbide a is a phorbin but does not have a "phorbin-type" spectrum.

9. Gurinovitch et al.(16) have suggested that this peak may be related to the n-π^* transition observed in cyclopentanone.(68) We regard this as unlikely, since n-π^* bands have little intensity and the 325 nm transition appears in many porphyrins.(40)

10. Since the completion of this manuscript, Knox (76) has done SCMO-CI calculations in excellent agreement with our assignment.

10a. Roos and Sundbom have, however, found second-order CI among these configurations in copper porphins.(100)

11. Since all α-saturated substituents seem to have identical effects on porphyrin spectra, derivatives which differ only in substituents with saturated carbons alpha to the ring are deemed spectroscopically equivalent.

12. Seely (99) has suggested that the prediction of the spectrum of the "phase test intermediate" would be a good additional test for an improved model.

LEGENDS TO FIGURES

Fig. 1. Structures of photosynthetic porphyrins.

Fig. 2. Absorption spectrum of chlorophyll a and protochlorophyll in ether. (10,11)

Fig. 3. Absorption spectrum in acetone of bacteriochlorophyll a (as in Fig. 7) and 2-desvinyl-2-acetyl chlorophyll a.(12)

Fig. 4. Molecular orbital energies in porphin, chlorin, OPP-THP, and ADJ-THP.[4] Orbitals are labeled by porphyrin symmetries. The a orbital is part of a cluster of closely spaced orbitals. (See Fig. 8 of Ref. 6.)

Fig. 5. Results of configuration interaction calculations for porphin, chlorin and OPP-tetrahydroporphin. Each line on the porphin diagram represents a pair of degenerate transitions; the oscillator strength is the sum of the two. Solid lines represent dipole allowed states; dotted lines represent dipole forbidden transitions. Predicted oscillator strengths calculated from transition gradients (7) are given in parentheses. The axes used here are the same as those used in previous work. (The labels Q_x and Q_y of Table IV of Ref. 6 were reversed through a typographical error.)

Fig. 6. (0-0) Experimental absorption levels in matched series of metal porphyrins. Note that the vertical scale is smaller than that of Fig. 5. All spectra in benzene except as noted. Numbers above state are oscillator strengths. Numbers in parentheses below state are extinction coefficients in thousands. Numbers followed by " /2" are the summed

values of two degenerate transitions.

a) Magnesium tetraphenyl porphin,(36) tetraphenyl chlorin,(43) and tetraphenyl OPP-THP.(37)

b) Copper chlorin,(38) porphin,(36) octamethyl porphin (in chlorobenzene),(39) deuteroporphyrin (in $CHCl_3$),(40) octaethyl chlorin, (39) octaethyl ADJ-THP.(41) The shape of the Soret band of octaethyl ADJ-THP is not in the literature.

c) Zinc tetraphenyl porphin,(42) tetraphenyl chlorin,(43) and tetraphenyl ADJ-THP.(42)

Fig. 7. Absorption spectrum of bacteriochlorophyll a in different solvents.(45)

Fig. 8. (0-0) Experimental absorption levels in a matched series of metal porphyrins related to chlorophyll a and bacteriochlorophyll a. Magnesium etioporphyrin (in EPA),(48) protochlorophyll a,(10) chlorophyll a (both in ether),(11) 2-desvinyl-2-acetyl chlorophyll a (in acetone),(12) bacteriochlorophyll (in acetone),(45) and hypochlorophyll.(47) N band and oscillator strengths in first column are for Mg deuteroporphyrin in chloroform.(40) Other notes as in Fig. 6.

Fig. 9. Absorption, circular dichroism and magnetic circular dichroism spectra of protochlorophyll a.(11) A small negative MCD at 440 nm does not appear in the drawing.(49) Optical path 1 cm, except 1 mm in (*) region (400-500 nm) in absorption spectrum, and 1 mm for MCD at $\lambda > 500$ nm.

Fig. 10. SCMO-PPP-CI results for carbonyl porphin. Experimental energies are those of Fig. 9. Song calculation is for protochlorophyll a.(50)

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