

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 2. Algebraic Solution of the Perimeter Model for the B Terms of Systems with a $(4N + 2)$ -Electron $[n]$ Annulene Perimeter^{1,2}

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Abstract. Effects of general symmetry-lowering perturbations on the B terms of the L and B transitions of a $(4N + 2)$ -electron $[n]$ annulene are worked out algebraically, starting with the perimeter model results of part 1. The results permit a prediction of MCD signs from the knowledge of the relative size of two orbital energy differences, which in turn can be usually estimated from molecular structure without calculations, using simple notions of the PMO theory. This is illustrated on the MCD of low-symmetry porphyrins. A simple pictorial physical interpretation of the origin of the MCD behavior is offered. The results also provide a rationale for some of the fortunate and seemingly fortuitous features of previous computations using semiempirical models. The good agreement between the results of a π -perimeter model and experimental data suggests that the magnetic mixing of the $n\pi^*$ - $\pi\pi^*$ type has an only minor effect on the B terms of $\pi\pi^*$ transitions in cyclic π -electron molecules.

Introduction

Part 1 of this series² stated the motivation for our attempt to develop simple rules relating absolute MCD signs of electronic transitions to molecular structure for cyclic π -electron systems and described the application of an improved but still very simple version of the simple π -perimeter model due to Platt³ and Moffitt⁴ to a general formulation of expressions for A and B terms of $G \rightarrow L$ and $G \rightarrow B$ transitions in $(4N + 2)$ -electron $[n]$ annulenes. It derived and tabulated the purely electronic magnetic moments of their L state (μ^+ , large and negative) and their B state (μ^- , small and negative except for some annulene anions) which result upon HOMO \rightarrow LUMO excitations reversing or preserving the sense of circulation of the promoted electron, respectively, and then proceeded to show that the A and B terms of the degenerate $G \rightarrow L$ and $G \rightarrow B$ transitions in those perturbed $[n]$ annulenes which possess an at least threefold axis of symmetry can be expressed as linear combinations of the μ^- and μ^+ moments in a way which permits easy predictions of absolute signs from molecular structure. An important role was played by the positive quantities ΔHOMO and ΔLUMO , the former describing the splitting of the originally degenerate HOMO and the latter that of the originally degenerate LUMO by the perturbation acting on the parent perimeter.

Presently, we describe an extension of the simple approach of part 1² to the derivation of expressions for B terms of $G \rightarrow L$ and $G \rightarrow B$ transitions in a perturbed $(4N + 2)$ -electron $[n]$ annulene of arbitrarily low symmetry. We adopt the notation and the simplifying assumptions of part 1² and refer the reader there for details. The results have an intuitively understandable form and permit a prediction of absolute MCD signs from the knowledge of the relative size of ΔHOMO and ΔLUMO . It is shown on the example of partially reduced porphyrins how these can be derived without any computations, using PMO-type⁵ notions. Finally, we relate the results to those of previous semiempirical computations and suggest an explanation for the apparent insignificance of magnetic $n\pi^*$ - $\pi\pi^*$ mixing for attempts to understand qualitatively the signs of the B terms of $\pi\pi^*$ transitions in cyclic π chromophores. Throughout, purely electronic terms are in the foreground of our attention and vibronic structure is not considered.

Part 3 presents a general classification of cyclic π -electron chromophores with a $(4N + 2)$ -electron perimeter and gives a nonmathematical description of the effect of inductive and mesomeric substituents on the MCD spectra of cyclic π

chromophores with a $(4N + 2)$ -electron perimeter, leading to general rules. As described in more detail in part 1,² in the following 15 papers of the series the MCD spectra of a large number of cyclic π systems are presented and interpreted.

Results and Discussion

1. Algebraic Description of the Effect of Structural Perturbations on the MCD of 2-Electron $[n]$ Annulenes and $(4N + 2)$ -Electron $[2(N + 1)]$ Annulenes. In the parent annulenes of these two kinds, one of the frontier orbitals is nondegenerate (HOMO or LUMO, respectively) and only one degenerate state results from HOMO \rightarrow LUMO excitations. In part 1,² we referred to it as the B state (ϵ_1, ϵ_1^* symmetry in the C_n group) and noted that its A term is given by $A(G \rightarrow B)/D(G \rightarrow B) = -\mu^-(n, N)/2$, so that it is positive for a 2-electron $[n]$ annulene and negative for a $(4N + 2)$ -electron $[2(N + 1)]$ annulene. Perturbations which preserve a threefold or higher axis of symmetry do not affect these results within our set of approximations.

Lower symmetry perturbations of interest here remove orbital and state degeneracies. Let $a = \langle \Psi_0^{-1} | \hat{A} | \Psi_0^0 \rangle$ characterize the perturbing operator \hat{A} . Then, real solutions of the perturbed CI problem for a 2-electron $[n]$ annulene are

$$\begin{aligned} \Phi(G) &= \Psi_G \\ \Phi(B_2) &= (e^{-i\gamma}\Psi_0^1 + e^{i\gamma}\Psi_0^{-1})/\sqrt{2} & W(B_2) &= B + |a| \\ \Phi(B_1) &= (e^{-i\gamma}\Psi_0^1 - e^{i\gamma}\Psi_0^{-1})/i\sqrt{2} & W(B_1) &= B - |a| \end{aligned}$$

where $\gamma = (\arg a)/2$, and the nonvanishing matrix elements of \hat{M} are

$$\begin{aligned} \langle G | \hat{M} | B_2 \rangle &= \sqrt{2}m(n, 1) \cdot e'_1 \\ \langle G | \hat{M} | B_1 \rangle &= \sqrt{2}m(n, 1) \cdot e'_2 \end{aligned}$$

and similar results are obtained for a $(4N + 2)$ -electron $[2(N + 1)]$ annulene. The unit vectors $e'_1 \times e'_2 = e_3$ are related to the unit vectors of the original coordinate system $e_1 \times e_2 = e_3$ by counterclockwise rotation around the e_3 axis by angle γ :

$$\begin{aligned} e'_1 &= e_1 \cdot \cos \gamma + e_2 \cdot \sin \gamma \\ e'_2 &= e_1 \cdot (-\sin \gamma) + e_2 \cdot \cos \gamma \\ e'_3 &= e_3 \end{aligned}$$

In this approximation, dipole strengths of the two transitions are equal, $D(G \rightarrow B_1) = D(G \rightarrow B_2) = 2m^2(n, 1)$ or $2m^2(2N$

matrix is shown in (I).

$$\begin{array}{cc}
 & \begin{array}{cc} X & Y \end{array} \\
 \begin{array}{c} X \\ Y \\ U \\ V \end{array} & \begin{pmatrix} \rho^{-1} & 0 \\ 0 & \rho^{-1} \\ \cos(\phi/2) & \cos\theta \sin(\phi/2) \\ -\sin(\phi/2) & \cos\theta \cos(\phi/2) \end{pmatrix}
 \end{array}
 \qquad
 \begin{array}{cc}
 & \begin{array}{cc} U & V \end{array} \\
 \begin{array}{c} U \\ V \end{array} & \begin{pmatrix} \cos(\phi/2) & -\sin(\phi/2) \\ \cos\theta \sin(\phi/2) & \cos\theta \cos(\phi/2) \\ c\rho^{-1} & 0 \\ 0 & -c\rho^{-1} \end{pmatrix}
 \end{array}
 \tag{I}$$

+ 2, 2N + 1). For a 2-electron [n]annulene, substitution into the general formulas for B terms yields

$$\begin{aligned}
 B(G \rightarrow B_1)/D(G \rightarrow B_1) &= -B(G \rightarrow B_2)/D(G \rightarrow B_2) \\
 &= -\mu^-(n, 0)W^{-1}(B_2 - B_1)
 \end{aligned}$$

for a (4N + 2)-electron [2(N + 1)]annulene the result is

$$\begin{aligned}
 B(G \rightarrow B_1)/D(G \rightarrow B_1) &= -B(G \rightarrow B_2)/D(G \rightarrow B_2) \\
 &= -\mu^-(2N + 2, N)W^{-1}(B_2 - B_1)
 \end{aligned}$$

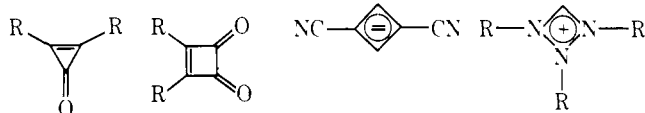
where $W^{-1}(B_2 - B_1) = [W(B_2) - W(B_1)]^{-1}$.

Since $\mu^-(n, 0) < 0$ and $\mu^-(2N + 2, N) > 0$ (part 1²), we conclude that the sign sequence of the B terms of the two B transitions is +, - in the order of increasing energy for a perturbed 2-electron [n]annulene and -, + for a perturbed (4N + 2)-electron [2(N + 1)]annulene. Since the latter prediction is specific for the LCAO MO model and is clearly not obtained in the free-electron MO model, the result suggests an interesting way of comparing the relative merits of the two simple descriptions. As noted in part 1,² available results for the symmetrical species such as Se₄²⁺ unambiguously favor the LCAO model.

Some specific predictions are shown below, but experimental verification may be difficult, since the B bands are expected at relatively high energies.

$$B_1 > 0, B_2 < 0$$

$$B_1 < 0, B_2 > 0$$



2. Algebraic Description of the Effect of Structural Perturbations on the MCD of a General (4N + 2)-Electron [n]-Annulene (0 < N < n/2 - 1). (i) The Formulation of the Problem. In the parent annulenes, both HOMO and LUMO are degenerate, and there are two sense-preserving excitations yielding the complex configurations Ψ_N^{N+1} and Ψ_N^{-N-1} which jointly describe the higher energy degenerate excited state B (symmetries ϵ_1 and ϵ_1^* , respectively, in C_n ; magnetic moments $\pm\mu^- \cdot e_3$). In addition, there are two sense-reversing excitations yielding the complex configurations Ψ_N^{N+1} and Ψ_N^{-N-1} which either jointly describe the lower energy degenerate excited state L if $n \neq 4N + 2$ (ϵ_{2N+1} and ϵ_{2N+1}^* , respectively; magnetic moments $\pm\mu^+ \cdot e_3$) or interact to give two real state wave functions: that of the $L_a(B_{1u})$ state $(\Psi_N^{N+1} + \Psi_N^{-N-1})/\sqrt{2}$ and that of the lower energy $L_b(B_{2u})$ state $(\Psi_N^{N+1} - \Psi_N^{-N-1})/i\sqrt{2}$, if $n = 4N + 2$ (connected by a magnetic dipole transition moment $\langle L_b | \hat{M} | L_a \rangle = i\mu^+ \cdot e_3$). Only the sense-preserving excitations carry transition intensity. The perturbations which preserve a threefold or higher axis of symmetry have been discussed in part 1;² lower symmetry perturbations are of interest here. We shall consider only one-electron perturbations and refer the reader to the numerical PPP results of parts 5⁷ and 8⁸ for verification of our claim that inclusion of typical 2-electron perturbations does not affect the results significantly. Let the perturbation be characterized by operator \hat{A} , and let $a = \langle \Psi_N^{N+1} | \hat{A} | \Psi_N^{N+1} \rangle$ and $b = \langle \Psi_N^{-N-1} | \hat{A} | \Psi_N^{-N-1} \rangle$. To the first order in degenerate perturbation theory, compatible with the approximations introduced in part 1,²

$$\begin{aligned}
 |a| &= \Delta\text{HOMO}/2 \\
 |b| &= \Delta\text{LUMO}/2
 \end{aligned}$$

We now introduce a real basis set

$$\begin{aligned}
 X &= (e^{-i\gamma}\Psi_N^{N+1} + e^{i\gamma}\Psi_N^{-N-1})/\sqrt{2} \\
 Y &= (e^{-i\gamma}\Psi_N^{N+1} - e^{i\gamma}\Psi_N^{-N-1})/i\sqrt{2} \\
 U &= (\Psi_N^{N+1} + \Psi_N^{-N-1})/\sqrt{2} \\
 V &= (\Psi_N^{N+1} - \Psi_N^{-N-1})/i\sqrt{2}
 \end{aligned}$$

where $\gamma = (\arg a + \arg b)/2$. We further introduce the notation $\cos\theta = (|a| - |b|)/(|a| + |b|)$, $0 \leq \theta \leq \pi$, $\phi = \arg a - \arg b$, $0 \leq \phi < 2\pi$, $\rho = (|a| + |b|)/(B - L)$, where B and L are the energies of the perturbed sense-preserving and sense-reversing configurations, respectively, and $c = \langle \Psi_N^{N-1} | \hat{H} | \Psi_N^{N+1} \rangle / (B - L)$. Note that c is a measure of the separation of the L_b and L_a states in the parent annulene and vanishes by symmetry unless $n = 4N + 2$, in which case its typical values are about 0.5.

The case of the unperturbed annulene ($\rho = 0$) was considered in part 1.² Here, we consider the range $0 < \rho < 5$; for stronger perturbations the simple theory is not likely to make sense (note that ρ^{-1} is the magnitude of the energy separation between the energy-preserving and energy-reversing excitations in the perturbed annulene in units of $|a| + |b|$). The variables ρ , θ , and ϕ are defined in a way which permits an easy visualization of all important aspects of the perturbation in a spherical-coordinate system, but this will not be further discussed here. While ρ is a measure of the strength of the perturbation and θ a measure of the relative splitting of the HOMO's and the LUMO's, ϕ characterizes the symmetry properties of the perturbation. If a reflection plane perpendicular to the molecular plane is present, $\phi = 0$ (MO ordering s, a, -a, -s or a, s, -s, -a) or $\phi = \pi$ (MO ordering s, a, -s, -a or a, s, -a, -s).

In this notation, and taking L for the zero of energy, the CI

(ii) **Soft MCD Chromophores.** Within the presently considered class of cyclic π chromophores, we define soft chromophores as those for which $\Delta\text{HOMO} = \Delta\text{LUMO}$ ($\theta = \pi/2$). In this case, the CI matrix acquires a block-diagonal form, and general properties of B terms in MCD spectra can be deduced easily.

Regardless of the values of c, γ , ρ , and ϕ , the eigenvectors have the form

$$\begin{aligned}
 \Phi(G) &= \Psi_G \\
 \Phi(B_2) &= c_X(B_2) \cdot X + c_U(B_2) \cdot U + c_V(B_2) \cdot V \\
 \Phi(B_1) &= Y \\
 \Phi(L_2) &= c_X(L_2) \cdot X + c_U(L_2) \cdot U + c_V(L_2) \cdot V \\
 \Phi(L_1) &= c_X(L_1) \cdot X + c_U(L_1) \cdot U + c_V(L_1) \cdot V
 \end{aligned}$$

labeled so that $W(B_2) > W(B_1) = \rho^{-1} > W(L_2) > W(L_1)$. The only possibly nonvanishing matrix elements of \hat{M} are

$$\begin{aligned}
 \langle G | \hat{M} | B_2 \rangle &= \sqrt{2}c_X(B_2) \cdot m(n, 2N + 1) \cdot e'_1 \\
 \langle G | \hat{M} | B_1 \rangle &= \sqrt{2}m(n, 2N + 1) \cdot e'_2 \\
 \langle G | \hat{M} | L_2 \rangle &= \sqrt{2}c_X(L_2) \cdot m(n, 2N + 1) \cdot e'_1 \\
 \langle G | \hat{M} | L_1 \rangle &= \sqrt{2}c_X(L_1) \cdot m(n, 2N + 1) \cdot e'_1
 \end{aligned}$$

where the coordinate system $\hat{e}_1, \hat{e}_2, \hat{e}_3$ is defined as in section 1, but with the present definition of the angle γ as $(\arg a + \arg b)/2$. B terms of those transitions whose dipole strength D happens to be zero vanish (this could be L_2 or L_1 if $c_X(L_2) = 0$ or $c_X(L_1) = 0$). For transitions of nonvanishing intensity, we obtain

$$B(B_2)/D(B_2) = \mu^-(n, N) \cdot W^{-1}(B_2 - B_1)$$

$$B(B_1)/D(B_1) = -\mu^-(n, N)[c_X^2(B_2) \cdot W^{-1}(B_2 - B_1) - c_X^2(L_2) \cdot W^{-1}(B_1 - L_2) - c_X^2(L_1) \cdot W^{-1}(B_1 - L_1)]$$

$$B(L_2)/D(L_2) = -\mu^-(n, N) \cdot W^{-1}(B_1 - L_2)$$

$$B(L_1)/D(L_1) = -\mu^-(n, N) \cdot W^{-1}(B_1 - L_1)$$

and we see that μ^+ contributions are absent. The μ^- contributions provide $B(B_2)$ with the sign of $\mu^-(n, N)$ while $B(L_2)$ and $B(L_1)$ have the sign of $-\mu^-(n, N)$. Since $c_X^2(B_2) > c_X^2(L_2)$, $c_X^2(L_1)$ and moreover, $W^{-1}(B_2 - B_1) \geq W^{-1}(B_1 - L_2)$, $W^{-1}(B_1 - L_1)$ for any magnitudes of ρ and c of interest here, also the sign of $B(B_1)$ will be that of $-\mu^-(n, N)$. Figure 2 of part 1² gives a list of calculated values of $\mu(n, N)$ for $(4N + 2)$ -electron $[n]$ annulene perimeters as a function of n and N and we note that for almost all perimeters of practical interest, $\mu^-(n, N)$ is negative. For these, our results predict the sign sequence $+, +, +, -$ for the B terms of the four transitions in the order of increasing energy. The positive B terms of both L bands should be quite small relative to those of the B bands, both because they have much smaller dipole strengths and because of unfavorable energy differences in their denominators [note that $B(L_2)$ and $B(L_1)$ are not due to the mutual magnetic mixing of the two L states but to their mixing with the distant B_1 state]. Consideration of vibronic effects will undoubtedly be essential for those transitions which have vanishing, or nearly vanishing, purely electronic intensity.

Since μ^- is a small quantity (typical values are $\sim -0.3 \beta_e$), the B/D values should be relatively small even for the two $G \rightarrow B$ transitions. Any additional perturbation which causes $\theta \neq \pi/2$ and thus introduces contributions containing the much larger quantity μ^+ can be expected to cause considerable changes in the MCD spectrum, particularly in the weak L bands but possibly even in the stronger B bands; hence the name "soft MCD chromophores" for those for which $\Delta\text{HOMO} = \Delta\text{LUMO}$: these chromophores have MCD spectra and signs offering little resistance to deformation even by weak additional perturbations. When a change of $\cos \theta$ from the value of 0 is considered as a small perturbation, perturbed values of the B terms contain first-order contributions proportional to $\mu^+ \cos \theta$, showing that these deformations can be in either direction depending on whether ΔHOMO or ΔLUMO is larger.

(iii) Hard MCD Chromophores. Within the presently considered class of cyclic π chromophores, we define hard chromophores as those for which ΔHOMO and ΔLUMO are quite different ($\theta \neq \pi/2$). Clearly, there will be a shady area of borderline cases in which ΔHOMO and ΔLUMO are close to each other but not equal, i.e., "almost soft" or "intermediate" chromophores (e.g., azulene⁹).

If $\theta \neq \pi/2$, explicit solutions to the CI problem are found easily if $c = 0$ or $\phi = 0$ or $\phi = \pi$. The dipole strengths are

$$D(G \rightarrow B_2) = 2m^2(n, 2N + 1) \cos^2 \alpha$$

$$D(G \rightarrow B_1) = 2m^2(n, 2N + 1) \cos^2 \beta$$

$$D(G \rightarrow L_2) = 2m^2(n, 2N + 1) \sin^2 \beta$$

$$D(G \rightarrow L_1) = 2m^2(n, 2N + 1) \sin^2 \alpha$$

where transitions to L_1 and B_2 are polarized along \hat{e}_1 and those to L_2 and B_1 along \hat{e}_2 , and the B terms are

$$B(G \rightarrow B_2)/D(G \rightarrow B_2) = \mu^-(n, N)[\cos^2 \beta \cdot W^{-1}(B_2 - B_1) + \sin^2 \beta \cdot W^{-1}(B_2 - L_2)] + \mu^+(n, N) \cdot (\sin 2\alpha \sin 2\beta/4 \cos^2 \alpha) \cdot [W^{-1}(B_2 - B_1) - W^{-1}(B_2 - L_2)]$$

$$B(G \rightarrow B_1)/D(G \rightarrow B_1) = \mu^-(n, N)[- \cos^2 \alpha \cdot W^{-1}(B_2 - B_1) + \sin^2 \alpha \cdot W^{-1}(B_1 - L_1)] + \mu^+(n, N) \cdot (\sin 2\alpha \sin 2\beta/4 \cos^2 \beta) \cdot [-W^{-1}(B_2 - B_1) - W^{-1}(B_1 - L_1)]$$

$$B(G \rightarrow L_2)/D(G \rightarrow L_2) = \mu^-(n, N)[- \cos^2 \alpha \cdot W^{-1}(B_2 - L_2) + \sin^2 \alpha \cdot W^{-1}(L_2 - L_1)] + \mu^+(n, N) \cdot (\sin 2\alpha \sin 2\beta/4 \sin^2 \beta) \cdot [W^{-1}(B_2 - L_2) + W^{-1}(L_2 - L_1)]$$

$$B(G \rightarrow L_1)/D(G \rightarrow L_1) = \mu^-(n, N)[- \cos^2 \beta \cdot W^{-1}(B_1 - L_1) - \sin^2 \beta \cdot W^{-1}(L_2 - L_1)] + \mu^+(n, N) \cdot (\sin 2\alpha \sin 2\beta/4 \sin^2 \alpha) \cdot [W^{-1}(B_1 - L_1) - W^{-1}(L_2 - L_1)]$$

with the following specifications:

(a) If the perimeter is charged ($n \neq 4N + 2$), $c = 0$, $\tan 2\alpha = 2\rho$, $\tan 2\beta = 2\rho \cos \theta$, the order of energies is $W(B_2) \geq W(B_1) > W(L_2) \geq W(L_1)$ (the equalities hold if $\theta = 0$ or π , which two cases were discussed in part 1²), and the state labels B_2, B_1, L_2 , and L_1 indicate parentage in states of the unperturbed perimeter.

(b) If the perimeter is uncharged ($n = 4N + 2$), $c \neq 0$, the order of energies is $W(B_a), W(B_b) > W(L_a), W(L_b)$, and the identification with parent perimeter states is as follows:

(α) for $\phi = 0$, $L_1 \equiv L_a, L_2 \equiv L_b, B_1 \equiv B_b, B_2 \equiv B_a$, and $\tan 2\alpha = 2\rho/(1 - c)$, $\tan 2\beta = 2\rho \cos \theta/(1 + c)$

(β) for $\phi = \pi$, $L_1 \equiv L_b, L_2 \equiv L_a, B_1 \equiv B_a, B_2 \equiv B_b$, and $\tan 2\alpha = 2\rho/(1 + c)$, $\tan 2\beta = 2\rho \cos \theta/(1 - c)$

The ranges of the angles α and β follow from $\rho \geq 0$, $0 \leq \theta \leq \pi$. The electric [$m(n, 2N + 1)$] and magnetic [$\mu^\pm(n, N)$] moments were defined and discussed in part 1.² Transitions into the L_b and B_b states are always polarized across the bonds and those into L_a and B_a bands through the atoms of the respective $[4N + 2]$ annulene perimeters.

If $c \neq 0$ and $\phi \neq 0, \pi$, i.e., for those perturbed $(4N + 2)$ -electron $[4N + 2]$ annulenes which are of symmetry C_h or C_s , explicit solution of the CI problem is still possible but the resulting expressions are very lengthy and uninformative. We have therefore performed a series of several hundred numerical calculations for systematically selected values of ρ , ϕ , and θ , and find that the results for the dipole strengths and the B terms represent a smooth interpolation from the explicit description obtained for $\phi = 0$ to the explicit description obtained for $\phi = \pi$ (if $\phi \neq 0$ or π , both $G \rightarrow L$ transitions are of nonvanishing intensity). Figure 1 illustrates this behavior. The behavior of polarization directions also interpolates in an easily comprehensible way but will not be discussed here.

The explicit expressions for B terms given above, combined with the numerical results for the case $c \neq 0$, $\phi \neq 0, \pi$, permit general conclusions about the μ^- and μ^+ contributions (note that the values of α and $|\beta|$ can be estimated from ratios of experimental dipole strengths and the W^{-1} s from experimental transition energies).

μ^- Contributions. In practice, these are only important if the difference $\Delta\text{HOMO} - \Delta\text{LUMO}$ is small in absolute value; otherwise, the μ^+ contributions will dominate. The signs of the contributions to $B(B_2)$ and $B(B_1)$ are dominated by the magnetic mixing of the B_2 and B_1 states. The higher energy one has the sign of $\mu^-(n, N)$, and the lower energy one the sign of $-\mu^-(n, N)$, just as in a soft chromophore. In case of an uncharged perimeter ($n = 4N + 2$), the separation of the L_1 and

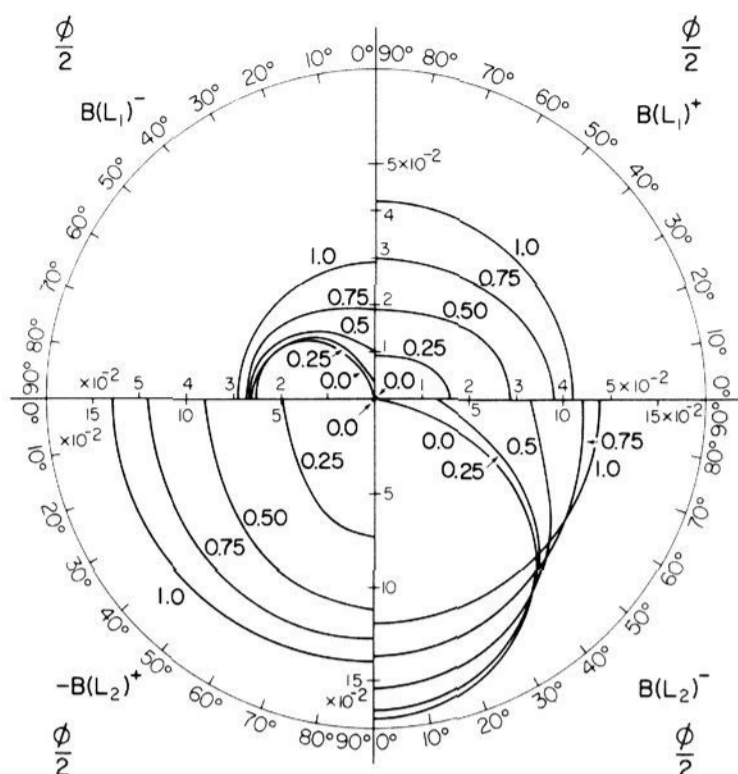


Figure 1. Polar plot of calculated contributions to B terms of the $G \rightarrow L$ transitions against $\phi/2$ for $\rho = c = 0.5$ and for five values of $\cos \theta$ (0, 0.25, 0.50, 0.75, 1.0, as shown): 1st quadrant, the μ^+ contribution to $B(L_1)$, in units of $[-2\mu^+m^2]$; 2nd quadrant, the μ^- contribution to $B(L_1)$, in units of $[-2\mu^-m^2]$; 3rd quadrant, minus the μ^+ contribution to $B(L_2)$, in units of $[-2\mu^+m^2]$; 4th quadrant, the μ^- contribution to $B(L_2)$, in units of $[-2\mu^-m^2]$. Note: the μ^+ contributions are odd and the μ^- contributions are even functions of $\cos \theta$. For $\cos \theta = \pm 1$, the results are independent of ϕ , whose value is arbitrary.

L_2 states is frequently considerable and then, $B(L_1)$ and $B(L_2)$ will be dominated by the L_1-B_1 and L_2-B_2 mixings, respectively, and both will have the sign of $-\mu^-(n, N)$, just as in a soft chromophore. On the other hand, in the case of a charged perimeter ($n \neq 4N + 2$) and in some cases of an uncharged perimeter (e.g., derivatives of anthracene) the two L states are nearly degenerate, and their mutual mixing may then be nonnegligible. Its contribution to the B term of the lower of the L states has the sign of $-\mu(n, N)$; its contribution to the B term of the upper L state has the sign of $\mu(n, N)$. As a result, there is no doubt that the overall sign of the μ^- contribution to the B term of the lower L transition is that of $-\mu(n, N)$, as in the case of a soft chromophore. For the upper L transitions the B-L and L-L mixing contributions are opposed, and the μ^- contribution to its B term will be very small and its sign hard to predict. For the case of a charged perimeter, where L_2 is the upper L state, direct substitution shows that for any α , $W^{-1}(B_2 - L_2)/W^{-1}(L_2 - L_1) \leq \tan^2 \alpha$ in the perimeter model (the equality holds for soft chromophores, $\beta = 0$), so that the sign of the overall μ^- contribution to $B(L_2)$ is dominated by the L_2-L_1 mixing and equals that of $\mu(n, N)$.

In summary, the signs of the μ^- contributions to the B terms in a hard chromophore are the same as they were for a soft chromophore, with the possible exception of the upper L state if the L states are nearly degenerate.

μ^+ Contributions. In contrast to the μ^- contributions, which were small and had the same signs for almost all possible structures, the potentially large μ^+ contributions to the four B terms show a striking structure dependence in a way which is unique for MCD spectroscopy: their sign is determined by the sign of β , i.e., by the sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$. Since $\mu^+(n, N) < 0$ and since $W^{-1}(L_2 - L_1) > W^{-1}(B_1 - L_1)$ and $W^{-1}(B_2 - B_1) > W^{-1}(B_2 - L_2)$, the predicted sign sequence for the μ^+ contributions to the B terms is $+, -, +, -$ if $\Delta\text{HOMO} - \Delta\text{LUMO} > 0$ and $-, +, -, +$ if $\Delta\text{HOMO} - \Delta\text{LUMO} < 0$. In the case of the B terms of the lower of the $G \rightarrow L$ transitions and the upper of the $G \rightarrow B$ transitions the effect of the L-L or B-B mixing is opposed to that of L-B mixing, but the former

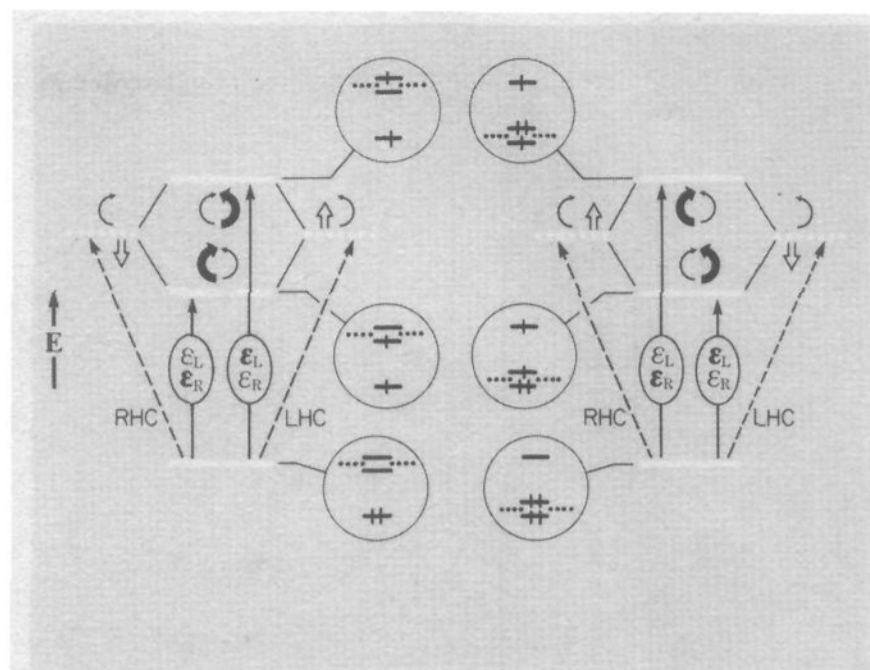


Figure 2. Physical origin of B terms (mutual mixing of excited states). Dotted lines represent the energies of nonstationary basis-set eigenstates of \hat{L}_z and \hat{M}_z in zero magnetic field, and the curved arrows indicate the kind of circularly polarized light required to reach them from the ground state. The double arrows show the Zeeman effect of the magnetic field. Molecular eigenstates (full lines) are produced by mixing of the two basis-set states in the magnetic field and are represented by typical MO configurations (electron-dominated excitation on the left, hole-dominated excitation on the right). Thickness of the curved arrows indicates the relative weight of the LHC and RHC polarized basis-set states, and the lean and the fat ϵ 's stand for the resulting smaller and larger extinction coefficients for CPL, respectively.

is clearly favored by the energy difference in the denominator.

The justification for the label "hard MCD chromophores" is now clear: small perturbations are not likely to change the sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$ and will thus have no effect on the signs of the observed B terms, which are dominated by the μ^+ contributions.

3. A Simple Pictorial View of the Origin of the μ^- and μ^+ Contributions to B Terms. Physical insight into the origin of the B terms is obtained by describing the molecular electronic states in the basis of the eigenstates of the e_3 -component of \hat{M} , and we shall exemplify this on a system with only two excited states. Excited states with nonzero angular momentum occur in degenerate pairs. One component can be reached from the ground state by absorption of LHC polarized light, and the other by absorption of RHC polarized light (Figure 2). In the absence of outside magnetic field, the two nonstationary states combine in exactly 1:1 ratio when the full molecular Hamiltonian is diagonalized and generally produce two eigenstates of two different energies, both equally likely to be reached by absorption of LHC as compared with RHC light. In the presence of outside magnetic field, the two eigenstates of \hat{M}_z which form the initial basis set are no longer degenerate and the one with a positive angular momentum (negative magnetic moment) lies above the other by the Zeeman term $2\mu_z B_z$. When we now diagonalize the molecular Hamiltonian in this basis, the mixing no longer is exactly 1:1; the upper of the two Zeeman components is a little more important in the upper molecular eigenstate, and the lower component is more important in the lower eigenstate. Thus, the probabilities of LHC and RHC light absorption by either state are no longer equal. If the eigenstate of \hat{M}_z which is reached by absorption of LHC light has positive angular momentum, the sequence of B terms will be $+, -$ in the order of increasing energy; if that reached by absorption of RHC light has positive angular momentum, the sequence will be $-, +$.

In our case, there are two distinct mechanisms by which the difference in the absorption of LHC and RHC light by the perturbed annulene arises, and they correspond to the μ^- and

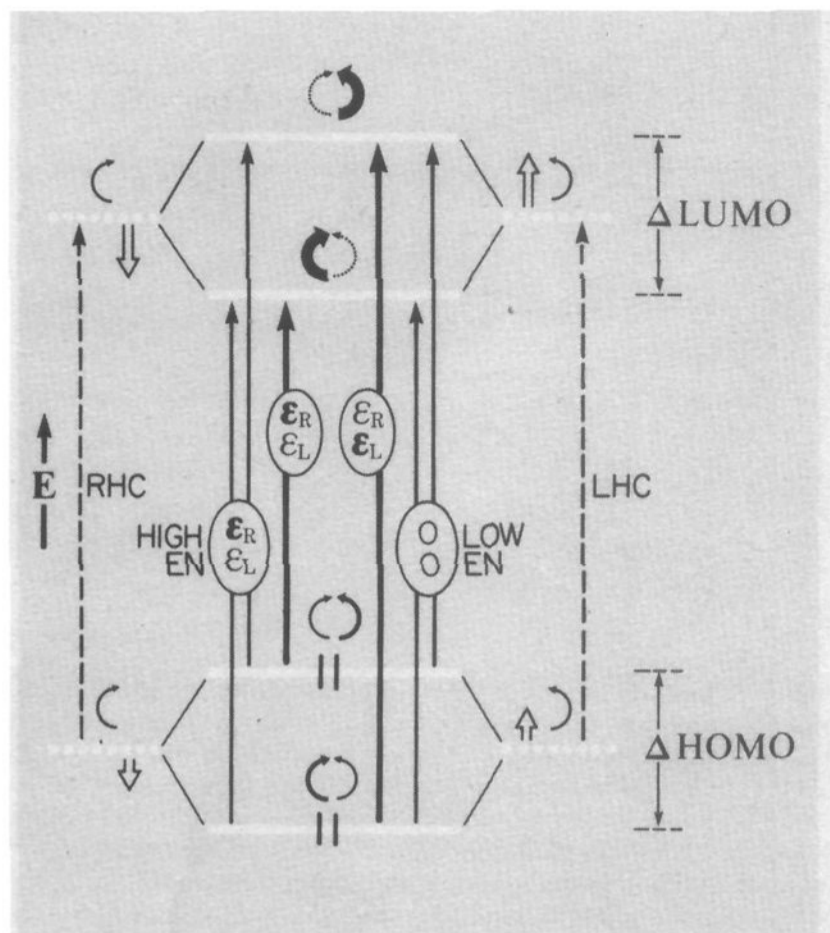


Figure 3. Physical origin of μ^- contributions to B terms. Dotted lines represent energies of the complex perimeter MO's in zero magnetic field and double arrows indicate their shifts by the Zeeman effect of the magnetic field (the curve arrows give the sense of electron circulation, viewed from the positive e_3 direction). Allowed transitions between the perimeter MO's are shown and their circular polarizations are indicated. Canonical MO's of the perturbed annulene (energy: full lines) are produced by pairwise mixing of the perimeter MO's. Thickness of the curved arrows indicates the relative weight of the two perimeter MO's in the mixture. The resulting differences in ϵ_L and ϵ_R for the $G \rightarrow L$ and $G \rightarrow B$ transitions are indicated, taking into account first-order CI mixing [the exact cancellation shown obtains only for $\phi = 0$ (L_b) or $\phi = \pi$ (L_a)].

μ^+ contributions of the algebraic description. Figure 3 shows the origin of the μ^- contribution on an MO level diagram, assuming $\Delta\text{HOMO} = \Delta\text{LUMO}$ in order to make the μ^+ contribution vanish. The energies of the (nonstationary) complex perimeter MO's of the perturbed annulene, which are eigenfunctions of the angular momentum operator, are shown as dotted lines. In the absence of outside magnetic field, they mix exactly 1:1 to produce the canonical MO's. In the presence of outside field, the HOMO pair of complex orbitals is Zeeman-split to a somewhat different degree, usually a little less, than the LUMO pair. Thus, when canonical orbitals are formed from the complex ones in the presence of the field, mixing will not be exactly 1:1 and this disparity will be larger for the LUMO's. The rest of the argument is best seen when the disparity for the HOMO's is neglected altogether. Since the promotion of an electron from ψ_N to ψ_{N+1} requires a LHC photon and that from ψ_{-N} to ψ_{-N-1} a RHC photon, the unequal mixing of ψ_{N+1} and ψ_{-N-1} to form the canonical orbitals clearly leads to a differential MCD effect as indicated in Figure 3. Its magnitude depends on the difference of the magnetic moments and thus the Zeeman splittings of the HOMO and the LUMO perimeter orbitals; this is the μ^- contribution.

Figure 4 shows the origin of the μ^+ contribution for a case in which the magnetic moments of the HOMO and the LUMO perimeter orbitals are equal, so that the μ^- contribution vanishes. Clearly, if $\Delta\text{HOMO} \neq \Delta\text{LUMO}$, the disparity in the ψ_N, ψ_{-N} and ψ_{N+1}, ψ_{-N-1} mixings, both of which were 1:1 in the absence of a field, still exists, since it is the ratio of the Zeeman shift to the total splitting which determines the mixing coefficients. As shown in Figure 4, this effect leads to signs of μ^+ contributions identical with those derived algebraically.

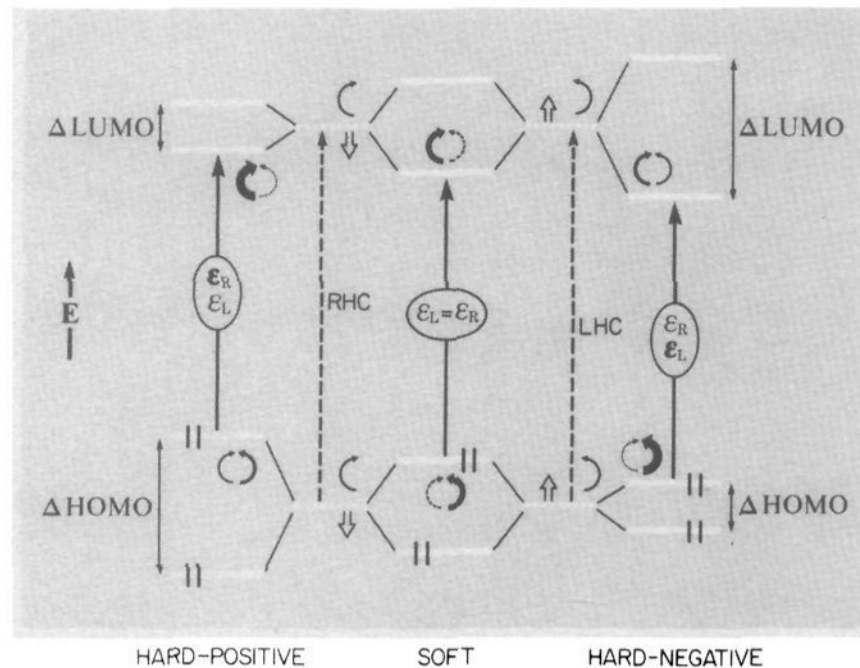


Figure 4. Physical origin of μ^+ contributions to B terms. See caption to Figure 3. The resulting differences in ϵ_L and ϵ_R are shown explicitly for only one of the four transitions.

4. An Example: Interpretation of the MCD Signs of Low-Symmetry Porphyrins and Chlorins without Computations.

D_{4h} porphyrins are predicted by the present simple model to always have positive purely electronic A terms for the $G \rightarrow L$ ("Q band") and $G \rightarrow B$ ("B band") transitions, since their LUMO is degenerate by symmetry (part 1²). On the other hand, porphyrins of lower symmetry can have either ΔHOMO or ΔLUMO larger and provide a nice example of molecules which can have either sign sequence for the μ^+ contributions. In a classical study of the porphyrin chromophore, Gouterman and collaborators¹⁰ calculated the MO levels of a series of partially hydrogenated derivatives. In the dihydro compound **1**, chlorin, and in the opposite tetrahydro derivative **2**, bacteriochlorin, they obtained $\Delta\text{HOMO} < \Delta\text{LUMO}$, whereas in the adjacent tetrahydro analogue **3**, ΔHOMO is slightly larger and in the hexahydro and octahydro porphyrins **4** and **5**, ΔHOMO is much larger (in **5**, $\Delta\text{LUMO} = 0$ by symmetry; the formulas **1-5** are shown in Figure 5). At that time, they did not draw any conclusions concerning MCD, but from the present results the consequences of the sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$ are clear. Experimentally, unlike most porphyrin derivatives, chlorins show the sign sequence $-, +, -, +$ for the four B terms in the order of increasing energy ("anomalous long-wavelength MCD", i.e., a negative B term for the first transition) and this was considered remarkable in view of the opposite sequence found in porphyrins and phthalocyanins¹¹ but is readily understood now (the numerical calculations of McHugh et al.¹² yield the incorrect signs). Similar variation in signs of the B terms should be found for azaporphyrins. Here, Gouterman and collaborators¹⁰ found $\Delta\text{HOMO} < \Delta\text{LUMO}$ for the monoaza and opposite diaza compounds and $\Delta\text{HOMO} > \Delta\text{LUMO}$ for the adjacent diaza, the triaza, and the tetraaza derivatives.

While PPP calculations of the type performed by Gouterman and collaborators are easy to do on present-day computers, the need for computer calculations would still tend to hinder the use of MCD spectroscopy in organic chemistry. It is therefore interesting to note that the relative size of ΔHOMO and ΔLUMO is also correctly deduced without any calculations by inspection of the perimeter orbitals using the PMO method,⁵ in spite of its crude nature. Figure 5 shows the nodal properties of the frontier MO's of the [16]annulene dianion and indicates the interactions with the proper symmetry combinations of the MO's of four ethylene units. Their union, plus four aza replacements, generate the porphyrin dianion. It is clear that its LUMO remains degenerate: even after the perturbation, the $-a$ and $-s$ orbitals are related by a 90°

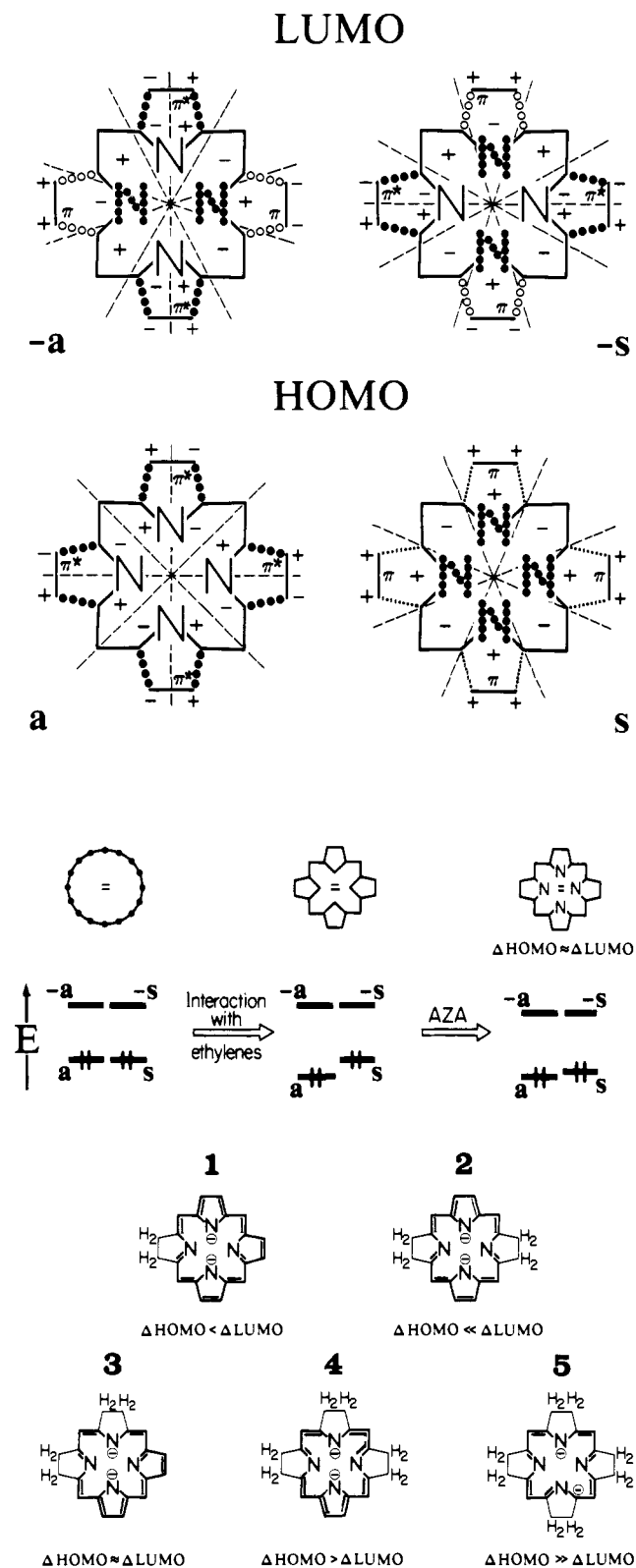


Figure 5. Nodal properties of the HOMO and LUMO of the [16]annulene dianion, and the interactions due to the union with four ethylenes and four aza nitrogens: black circles, interactions which lower the orbital energy; white circles, interactions which raise the orbital energy. The effect of the perturbations on orbital energies in the process [16]annulene dianion \rightarrow porphyrin dianion is shown below. In the hydrogenated analogues **1–5**, the interactions with one or more of the ethylene units are missing, with predictable effects on the relative size of Δ HOMO and Δ LUMO.

rotation. The HOMO of porphyrin dianion is accidentally also almost degenerate (this follows from the very low intensity of its $G \rightarrow L$ transition,¹⁰ in a more rigorous description one

would need to distinguish between the relative magnitude of orbital energy differences and that of configuration energies). In **s**, the energy is lowered by the aza replacement, while the ethylenes are attached at points where **s** has nodes and do not affect its energy. In **a**, the energy is lowered by interaction with the four π^* ethylene orbitals, while the nitrogens lie on nodal planes and are inactive. In the hydrogenated derivatives, one or both degeneracies are removed. For instance, in bacteriochlorin, **2**, Δ LUMO is greatly increased since in **-a**, two interactions with the ethylene π MO are missing while in **-s**, two interactions with the ethylene π^* MO are missing. At the same time, Δ HOMO is increased less since no change occurs with **s** (two interactions with ethylene π^* MO are now missing for **a**). In the adjacent tetrahydro compound **3**, Δ HOMO is the same as in **2**, but there is now no effect on **-a** and **-s**, so that Δ LUMO = 0 is expected. Similar qualitative considerations account for the other calculated MO energy differences and illustrate how extremely simple arguments permit a rationalization of MCD signs of even quite complex molecules. In part 3,⁶ we shall use similar simple notions for the formulation of general rules for substituent effects.

5. Relation to Numerical Computations. (i) Two Fortunate Features of Numerical Calculations. Two features of previous numerical semiempirical calculations of B terms of low-energy transitions in cyclic π systems, summarized in part 1,² have been most fortunate. These are the fact that so few contributions to a given B term are important although the sums run over all electronic states of the molecule and the fact that the resultant B terms, as well as these individual contributions, are almost totally insensitive to the choice of origin even in molecules of low symmetry for which origin-dependence must generally be expected.¹³ We propose that the close relation of the B terms of low-symmetry cyclic π -electron systems to those of the high-symmetry parent perimeters discussed here accounts for both of these features. For any system whose MO's are those of an annulene, $B_{F,G}^E + B_{G,F}^E$ always vanishes and very few $B_{L,F}^E$ or $B_{F,G}^E$ expressions are nonzero since the magnetic dipole transition moment operator connects only orbitals which are degenerate. Also, for this system all of these expressions are origin-independent individually, since the magnitude of change of the magnetic moment $\langle A | \hat{M} | B \rangle$ with change of origin is proportional to $\langle A | \hat{P} | B \rangle$, which vanishes whenever the other two vectors contained in the expression do not. In a sense then, the fact that MCD of cyclic π systems is dominated by the nodal properties of the MO's of the perimeter which resists change upon perturbation is essential for the success of simple PPP calculations of MCD of these systems. Conversely, neither of these two fortunate features first discovered numerically¹³ and now rationalized generally needs to apply to linear π systems nor to all-valence electron calculations for molecules exhibiting other types of transitions.

(ii) The Significance of Standard PPP Calculations. In the usual version of the PPP model, non-neighbor resonance integrals are assumed to vanish. If matrix elements of the linear momentum operator are derived from the resonance integrals according to Linderberg,¹⁴ so as to guarantee origin-independence of the B terms calculated for molecules of any symmetry from exact solutions of the model,¹³ the μ_2^+ and μ_2^- contributions to the magnetic moments μ^+ and μ^- are neglected. While this appears to be quite acceptable for μ^+ , it means disaster for μ^- , whose major part and, in the case of uncharged perimeters, the only part, originates in next-neighbor interactions.

The simplest PPP calculations will thus deviate in a systematic manner from the present results. The deviation is negligible for very hard chromophores in which μ_2^\pm contributions play a subordinate role, e.g., for the hydrocarbon ions on which the pairing theorem was tested.¹⁵ However, the deviation is considerable for soft chromophores, in which the μ^-

contributions are essential. Simple PPP calculations for derivatives of soft chromophores are therefore best viewed as a calculation of the difference with respect to the parent. The best way to further improvement may be in adopting a CNDO or INDO type of approach, which, however, underestimates the extent of orbital and state pairing in alternant π systems and thus produces significant μ^+ contributions even where essentially none should exist.¹⁶

(iii) Neglects Inherent to the Perimeter Model. Some of the shortcomings of the present approach were already mentioned in part 1.² Perhaps the most drastic approximation made in the evaluation of B terms is the extremely small number of states considered. Omission of higher energy $\pi\pi^*$ configurations is likely to affect the results for the higher energy $G \rightarrow B$ transitions, and the results for the $G \rightarrow B_2$ transition cannot be taken very seriously (e.g., in fluoranthenes¹⁷ and phenanthrenes¹⁸). We therefore prefer to claim general predictability only for the $G \rightarrow L$ transitions and the lower $G \rightarrow B_1$ transition. Another potentially very serious omission is that of magnetic mixing with all states other than $\pi\pi^*$, e.g., with $\sigma\pi^*$ and $n\pi^*$ states. Luckily, even in molecules whose lowest excited states are of the $n\pi^*$ type, agreement for signs of B terms of $\pi\pi^*$ transitions in the present crude theory is excellent, and it appears that magnetic $n\pi^*-\pi\pi^*$ and similar mixing is only of secondary importance for the B terms of the $G \rightarrow L$ and $G \rightarrow B$ transitions. Supporting evidence for this comes from the extreme weakness of the B terms of $n\pi^*$ transitions where these are observed (azines,^{7,19} azanaphthalenes,²⁰ etc.) and from the observation that upon protonation of the lone pair in aza heterocycles, the B terms of the $\pi\pi^*$ transitions are either unaffected or affected in ways which can be accounted for by the effect of increased electronegativity of the nitrogen on π electrons alone.^{19,20}

This lack of $n\pi^*-\pi\pi^*$ and similar mixing is absolutely essential for the success of simple MCD interpretations for $\pi\pi^*$ transitions. It is probably due to the much smaller value of not only the electric dipole transition moments into a typical $n\pi^*$ compared with a typical $\pi\pi^*$ state but also, most likely, of the magnetic dipole transition moments linking $n\pi^*$ states with $\pi\pi^*$ states compared with those mutually linking the perimeter $\pi\pi^*$ states: even a fully localized lone-pair orbital will have magnetic dipole matrix elements with all π orbitals except those which have a node at the atom with the lone pair, but no single one among them will be large (a fraction of β_e at best). This dilution produces a propensity for indiscriminate mixing of the $n\pi^*$ state with many $\pi\pi^*$ states, affecting the B term of none of them very much, particularly in larger π systems. The dilution is only likely to increase with the delocalization of the lone pair or upon going to a $\sigma\pi^*$ or $\pi\sigma^*$ state. The effects of the numerous mixing terms on the $n\pi^*$ B term are likely to partially cancel, in contrast to the situation just described for the perimeter π orbitals.

6. Conclusions. The B terms of the two $G \rightarrow B$ transitions of a perturbed 2-electron [n]annulene have the sign sequence +, - in the order of increasing energy, and those of the corre-

sponding transitions of a perturbed ($4N + 2$)-electron [$2(N + 1)$]annulene have the sign sequence -, +. The B terms of the $G \rightarrow L$ and $G \rightarrow B$ transitions of other ($4N + 2$)-electron [n]annulenes are composed of two parts. One is proportional to μ^- and therefore always small; the other is proportional to μ^+ and therefore potentially large. A pictorial and intuitive description of the origin of the two contributions can be given. The μ^- contribution is structure-insensitive and represents an intrinsic property of the ($4N + 2$)-electron perimeter. The sign and magnitude of the μ^+ contribution depend on the quantity $\Delta\text{HOMO} - \Delta\text{LUMO}$ and thus are a very sensitive yet straightforward function of molecular structure. Since the relative size of the orbital energy differences ΔHOMO and ΔLUMO is usually predictable by qualitative considerations of the PMO type, absolute MCD sign predictions are possible without computations, as illustrated on low-symmetry porphyrins. The results also provide a rationalization of some features of previous numerical calculations.

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