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## Magnetic Circular Dichroism of Cyclic $\pi$ -Electron Systems. 1. Algebraic Solution of the Perimeter Model for the $A$ and $B$ Terms of High-Symmetry Systems with a $(4N + 2)$ -Electron $[n]$ Annulene Perimeter<sup>1</sup>

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**Abstract:** Algebraic solutions are given for the purely electronic contributions to the  $A$  and  $B$  terms of the L and B transitions of  $(4N + 2)$ -electron  $[n]$ annulenes, using the LCAO version of the  $\pi$ -electron perimeter model with overlap through second-order and experimental excitation energies. Effects of perturbations which preserve a threefold or higher axis of symmetry are then incorporated in the solutions, and general rules relating MCD signs to structure are formulated (lower symmetry is considered in part 2). A relation to vibronic effects in MCD spectra of the annulenes is pointed out. The results pinpoint the origin of the long-recognized need for the use of an orthogonalized basis set in MCD calculations which use ZDO models and favor the LCAO MO over the FEMO model. MCD signs of  $D_{4h}$  porphyrins and phthalocyanins are discussed as an illustration, using symmetry to predict signs and PMO theory to predict relative magnitudes of the purely electronic contributions to  $A$  terms.

### Introduction

If magnetic circular dichroism spectroscopy is to shed its reputation of a highly specialized method useful mainly to the inorganic physical spectroscopist and acquire a place in the arsenal of physical tools useful to the organic chemist, it is essential to develop simple rules relating absolute MCD signs of electronic transitions to molecular structure. In preliminary communications,<sup>1-3</sup> we have pointed out how general rules for structural effects can be derived from first principles for cyclic  $\pi$ -electron systems. In the present series of papers, we describe in detail our results for those cyclic  $\pi$  systems which can be at least remotely derived from a  $(4N + 2)$ -electron perimeter and thus possess two B and usually also two L states in Platt's notation.<sup>4</sup> In recent years the purely electronic MCD signs for many individual cyclic  $\pi$ -electron systems have been computed numerically using methods such as PPP<sup>5</sup> and CNDO/S,<sup>6</sup> generally in good agreement with experiment.<sup>7-41</sup> The present formulation of theory is complementary to these computational studies: we shall not attempt to obtain quantitative results and detailed understanding for a large number of transitions of a given molecule but rather shall seek an algebraic formulation of simple expressions for  $A$  and  $B$  terms of the most prominent four low-energy bands in a large class of molecules from first principles using a simple model of the  $\pi$ -electron system. We shall find that this approach permits the absolute MCD signs to be derived from a relative size of two orbital energy differences. For most molecules, this relative size is obvious from molecular structure and qualitative theoretical notions, so that absolute MCD sign predictions for a very large number of molecules become easily possible without any calculations

whatever, and general rules for substituent effects and the like can be formulated.

The present analysis is accompanied by a series of experimental papers which present results for selected cyclic  $\pi$  systems and illustrate the various predictions reached. The general layout of this series of papers is as follows. The first two papers present the general theory for purely electronic MCD signs and discuss the approximations used. In the present paper (part 1), expressions for the  $A$  and  $B$  terms of a symmetrically perturbed  $(4N + 2)$ -electron  $[n]$ annulene with a threefold or higher axis of symmetry are derived. In part 2,<sup>42</sup> expressions for the  $B$  terms of a perturbed  $(4N + 2)$ -electron  $[n]$ annulene of low symmetry (no degenerate states) are derived. Those interested only in application of the results to organic molecules may find it profitable to skip most of the derivations in parts 1 and 2. Part 3<sup>43</sup> is nonmathematical and requires only a knowledge of the basic principles of PMO theory.<sup>44</sup> It proposes a general classification of chromophores with a  $(4N + 2)$ -electron perimeter and derives rules for substituent effects on MCD spectra of various types of such  $\pi$  systems. Part 4<sup>45</sup> shows that the aza analogues of benzene show very weak MCD bands, as expected for purely inductive substitution on a  $(4N + 2)$ -electron  $[4N + 2]$ annulene and in contrast to the large effects of mesomeric substitution on such annulenes. Effects of simultaneous inductive and mesomeric substitution on benzene are investigated in part 5,<sup>46</sup> and some very strongly perturbed derivatives, such as the pyridones, are considered in part 6.<sup>47</sup> We then turn to polycyclic benzenoid hydrocarbons and find the expected dramatic effects of perturbations on these odd-soft<sup>43</sup> chromophores. Aza replacement (part 7<sup>48</sup>), substitution

(part 8<sup>49</sup>), and simultaneous aza and amino substitution (part 9<sup>50</sup>) on naphthalene are explored first; some more distantly related heterocycles such as the quinolones are taken up in part 10.<sup>51</sup> Aza and substituted derivatives of anthracene (part 11<sup>52</sup>) as well as aza analogues of phenanthrene (part 12<sup>53</sup>) show the expected large effects of perturbations. A striking sensitivity of MCD signs of pyrene to aza replacement has already been reported;<sup>35</sup> in part 13<sup>54</sup> we find the expected analogous structural sensitivity for the effect of mesomeric substitution. After benzenoid hydrocarbons, we turn attention to azulene, which is a borderline case between an even-soft<sup>43</sup> and a positive-hard<sup>43</sup> chromophore. Its alkyl derivatives (part 14<sup>55</sup>) and benzo analogues (part 15<sup>56</sup>) behave as predicted. The expected lack of sensitivity to perturbations in a hard<sup>43</sup> chromophore is then demonstrated on derivatives of acenaphthylene in part 16<sup>57</sup> and of fluoranthene in part 17,<sup>58</sup> as well as on three benzofluoranthenes in part 18.<sup>59</sup>

In a sequel to the present group of papers, we shall show that tropolones,<sup>60</sup> five-membered ring heterocycles analogous to indene<sup>61</sup> and fluorene<sup>62</sup> and isoelectronic with the indenide<sup>63</sup> and fluorenyl<sup>64</sup> anions, as well as various additional heterocycles<sup>65</sup> can also be viewed as perturbed annulenes and their observed MCD signs can be understood accordingly. In summary, we believe that it will be generally profitable to use the  $\pi$ -perimeter model for all cyclic  $\pi$ -electron systems derivable, at least remotely, from a  $(4N + 2)$ -electron perimeter, and we are currently engaged in investigations of more complex substituted heterocycles such as flavins, pteridines, and purines, in search for the limits of the simple approach.

An additional result of the present series of investigations is an improved understanding of the number and nature of the electronic states of the chromophores involved. New excited states are identified in phenanthrene,<sup>53</sup> azulene,<sup>55</sup> and acenaphthylene;<sup>57</sup> identification of the states of  $\gamma$ -pyridone,<sup>47</sup> pyrene,<sup>54</sup> and of the two presumed  $n\pi^*$  states of phthalazine<sup>48</sup> is improved, states of three benzofluoranthenes<sup>59</sup> are assigned, and last but not least, a more reliable assignment of the much disputed  $L_b$  band of anthracene is reached.<sup>52</sup>

## Results and Discussion

**1. General Considerations.**<sup>66</sup> An MCD spectrum is a plot of magnetically induced molar ellipticity  $[\theta]_M$  per unit magnetic field (deg L m<sup>-1</sup> mol<sup>-1</sup> G<sup>-1</sup>) against some measure of photon energy. Each electronic transition makes a contribution to  $[\theta]_M$ . For an isotropic sample, this is given by

$$[\theta]_M = -21.3458[f_2(B + C/kT) + f_1A]$$

where the line shape function  $f_2$  is that of an absorption line, while  $f_1$  corresponds to a derivative of an absorption line, i.e., is s-shaped.  $A$  ( $D^2 \beta_c$ ),  $B$  ( $D^2 \beta_c/cm^{-1}$ ) and  $C$  are the Faraday parameters of the transition ( $C/kT$  is in units of  $D^2 \beta_c/cm^{-1}$ ,  $T$  is absolute temperature). The MCD spectrum contains a sum of these contributions from all transitions. In a molecule with a nondegenerate ground state,  $C$  vanishes, and this is the case for all molecules of interest to us now. If the excited state is nondegenerate,  $A$  vanishes as well, so that for the vast majority of organic molecules, the electronic part of the MCD effect of any transition is characterized by its  $B$  term alone. Note that a positive contribution to the ellipticity  $[\theta]_M$  will be provided by a transition with a negative  $B$  term and vice versa. In the absence of strong vibronic effects, the shape imparted to the MCD spectrum by the  $B$  term of a transition is the same as the shape of its absorption band.

In molecules with a threefold or higher symmetry axis, an excited state may be degenerate and  $A$  then need not vanish. The contribution of the transition to  $[\theta]_M$  then consists of (i) a positive ( $B < 0$ ) or negative ( $B > 0$ ) band of absorption-like shape centered at the position of the absorption band and (ii) a superimposed s-like shape centered at the position of the

absorption band, with a positive wing at lower energies and a negative one at higher energies ( $A < 0$ ) or with a negative wing at lower energies and a positive one at higher energies ( $A > 0$ ).

Because of the complicated structure of many absorption bands and their frequent mutual overlap, it is often difficult to obtain reliable experimental values for the  $A$  and  $B$  terms. The best procedure is the method of moments:

$$A = 33.53^{-1} \int d\tilde{\nu}(\tilde{\nu} - \tilde{\nu}_0)[\theta]_M/\tilde{\nu}$$

$$B = -33.53^{-1} \int d\tilde{\nu}[\theta]_M/\tilde{\nu}$$

where  $\tilde{\nu}$  is wavenumber and  $\tilde{\nu}_0$  is the center of the absorption band (in isotropic solution).

It is customary to characterize the MCD effect of a transition by the quantities  $A/D$  and  $B/D$ , where  $D$  is the dipole strength of the transition. Using ordinary first-order perturbation theory for the effect of the magnetic field,  $A/D$  can be expressed as

$$\frac{A(G \rightarrow F)}{D(G \rightarrow F)} = \frac{\langle F_i | \hat{M} | F_i \rangle \cdot \text{Im}\{ \langle G | \hat{M} | F_i \rangle \times \langle F_i | \hat{M} | G \rangle \}}{2 | \langle G | \hat{M} | F_i \rangle |^2} = -\mu/2$$

$$i = 1 \text{ or } 2$$

for a transition from a nondegenerate ground state  $G$  to a doubly degenerate state  $F$ , where  $F_1$  and  $F_2$  are the two complex components of  $F$  which diagonalize the component of  $\hat{M}$  along the symmetry axis and  $\mu$  is the magnetic moment of the excited state.  $\text{Im}$  stands for "imaginary part of",  $\hat{M} = \sum_i \hat{m}_i$  is the electric dipole moment operator, and  $\hat{M} = \sum_i \hat{m}_i$  is the magnetic dipole moment operator ( $i$  runs over all electrons).

The quantity  $B/D$  is expressed as a sum of contributions  $B_{l,G}^F$  due to magnetic mixing of electronic states  $l \neq F$  into the ground state, a contribution  $B_{F,G}^F + B_{G,F}^F$  due to mutual magnetic mixing of the ground and final states, and, usually most important, contributions  $B_{l,F}^F$  due to magnetic mixing of molecular states  $l \neq G$  into the final state:

$$\frac{B(G \rightarrow F)}{D(G \rightarrow F)} = \left[ \sum_{l,l \neq G,F} B_{l,G}^F + (B_{F,G}^F + B_{G,F}^F) + \sum_{l,l \neq G,F} B_{l,F}^F \right] / | \langle G | \hat{M} | F \rangle |^2$$

$$B_{l,G}^F = \text{Im}\{ \langle l | \hat{M} | G \rangle \cdot \langle G | \hat{M} | F \rangle \times \langle F | \hat{M} | l \rangle / [W(l) - W(G)] \}$$

$$B_{F,G}^F + B_{G,F}^F = \text{Im}\{ \langle F | \hat{M} | G \rangle \cdot \langle G | \hat{M} | F \rangle \times (\langle F | \hat{M} | F \rangle - \langle G | \hat{M} | G \rangle) / [W(F) - W(G)] \}$$

$$B_{l,F}^F = \text{Im}\{ \langle F | \hat{M} | l \rangle \cdot \langle G | \hat{M} | F \rangle \times \langle l | \hat{M} | G \rangle / [W(l) - W(F)] \}$$

where the sums run over all molecular electronic states  $l$  except as indicated and  $W(J)$  is the energy of  $J$ th state. Throughout, the state wave functions are those of the molecule in the absence of the magnetic field.

**2. MCD of Perturbed  $(4N + 2)$ -Electron  $[n]$ Annulenes. The Procedure.** For an a priori derivation of general rules, we need a model simple enough to permit an algebraic solution, yet realistic enough to correctly describe the fundamental physics of the MCD phenomenon. We propose that the classical  $\pi$ -perimeter model<sup>4,67,68</sup> satisfies these requirements. Derivation of explicit algebraic expressions for  $A$  and  $B$  terms is based on the neglect of all terms of third or higher order in overlap  $S$  and proceeds as follows.

For the parent  $(4N + 2)$ -electron  $[n]$ annulenes, we define a basis set of nonorthogonal  $2p_z$ -type orbitals along the periphery of a circle whose center is the origin of the coordinate system, define matrix elements of the one-electron electric ( $\hat{m}$ )

and magnetic ( $\hat{\mu}$ ) dipole moment operators employing the Linderberg relation<sup>69</sup> and assuming that the ratio of the matrix element of  $\hat{\mu}$  between next-nearest-neighbor Löwdin AO's to that for nearest neighbors is  $-0.15$ , as suggested by direct integration for STO's (see Appendix), transform to a basis of Löwdin-orthogonalized<sup>70</sup> AO's for which the zero differential overlap approximation is known to be reasonable,<sup>71</sup> determine MO's  $\psi_k$  by symmetry ( $k$  is the angular momentum quantum number), use configuration interaction among all single excitations from the HOMO (highest occupied MO) to the LUMO (lowest unoccupied MO) for construction of the singlet wave functions of the L and B states, and use the latter to evaluate  $A$  and  $B$  terms. For molecules derived from the parent circular  $(4N + 2)$ -electron annulenes by geometric in-plane distortions, by transannular cross-linking, by union with inside fragments containing one or more atoms in conjugation (bridging), by replacement of carbon atoms by heteroatoms, and by attachment of substituents on the ring, we start with the result for the unperturbed perimeter, disregard the effect of changes in molecular geometry and in MO coefficients, and analyze the effects of the perturbation on the mixing of configurations. It will be seen that in the final analysis, the effect of a perturbation on the MCD signs is simply related to its effect on MO energies.

Possible effects of magnetic mixing of states such as  $\sigma\pi^*$  and  $n\pi^*$  into the ground state or into the  $\pi\pi^*$  states on the  $B$  terms will be ignored. The justification for this is mostly empirical and is discussed in part 2.<sup>42</sup>

**3. Algebraic Solution of the  $\pi$ -Perimeter Model for MCD of a Regular-Polygon  $(4N + 2)$ -Electron  $[n]$ Annulene.** The following results for the matrix elements of  $\hat{\mathbf{M}}$  and  $\hat{\mathcal{M}}$  in the configuration basis are obtained ( $C_n$  symmetry group).

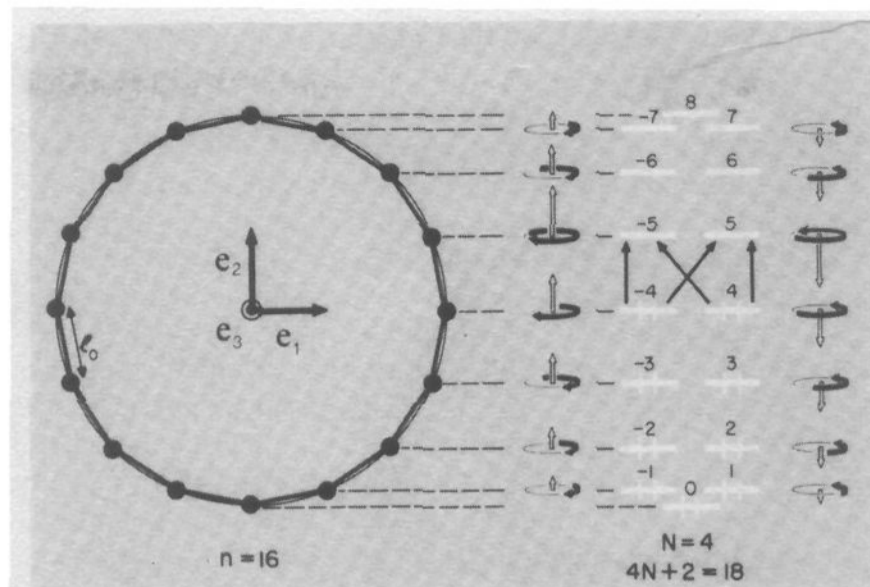
(i) **2-Electron  $[n]$ Annulenes ( $N = 0$ ).** The HOMO,  $\psi_0$ , is of symmetry A and is not degenerate. The LUMO,  $\psi_1$  and  $\psi_{-1}$ , is degenerate and belongs to the complex representations  $\epsilon_1$  and  $\epsilon_1^*$ . Single HOMO  $\rightarrow$  LUMO excitation from  $\Psi_G$  produces two singlet configurations  $\Psi_0^1$  and  $\Psi_0^{-1}$ . The only nonvanishing matrix elements of  $\hat{\mathbf{M}}$  and  $\hat{\mathcal{M}}$  involving these three configurations are

$$\begin{aligned} \langle \Psi_G | \hat{\mathbf{M}} | \Psi_0^1 \rangle &= \sqrt{2}m(n,1) \cdot \mathbf{e}^+ \\ \langle \Psi_G | \hat{\mathbf{M}} | \Psi_0^{-1} \rangle &= \sqrt{2}m(n,1) \cdot \mathbf{e}^- \\ -\langle \Psi_0^{-1} | \hat{\mathcal{M}} | \Psi_0^{-1} \rangle &= \langle \Psi_0^1 | \hat{\mathcal{M}} | \Psi_0^1 \rangle = \mu^-(n,0) \cdot \mathbf{e}_3 \end{aligned}$$

The symbols  $m(i,j)$  and  $\mu(i,j)$  are defined below,  $\mathbf{e}_1 \times \mathbf{e}_2 = \mathbf{e}_3$ ,  $\mathbf{e}_1$ ,  $\mathbf{e}_2$ , and  $\mathbf{e}_3$  are unit vectors with  $\mathbf{e}_1$  going through an atom and  $\mathbf{e}_3$  perpendicular to the molecular plane,  $\mathbf{e}^+ = (\mathbf{e}_1 + i\mathbf{e}_2)/\sqrt{2}$ , and  $\mathbf{e}^- = (\mathbf{e}_1 - i\mathbf{e}_2)/\sqrt{2}$ . In  $\Psi_G \rightarrow \Psi_0^1$  a photon with an  $e_3$  component of angular momentum  $\hbar$  must be absorbed, so that the transition is LHC polarized; in  $\Psi_G \rightarrow \Psi_0^{-1}$  a  $-\hbar$  photon is absorbed, so that the transition is RHC polarized (we take  $\mathbf{e}_3$  to be the light propagation direction as well as the direction of the magnetic field). The excited configuration  $\Psi_0^1$  has a negative  $e_3$  component of the magnetic moment, while  $\Psi_0^{-1}$  has a positive magnetic moment, so that in the magnetic field,  $\Psi_0^{-1}$  lies below  $\Psi_0^1$ , and we anticipate  $A/D > 0$  in analogy to the atomic Zeeman effect.

(ii)  **$(4N + 2)$ -Electron  $[2(N + 1)]$ Annulenes.** In this case, the HOMO,  $\psi_N$  and  $\psi_{-N}$ , is degenerate and belongs to the complex representations  $\epsilon_N$  and  $\epsilon_N^*$ , while the nondegenerate LUMO,  $\psi_{N+1}$ , belongs to the B representation. Single HOMO  $\rightarrow$  LUMO excitation from  $\Psi_G$  produces two singlet configurations  $\Psi_N^{N+1}$  and  $\Psi_{-N}^{N+1}$ . The only nonvanishing matrix elements of  $\hat{\mathbf{M}}$  and  $\hat{\mathcal{M}}$  involving these three configurations are

$$\begin{aligned} \langle \Psi_G | \hat{\mathbf{M}} | \Psi_N^{N+1} \rangle &= \sqrt{2}m(2N+2,2N+1) \cdot \mathbf{e}^+ \\ \langle \Psi_G | \hat{\mathbf{M}} | \Psi_{-N}^{N+1} \rangle &= \sqrt{2}m(2N+2,2N+1) \cdot \mathbf{e}^- \\ -\langle \Psi_{-N}^{N+1} | \hat{\mathcal{M}} | \Psi_{-N}^{N+1} \rangle &= \langle \Psi_N^{N+1} | \hat{\mathcal{M}} | \Psi_N^{N+1} \rangle \\ &= \mu^-(2N+2,N) \cdot \mathbf{e}_3 \end{aligned}$$



**Figure 1.** Geometry and MO occupancy for a  $(4N + 2)$ -electron  $[n]$ annulene,  $C_{16}H_{16}^{2-}$ . For each MO, the angular momentum quantum number  $k$  is given and the sense and amount of electron circulation and of the resulting orbital magnetic moment are shown schematically. The MO's  $\psi_0$  and  $\psi_8$  have no net electron circulation and no magnetic moment.

Remembering that absorption of a LHC ( $+\hbar$ ) photon always increases the orbital angular momentum quantum number  $k$ , while absorption of a RHC ( $-\hbar$ ) photon decreases it, we can again attach simple physical significance to these results. The LHC-polarized  $\Psi_N^{N+1}$  has a positive  $e_3$  component of the magnetic moment, and the RHC-polarized  $\Psi_{-N}^{N+1}$  a negative one, in the magnetic field  $\Psi_N^{N+1}$  lies below  $\Psi_{-N}^{N+1}$ , and we anticipate  $A/D < 0$ . In general, an excitation from a nondegenerate closed-shell ground state to a degenerate final state in which the angular momentum of an electron is increased will have  $A > 0$ , and an excitation in which angular momentum of an electron is decreased or, in an alternative description, that of a hole increased, will have  $A < 0$ .

(iii) **The General Case:  $0 < N < n/2 - 1$ .** In this case, which requires  $n \geq 5$ , both the HOMO,  $\psi_N$  and  $\psi_{-N}$  (representations  $\epsilon_N$  and  $\epsilon_N^*$  of the  $C_n$  group), and the LUMO,  $\psi_{N+1}$  and  $\psi_{-N-1}$  (representations  $\epsilon_{N+1}$  and  $\epsilon_{N+1}^*$ ), are degenerate. Single HOMO  $\rightarrow$  LUMO excitation from  $\Psi_G$  produces four singlet configurations (Figure 1),  $\Psi_N^{N+1}$ ,  $\Psi_{-N}^{N+1}$ ,  $\Psi_{-N}^{N-1}$ , and  $\Psi_N^{N-1}$ , which transform like  $\epsilon_1$ ,  $\epsilon_1^*$ ,  $\epsilon_{2N+1}$ , and  $\epsilon_{2N+1}^*$ , respectively. The only nonvanishing matrix elements of  $\hat{\mathbf{M}}$  and  $\hat{\mathcal{M}}$  involving these five configurations are

$$\begin{aligned} \langle \Psi_G | \hat{\mathbf{M}} | \Psi_N^{N+1} \rangle &= \sqrt{2}m(n,2N+1) \cdot \mathbf{e}^+ \\ \langle \Psi_G | \hat{\mathbf{M}} | \Psi_{-N}^{N+1} \rangle &= \sqrt{2}m(n,2N+1) \cdot \mathbf{e}^- \\ -\langle \Psi_{-N}^{N-1} | \hat{\mathcal{M}} | \Psi_{-N}^{N-1} \rangle &= \langle \Psi_N^{N+1} | \hat{\mathcal{M}} | \Psi_N^{N+1} \rangle = \mu^-(n,N) \cdot \mathbf{e}_3 \\ -\langle \Psi_N^{N-1} | \hat{\mathcal{M}} | \Psi_N^{N-1} \rangle &= \langle \Psi_{-N}^{N+1} | \hat{\mathcal{M}} | \Psi_{-N}^{N+1} \rangle = \mu^+(n,N) \cdot \mathbf{e}_3 \end{aligned}$$

Now, both an electron and a hole acquire finite angular momentum upon excitation. The nondegenerate  $\Psi_G$  has no magnetic moment, and excited configurations have a magnetic moment equal to the sum of the moments of the electron in its new orbital and of the hole in its new orbital.

In the special but important case of a  $(4N + 2)$ -electron  $[4N + 2]$ annulene,  $2N + 1$  is equal to  $n/2$  and representations  $\epsilon_{2N+1}$  and  $\epsilon_{2N+1}^*$  do not exist in the  $C_n$  group. Instead,  $\Psi_N^{N+1}$  and  $\Psi_{-N}^{N-1}$  belong to the B representation and interact through the two-electron part of the Hamiltonian. Their symmetry adaptation to the full  $D_{nh}$  group of the  $[n]$ annulene will be considered below.

The sense-preserving excitations  $\Psi_G \rightarrow \Psi_N^{N+1}$  and  $\Psi_G \rightarrow \Psi_{-N}^{N-1}$ , in which the circulation directions of the hole and of

the electron are identical and their magnetic moments opposed, yield excited configurations with small magnetic moments,  $\mu^-(n,N)$  and  $-\mu^-(n,N)$ , respectively. The sense-reversing excitations  $\Psi_G \rightarrow \Psi_N^{N+1}$  and  $\Psi_G \rightarrow \Psi_N^{N-1}$ , in which the electron and the hole circulate in opposite directions, so that their magnetic moments add up, yield excited states with large magnetic moments  $\mu^+(n,N)$  and  $-\mu^+(n,N)$ , respectively (cf. Figure 1). Only the sense-preserving excitations (excited state of  $E_1$  symmetry) are electric dipole allowed:  $\Psi_G \rightarrow \Psi_N^{N+1}$  is LHC polarized,  $\Psi_G \rightarrow \Psi_N^{N-1}$  is RHC polarized. We anticipate  $A/D > 0$  if  $W(\Psi_N^{N-1}) < W(\Psi_N^{N+1})$  in the magnetic field, i.e., if  $\mu^-(n,N) < 0$  (electron-dominated magnetic moment), and  $A/D < 0$  if  $W(\Psi_N^{N-1}) > W(\Psi_N^{N+1})$  in the field, i.e., if  $\mu^-(n,N) > 0$  (hole-dominated magnetic moment).

The magnetic moments  $\mu^-(n,N)$  and  $\mu^+(n,N)$  introduced in the above expressions play a key role in the MCD of most  $(4N + 2)$ -electron  $[n]$ annulenes. Introducing the net charge in the  $\pi$  system  $q = n - (4N + 2)$ , using the units of Bohr magneton  $\beta_e$  for  $\mu$ , Å for the distance between neighboring atoms ( $l_0$ ), and eV for the resonance integral between neighbors in the Löwdin basis ( $\beta_1$ ), and separating the "nearest-neighbor current" ( $\mu_1$ ) and "next-nearest-neighbor current" ( $\mu_2$ ) contributions to the magnetic moments where applicable, they are given by

$$\mu^-(3,0) = -0.065|\beta_1|l_0^2/(1+S)$$

$$\mu^-(4,0) = -\mu(4,1) = -0.13|\beta_1|l_0^2$$

$$\mu^-(n,N) = \mu_1^-(n,N) + \mu_2^-(n,N) \quad n \geq 5$$

$$\mu^+(n,N) = \mu_1^+(n,N) + \mu_2^+(n,N) \quad n \geq 5$$

$$\mu_1^-(n,N) = -0.26|\beta_1|l_0^2 \cos(\pi/n) \sin(\pi q/2n)$$

$$\mu_2^-(n,N) = -0.078|\beta_1|l_0^2 \cos^2(\pi/n) \cos(\pi q/n)$$

$$\mu_1^+(n,N) = -0.26|\beta_1|l_0^2 \cot(\pi/n) \cos(\pi/n) \cos(\pi q/2n)$$

$$\mu_2^+(n,N) = 0.039|\beta_1|l_0^2 \cot(\pi/n) \cos(2\pi/n) \sin(\pi q/n)$$

If  $n$  is even,  $q$  is even, its limits are  $2 - n \leq q \leq n - 2$ , both  $q$  and  $-q$  are possible charges,  $\mu_1^-(q) = -\mu_1^-(-q)$ ,  $\mu_2^+(q) = -\mu_2^+(-q)$ , so that  $\mu_1^- = \mu_2^+ = 0$  if  $q = 0$ , and  $\mu_1^+(q) = \mu_1^+(-q)$ ,  $\mu_2^-(q) = \mu_2^-(-q)$ . The resulting pairing properties of the  $+q$ - and  $-q$ -charged versions of the perimeter are of the form required<sup>72</sup> by the pairing theorem for alternant systems. If  $n$  is odd,  $q$  is odd, its limits are  $4 - n \leq q \leq n - 2$ , and  $q$  and  $-q$  cannot both be admissible charges for a  $(4N + 2)$ -electron system; there are no analogous pairing properties for such a nonalternant ring. Inspection of the above expressions shows that

$$\mu^- < 0 \quad \text{if } q \geq 0$$

$$\mu^- < 0 \quad \text{if } q \text{ is weakly negative, particularly if } n \text{ is large}$$

$$\mu^- > 0 \quad \text{if } q \text{ is at or near its maximum possible negative value}$$

Using  $|\beta_1| = 2.4$  eV and  $l_0 = 1.4$  Å, direct substitution leads to the values shown in Figure 2.

The values of  $m(i,j)$  are

$$m(3,1) = -el_0(1 + 9S^2/8)/\sqrt{6}$$

$$m(4,1) = m(4,3) = -el_0(1 + S^2/2)/2$$

$$m(n,j) = [-el_0/2\sqrt{2} \sin(\pi/n)] \times [1 + 2S^2 \sin^2(\pi/n) \sin^2(\pi j/n)] \quad n > 4$$

where  $e > 0$  is the magnitude of electron charge.

In the unperturbed annulene, the Hamiltonian is diagonal in the configuration basis. Only in the case of a  $(4N + 2)$ -electron  $[4N + 2]$ annulene, the two configurations of B symmetry in the  $C_n$  group,  $\Psi_N^{N+1}$  and  $\Psi_N^{N-1}$ , will interact through

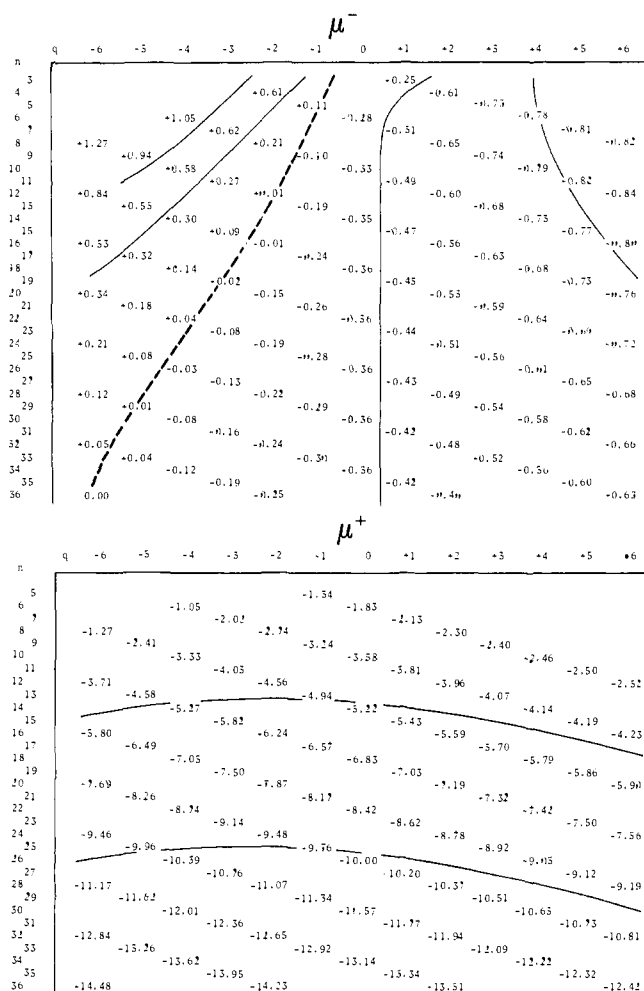


Figure 2. Magnetic moments  $\mu^-$  and  $\mu^+$  in units of  $\beta_e$  for various  $(4N + 2)$ -electron  $[n]$ annulenes ( $q =$  net charge), assuming  $|\beta_2|/|\beta_1| = 0.15$ .

an electron-repulsion term. In the full  $D_{nh}$  symmetry of the problem, the mixing is determined by symmetry. A  $B_{2u}$  state and a  $B_{1u}$  state result, of which the former is well-known<sup>4,67</sup> to be of lower energy.

A summary of state labels, wave functions chosen as eigenfunctions of  $\hat{M}$  wherever possible and real otherwise, and symmetries, arranged in order of increasing energy, is shown in Chart I.

#### Chart I

(i) 2-Electron $[n]$ Annulene or $(4N + 2)$ -Electron $[2(N + 1)]$ Annulene			
		$C_n$	$D_{nh}$
$\Phi(G):$	$\Psi_G$	A	$A_{1g} (A_1')$
$B \left\{ \begin{array}{l} \Phi(B'): \\ \Phi(B''): \end{array} \right.$	$\Psi_0^1$ or $\Psi_N^{N+1}$ $\Psi_0^{-1}$ or $\Psi_N^{N-1}$	$\epsilon_1$ $\epsilon_1^*$	$E_{1u} (E_1')$
(ii) $(4N + 2)$ -Electron $[4N + 2]$ Annulene			
$\Phi(G):$	$\Psi_G$	A	$A_{1g}$
$\Phi(L_b):$	$(\Psi_N^{N+1} - \Psi_N^{N-1})/i\sqrt{2}$	B (nodes through atoms)	$B_{2u}$
$\Phi(L_a):$	$(\Psi_N^{N+1} + \Psi_N^{N-1})/\sqrt{2}$	B (nodes through bonds)	$B_{1u}$
$B \left\{ \begin{array}{l} \Phi(B'): \\ \Phi(B''): \end{array} \right.$	$\Psi_N^{N+1}$ $\Psi_N^{N-1}$	$\epsilon_1$ $\epsilon_1^*$	$E_{1u}$
(iii) General $(4N + 2)$ -Electron $[n]$ Annulene ( $0 < N < n/2 - 1, 4N + 2 \neq n$ )			
$\Phi(G):$	$\Psi_G$	A	$A_{1g} (A_1')$
$L \left\{ \begin{array}{l} \Phi(L'): \\ \Phi(L''): \end{array} \right.$	$\Psi_N^{N+1}$ $\Psi_N^{N-1}$	$\epsilon_{2N+1}$ $\epsilon_{2N+1}^*$	$E_{2N+1,u} (E_{2N+1}')$
$B \left\{ \begin{array}{l} \Phi(B'): \\ \Phi(B''): \end{array} \right.$	$\Psi_N^{N+1}$ $\Psi_N^{N-1}$	$\epsilon_1$ $\epsilon_1^*$	$E_{1u} (E_1')$

In the case of a  $(4N + 2)$ -electron  $[4N + 2]$ annulene, it is also customary to use the real functions  $\Phi(\mathbf{B}_b) = (\Psi_N^{N+1} - \Psi_{-N}^{-N-1})/i\sqrt{2}$  and  $\Phi(\mathbf{B}_a) = (\Psi_N^{N+1} + \Psi_{-N}^{-N-1})/\sqrt{2}$ .

The dipole strength of the allowed transition is

$$D(G \rightarrow B) = |\langle G | \hat{M} | B' \rangle|^2 + |\langle G | \hat{M} | B'' \rangle|^2 = 4m^2(n, 2N+1)$$

The formulas for  $A$  and  $B$  terms yield a general prediction for the purely electronic contributions:

$$A(G \rightarrow L) = B(G \rightarrow L) = B(G \rightarrow B) = 0$$

$$\frac{A(G \rightarrow B)}{D(G \rightarrow B)} = -\frac{\mu^-(n, N)}{2}$$

so that the magnetic moment of the  $B$  state is  $-2A/D = \mu^-(n, N)$ . The magnetic moment of the  $L$  state,  $\mu^+(n, N)$ , is high, but its  $A$  term vanishes, since the dipole strength from the ground state is zero (this state is absent if  $N = 0$  or  $n/2 - 1$ ).

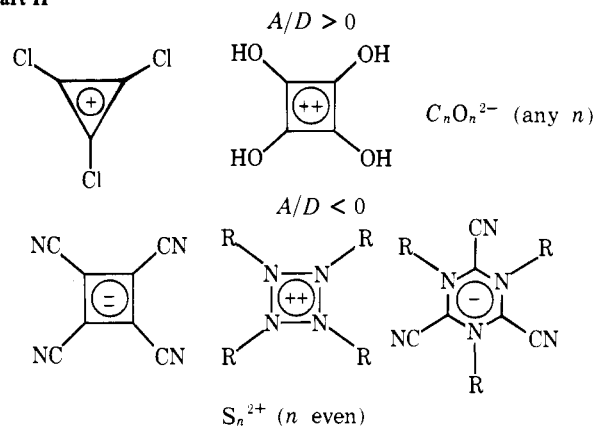
The experimental intensity of the absorption and the MCD effects of the  $G \rightarrow L$  transition are quite weak but nonzero and suggest a large magnetic moment in agreement with the perimeter model. Since all of the effect is due to vibronic intensity borrowing from the  $B$  state, neglected in the present treatment, no meaningful comparison is possible. Since either or both components of the  $L$  transition can easily acquire a positive or a negative MCD sign upon suitable perturbation, we shall refer to MCD chromophores of this type as "double-soft" in the classification scheme described in part 3.<sup>43</sup>

For the  $B$  state, the neglect of vibronic interactions is of little consequence when absorption spectra are discussed, but this is not so for MCD of annulenes which have both  $L$  and  $B$  states. The expected purely electronic excited state magnetic moment  $\mu^-$  of the  $B$  state is so small that vibronic borrowing of the large magnetic moment  $\mu^+$  from the  $L$  state is likely to have considerable influence on the observed spectra. The complex shapes of the MCD curve in the region of the  $G \rightarrow B$  transition observed for benzene<sup>73</sup> and the tropylium cation<sup>60</sup> might result from such magnetic moment borrowing, and the apparently uncomplicated small  $A$  term of the  $C_9H_9^-$  anion ( $-2A/D = -0.34$ )<sup>63</sup> is probably partially due to it as well. All that can be said from purely electronic calculations is that our predicted  $\mu^-$  values are of the right order of magnitude. A general consideration of the vibronic effects in  $(4N + 2)$ -electron  $[4N]$ -annulenes and  $[4N + 2]$ annulenes published some time ago<sup>74</sup> points the way to further progress in the algebraic approach to the problem, and recent numerical computations for the case of benzene are also of considerable interest.<sup>39,41,75</sup> We shall briefly return to vibronic interactions in section 5.

The predicted  $A$  terms of the  $G \rightarrow B$  transition in 2-electron  $[n]$ annulenes (positive) and in  $(4N + 2)$ -electron  $[2(N + 1)]$ annulenes (negative) should not be subject to these uncertainties. No experimental data appear to be available for 2-electron annulenes, but three inorganic analogues of the 6-electron  $[4]$ annulene dianion have been investigated and all show the expected small negative  $A$  terms for the transition assigned as  $G \rightarrow B$  in our notation. The reported  $-2A/D$  values are  $0.66 \beta_e$  for  $Se_4^{2+}$  and  $0.50 \beta_e$  for  $Te_4^{2+}$ ;<sup>76</sup> no numerical value was given for  $S_4^{2+}$ .<sup>77</sup>

**4. Algebraic Description of the Effect of Structural Perturbations on the MCD of a  $(4N + 2)$ -Electron  $[n]$ Annulene.** We shall neglect the effect of perturbations on MO's other than the mixing within degenerate pairs, with obvious justification as well as limitations. The perturbations considered here either preserve the  $n$ -fold rotation axis of the AO framework of the parent  $[n]$ annulene or convert it to a  $(n/m)$ -fold axis, where  $m \neq 1$  is an integer such that  $n/m \geq 3$  (see part 2<sup>42</sup> for other types of perturbations). In the new group  $C_{n/m}$ , the  $\epsilon_{2N+1}$ ,  $\epsilon_{2N+1}^*$  representation remains  $\epsilon_{2N+1}$ ,  $\epsilon_{2N+1}^*$  ( $2N + 1$  is to be taken

Chart II



modulo  $n/m$ , i.e., ignoring integer multiples of  $n/m$ ) if such a representation exists in the subgroup  $C_{n/m}$ ; otherwise it decomposes; if  $2N + 1$  is an odd integer multiple of  $n/2m$ , it produces  $2 \times B$ , and if  $2N + 1$  is an even integer multiple of  $n/2m$ , it produces  $2 \times A$ . The two species of  $B$  symmetry which are present for a  $(4N + 2)$ -electron  $[4N + 2]$ annulene remain  $2 \times B$  in the subgroup  $C_{n/m}$  if  $m$  is odd and they become  $2 \times A$  if  $m$  is even.

For  $0 < N < n/2 - 1$ , we shall find it useful to introduce the symbols  $\Delta\text{HOMO}$  for the absolute value of the energy difference of the two orbitals of the perturbed annulene which originate in the HOMO orbitals of the parent ( $\psi_N, \psi_{-N}$ ) and  $\Delta\text{LUMO}$  for that of the two orbitals which originate in the LUMO orbitals of the parent ( $\psi_{N+1}, \psi_{-N-1}$ ).

(i) **Highly Symmetrical Perturbed 2-Electron  $[n]$ Annulenes and  $(4N + 2)$ -Electron  $[2(N + 1)]$ Annulenes.** As long as we neglect the effect of the perturbation on the matrix elements of  $\hat{m}$  and  $\hat{\mu}$  over the MO's, the perturbation has no effect on the expected MCD spectrum:

$$\frac{A(G \rightarrow B)}{D(G \rightarrow B)} = -\frac{\mu^-(n, N)}{2} \quad B(G \rightarrow B) = 0$$

Thus,  $A/D$  for the  $B$  band of a 2-electron  $[n]$ annulene is positive, and  $A/D$  for the  $B$  band of a  $(4N + 2)$ -electron  $[2(N + 1)]$ annulene is negative, regardless of perturbations, as long as a threefold or higher symmetry axis is preserved.

Some specific examples of predicted signs are shown in Chart II, but experimental verification may be difficult, since the  $B$  band is expected at relatively high energies (however, see Note Added in Proof).

(ii) **General Results for Perturbed  $(4N + 2)$ -Electron  $[n]$ -Annulenes ( $0 < N < n/2 - 1$ ). Double-Soft Chromophores ( $\Delta\text{HOMO} = \Delta\text{LUMO} = 0$ ;** neither  $N$  nor  $N + 1$  is an integer multiple of  $n/2m$ ). This situation occurs whenever the  $n$ -fold axis is preserved ( $m = 1$ ) and in most other cases, with exceptions listed in Table I up to  $n = 22$ . Since  $L$  is of symmetry other than  $E_1$ , the Hamiltonian matrix is already diagonal and configuration interaction is absent, except possibly for producing nondegenerate  $L_b$  and  $L_a$  states, and sense-preserving and sense-reversing excitations do not mix, just as in the parent annulene. The resulting dipole strengths and  $A$  and  $B$  terms are identical with those of the unperturbed parent annulenes. For all molecules and ions of this type for which experimental data are available, very small positive values of  $A(G \rightarrow B)$  are expected. Once again, vibronic effects have to be added to these purely electronic considerations before a meaningful comparison with experimental data is possible, even for the strongly allowed  $G \rightarrow B$  transitions. The order of magnitude is as expected for the purely electronic effect, and even the signs almost always agree. The reported values for  $-2A(G \rightarrow B)/D(G \rightarrow B)$  are as follows:  $C_{16}H_{16}^{2-}$  (probably  $D_{4h}$ ),  $-0.1$ ;<sup>20</sup>  $C_{18}H_{18}$  (probably  $D_{6h}$ ),  $+0.12$ ;<sup>78</sup>  $C_5(CN)_5^-$ ,  $-0.26$ ;<sup>79</sup>  $C_6Cl_6$ ,

**Table I.** Lifting of Orbital Degeneracy in  $[n]$ Annulenes upon Symmetry Reduction  $C_n \rightarrow C_{n/m}$  ( $n/m \geq 3$ )

$(CH)_n$	$n/m$	$k^a$	$\Delta\text{HOMO} \neq 0$	charge required <sup>b</sup>	$\Delta\text{LUMO} \neq 0$
C <sub>8</sub> H <sub>8</sub>	4	2	-2		+2
C <sub>9</sub> H <sub>9</sub>	3	3	-5		-1
C <sub>12</sub> H <sub>12</sub>	3	3	-2		+2
C <sub>12</sub> H <sub>12</sub>	4	2, 4	+2, -6		+6, -2
C <sub>12</sub> H <sub>12</sub>	6	3	-2		+2
C <sub>15</sub> H <sub>15</sub>	3	3, 6	+1, -11		+5, -7
C <sub>15</sub> H <sub>15</sub>	5	5	-7		-3
C <sub>16</sub> H <sub>16</sub>	4	2, 4, 6	+6, -2, -10		+10, +2, -6
C <sub>16</sub> H <sub>16</sub>	8	4	-2		+2
C <sub>18</sub> H <sub>18</sub>	3	3, 6	+4, -8		+8, -4
C <sub>20</sub> H <sub>20</sub>	4	2, 4, 6, 8	+10, +2, -6, -14		+14, +6, -2, -10
C <sub>20</sub> H <sub>20</sub>	5	5	-2		+2
C <sub>20</sub> H <sub>20</sub>	10	5	-2		+2
C <sub>21</sub> H <sub>21</sub>	3	3, 6, 9	+7, -5, -17		+11, -1, -13
C <sub>21</sub> H <sub>21</sub>	7	7	-9		-5

<sup>a</sup> The subscript of the orbital pair  $\psi_k, \psi_{-k}$  which splits. <sup>b</sup> The charge on the annulene required to achieve either  $\Delta\text{HOMO} \neq 0$  or  $\Delta\text{LUMO} \neq 0$ .

-0.36;<sup>21</sup> C<sub>6</sub>Br<sub>6</sub>, -0.42;<sup>21</sup> 1,3,5-C<sub>6</sub>H<sub>3</sub>X<sub>3</sub> (X = Cl, Br, CN, OH, OCH<sub>3</sub>), -0.26 to -0.64;<sup>21</sup> triphenylene, -0.36;<sup>80</sup> coronene, -0.38;<sup>80</sup> 1,7,13-tridehydro[18]annulene, -0.40;<sup>78</sup> [18]annulene trioxide, -0.08.<sup>78</sup>

(iii) **General Results for Perturbed  $(4N + 2)$ -Electron  $[n]$ -Annulenes ( $0 < N < n/2 - 1$ ). Positive-Hard Chromophores ( $\Delta\text{HOMO} \neq 0, \Delta\text{LUMO} = 0$ ;**  $N$  is an integer multiple of  $n/2m$ ). All cases up to  $n = 22$  are listed in Table I. In the  $C_{n/m}$  group, both  $\Psi_N^{N+1}$  and  $\Psi_N^{N-1}$  transform like  $\epsilon_1$  and interact. Their complex conjugates,  $\Psi_N^{-N-1}$  and  $\Psi_N^{-N-1}$ , transform like  $\epsilon_1^*$  and interact analogously. The state wave functions can be written as

$$\begin{aligned}\Phi(G) &= \Psi_G \\ \Phi(B') &= \Psi_N^{N+1} \cos \alpha + \Psi_N^{N-1} \sin \alpha & \epsilon_1 \\ \Phi(B'') &= \Psi_N^{-N-1} \cos \alpha + \Psi_N^{-N-1} \sin \alpha & \epsilon_1^* \\ \Phi(L') &= \Psi_N^{N+1}(-\sin \alpha) + \Psi_N^{N-1} \cos \alpha & \epsilon_1 \\ \Phi(L'') &= \Psi_N^{-N-1}(-\sin \alpha) + \Psi_N^{-N-1} \cos \alpha & \epsilon_1^*\end{aligned}$$

where  $\alpha$  ranges from 0 for the unperturbed system to  $\pi/4$  for the most strongly perturbed. It is related to the energy of the perturbed sense-preserving configurations ( $B$ ), sense-reversing configurations ( $L$ ), and the off-diagonal matrix element of the perturbation connecting the two ( $a$ ):  $\tan 2\alpha = 2|a|/(B - L)$ . The dipole strengths are

$$\begin{aligned}D(G \rightarrow B) &= 4m^2(n, 2N+1) \cos^2 \alpha \\ D(G \rightarrow L) &= 4m^2(n, 2N+1) \sin^2 \alpha\end{aligned}$$

and substitution into the formulas for MCD parameters yields

$$\begin{aligned}\frac{A(G \rightarrow B)}{D(G \rightarrow B)} &= -\frac{\mu^-(n, N) \cos^2 \alpha + \mu^+(n, N) \sin^2 \alpha}{2} \\ \frac{A(G \rightarrow L)}{D(G \rightarrow L)} &= -\frac{\mu^-(n, N) \sin^2 \alpha + \mu^+(n, N) \cos^2 \alpha}{2}\end{aligned}$$

We conclude that the  $A$  terms of both the L and B transitions are positive in all perturbed annulenes of this kind, except perhaps for those rare choices of  $n$  and  $N$  for which  $\mu^-(n, N) > 0$ , and then only as long as the perturbation is very weak. Physically, this makes good sense: the excitation is from a nondegenerate orbital into a degenerate one and it therefore imparts angular momentum to an electron, not to a hole.

For the first time, we also obtain nonvanishing  $B$  terms:

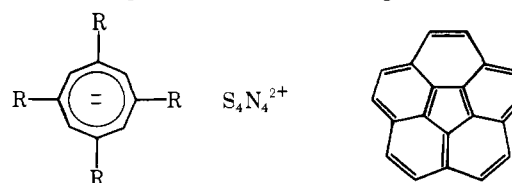
$$\begin{aligned}\frac{B(G \rightarrow B)}{D(G \rightarrow B)} &= (\sin^2 \alpha) \frac{\mu^-(n, N) - \mu^+(n, N)}{W(B) - W(L)} \\ \frac{B(G \rightarrow L)}{D(G \rightarrow L)} &= (-\cos^2 \alpha) \frac{\mu^-(n, N) - \mu^+(n, N)}{W(B) - W(L)}\end{aligned}$$

Since  $\mu^-(n, N) - \mu^+(n, N)$  is positive and  $W(B) > W(L)$ , we expect a positive  $B$  term for the  $G \rightarrow B$  transition and a negative  $B$  term for the  $G \rightarrow L$  transition. Note that the results are independent of the actual ordering of the MO's which resulted from the HOMO of the parent annulene upon perturbation. Thus, perturbations due to electron-withdrawing and electron-donating substituents or heteroatoms lead to the same MCD signs. Experimental data appear to be limited to  $D_{4h}$  porphyrins and phthalocyanins and are discussed in more detail in section 6.

A source of potential difficulty in the evaluation of electronic contributions to  $B$  terms, inherent to all  $\pi$ -electron models, is our neglect of contributions from magnetic mixing with states other than  $\pi\pi^*$ . This point is discussed in more detail in part 2;<sup>42</sup> it appears that the difficulty is not severe and that the  $B$  terms of  $\pi\pi^*$  transitions are dominated by  $\pi\pi^* - \pi\pi^*$  mixing.

As long as  $a$  and  $\alpha$  are reasonably large, e.g., in phthalocyanins, the  $-, +, -, +$  sequence of MCD signs is very unlikely to be disturbed by symmetry-lowering perturbations which convert the  $A$  terms into pairs of  $B$  terms; thus the label "positive-hard". As  $a$  and  $\alpha$  approach zero (e.g., in porphyrins), the chromophore gradually becomes "double-soft".

To illustrate the use of Table I, some predictions of positive  $A/D$  terms of B and L bands for compounds in which HOMO should be nondegenerate and LUMO degenerate are listed:



(iv) **General Results for Perturbed  $(4N + 2)$ -Electron  $[n]$ -Annulenes ( $0 < N < n/2 - 1$ ). Negative-Hard Chromophores ( $\Delta\text{HOMO} = 0, \Delta\text{LUMO} \neq 0$ ;**  $N + 1$  is an integer multiple of  $n/2m$ ). Cases up to  $n = 22$  are listed in Table I. In the  $C_{n/m}$  group, both  $\Psi_N^{N+1}$  and  $\Psi_N^{N-1}$  transform like  $\epsilon_1$  and interact. Their complex conjugates,  $\Psi_N^{-N-1}$  and  $\Psi_N^{N+1}$ , transform like  $\epsilon_1^*$  and interact in an analogous fashion.

Dipole strengths are the same as in the preceding case. The MCD parameters are

$$\frac{A(G \rightarrow B)}{D(G \rightarrow B)} = -\frac{\mu^-(n,N) \cos^2 \beta - \mu^+(n,N) \sin^2 \beta}{2}$$

$$\frac{A(G \rightarrow L)}{D(G \rightarrow L)} = -\frac{\mu^-(n,N) \sin^2 \beta - \mu^+(n,N) \cos^2 \beta}{2}$$

and we conclude that the  $A$  term of the L transition is negative in all perturbed annulenes of this kind, and that of the B transition as well unless the perturbation is very weak (LUMO almost degenerate; in which case vibronic effects may dominate anyway). Physically, this is reasonable: the excitation is from a degenerate orbital into a nondegenerate one, so that it imparts angular momentum to a hole, not to an electron. In this respect, each of the two transitions resembles the B transition of a  $(4N - 2)$ -electron  $[2N]$ annulene.

For the  $B$  terms, we obtain

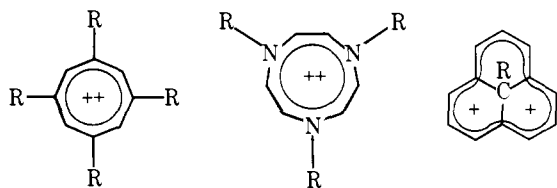
$$\frac{B(G \rightarrow B)}{D(G \rightarrow B)} = (\sin^2 \beta) \frac{\mu^-(n,N) + \mu^+(n,N)}{W(B) - W(L)}$$

$$\frac{B(G \rightarrow L)}{D(G \rightarrow L)} = (-\cos^2 \beta) \frac{\mu^-(n,N) + \mu^+(n,N)}{W(B) - W(L)}$$

and we expect a negative  $B$  term for the  $G \rightarrow B$  transition and a positive  $B$  term for the  $G \rightarrow L$  transition.

As long as the structural perturbation is reasonably large, the  $+, -, +, -$  sequence of MCD signs is very unlikely to be disturbed by symmetry-lowering perturbations which convert the  $A$  terms into pairs of  $B$  terms; thus the label "negative-hard". As the perturbation approaches zero, the chromophore gradually becomes "double-soft".

No experimental data for perturbed annulenes of this type appear to be available at present. We again refer to Table I and provide a few predictions of negative  $A/D$  terms for B and L bands of compounds in which  $\psi_N$  should be degenerate and  $\psi_{N+1}$  nondegenerate:



### 5. Relation of Structural to Vibrational Perturbations.

The published treatment of vibronic perturbations in MCD spectra of  $(4N + 2)$ -electron  $[4N]$ annulenes and  $[4N + 2]$ annulenes<sup>74</sup> is easily generalized to any  $[n]$ annulene. Considerations similar to those outlined above show that for  $n \neq 4N + 2$ , vibronic mixing causes levels with one quantum of vibration of  $e_{2N}$  symmetry (b symmetry if  $n = 4N$ ) to appear with positive  $A$  terms in the  $G \rightarrow L$  transition, at the same time providing positive contributions to the  $A$  terms of all allowed vibrational levels of the  $G \rightarrow B$  transition (averaging over this type of vibration gives  $\Delta\text{HOMO} \neq 0$ ), and it causes levels with one quantum of vibration of  $e_{2N+2}$  symmetry (b symmetry if  $n = 4N + 4$ ) to appear with negative  $A$  terms in the  $G \rightarrow L$  transition, at the same time providing negative contributions to the  $A$  terms of all allowed vibrational levels of the  $G \rightarrow B$  transition (this type of vibration causes  $\Delta\text{LUMO} \neq 0$ ).

If  $n = 4N + 2$ , the situation is more complicated, since the symmetry species  $e_{2N}$  and  $e_{2N+2}$  are one and the same, and adding a quantum of this vibration has the capacity of causing both  $\Delta\text{HOMO}$  and  $\Delta\text{LUMO}$  to be nonzero. These resulting effects could mutually compensate to a considerable degree, and from group theory alone, we cannot predict which will prevail. Since the L state is now nondegenerate, the result should be oppositely signed  $B$  terms in  $e_{2N}$  vibronic components of  $G \rightarrow L_b$  and  $G \rightarrow L_a$  transitions, plus contributions to the  $A$  terms of the allowed vibronic components of the  $G \rightarrow B$  transition. The  $e_{2N}$  vibronic components of the  $L_b$  and  $L_a$  states may still acquire nonzero  $A$  terms by borrowing both intensity

and magnetic moment from the B state, but these will be small, since the magnetic moment of the B state,  $\mu^-$ , is quite small. These conclusions are in agreement with recent analyses of the spectrum of benzene.<sup>39,41,75,81</sup>

**6. An Example: MCD of  $D_{4h}$  Porphyrins and Phthalocyanins.** According to the present simple model, all  $D_{4h}$  porphyrins and phthalocyanins have positive purely electronic  $A(G \rightarrow L)$  and  $A(G \rightarrow B)$ , since they have a nondegenerate HOMO and a degenerate LUMO. We shall use these examples to illustrate the use of qualitative MO arguments for prediction of MCD signs in some detail for the sake of those readers interested in applications. Simultaneously, we prepare the ground for an analysis of MCD signs of  $D_{2h}$  porphyrin derivatives given in part 2.<sup>42</sup> In those instances in which HOMO is nearly degenerate and the  $G \rightarrow L$  transition very weak, vibronic perturbations should be considered along the lines just discussed, but we shall disregard them for the present. We shall also ignore any effects of the metal.

The MO structures of porphyrins and phthalocyanins, as well as their MCD spectra, have been analyzed by various authors in the past. Useful summaries relevant to our needs (no explicit consideration of the metal) are found in ref 8, 68, and 82.

In this and most other practical applications, it is useful to introduce real MO's. The MO's  $\psi_0$  and  $\psi_{n/2} = \psi_{-n/2}$  ( $n$  even) are already real. For  $k \neq 0, k \neq n/2$ , we define real MO's  $\psi_k^\pm$  ( $k > 0$ ) by the relations

$$\psi_k^+ = (\psi_k + \psi_{-k})/\sqrt{2}$$

$$\psi_k^- = (\psi_k - \psi_{-k})/i\sqrt{2}$$

For the four frontier orbitals and their energies, we introduce the simplified notations

$$\mathbf{s} = \psi_N^+, \quad \epsilon(\mathbf{s})$$

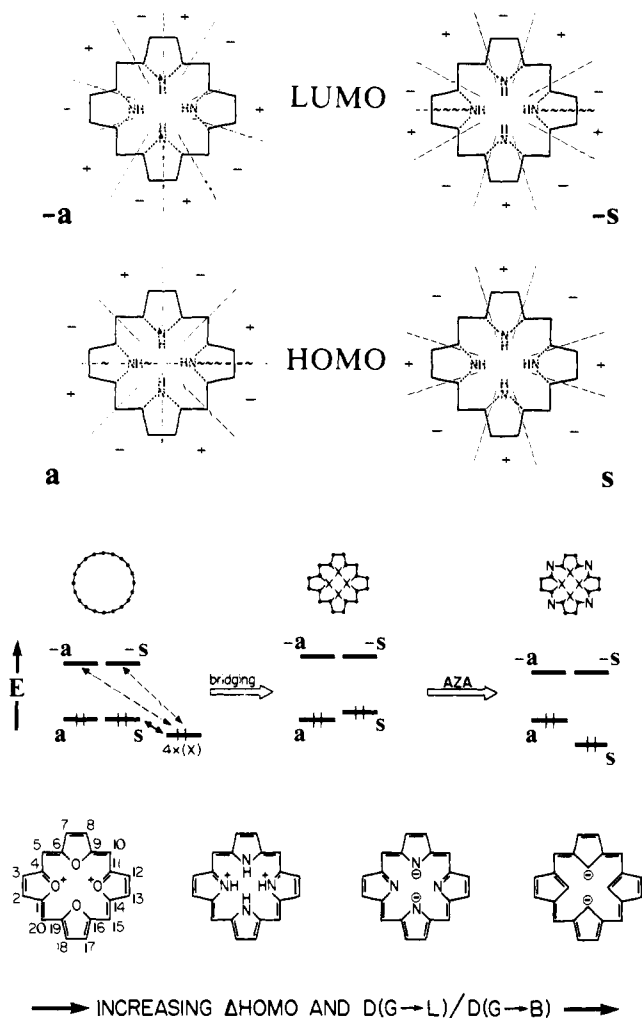
$$\mathbf{a} = \psi_N^-, \quad \epsilon(\mathbf{a})$$

$$-\mathbf{s} = \psi_{N+1}^+, \quad \epsilon(-\mathbf{s})$$

$$-\mathbf{a} = \psi_{N+1}^-, \quad \epsilon(-\mathbf{a})$$

The outer perimeter of a porphyrin contains 20 carbon atoms.  $D_{4h}$  porphyrins are formally derived from the  $C_{20}H_{20}^{2+}$  dication by introduction of four nitrogen-containing bridges (Figure 3). If these are the neutral bivalent  $-\text{NH}-$  links, the union results in the porphyrin dication  $C_{20}H_{20}(\text{NH})_4^{2+}$ ; if they are the negatively charged  $-\text{N}^-$  links, the union results in the porphyrin dianion  $C_{20}H_{20}N_4^{2-}$ , which can then be further formally transformed into various metalloporphyrins by placing a metal ion in the center where it can interact with the four nitrogen atoms (metal-centered transitions are not considered here).

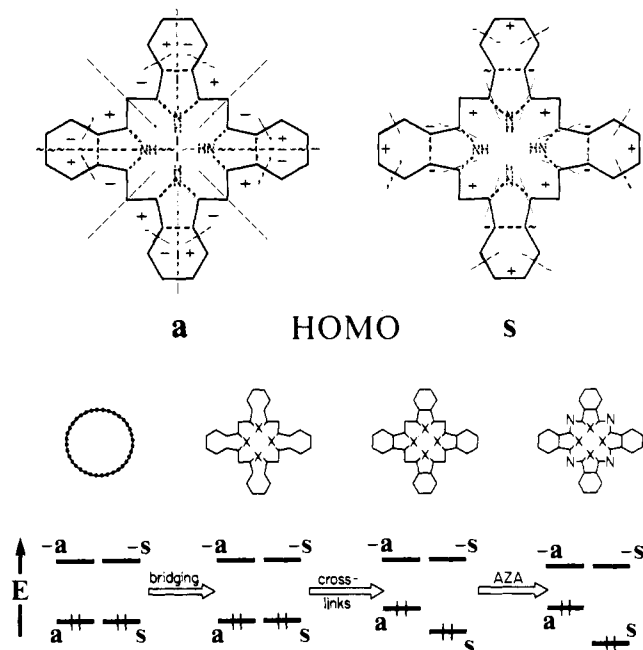
In  $C_{20}H_{20}^{2+}$ ,  $\epsilon(\mathbf{s}) = \epsilon(\mathbf{a})$  and  $\epsilon(-\mathbf{s}) = \epsilon(-\mathbf{a})$ . The nodal properties of the four orbitals are shown in Figure 3. We now neglect the effects of distorting the perimeter from the shape of a regular polygon and concentrate on the effects of the nitrogen bridging in the spirit of the simple PMO theory. The four NH groups have no effect on  $\epsilon(\mathbf{a})$  since they are located on nodes. Their effect on  $\epsilon(\mathbf{s})$  is small since they are attached to perimeter carbons on which  $\mathbf{s}$  has small coefficients (a node lies nearby). For each of the four bridging atoms, these coefficients have the same sign. A net interaction between  $\mathbf{s}$  and the in-phase combination of the four "lone-pair" orbitals of the NH groups results and produces two orbitals, extending over the bridges and delocalizing the nitrogen electrons over the perimeter. The higher energy orbital represents a modified HOMO and we shall label it  $\mathbf{s}$ . Clearly,  $\epsilon(\mathbf{s}) - \epsilon(\mathbf{a}) > 0$ , and the original degeneracy of HOMO is split. If the  $-\text{N}^-$  bridges are used for the union, the interaction is stronger and  $\epsilon(\mathbf{s})$  increases more, since the "lone pairs" now are at higher energy;



**Figure 3.** Top, nodal properties of the HOMO and LUMO of the [20]-annulene dication, and the location of perturbing bridges; center, the effect of bridging and aza substitution on orbital energies; bottom, a sequence of expected increase in perturbation by the bridges.

if  $-\text{CH}^-$  bridges are used, the effect should be stronger still. On the other hand,  $-\text{O}^-$  bridges should have a smaller effect. Similar considerations, or, more simply, application of group theory, show that  $\epsilon(-s) = \epsilon(-a)$  even after the perturbations are introduced, since the energies of both orbitals are raised equally (Figure 3).

Accordingly, we expect  $D(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{B}) = \tan^2 \alpha$  to increase from zero for  $\text{C}_{20}\text{H}_{20}^{2+}$  itself, through the O-bridged, NH-bridged, N<sup>-</sup>-bridged, and  $\text{CH}^-$ -bridged derivatives. Remembering that the points of attachment of the bridges to the perimeter are almost exactly on a node, we only expect the increase to be moderate. Further, we expect  $-2A(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{L})$  to be large, negative (Figure 2), and almost constant, since  $\cos^2 \alpha$  is a slowly decreasing function of  $\alpha$  for small values of  $\alpha$  and  $\alpha$  will be small if  $\Delta\text{HOMO} = |\epsilon(s) - \epsilon(a)|$  is small. Experimentally,  $D(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{B}) = 11.4/94 = 0.12$  ( $\alpha = 19^\circ$ ) in copper porphyrin<sup>8</sup> and similar small values are characteristic of other simple  $D_{4h}$  porphyrins as well. The value of  $D(\text{G} \rightarrow \text{L})$  is generally somewhat higher in  $D_{4h}$  porphyrin dianions than in the corresponding dications,<sup>83</sup> in agreement with expectations. The expected constancy of  $-2A(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{L})$  is only approximate; some decrease is observed upon going from the dianions to the dications (for octaethylporphyrin dianion,  $-2A(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{L}) = -3.1 \beta_e$ , for the dication,  $-2.3 \beta_e$ , taking values for the 0-0 band<sup>83</sup>; the values reported for metalloporphyrins are in the range  $-5.4$  to  $-7.0 \beta_e$ <sup>8</sup>).



**Figure 4.** Top, nodal properties of the HOMO of [36]annulene dication and the location of perturbing bridges; bottom, the effect of bridging, cross-linking, and aza substitution on orbital energies.

Large substituent effects can be expected for  $D_{4h}$  substitution in the inter-ring positions 5, 10, 15, and 20, in which **a** has a node and **s** an antinode. These should be easily able to override the  $\epsilon(s) - \epsilon(a)$  splitting induced by the nitrogen bridges. For strong electron donors such as methoxy, we expect  $\epsilon(s) - \epsilon(a) \gg 0$ ; for strong electron acceptors such as cyano or aza, we expect, for the first time,  $\epsilon(s) - \epsilon(a) \ll 0$ . Either of these situations should lead to  $\Delta\text{HOMO} \neq 0$  and to a considerable increase in the  $D(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{B})$  ratio as well as some decrease in the magnitude of  $-2A(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{L})$ , which should, however, definitely remain negative regardless of the ordering of the orbitals **a** and **s**. In magnesium 5,10,15,20-tetraazaporphine, the  $D(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{B})$  ratio is indeed quite high<sup>8</sup> ( $42.5/102.5 = 0.41$  ( $\alpha = 33^\circ$ )).

Tetrazabenzoporphyrins and phthalocyanins are derived similarly from the  $\text{C}_{36}\text{H}_{36}^{2+}$  annulene dication (Figure 4). The perimeter is first distorted to fourfold symmetry, and then  $-\text{NH}-$  bridges are built in as before. They are now almost without effect, since they are attached even closer to nodes of **s** than in the porphyrins, and again lie on the nodes of **a**. Larger effects should result from the introduction of the four cross-links to produce the four benzene rings. It occurs between atoms which carry identical MO coefficient signs in **s**, but opposite ones in **a**, so that this cross-linking perturbation strongly lowers  $\epsilon(s)$  and increases  $\epsilon(a)$ . We are thus led to expect  $\epsilon(s) - \epsilon(a) \ll 0$ , and since  $\epsilon(-s) = \epsilon(-a)$  by symmetry, a relatively large  $D(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{B})$  ratio should result. The visible band of tetrazabenzoporphyrins is in fact quite intense; for zinc tetrazabenzoporphyrin the ratio is<sup>8</sup>  $40/136 = 0.29$  ( $\alpha = 28^\circ$ ). The tetraaza substitution leading to phthalocyanins should further enhance this ratio since it occurs in positions where **a** has nodes and **s** antinodes and makes  $\epsilon(s) - \epsilon(a)$  even more negative. The reported<sup>8</sup> ratio for zinc phthalocyanin is  $57/91 = 0.63$  ( $\alpha = 38^\circ$ ). Throughout,  $-2A(\text{G} \rightarrow \text{L})/D(\text{G} \rightarrow \text{L})$  should remain negative as long as the symmetry is  $D_{4h}$  and  $-a$  and  $-s$  are degenerate. For these relatively large values of  $\Delta\text{HOMO}$ , its magnitude ought to be significantly smaller than  $\mu^+$ , since  $\cos^2 \alpha$  no longer is even approximately equal to unity. Moreover,  $\mu^+$  should be reduced compared with the regular-polygon value listed in Figure 2, due to the considerably decreased area encircled by the  $\pi$  perimeter compared with that



**Table II.**  $-2A/D$  Parameters for  $(4N + 2)$ -Electron  $[n]$ Annulenes ( $0 < N < n/2 - 1$ ) and Their Symmetrical Derivatives<sup>a</sup>

$\Delta$ HOMO	$\Delta$ LUMO	$-2A(G \rightarrow B)/D(G \rightarrow B)$	$-2A(G \rightarrow L)/D(G \rightarrow L)$	example
$\neq 0$	0	$\mu^-(n, N) \cos^2 \alpha + \mu^+(n, N) \sin^2 \alpha$	$\mu^-(n, N) \sin^2 \alpha + \mu^+(n, N) \cos^2 \alpha$	1,3,5,7-tetrasubstituted $C_8H_8^{2-}$
0	0	$\mu^-(n, N)^b$	... <sup>c</sup>	benzene, triphenylene
0	$\neq 0$	$\mu^-(n, N) \cos^2 \beta - \mu^+(n, N) \sin^2 \beta$	$\mu^-(n, N) \sin^2 \beta - \mu^+(n, N) \cos^2 \beta$	1,4,7-trisubstituted $C_9H_9^-$

<sup>a</sup> For the values of  $\mu^-(n, N)$  and  $\mu^+(n, N)$  see Figure 2;  $\mu^-$  is small and usually negative;  $\mu^+$  is large and always negative. The values of  $\alpha$  and  $\beta$ ,  $0 \leq \alpha, \beta < \pi/4$ , are related to the ratio of experimental intensities:  $\tan^2 \alpha = D(G \rightarrow L)/D(G \rightarrow B)$ ;  $\tan^2 \beta = D(G \rightarrow L)/D(G \rightarrow B)$ . If  $\Delta$ HOMO or  $\Delta$ LUMO are almost equal to zero, vibronic interactions are probably important and need to be considered. <sup>b</sup> Vibronic mixing of the L and B states may mask  $\mu^-$  by admixture of the much larger  $\mu^+$  (see section 5). <sup>c</sup> Purely electronic  $A$  and  $D$  vanish for the L state; the MCD spectrum will be dominated by vibronic effects due to mixing with the B state (see section 5).

of a regular polygon (a similar but weaker reduction should be operative in porphyrins). The experimental values for metallocyanins are indeed negative and generally smaller than those for porphyrins:  $-2A(G \rightarrow L)/D(G \rightarrow L) = -1.2$  to  $-3\beta_e$ .<sup>8</sup>

The automatic expectation of generally positive purely electronic contributions to  $A(G \rightarrow L)$  and  $A(G \rightarrow B)$  values for porphyrins and related compounds is only justified as long as the  $D_{4h}$  symmetry is preserved. As soon as symmetry is lowered,  $\epsilon(-s) \neq \epsilon(-a)$ , and we shall see in a discussion of chlorins and other low-symmetry porphyrins in part 2<sup>42</sup> that either sign can result for  $B$  terms, depending on the relative magnitude of  $\Delta$ HOMO and  $\Delta$ LUMO.

**7. Relation to Previous Numerical Computations.** Our analysis shows that in high-symmetry perturbed annulenes symmetry and degree of orbital occupancy alone determine whether  $\Delta$ HOMO and  $\Delta$ LUMO are different from zero. If  $\Delta$ HOMO  $\neq 0$  or  $\Delta$ LUMO  $\neq 0$ , the moments  $\mu^+$  tend to dominate the  $A$  terms. The magnitudes of these moments are so large that any reasonable method is virtually guaranteed to obtain their signs correctly and thus to reproduce the experimental signs of the  $A$  terms. Indeed, successful calculations of the signs of  $A$  terms for porphyrins by free-electron<sup>84</sup> and LCAO<sup>8</sup> MO methods were among the first performed for organic molecules.

A much more difficult task is the calculation of the signs of  $A$  terms in those instances where they are dominated by the moments  $\mu^-$ , i.e., if  $\Delta$ HOMO =  $\Delta$ LUMO = 0. The moment  $\mu^-$  is a measure of the generally quite small increase in the magnetic moment of an electron in HOMO upon passing to LUMO while preserving its sense of circulation, and its calculated sign frequently depends on the method of calculation. In the simple free-electron model, the angular momentum of the electron always increases upon excitation, and  $\mu^-$  is always negative. In the LCAO model, the angular momentum of  $\psi_k$  first increases with the quantum number  $|k|$  until the vicinity of  $n/4$  is passed, but then it starts to decrease, so that  $\mu^-$  can be positive (Figure 2). An experimental result for a  $(4N + 2)$ -electron  $[2(N + 1)]$ annulene system such as one isoelectronic with  $C_4H_4^{2-}$  or  $C_6H_6^{4-}$  puts the two methods to an interesting test, and the results for  $S_4^{2+}$ ,  $Se_4^{2+}$ , and  $Te_4^{2+}$  definitely favor the LCAO model. In an LCAO method, the location of the exact limit beyond which  $\mu^-$  is positive is sensitive to details of the calculation and in particular to the balance between nearest-neighbor and next-nearest-neighbor matrix elements of the linear momentum operator  $\hat{p}$ . We can now pinpoint the source of the difficulty experienced in ZDO methods when using a nonorthogonalized Slater AO basis set for a calculation of these matrix elements: the sign of the proportionality constant relating the matrix elements of  $\hat{p}$  to the difference of the position vectors of two AO's is the same for any two AO's, while in the orthogonalized basis, the sign for the next-nearest-neighbor term is opposed to that of the nearest neighbor term (Appendix). The discrepancy is particularly marked in  $\pi$ -electron calculations on uncharged alternant hydrocarbons in which the next-nearest-neighbor terms

alone determine the sign of  $\mu^-$ : opposite signs are obtained in the two approximations, and zero is obtained if these terms are neglected<sup>7,81</sup> (nonzero values are obtained if perfect pairing is removed by use of the CNDO/S method, but this method exaggerates the deviation from perfect pairing and leads to incorrect predictions of MCD signs<sup>40b</sup>). The experimental results demand  $\mu^- < 0$  for these systems; this is automatically obtained in the FEMO model. In the LCAO MO ZDO model, it requires opposite signs for the two matrix elements. These cannot be obtained from a nonorthogonal Slater basis but may result if an orthogonalized basis is used (Appendix). The discrepancy between the signs calculated by ZDO methods in orthogonalized and nonorthogonalized bases should also exist for charged annulenes as long as the net charge is small, and in perturbed annulenes; it accounts for the wrong sign of  $A(G \rightarrow B)$  calculated for the [16]annulene dianion<sup>20</sup> and for  $D_{4h}$  porphyrins<sup>8</sup> in the nonorthogonalized basis and appears in some of the published numerical results for annuleny ions,<sup>79</sup> weakly perturbed benzenes,<sup>40a</sup> and for a trisdehydrotribenzo[12]annulene.<sup>23</sup>

**8. Summary of Results and Conclusions.** A qualitative summary of results for  $A$  terms of  $(4N + 2)$ -electron  $[n]$ annulenes ( $0 < N < n/2 - 1$ ) and their symmetrically perturbed derivatives (threefold or higher axis of rotation) is given in Table II.

Results for the rarer 2-electron  $[n]$ annulenes and  $(4N + 2)$ -electron  $[2(N + 1)]$ annulenes and their symmetrical derivatives are given in Table III.

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## Appendix

Some of the intermediate results in the derivation are given below. The position vector of  $\nu$ th atom is  $\mathbf{r}_\nu$ . For nonorthogonal AO's  $\phi_\nu$ ,  $\langle \phi_\nu | \phi_{\nu+1} \rangle = S$ , and  $\langle \phi_\nu | \phi_{\nu+2} \rangle = S'$ , which is taken to be of the order of  $S^2$  if  $n > 3$ . Overlap of more distant AO's is neglected. Standard procedures yield

$$\langle \phi_\nu | \hat{\mathbf{m}} | \phi_\nu \rangle = -e\mathbf{r}_\nu$$

$$\langle \phi_\nu | \hat{\mathbf{m}} | \phi_{\nu+1} \rangle = -eS(\mathbf{r}_{\nu+1} + \mathbf{r}_\nu)/2$$

$$\langle \phi_\nu | \hat{\mathbf{m}} | \phi_{\nu+2} \rangle = -eS'(\mathbf{r}_{\nu+2} + \mathbf{r}_\nu)/2$$

$$\langle \phi_\nu | \hat{\mathbf{m}} | \phi_{\nu+k} \rangle = 0 \text{ if } k > 2$$

and

**Table III.** *A/D* Parameters for 2-Electron [*n*]Annulenes and (4*N* + 2)-Electron [2(*N* + 1)]Annulenes and Their Symmetrical Derivatives<sup>a</sup>

	$-2A(G \rightarrow B)/D(G \rightarrow B)$	sign of <i>A</i>	examples
2-electron [ <i>n</i> ]annulene	$\mu^-(n, N)$	+	$C_3H_3^+$
(4 <i>N</i> + 2)-electron [2( <i>N</i> + 1)]annulene	$\mu^-(n, N)$	-	$C_4H_4^{2-}$

<sup>a</sup> For the values of  $\mu^-(n, N)$ , see Figure 2.

$$\langle \phi_\nu | \hat{\mu} | \phi_{\nu+1} \rangle = i(\beta_c/\hbar)(\mathbf{r}_\nu \times \mathbf{r}_{\nu+1}) \cdot \mathbf{P} = (i\beta_c l_0^2/2\hbar) \cot(\pi/n) \cdot \mathbf{P} \cdot \mathbf{e}_3$$

$$\langle \phi_\nu | \hat{\mu} | \phi_{\nu+2} \rangle = i(\beta_c/\hbar)(\mathbf{r}_\nu \times \mathbf{r}_{\nu+2}) \cdot \mathbf{P}' = (i\beta_c l_0^2/2\hbar) \cos(2\pi/n) \cot(\pi/n) \cdot \mathbf{P}' \cdot \mathbf{e}_3$$

$$\langle \phi_\nu | \hat{\mu} | \phi_{\nu+\kappa} \rangle = 0 \text{ if } \kappa > 2$$

where  $\beta_c$  is Bohr magneton,  $\mathbf{P} = l_0^{-1} |\langle \phi_\nu | \hat{\mathbf{p}} | \phi_{\nu+1} \rangle|$  and  $\mathbf{P}' = [2l_0 \cos(\pi/n)]^{-1} |\langle \phi_\nu | \hat{\mathbf{p}} | \phi_{\nu+2} \rangle|$ . We take  $\mathbf{P}$  to be of the order  $S$  and  $\mathbf{P}'$  of the order  $S^2$  if  $n > 3$ . Matrix elements of  $\hat{\mathbf{p}}$  between more distant AO's are neglected.

For Löwdin-orthogonalized AO's  $\chi$  we obtain

$$\langle \chi_\nu | \hat{\mathbf{m}} | \chi_\nu \rangle = -e \cdot \mathbf{r}_\nu [1 + S^2 \sin^2(\pi/n)] \quad (n \geq 3)$$

$$\langle \chi_\nu | \hat{\mathbf{m}} | \chi_{\nu+1} \rangle = 0 \quad (n \geq 4)$$

$$= e \cdot \mathbf{r}_{\nu-1} (S^2/2) \sin^2(\pi/n) \quad (n = 3)$$

$$\langle \chi_\nu | \hat{\mathbf{m}} | \chi_{\nu+2} \rangle = e \cdot \mathbf{r}_{\nu+1} (S^2/2) \sin^2(\pi/n) \quad (n \geq 5)$$

$$= 0 \quad (n = 4)$$

$$\langle \chi_\nu | \hat{\mathbf{m}} | \chi_{\nu+\kappa} \rangle = 0 \text{ if } \kappa > 2 \quad (n \geq 5)$$

and

$$\langle \chi_\nu | \hat{\mu} | \chi_{\nu+1} \rangle = (i\beta_c l_0^2/2\hbar) \cot(\pi/n) \cdot \mathbf{P} \cdot \mathbf{e}_3 \quad (n \geq 4)$$

$$= (i\beta_c l_0^2/2\hbar) \cot(\pi/n) \cdot \mathbf{P}(1 + S) \cdot \mathbf{e}_3 \quad (n = 3)$$

$$\langle \chi_\nu | \hat{\mu} | \chi_{\nu+2} \rangle = -(i\beta_c l_0^2/2\hbar) \cot(\pi/n) \cdot [SP - 2P' \cos(2\pi/n)] \cdot \mathbf{e}_3 \quad (n \geq 5)$$

$$= 0 \quad (n = 4)$$

$$\langle \chi_\nu | \hat{\mu} | \chi_{\nu+\kappa} \rangle = 0 \text{ if } \kappa > 2 \quad (n \geq 5)$$

We use  $\mathbf{P} = -\beta m/\hbar$  according to Linderberg.<sup>69</sup> To estimate the ratio  $\langle \chi_\nu | \hat{\mu} | \chi_{\nu+2} \rangle / \langle \chi_\nu | \hat{\mu} | \chi_{\nu+1} \rangle$  ( $n \geq 5$ ), we assume the  $\phi$ 's to be Slater orbitals with exponent 1.625, take  $l_0 = 1.4 \text{ \AA}$ , and use standard formulas given, e.g., in ref 8 [ref 9 contains a misprint:  $R_{ij}^3$  should be replaced by  $R_{ij}^2$  in eq 10]. We obtain values between -0.14 and -0.16;  $\{\langle \chi_\nu | \hat{\mu} | \chi_{\nu+2} \rangle / \langle \chi_\nu | \hat{\mu} | \chi_{\nu+1} \rangle\} = -[S - 2(P'/P) \cos(2\pi/n)] = -\{0.24 - [2 \cos(2\pi/n)] \cdot (p^2 l_1^2 + 3pl_1 + 3)(p^2 l_0^2 + 3pl_0 + 3)^{-1} \exp[p(l_0 - l_1)]\}$ , where  $p = 1.625/a_0 = 3.078$ , and  $l_1 = 2l_0 \cos(\pi/n)$ . While it is not at all obvious that this AO choice represents the best minimum basis set for the model, it is encouraging that it produces the sign and order of magnitude demanded by the experimental data, and we shall adopt the value -0.15 for the ratio. Thus, we use

$$\langle \chi_\nu | \hat{\mu} | \chi_{\nu+1} \rangle = |\beta_1| (im\beta_c l_0^2/2\hbar^2) \cot(\pi/n) \cdot \mathbf{e}_3 \quad (n \geq 4)$$

$$= |\beta_1| (im\beta_c l_0^2/2\hbar^2) \cot(\pi/n)(1 + S) \cdot \mathbf{e}_3 \quad (n = 3)$$

$$\langle \chi_\nu | \hat{\mu} | \chi_{\nu+2} \rangle = -0.15 |\beta_1| (im\beta_c l_0^2/2\hbar^2) \cot(\pi/n) \cdot \mathbf{e}_3 \quad (n \geq 5)$$

$$= 0 \quad (n = 4)$$

It should be noted that the sign of the next-nearest-neighbor element of  $\hat{\mu}$  is different in the  $\phi$  basis and in the  $\chi$  basis.

MO's are given by symmetry:

$$\psi_k = n^{-1/2} \sum_{\nu=0}^{n-1} [\exp(2\pi i k \nu/n)] \chi_\nu$$

$$k = 0, \pm 1, \dots, \pm(n/2 - 1), n/2 \quad \text{if } n \text{ is even}$$

$$k = 0, \pm 1, \dots, \pm(n-1)/2 \quad \text{if } n \text{ is odd}$$

The only nonvanishing matrix elements of  $\hat{\mu}$  and  $\hat{\mathbf{m}}$  are

$$\langle \psi_k | \hat{\mu} | \psi_k \rangle = -\langle \psi_{-k} | \hat{\mu} | \psi_{-k} \rangle = \mu(n, k) \cdot \mathbf{e}_3$$

$$\langle \psi_k | \hat{\mathbf{m}} | \psi_{k \pm 1} \rangle = m(n, |2k \pm 1|) \cdot \mathbf{e}^\pm$$

where

$$\mu(3, \pm 1) = \mp |\beta_1| (m\beta_c l_0^2/2\hbar^2)(1 + S)$$

$$\mu(n, k) = -|\beta_1| (m\beta_c l_0^2/\hbar^2) \cot(\pi/n) \cdot [\sin(2\pi k/n) - 0.15 \sin(4\pi k/n)] \quad n > 3$$

and  $m(i, j)$  was given in the text.

The moment  $\mu(n, k) \cdot \mathbf{e}_3$  contains two contributions, one proportional to  $\sin(2\pi k/n)$  with a large proportionality constant, the other, absent if  $n = 3$  or  $n = 4$ , proportional to  $-\sin(4\pi k/n)$  with a small proportionality constant. Physically, the former can be viewed as due to a circular electron current passing from a Löwdin AO centered on one atom to the next Löwdin AO centered on the neighboring atom, and so on around the ring. The latter can be viewed similarly as a superposition of two additional weaker circular electron currents which proceed from the Löwdin AO centered on a given atom to the Löwdin AO centered not on the nearest but on the next nearest neighbor, one directly through space, and the other, somewhat stronger and opposed in sense, indirectly by taking advantage of the slight delocalization of the Löwdin orbital centered at atom  $\kappa$  to the neighboring atoms  $\kappa + 1$  and  $\kappa - 1$ .

Finally, we define

$$\mu^-(n, 0) = \mu(n, 1)$$

$$\mu^-(2N+2, N) = -\mu(2N+2, N)$$

$$\mu^\pm(n, N) = \mu(n, N+1) \pm \mu(n, N)$$

**Notes Added in Proof.** MCD of the  $C_4O_4^{2-}$ ,  $C_5O_5^{2-}$ , and  $C_6O_6^{2-}$  oxocarbon anions have now been measured (R. C. West, S. Inagaki, and J. Michl, unpublished results). The *A* terms of their B bands are positive as predicted in Chart II.

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