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CIRCULAR DICHROISM OF CHLOROPHYLL AND RELATED MOLECULES CALCULATED USING A POINT MONOPOLE MODEL FOR THE ELECTRONIC TRANSITIONS

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J. Phys. Chem.

**Circular Dichroism of Chlorophyll and Related Molecules Calculated  
Using a Point Monopole Model for the Electronic Transitions**

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Abstract: Agreement between calculated and observed rotational strengths for solution monomers of chlorophyll, bacteriochlorophyll, and related molecules has been improved by an order of magnitude through the use of a model which distributes the  $\pi$ - $\pi^*$  transitions over the porphyrin ring. Using the Kirkwood-Tinoco coupled oscillator approach, the electronic transitions are described using point monopoles located at the porphyrin macrocycle nuclei. Asymmetrically-placed substituents are replaced by anisotropic polarizabilities and the sum of monopole-polarizability potentials is used to calculate the rotational strengths. An improved geometry for the chlorin ring system is based on recent X-ray diffraction data. The discussion considers the possibilities for theoretical treatment of more complicated systems of molecules.

The application of circular dichroism measurements to materials of photosynthetic origin promises to provide important information about the internal organization and structure of the photoactive pigmented membranes.<sup>1</sup> In order to provide a sound basis for interpreting the CD spectra of these complex biological materials, it is important to develop a better understanding of the corresponding properties of the individual (isolated) molecules.

The present paper is an extension of a previous study of the origins of molecular optical activity in chlorophyll and related molecules.<sup>2</sup> These molecules consist of an extended, planar porphyrin chromophore, whose symmetry can be considered to be perturbed by substituents placed

asymmetrically around the periphery. The absolute configuration at the asymmetric centers in many of these molecules is known,<sup>3,4</sup> which enables them to provide a rigorous test for the theoretical treatment. The agreement between experiment and calculations utilizing a model involving a point monopole approximation for the electric transition moment is a considerable improvement over that resulting from the use of point dipole transition moments, but there is still some discrepancy in the quantitative nature of the calculations.

### Theory

In the Kirkwood coupled oscillator model, the origin of optical activity is the interaction potential between electric transition dipoles located asymmetrically with respect to one another.<sup>5</sup> Tinoco has derived a general formalism for the rotational strength ( $R_A$ ) for the case of an electrically allowed, magnetically forbidden transition,  $a \leftarrow 0$ , located on group  $i$ , starting from perturbation theory.<sup>6</sup> The pertinent equation contains two sets of terms:

$$R_A = - \left[ \frac{2\pi}{c} \sum_{j \neq i} \sum_{b \neq a} \frac{V_{ioa;job} \nu_a \nu_b (\underline{R}_j - \underline{R}_i) \cdot (\underline{\mu}_{job} \times \underline{\mu}_{ioa})}{h(\nu_b^2 - \nu_a^2)} \right] \quad (1a)$$

$$+ 2 \sum_{j \neq i} \sum_{b \neq a} \left[ \frac{\text{Im } V_{ioa;job} \nu_a \underline{\mu}_{ioa} \cdot \underline{m}_{jbo}}{h(\nu_b^2 - \nu_a^2)} \right] \quad (1b)$$

where  $\underline{R}_j$  and  $\underline{R}_i$  are position vectors of the  $j$ th and  $i$ th group respectively, and  $\underline{\mu}$ 's are electric dipole transition moments in groups  $i$  and  $j$  for transitions  $a \leftarrow 0$  and  $b \leftarrow 0$  where the subscript  $0$  represents the ground state.

$V_{ioa;job}$  is the coulomb potential energy due to the interaction of

transition charge densities in group  $i$  with those in group  $j$ .  $\nu_a$  and  $\nu_b$  are the frequencies of the transitions  $a \rightarrow 0$  and  $b \rightarrow 0$ ,  $h$  is Planck's constant, and  $c$  is the velocity of light.  $\text{Im}$  means "the imaginary part of" and  $\underline{m}_{jbo}$  is the magnetic dipole transition moment for the transition  $b \rightarrow 0$  on group  $j$ . The second term in this formula is extremely difficult to calculate and is usually ignored. It is expected on theoretical grounds<sup>7</sup> to be much smaller than the first term and one explicit calculation<sup>8</sup> has it accounting for about 1/10 of the observed rotational strength in cyclopentanone derivatives. Hence, only the more familiar first term, equivalent to the Kirkwood contribution, will be considered in this paper.

For each of the pigments the long wavelength  $Q_y$  and  $Q_x$  transitions are examined.<sup>9,10</sup> These electrically allowed transitions are  $\pi \rightarrow \pi^*$  in nature and are delocalized over the porphyrin chromophore. For each of the molecules considered here the  $Q_y$  band is lower in energy and has a greater absorption intensity (Table I). The  $x$ - and  $y$ -axes are defined in Fig. 1. Typical absorption and circular dichroism spectra are shown in Fig. 2. The band assignments are from experimental studies of fluorescence polarization and linear dichroism,<sup>11,12</sup> and from the theoretical studies of Gouterman.<sup>9,10</sup> Each of the bands is slightly complicated by higher vibrational components. These components, however, are not strongly polarized,<sup>10</sup> due to mixing with higher electronic states. Because of this, the higher vibrational components tend not to contribute to the circular dichroism and are ignored in the calculations. The shorter wavelength Soret bands (occurring in the range 350-450 nm) overlap one another strongly, and no calculations were attempted on them.

From the fundamental equation of rotational strength:<sup>13</sup>

$$R_A = \text{Im } \underline{\mu}_{0a} \cdot \underline{m}_{a0} \quad (2)$$

a molecule must possess non-perpendicular electric and magnetic transition dipole moments in order to be optically active. Electrically allowed transitions of planar aromatic chromophores, such as the Q-transitions of the simple porphyrins, cannot possess the required magnetic dipole from symmetry considerations. The necessary magnetic dipole, in the case of chlorophyll and related biological pigments, is supplied as a perturbation resulting from interaction with asymmetrically-placed substituents.

With this in mind, we can make the form of eq. (1a) seem plausible. The interaction potential,  $V_{i0a;j0b}$ , and the dependence on frequency originate in the perturbation method. The vector relationships come from equations such as:

$$\underline{m}_{j0b} = \frac{i\pi}{c} \nu_b (\underline{R}_j \times \underline{\mu}_{j0b}) \quad (3)$$

where  $i = \sqrt{-1}$ . The two summations of eq. (1a) indicate that the transition of interest,  $\underline{\mu}_{i0a}$ , is interacting with all the transitions, b-o, of each of the asymmetrically-placed substituents, j.

The specific molecules for which calculations were done are chlorophyll a (Chl a), pyrochlorophyll a (pyroChl a), bacteriochlorophyll (BChl), and pyrobacteriochlorophyll (pyroBChl). Calculated rotational strength is compared with experimental circular dichroism (CD) results for the first three of these for both the  $Q_y$  and  $Q_x$  bands. The relevant experimental absorption and CD data for these molecules are shown in Table I. The molecular structures of these molecules differ in two important



respects: (1) the number of asymmetric substituents and (2) the number of rings which have reduced outer bonds. As shown in Fig. 1, BChl has five porphyrin ring carbon atoms substituted asymmetrically at positions C-3, C-4, C-7, C-8, and C-10. In pyroBChl, the carboxymethyl group is replaced with a hydrogen atom and so the C-10 position is no longer asymmetrically substituted. Likewise Chl a and pyroChl a are asymmetrically substituted at positions C-7, C-8, C-10, and at C-7, C-8, respectively. The absorption spectra of these molecules, in contrast to the CD, are relatively insensitive to the nature of the asymmetric substituents and are more a function of the extent of unsaturation of the pyrrole rings. Therefore, it is expected, and found experimentally, that the absorption spectrum of Chl a closely resembles that of pyroChl a. The same relationship holds between BChl and pyroBChl.

In a previous model used to calculate the interaction potential,  $V_{ioa;job}$ , was evaluated by treating the porphyrin transitions as point dipoles, substituting a dipole-dipole interaction expression in eq. (1a) and then using the Kirkwood polarizability approximation.<sup>2</sup> The actual  $\pi-\pi^*$  transitions involved, however, are delocalized over the entire porphyrin ring, which has a radius of the order of 5 Å, while the distance between the asymmetric centers and the nearest carbon of the aromatic part of the porphyrin ring can be as small as 2 Å. Thus, a more realistic attempt must take into account the effect of this delocalization of the transition on the interaction potential. For the results presented here, this was done by considering the transition dipole to be the sum of transition electric monopole moments located at each of the conjugated atoms of the ring. The potential can then be determined

by treating separately the interaction of each of the monopoles of the porphyrin ring with the effective transition dipoles of the asymmetric centers according to the equation:

$$V_{ioa;job} = - \sum_t \frac{q_{it0a} \underline{R}_{it0a;j} \cdot \underline{\mu}_{job}}{|\underline{R}_{it0a;j}|^3} \quad (4)$$

where  $q_{it0a}$  is the electric transition monopole located at the  $t^{\text{th}}$  atom for transition  $a \leftarrow 0$  (the  $Q_y$  or  $Q_x$  transition) for group  $i$  (the porphyrin ring) and  $\underline{R}_{it0a;j}$  is a position vector from the  $j^{\text{th}}$  asymmetrically-placed substituent to monopole  $t$ .

The transition monopoles were obtained from the self-consistent field molecular orbital calculations of Weiss,<sup>14</sup> who used the configuration interaction method of Pariser, Parr and Pople (SCMO-PPP-CI).<sup>15</sup> Good qualitative agreement with the visible and near-UV absorption spectra was obtained. The monopole charge at the  $t^{\text{th}}$  atom of a  $\pi$  system is proportional to  $C_{t0} C_{ta}$  for a transition from the ground state to a singly excited state,  $a$ , where  $C_{t0}$  and  $C_{ta}$  are, respectively, the molecular orbital coefficients at the  $t^{\text{th}}$  center for the ground and excited state molecular orbitals. The monopoles (Table II) for BChl and pyroBChl were derived from a calculation for 2,6-dicarbonyl OPP-tetrahydroporphin and those for Chl a and pyroChl a from 2-vinyl-6-carbonyl chlorin. The calculated monopoles were scaled so that the summation:

$$\sum_t \underline{R}_{it0a} q_{it0a}$$

equalled the experimental value for  $\underline{\mu}_{ioa}$ . In order to improve the approximation to the transition charge densities of  $\pi$  type orbitals,

each monopole strength was separated into two parts. New monopoles, with magnitudes equal to half those of the calculated monopoles, were placed 1 Å above and below the conjugated atom.<sup>16</sup> The number of monopoles used, therefore, was actually twice the number of conjugated atoms. Molecular orbital calculations on protochlorophyll were not very successful. For this more symmetric molecule polarized transitions for the long wavelength absorption bands, in contrast to experiment,<sup>2</sup> were not predicted and therefore a rotational strength calculation was not attempted.

If we now substitute eq. (4) into eq. (1a):

$$R_A = -\frac{2\pi}{c} \sum_{j \neq i} \sum_{b \neq a} \sum_t \frac{\nu_a \nu_b}{h(\nu_b^2 - \nu_a^2)} \frac{q_{i\text{to}a}}{|R_{i\text{to}a;j}|^3} (R_{i\text{to}a;j} \cdot \underline{\mu}_{j\text{ob}}) [\underline{\mu}_{j\text{ob}} \cdot (R_{i\text{oa};j} \times \underline{\mu}_{i\text{oa}})] \quad (5)$$

we find that any calculation would be extremely difficult, because knowledge of the transition dipoles of each of the asymmetric groups,  $j$ , for all transitions,  $b \leftarrow a$ , is needed. A majority of these transitions occur in the far ultraviolet region and have never been classified. To overcome this, we use Kirkwood's polarizability approximation:

$$(2/h\nu_0) \sum_b \underline{\mu}_{j\text{ob}} \underline{\mu}_{j\text{ob}} = (\alpha_{33} - \alpha_{11})_j \underline{e}_j \underline{e}_j \quad (6)$$

where  $\nu_0$  is an average frequency of the transitions,  $\alpha_{33}$  and  $\alpha_{11}$  are the polarizabilities parallel and perpendicular to the axis of symmetry for each group (assuming cylindrical symmetry), and  $\underline{e}_j$  is a unit vector pointing along the axis of cylindrical symmetry. Each covalent bond in an asymmetric center is considered in the calculations to be a group,  $j$ . A polarizability anisotropy  $(\alpha_{33} - \alpha_{11})_j$  is associated with each bond,

and its magnitude is based on values found in the literature. By considering each bond separately, and therefore distributing each asymmetric substituent in space, better results can be expected than if each group is approximated by a single polarizability value. Bond polarizabilities are difficult to determine and considerable variation in values is found in the literature. The values used for the C-H,<sup>17-19</sup> C-C,<sup>20,21</sup> C=O,<sup>21,22</sup> and C-O<sup>21,22</sup> bonds are shown in Table III and are judged to be the best available. By putting eq. (6) into eq. (5) and by using the good approximation

$$\frac{v_0^2}{v_0^2 - v_a^2} \approx 1$$

we obtain our final equation:

$$R_A = -\frac{\pi}{c} \sum_{j \neq i} \sum_t \frac{v_a q_{jtoa}}{|R_{jtoa;j}|^3} (\alpha_{33} - \alpha_{11})_j (R_{jtoa;j} \cdot \underline{e}_j) [\underline{e}_j \cdot (R_j - R_{jtoa}) \times \underline{u}_{jtoa}] \quad (7)$$

Coordinates for the molecules (Table II) are taken from a recent crystal structure determination of methyl chlorophyllide a<sup>23</sup> (Chl a with the central Mg atom removed and with a methyl group replacing the phytol chain). Thus, the geometry of the side groups in solution is taken to be the same as that in the crystal. Although this may seem to be a crude approximation, molecular models show that each side group has significant steric hindrances. Thus, the assumption used is that, even in solution, the side groups are unable to rotate freely. Because eq. (7) predicts a dependence of rotational strength on the inverse square of the distance of separation, the part of the side group which makes the

greatest contribution to the optical activity is expected to be that which is closest to the conjugated ring, and it is precisely this part of the group which will feel the bulk of the steric forces. Calculations in which all side groups were allowed to rotate freely (Table IV) were also attempted. In all cases the agreement with experiment was not so good as that in which the "crystal conformation in solution" was assumed. In certain cases the results did not even agree with the sign of the experimental rotational strength.

The phytol chain is ignored in the calculations. This probably introduces no serious error since this substituent is a larger distance from the porphyrin ring than any other group, thereby decreasing its interaction potential. Evidence from NMR measurements<sup>24,25</sup> indicates that the phytol does not strongly interact with the other substituents. Measurements in this laboratory show that the CD of methyl chlorophyllide a is identical to that of Chl a, implying that the phytol may safely be ignored in a theoretical treatment. This result would seem to resolve a conflict between the results of Houssier and Sauer<sup>2</sup> on pheophytin a and those of Briat et al.<sup>26</sup> on methyl pheophorbide a (pheophytin a with a methyl replacing the phytol). The difference in the magnitude of the CD reported for these molecules can most likely be attributed to a calibration problem of one of the spectrometers or to a partial epimerization of the substituents at C-10, as has already been suggested.<sup>2</sup>

### Results

Results of the calculations are given in Table IV. All experimental measurements<sup>2,27</sup> were made on solutions in ether and, to account

for the dielectric effect of the solvent,<sup>28</sup> all calculated rotational strengths were multiplied by  $(n^2 + 2)/3$ , where  $n$  is the refractive index of the solvent. In all cases there is qualitative agreement between the theoretically derived rotational strengths and the experimental values. In the previous study,<sup>2</sup> in which the Q transitions were approximated by a point dipole, the experimental measurements gave larger rotational strengths than the calculations by factors from 8 to 40. In one case (Chl a;  $Q_y$  transition) the wrong sign was predicted. In the point monopole calculations (Table IV) the range of discrepancies is reduced to 1.5 to 6 and the signs are all correctly predicted. Most of the improvement reported here can be attributed to the use of monopoles and the use of a fixed geometry for the substituents. It is clear that in calculations, such as these, a highly delocalized transition cannot be accurately represented as a point dipole.

Results are also presented for a calculation in which all monopoles were placed in the plane of the chromophore (for all other calculations, monopoles were divided by two and placed 1 Å above and below the plane; see above). It is seen that this can change the contribution of an individual asymmetric center by as much as a factor of two. The implication from this is that if the true wave function (with the transition charge densities distributed continuously through space) was used to calculate the interaction potential, the result would be an improvement over that obtained by using monopoles (even if the monopoles were an extremely accurate set). That is, there is still an inherently large approximation in the use of point monopoles.

A calculation is presented for Chl a in which BChl monopoles were used. This changes the result by a large amount and appreciably reduces the agreement with experiment. Since Chl a and BChl are closely related molecules with monopole patterns which are rather similar, this test shows that relatively small changes in monopoles can cause large changes in the calculated rotational strengths. Fairly accurate monopoles are, therefore, essential for this type of calculation.

Attempts were made to prepare and to obtain a CD spectrum for pyroBChl. For this molecule the contribution to the rotational strength induced by the groups at C-3 and C-4 is expected approximately to cancel the contributions of the asymmetric centers at C-7 and C-8 (these groups are related by an approximate center of inversion) and a small CD signal is expected. However, just the opposite result ( $R_A = 37.2 \times 10^{-40}$  c.g.s. for the  $Q_y$  transition in pyroBChl) was obtained. Although the infrared spectrum confirmed the absence of the C-10 carboxymethyl group and the visible and near-infrared absorption was virtually indistinguishable from that of BChl, the extraordinarily large CD peaks lead us to doubt whether we had the correct molecule. As a consequence, the experimental rotational strengths for pyroBChl are not included in Table IV.

### Conclusions

The nature of the optical activity of the chlorophyll molecules studied can now be considered to be reasonably well understood. The CD spectra can be accounted for in terms of the interactions described

by the Kirkwood-Tinoco approach. It is possible that this type of calculation may prove useful in assigning absolute configurations to molecules where this information is not known.

The origin of the circular dichroism of chlorophylls in photosynthetic membranes differs from that described here. Exciton interactions between chlorophylls cause rotational strengths of a much larger magnitude than those exhibited by monomers. Nevertheless, the theory for such interactions has much in common with that presented here. The results presented above thus make calculations on more complicated systems feasible.

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Table I: Experimental Values of Absorption and Rotational Strengths (in Ether)

		Chl <u>a</u>	pyroChl <u>a</u>	BChl	pyroBChl
$\lambda_{\max}$ (nm)	$\left\{ \begin{array}{l} Q_y \\ Q_x \end{array} \right.$	661	661	770	770
		575	578	570	583
$\omega_{\max}$ (cm <sup>-1</sup> )	$\left\{ \begin{array}{l} Q_y \\ Q_x \end{array} \right.$	15,130	15,130	12,987	12,987
		17,390	17,300	17,540	17,150
Bandwidth $\Delta\omega$ (cm <sup>-1</sup> )	$\left\{ \begin{array}{l} Q_y \\ Q_x \end{array} \right.$	390	420	550	490
		760	780	910	920
$10^{-3} \epsilon_{\max}$ (mole/l) <sup>-1</sup> cm <sup>-1</sup>	$\left\{ \begin{array}{l} Q_y \\ Q_x \end{array} \right.$	86.3	80	96	96
		6.8	8	22	22
Oscillator strength $f = 4.33 \times 10^{-9} \int \epsilon(\omega) d\omega$	$\left\{ \begin{array}{l} Q_y \\ Q_x \end{array} \right.$	0.155	0.155	0.309	0.30
		0.024	0.029	0.110	0.110
Rotational strength $10^{40} R_A$ (cgs)	$\left\{ \begin{array}{l} Q_y \\ Q_x \end{array} \right.$	-8.7	-14.3	5.0	----
		$\sim 0^-$	$\sim 0^-$	-4.4	----

Table II: Atomic Coordinates and Transition Monopoles

Atom <sup>a</sup>	Coordinates (Å) for methyl pheophorbide <u>a</u> <sup>23</sup>	Transition monopoles <sup>14</sup>			
		BChl		Chl <u>a</u>	
		Q <sub>y</sub>	Q <sub>x</sub>	Q <sub>y</sub>	Q <sub>x</sub>
N <sub>1</sub>	(.20, -2.01, .02)	-.035	.007	-.049	.001
N <sub>2</sub>	(2.10, 0., -.04)	.001	-.115	.005	-.055
N <sub>3</sub>	(-.13, 2.07, -.04)	.035	-.007	.047	.004
N <sub>4</sub>	(-2.16, -.06, .06)	-.001	.115	.004	.109
C <sub>α</sub>	(2.33, 2.46, -.03)	.035	-.129	.107	-.112
C <sub>β</sub>	(2.63, -2.40, .03)	-.033	-.124	-.086	-.136
C <sub>γ</sub>	(-2.30, -2.45, -.02)	-.035	.129	-.054	.108
C <sub>δ</sub>	(-2.57, 2.35, .03)	.033	.123	.044	.109
C <sub>1</sub>	(-.85, 4.25, .02)	-.051	.037	-.039	.029
C <sub>2</sub>	(.52, 4.26, -.01)	-.046	-.035	-.028	-.041
C <sub>3</sub>	(4.26, .83, .07)	.000	.000	.040	.027
C <sub>4</sub>	(4.36, -.54, .07)	.000	.000	-.046	.017
C <sub>5</sub>	(.80, -4.20, -.02)	.051	-.037	.045	-.037
C <sub>6</sub>	(-.61, -4.11, -.03)	.046	.035	.036	.031
C <sub>7</sub>	(-4.38, -.92, .30)	.000	.000	.000	.000
C <sub>8</sub>	(-4.46, .61, .01)	.000	.000	.000	.000
C <sub>9</sub>	(-1.83, -4.88, -.09)	.000	.001	-.001	.002
C <sub>10</sub>	(-3.02, -3.81, -.13)	.000	.000	.000	.000
C <sub>11</sub>	(-.93, -2.73, -.02)	.081	-.078	.067	-.079
C <sub>12</sub>	(1.30, -2.89, .02)	.091	.070	.075	.059
C <sub>13</sub>	(2.99, -1.06, .01)	.112	.055	.069	.062
C <sub>14</sub>	(2.85, 1.13, .01)	-.103	.063	-.084	.050
C <sub>15</sub>	(1.00, 2.87, -.02)	-.081	.078	-.085	.050
C <sub>16</sub>	(-1.26, 2.84, -.00)	-.091	-.070	-.075	-.085
C <sub>17</sub>	(-3.01, 1.00, .04)	-.112	-.055	-.111	-.058
C <sub>18</sub>	(-2.92, -1.19, .08)	.103	-.063	.106	-.056
C <sub>19</sub>	(1.43, 5.43, .00)	.000	-.001	.000	.000
C <sub>20</sub> <sup>b</sup>	(1.12, 6.61, -.22)	-.015	-.008	.000	.000
O <sub>1</sub>	(-2.01, -6.09, -.11)	.015	.008	.019	.010

<sup>a</sup> See Fig. 1 for numbering system

<sup>b</sup> C<sub>20</sub> is replaced with an oxygen in BChl

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Table III: Bond-bond Polarizabilities

Bond	Polarizability Anisotropy $10^{24} (\alpha_{33} - \alpha_{11}), \text{cm}^3$
C-C	.71
C=O	1.24
C-O	.96
C-H	-.312

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Table IV: Comparison of Calculated and Experimental Rotational Strengths

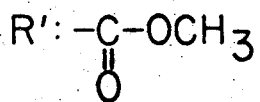
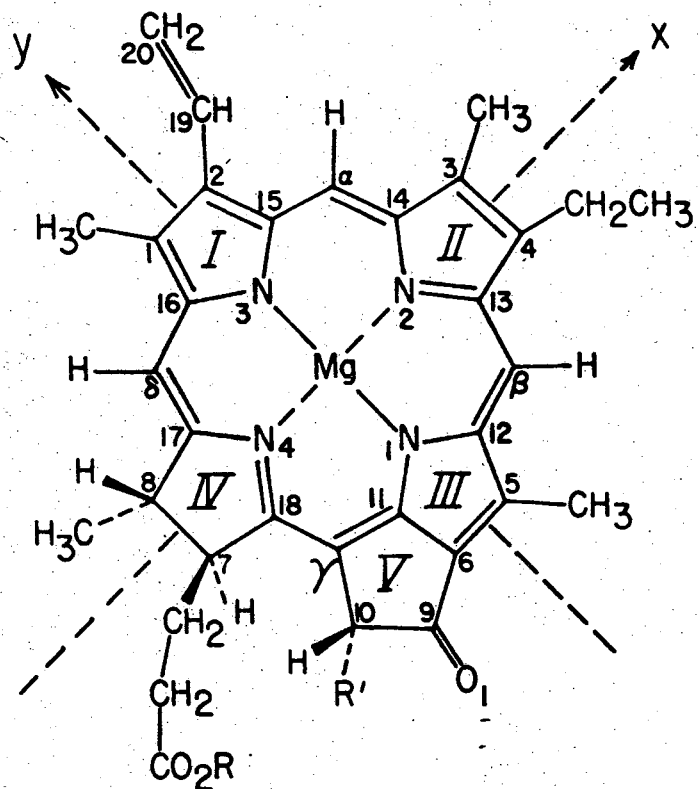
Molecule	Transition	Point dipole Model <sup>a</sup>	Calculated $R_A$ ( $\times 10^{40}$ cgs) contribution for each asymmetry center					Calculated sum	Experimental
		$R_A$ ( $\times 10^{40}$ cgs)	C-3	C-4	C-7	C-8	C-10	$R_A$ ( $\times 10^{40}$ cgs)	$R_A$ ( $\times 10^{40}$ cgs)
BCh1	$Q_y$	1.3	1.9	1.9	-3.3	-2.3	5.2	3.4	5.0
	$Q_x$	-.1	-.005	-.31	.14	.20	-3.1	-3.1	-4.4
pyroBCh1	$Q_y$	0	1.9	1.9	-3.3	-2.3		-1.8	---
	$Q_x$	0	-.005	-.31	.14	.20		.03	---
Ch1 <u>a</u>	$Q_y$	.5			-2.9	-2.1	3.6	-1.4	-8.7
	$Q_x$	.02			.07	.1	-1.6	-1.4	$\sim 0^-$
pyroCh1 <u>a</u>	$Q_y$	0.4			-2.9	-2.1		-5.0	-14.3
	$Q_x$	.3			.07	.1		.2	$\sim 0^-$
Bch1 (monopoles in plane)	$Q_y$		3.2	3.9	-5.0	-4.1	5.2	2.8	5.0
Ch1 <u>a</u> (with BCh1 monopoles)	$Q_y$				-1.6	-1.0	2.4	-.2	-8.7
BCh1 (with freely rotating side groups)	$Q_y$		.1	.8	-.4	-.8	.4	.1	5.0

<sup>a</sup>Calculated from data in Ref. 2

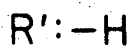
Figure Legends

Fig. 1. Molecular structures of chlorophyll a, pyrochlorophyll a, bacteriochlorophyll and pyrobacteriochlorophyll, showing the absolute configuration of the asymmetrically placed ring substituents. R = phytyl.

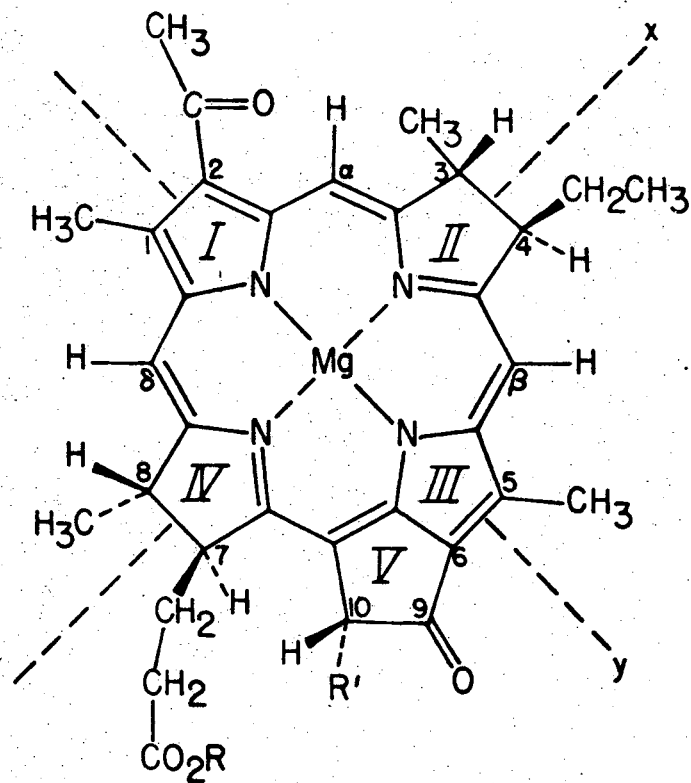
Fig. 2. Circular dichroism and absorption spectra of chlorophyll a and pyrochlorophyll a in ether (from Ref. 2).



CHLOROPHYLL-A



PYROCHLOROPHYLL-A

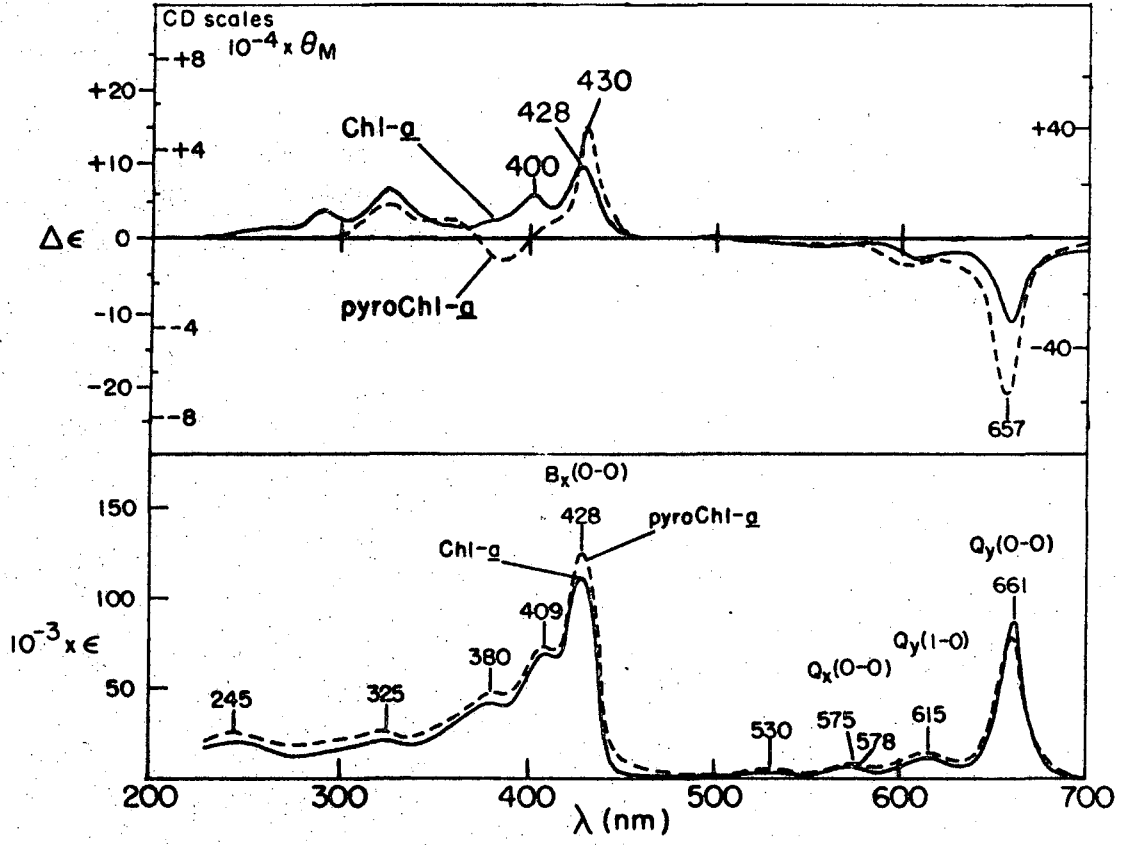


BACTERIOCHLOROPHYLL

PYROBACTERIOCHLOROPHYLL



Optical activity of Chl-a and pyroChl-a in ether



XBL 709-5393

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