

# Magnetic Circular Dichroism of Cyclic $\pi$ -Electron Systems.

## 3.<sup>1</sup> Classification of Cyclic $\pi$ Chromophores with a $(4N + 2)$ -Electron $[n]$ Annulene Perimeter and General Rules for Substituent Effects on the MCD Spectra of Soft Chromophores

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**Abstract:** The theory of parts 1 and 2 is used to propose a unified classification of cyclic  $\pi$  chromophores with a  $(4N + 2)$ -electron  $[n]$ annulene perimeter based on their MCD behavior. Simple PMO arguments permit a derivation of general rules for the response of various kinds of soft MCD chromophores to inductive and mesomeric effects of substituents.

### Introduction

The results of parts 1<sup>2</sup> and 2<sup>1</sup> suggest a general classification of all chromophores derived from a  $(4N + 2)$ -electron  $[n]$ -annulene perimeter, which represents an elaboration of the notions of soft and hard chromophores. The present paper describes such a classification and systematizes the MCD behavior of the  $G \rightarrow L$  and  $G \rightarrow B$  transitions. The same classification also describes their intensities and polarizations, but the latter aspects will not be discussed presently.

The second objective of the paper is to develop general rules for the MCD effects of perturbations which convert soft chromophores to hard chromophores. We choose substituent effects as a prime example of such perturbations and find different behavior for different types of soft chromophores. The ease with which predictions of MCD signs induced by a specific substituent in a specific position can be made suggests that MCD spectroscopy will be of diagnostic value for derivatives of soft chromophores as well as for investigations of the nature of substituent effects. Since similar perturbations of hard chromophores leave the signs of their  $B$  terms intact, MCD will not be useful for investigations of substitution patterns on derivatives of these chromophores but rather will provide a characteristic and predictable structural "signature" for each such chromophore which may help to recognize it even if it is masked, say, in the UV spectrum, by heavy perturbations.

### Results and Discussion

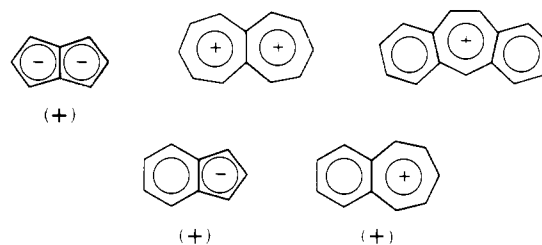
**1. A Classification of  $\pi$  Chromophores with a  $(4N + 2)$ -Electron Perimeter.** A general classification scheme for cyclic  $\pi$  systems which can be related, at least remotely, to a  $(4N + 2)$ -electron  $[n]$ annulene perimeter is outlined in Table I (hard chromophores) and Table II (soft chromophores), which also summarize the expected signs of  $\mu^-$  and  $\mu^+$  contributions to the  $B$  terms of  $G \rightarrow L$  and  $G \rightarrow B$  transitions. The labels chosen for the various types of chromophores are partly self-explanatory. The qualifiers "double", "single", and "zero" state the number of  $G \rightarrow L$  transitions with vanishing  $B$  terms, whose MCD signs should be particularly sensitive to even small perturbations (and which should show strong vibronic effects). Single-soft, odd-soft, and even-soft chromophores all have one such  $L$  transition, but we need to distinguish between them, both to indicate which of the two  $L$  transitions it is, and since they respond differently to substituent effects. The origin of the qualifiers "odd" and "even" will become clear below.

**2. Examples of Various Classes of Hydrocarbons.** It is possible to make some general statements about the relation between structure and the positive or negative nature of hard chromophores. For instance, in part 16<sup>3</sup> we show that peri-

condensed hydrocarbons with a single internal carbon atom are likely to be positive-hard if they have a  $[4N + 1]$ annulene perimeter and negative-hard if they have a  $[4N + 3]$ annulene perimeter. Presently, however, we shall focus attention on the perhaps more intriguing soft chromophores and provide examples of hydrocarbons which belong to various classes of this category. Exact equality of  $\Delta HOMO$  and  $\Delta LUMO$  is hard to find in any real perturbed annulene, and most of our examples of soft chromophores deviate more or less from the ideal. In double-soft chromophores, the equality is guaranteed by symmetry, and these are probably the only perfect soft chromophores (part 1<sup>2</sup>). To a good approximation, orbital and state pairing holds in alternant hydrocarbons (it is exact at the Hückel and PPP levels) and provides our next best examples of  $\Delta HOMO = \Delta LUMO$  (odd-soft chromophores). In most other examples, ideal softness is only approached.

(i) **Double-Soft Chromophores.** Hydrocarbons of this class possess high symmetry and were discussed in part 1.<sup>2</sup>

(ii) **Single-Soft Chromophores.** Introduction of a single cross-link into a charged  $(4N + 2)$ -electron  $[n]$ annulene ( $n \neq 4N + 2$ ) preserves at least  $C_{2v}$  symmetry and frequently produces an approximately equal splitting of the annulene HOMO's and its LUMO's. Judging by Hückel energies, the following are nearly single-soft chromophores [the signs in parentheses indicate whether they deviate toward positive-hard (+) or negative-hard (-)].



(iii) **Odd-Soft Chromophores.** One or more cross-links between positions  $\mu$  and  $\nu$  of a  $(4N + 2)$ -electron  $[4N + 2]$ annulene, where  $\mu + \nu$  is odd, represent an odd perturbation as defined by Moffitt<sup>4</sup> and produce an odd-soft chromophore. Thus, all uncharged alternant hydrocarbons with a  $[4N + 2]$ annulene perimeter and no threefold or higher symmetry axis belong to this category. Benzenoid hydrocarbons represent the most important example.

(iv) **Even-Soft Chromophores.** A cross-link between positions  $\mu$  and  $\nu$  of a  $(4N + 2)$ -electron  $[4N + 2]$ annulene, where  $\mu + \nu$  is even, represents an even perturbation as defined by Moffitt<sup>4</sup> and produces an approximately even-soft chromophore

**Table I.** Hard Chromophores Derived from  $(4N + 2)$ -Electron  $[n]$ Annulenes<sup>a</sup>

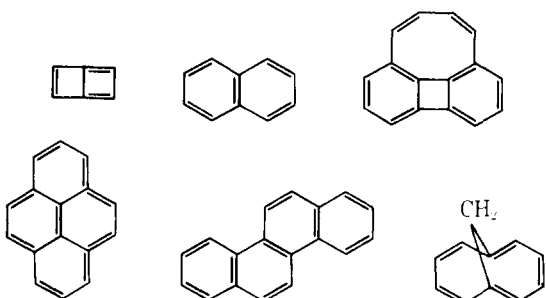
$4N + 2$	sign of $\mu^-$ contribution to $B$ or $A$ term				sign of $\mu^+$ contribution to $B$ or $A$ term				example
	$G \rightarrow L'$	$G \rightarrow L''$	$G \rightarrow B'$	$G \rightarrow B''$	$G \rightarrow L'$	$G \rightarrow L''$	$G \rightarrow B'$	$G \rightarrow B''$	
Positive-Hard: $\Delta\text{HOMO} > \Delta\text{LUMO}$									
$2^b$			+	-					
$n$	$-\text{sgn } \mu^-$ (w)	$-\text{sgn } \mu^-$ (w) <sup>c</sup>	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	+	-	+	-	cyclopropenone
$\neq 2, n$	$-\text{sgn } \mu^-$ (w)	$+\text{sgn } \mu^-$ (w)	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	+	-	+	-	benz[a]azulene pleiadiene
Negative-Hard: $\Delta\text{HOMO} < \Delta\text{LUMO}$									
$2n - 2^b$			-	+					
$n$	$-\text{sgn } \mu^-$ (w)	$-\text{sgn } \mu^-$ (w) <sup>c</sup>	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	-	+	-	+	$\text{Se}_4^{2+}$ dication benz[e]azulene
$\neq 2n - 2, n$	$-\text{sgn } \mu^-$ (w)	$+\text{sgn } \mu^-$ (w)	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	-	+	-	+	acenaphthylene

<sup>a</sup>  $L'$ ,  $L''$ ,  $B'$ , and  $B''$  are the four states in the order of increasing energy. When  $L'$  and  $L''$  or  $B'$  and  $B''$  are degenerate, the sign of the contribution to the  $A$  term is that given for  $L'$  or  $B'$ , respectively. Particularly small contributions are indicated by (w).  $\text{Sgn } \mu^- = -1$  in almost all cases; cf. Figure 2 of part 1. The results for  $G \rightarrow B''$  are usually less reliable. <sup>b</sup> If HOMO is not degenerate,  $\Delta\text{HOMO} = \infty$ ; if LUMO is not degenerate,  $\Delta\text{LUMO} = \infty$ . <sup>c</sup> If the two  $G \rightarrow L$  transitions are nearly degenerate, this may be zero or even  $+\text{sgn } \mu^-$  (the L-L mixing and the B-L mixing oppose each other).

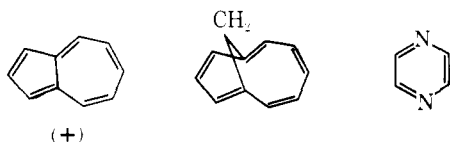
**Table II.** Soft Chromophores Derived from  $(4N + 2)$ -Electron  $[n]$ Annulenes<sup>a</sup>

$4N + 2$	$\Delta\text{HOMO} = \Delta\text{LUMO}$	$\phi^b$	type	sign of $\mu^-$ contribution to $B$ or $A$ term				example
				$G \rightarrow L'$	$G \rightarrow L''$	$G \rightarrow B'$	$G \rightarrow B''$	
any	$0 \neq$	-	double-soft	0	0	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	benzene, tropylium
$\neq n$	$0 \neq$	any	single-soft	$-\text{sgn } \mu^-$ (w)	0	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	pentalene dianion
$n$	0	0	odd-soft	0 ( $L_b$ )	$-\text{sgn } \mu^-$ (w) ( $L_a$ )	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	naphthalene
		$\pi$	even-soft	$-\text{sgn } \mu^-$ (w) ( $L_b$ )	0 ( $L_a$ )	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	(azulene)
		$\neq 0, \pi$	zero-soft	$-\text{sgn } \mu^-$ (w)	$-\text{sgn } \mu^-$ (w)	$-\text{sgn } \mu^-$	$+\text{sgn } \mu^-$	(benz[f]azulene)

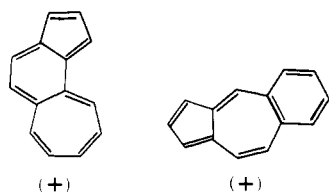
<sup>a</sup>  $L'$ ,  $L''$ ,  $B'$ , and  $B''$  are the four states in the order of increasing energy, except where indicated otherwise. When  $L'$  and  $L''$  or  $B'$  and  $B''$  are degenerate, the sign of the contribution to the  $A$  term is that given for  $L'$  or  $B'$ , respectively. Particularly small contributions are indicated by (w).  $\text{Sgn } \mu^- = -1$  in almost all cases; cf. Figure 2 of part 1. The results for  $G \rightarrow B''$  are usually less reliable. <sup>b</sup> For  $\phi = 0$ , the orbital sequence is  $s, a, -a, -s$  or  $a, s, -s, -a$ ; for  $\phi = \pi$ , the orbital sequence is  $s, a, -s, -a$  or  $a, s, -a, -s$ . If the molecule has no plane of reflection symmetry perpendicular to the molecular plane ( $C_s, C_{2h}$ ),  $\phi \neq 0, \pi$ .



( $\Delta\text{HOMO} = \Delta\text{LUMO}$  only to the first order of perturbation theory when the cross-link is viewed as a perturbation). Azulene is a good example of this type of chromophore. Another important class of perturbation of a  $(4N + 2)$ -electron  $[4N + 2]$ annulene which produces an even-soft chromophore is inductive perturbation, say by one or more aza nitrogens.



(v) **Zero-Soft Chromophores.** If cross-links of both kinds are present in a hydrocarbon, e.g., in benzazulenes, the equality of  $\Delta\text{HOMO}$  and  $\Delta\text{LUMO}$  is rarely achieved. Two examples of near equality follow. It may be easier to find chromophores of this kind among cyclic  $\pi$ -electron systems containing substituents and heteroatoms.



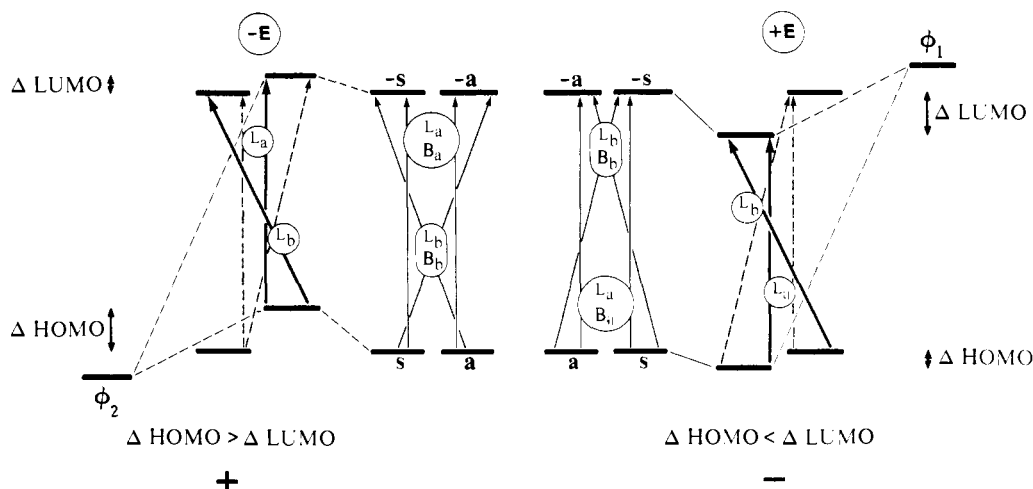
**3. Inductive (I) and Mesomeric (E) Electron Donation (-) and Withdrawal (+).** Before formulating general rules for substituent effects on MCD spectra, we need to specify clearly what is meant by I and E effects in the present context and how it translates into a quantum mechanical description in terms of one-electron perturbations.

We shall understand under I effects of a substituent those which propagate through polarization of the  $\sigma$  electrons of the aromatic molecule and under E effects those which propagate through polarization of the  $\pi$  electrons. The effects change the properties of the atoms which comprise the aromatic system, such as their valence state ionization potential and electron affinity, and those of the aromatic MO's, such as coefficients and energies, which will be of prime interest to us. We shall describe these changes in terms of low-order perturbation theory in the PMO spirit<sup>5</sup> since we always assume that even in the substituted molecule the parent system is still clearly recognizable. Since the perimeter model treats explicitly only  $\pi$  electrons, the formal descriptions of the two types of electron donation and withdrawal by substituents will differ, although in an all-valence model the physical nature of both would clearly be the same, i.e., displacement of electrons toward regions of low potential energy within the limits imposed by the Pauli exclusion principle.

The size of the  $\pi$  system is not affected by a substituent with an I effect. The effect on the energy of  $i$ th MO is taken to be

$$\Delta\epsilon(i) = \sum_{\nu} c_{\nu i}^2 \Delta\alpha_{\nu}$$

where  $\nu$  runs over all atoms affected by the perturbation,  $c_{\nu i}$  is the coefficient of  $i$ th MO on  $\nu$ th atom, and  $\Delta\alpha_{\nu}$  is the change in the effective electronegativity (Coulomb integral) of  $\nu$ th atom (usually, only the one which carries the substituent needs to be considered). Replacement of CH in the  $\sigma$  skeleton by a



**Figure 1.** An example of the effect of mesomeric (E) substitution on the  $\Delta$ HOMO and  $\Delta$ LUMO values of a  $(4N + 2)$ -electron  $[4N + 2]$ annulene, and the induced signs of the  $\mu^+$  contributions to the  $B$  terms of the lowest  $\pi\pi^*$  transition [ $B(L_1)$ ].

heteroatom such as N,  $\text{NH}^+$ ,  $\text{O}^+$ ,  $\text{BH}^-$ , etc. can be viewed as a special case of an I effect.

A substituent with an E effect increases the size of the system under consideration. If it carries an empty antibonding orbital of  $\pi$  symmetry ( $-\text{BH}_2$ ), its effect will be  $+E$ ; if it carries a filled bonding orbital of  $\pi$  symmetry ( $-\text{OH}$ ), its effect will be  $-E$ . If the substituent consists of several  $\pi$  centers and carries some filled and some empty orbitals with nonvanishing coefficients at the point of attachment, its effect may be  $+E$ ,  $\pm E$ , or  $-E$ , depending on the substrate. The dominant action will be usually determined by either the substituent LUMO or its HOMO, depending on which is closer to the Fermi level of the substrate ( $+E$ ,  $-E$ , respectively, and  $\pm E$  if the separations are the same). One and the same substituent of this type may be electron withdrawing on the  $\text{C}_5\text{H}_5^-$  anion and electron donating on the  $\text{C}_7\text{H}_7^+$  cation.

To estimate the effect of an E substituent on  $i$ th MO, we shall use first-order perturbation theory in the rare instances of degeneracy, but otherwise we shall use the second-order expression. If only one substituent orbital is important, say,  $\phi$

$$\Delta\epsilon(i) = \frac{(c_{\mu\phi}c_{vi}\beta_{\mu\nu})^2}{\epsilon(i) - \epsilon(\phi)}$$

where  $\beta_{\mu\nu}$  is the resonance integral of the bond between the substituent and the substrate,  $c_{\mu\phi}$  is the coefficient of the substituent orbital at the point of attachment, and  $c_{vi}$  is the coefficient of the  $i$ th MO at the point of attachment.

Clearly, while I and  $\pm E$  substituents show no bias in acting on the occupied and the unoccupied MO's of the substrate, the energy difference in the denominator will make  $+E$  substituents preferentially affect the low-lying empty MO's of the substrate, while  $-E$  substituents will work predominantly on the high-lying occupied levels. Consequently, E substitution has a particularly strong potential for inducing  $\Delta\text{HOMO} \neq \Delta\text{LUMO}$  in soft chromophores. In the limit of very strong  $+E$  monosubstitution, when all other perturbations of the perimeter which are present become unimportant and the  $+E$  effect alone dominates, we shall clearly obtain  $\Delta\text{HOMO} < \Delta\text{LUMO}$ , since  $c_{vi} \neq 0$  for  $i = -s$  but  $c_{vi} = 0$  for  $i = -a$ , while such a natural limit for domination by a  $-E$  substituent is  $\Delta\text{HOMO} > \Delta\text{LUMO}$ , since  $c_{vi} \neq 0$  for  $i = s$  but  $c_{vi} = 0$  for  $i = a$ .

**4. Substituent Effects on MCD Spectra.** In the following, we discuss the effects of substituents on the difference  $\Delta\text{HOMO} - \Delta\text{LUMO}$ . As shown in parts 1<sup>2</sup> and 2,<sup>1</sup> if this is positive, the induced  $\mu^+$  contributions to the  $B$  terms of  $B \rightarrow L$  and  $G \rightarrow B$  transitions will have the sign sequence  $+, -, +, -$  in the order

of increasing energy and if it is negative, the sign sequence will be  $-, +, -, +$ .

Substituent effects on uncharged-perimeter soft chromophores ( $n = 4N + 2$ ) are particularly easy to systematize because the pairing theorem is valid for  $(4N + 2)$ -electron  $[4N + 2]$ annulenes in the Hückel and PPP models and provides a simple relation between the mutually paired perimeter MO's  $s, -s$ , and  $a, -a$ :  $c_{\nu,s}^2 = c_{\nu,-s}^2$  and  $c_{\nu,a}^2 = c_{\nu,-a}^2$  for any  $\nu$ .

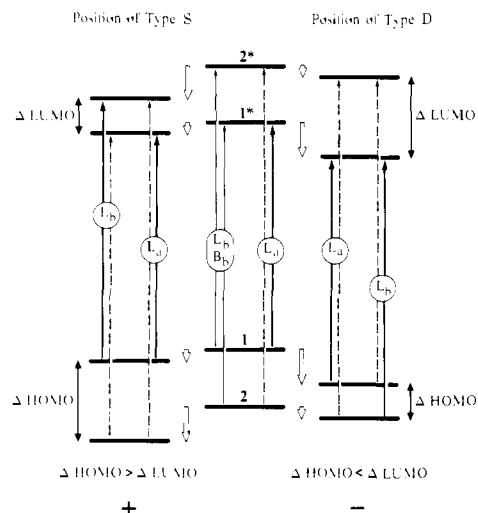
(i) **Double-Soft Chromophores.** In these chromophores, the signs of both  $B(G \rightarrow L_b)$  and  $B(G \rightarrow L_a)$  should be very sensitive to substituent effects since their  $\mu^-$  contributions vanish. For a perturbation due to one or more I substituents,  $\Delta\text{HOMO} = \Delta\text{LUMO}$  to the first order, and the orbital order is such that an even-soft chromophore results. In second order,  $\Delta\text{HOMO} \neq \Delta\text{LUMO}$  but the difference is small, so that even then, an approximately even-soft chromophore results. This situation is discussed and compared with experiments on the case of the azines in part 4.<sup>6</sup>

For  $+E$  substitution,  $\Delta\text{HOMO} < \Delta\text{LUMO}$ ; for  $-E$  substitution,  $\Delta\text{HOMO} > \Delta\text{LUMO}$  (Figure 1). Clearly, the natural preference of the E substituent dominates the signs of the  $B$  terms regardless of the position of substitution. This result provides a rational physical explanation of the rule of thumb published a decade ago for substituted benzenes<sup>7</sup> and confirmed by subsequent numerical work, as discussed in more detail in part 4.<sup>6</sup> It also provides a priori predictions for molecules like triphenylene.

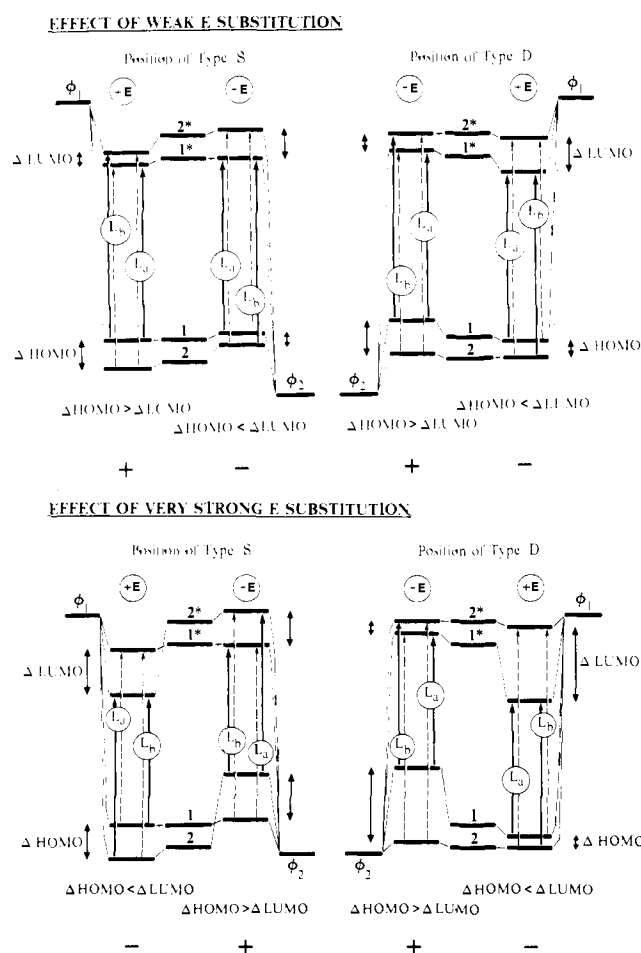
If both I and E substituents are present, it is best to view the molecule as an even-soft chromophore perturbed by an E substituent as discussed in more detail in part 5.<sup>8</sup>

(ii) **Odd-Soft Chromophores.** In these, the sign of  $B(G \rightarrow L_b)$  should be particularly sensitive to substituent effects since its  $\mu^-$  contribution vanishes. The orbitals are ordered  $s, a, -a, -s$  or  $a, s, -s, -a$ , and we shall refer to them as 2, 1,  $-1, -2$  in the order of increasing energy. Clearly, a  $+I$  effect in position  $\nu$  will cause  $\Delta\text{HOMO} > \Delta\text{LUMO}$  if  $c_{\nu,1}^2 < c_{\nu,2}^2$  and  $\Delta\text{HOMO} < \Delta\text{LUMO}$  if  $c_{\nu,1}^2 > c_{\nu,2}^2$ , and the opposite will hold for the  $-I$  effect (Figure 2). This behavior is illustrated on aza analogues of naphthalene,<sup>9</sup> phenanthrene,<sup>10</sup> anthracene,<sup>11</sup> and pyrene.<sup>12</sup>

In the positions of substitution in which  $c_{\nu,1}^2 > c_{\nu,2}^2$  (and  $c_{\nu,-1}^2 > c_{\nu,-2}^2$ ), the natural tendency of  $+E$  substitution to induce  $\Delta\text{HOMO} < \Delta\text{LUMO}$  whenever it can dominate the scene is not opposed nor is the tendency of  $-E$  effect to induce  $\Delta\text{HOMO} > \Delta\text{LUMO}$ . We shall refer to these positions as "dominant" (D) since they permit even a very weak substituent E effect to dominate and impose that sign of the  $\Delta\text{HOMO} - \Delta\text{LUMO}$  difference which it finds natural (Figure 3).



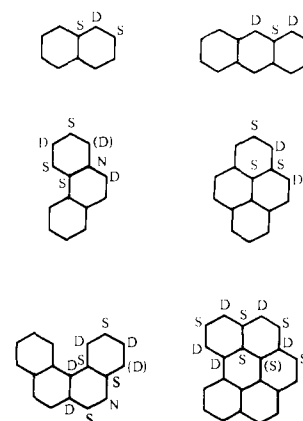
**Figure 2.** An example of the effect of inductively withdrawing (+I) substitution on the  $\Delta\text{HOMO}$  and  $\Delta\text{LUMO}$  values of an odd-soft chromophore, and the induced signs of the  $\mu^+$  contributions to the  $B$  terms of the lowest  $\pi\pi^*$  transition [ $B(L_1)$ ]. Orbital pairing: 1,1\* and 2,2\*.



**Figure 3.** Examples of the effect of weak and strong E substitution on the  $\Delta\text{HOMO}$  and  $\Delta\text{LUMO}$  values of an odd-soft chromophore, and the induced signs of  $\mu^+$  contributions to the  $B$  terms of the lowest  $\pi\pi^*$  transition [ $B(L_1)$ ]. Orbital pairing: 1,1\* and 2,2\*.

In those positions in which  $c_{\nu,1^2} < c_{\nu,2^2}$  (and  $c_{\nu,-1^2} < c_{\nu,-2^2}$ ), the natural tendencies of E substituents are at first perverted by the orbital ordering: a weak +E effect will cause  $\Delta\text{HOMO} > \Delta\text{LUMO}$  and a weak -E effect will cause  $\Delta\text{HOMO} < \Delta\text{LUMO}$ . Only when the E effect becomes strong enough to

**Chart I**



cause a reversal in the order of the orbitals, either by actual or by avoided crossing, will the natural tendencies prevail. Once this occurs, the E effect will dominate the scene in the usual fashion, and very strong +E substituents will cause  $\Delta\text{HOMO} < \Delta\text{LUMO}$  while very strong -E substituents will cause  $\Delta\text{HOMO} > \Delta\text{LUMO}$ . We shall refer to these positions as "subdominant" (S) since they cause the natural tendencies of E substituents to lay dormant for a while (weak E effect) and only eventually allow them to dominate as the substituent gathers strength (strong E effect, cf. Figure 3). In part 8<sup>13</sup> we shall investigate in some detail just how the change of sign occurs.

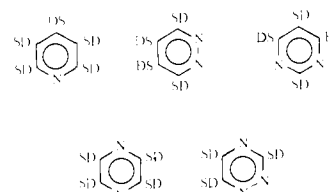
An illustration of various facets of the behavior of odd-soft chromophores is available for the cases of naphthalene,<sup>9,13</sup> anthracene,<sup>11</sup> and pyrene.<sup>12,14</sup> A list of D and S positions in some common odd-soft chromophores is given in Chart I. Positions for which  $c_{\nu,1^2} \approx c_{\nu,2^2}$  should show little response to weak E effects and have been labeled N for neutral.

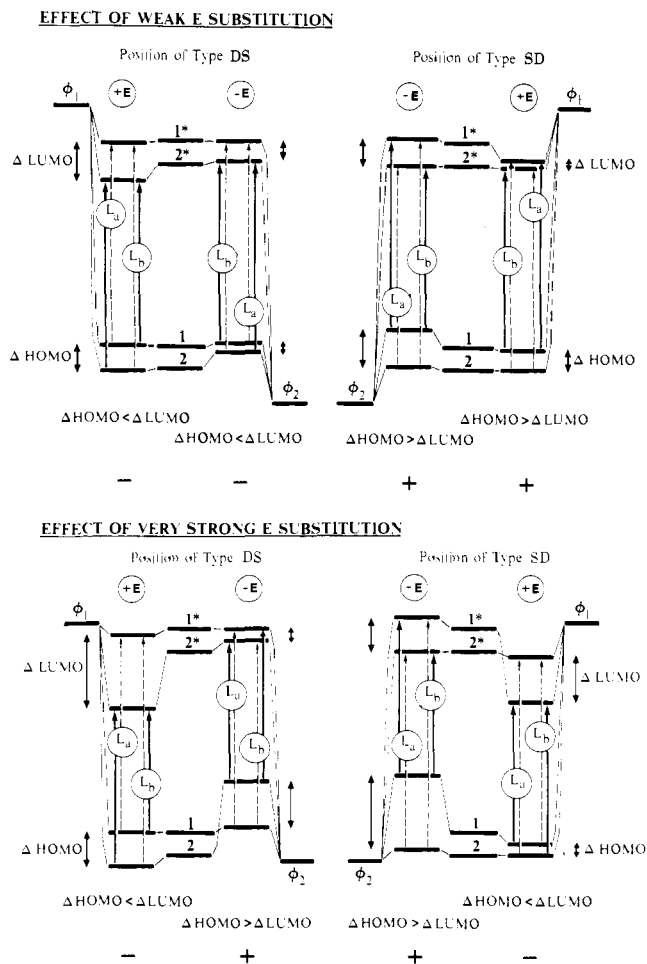
(iii) **Even-Soft Chromophores.** In these, the sign of  $B(G \rightarrow L_a)$  should be particularly sensitive to substituent effects since its  $\mu^-$  contribution vanishes. The orbitals are ordered s, a, -s, -a or a, s, -a, -s, and we shall again refer to them as 2, 1, -1, -2 in the order of increasing energy. Given this orbital sequence, an I effect does not remove the equality  $\Delta\text{HOMO} = \Delta\text{LUMO}$  to the first order in the perturbation regardless of the position of substitution. This behavior is documented by the comparison of pyridine with the diazines in part 4.<sup>6</sup> In only approximately even-soft chromophores, in which MO coefficient pairing is imperfect, nonvanishing effects are to be expected from I substituents, but they should be generally smaller than was the case for odd-soft chromophores.

The positions of substitution in which  $c_{\nu,1^2} < c_{\nu,2^2}$  and  $c_{\nu,-2^2} < c_{\nu,-1^2}$  are dominant for +E substitution and subdominant for -E substitution (DS), while those in which the opposite holds are +E subdominant and -E dominant (SD), with the obvious consequences for the  $\Delta\text{HOMO}-\Delta\text{LUMO}$  difference (Figure 4). In part 5,<sup>8</sup> we shall describe in some more detail the process of sign reversal caused by increasing the E effect of the substituent.

We do not have a very good illustration of this type of behavior on a hydrocarbon, since the pairing of the orbitals of even-soft chromophores, which are nonalternant, reflects only

**Chart II**





**Figure 4.** Examples of the effect of weak and strong E substitution on the  $\Delta \text{HOMO}$  and  $\Delta \text{LUMO}$  values of an even-soft chromophore, and the induced signs of  $\mu^+$  contributions to the  $B$  terms of the lowest  $\pi\pi^*$  transition [ $B(L_1)$ ]. Orbital pairing: 1,1\* and 2,2\*.

rather approximately the perfect pairing which was present in the unperturbed perimeter. In part 14<sup>15</sup> we discuss the case of azulene, whose positions indeed are approximately of the SD and DS types. A better illustration is available in the case of E-substituted pyridines, discussed in part 5.<sup>8</sup> Chart 11 gives a list of SD and DS positions in some azines to give an indication of the variety to be expected.

(iv) **Zero-Soft Chromophores.** These have all  $\mu^-$  contributions nonvanishing and the signs of their  $B$  terms should show less sensitivity to small perturbations. Chromophores of this kind will probably have to be handled on a one-by-one basis.

Substituent effects on charged-perimeter soft chromophores ( $n \neq 4N + 2$ ) are more difficult to handle en masse. Since orbital pairing is absent already in the parent perimeter, let alone in the derived chromophores, all four orbitals behave independently and all four coefficients in the position of substitution will in general have to be inspected before prediction of substituent effects can be made. One generalization which appears possible for double-soft chromophores of this type is that a single I substituent weak enough to be reasonably described by first-order perturbation will convert annulene ions to single-soft chromophores (e.g., from  $\text{C}_5\text{H}_5^-$ , the pyrrole nitranion  $\text{C}_4\text{H}_4\text{N}^-$ , or the tetrazole nitranion  $\text{CHN}_4^-$ ,  $\Delta \text{HOMO} \approx \Delta \text{LUMO}$ ), while multiple I substitution will generally produce hard chromophores (imidazole nitranion,  $\text{C}_3\text{H}_3\text{N}_2^-$ ,  $\Delta \text{HOMO} > \Delta \text{LUMO}$ , and pyrazole nitranion,  $\Delta \text{HOMO} < \Delta \text{LUMO}$ ). Similarly, a single  $-E$  substituent should yield  $\Delta \text{HOMO} > \Delta \text{LUMO}$ .

In the present group of papers, we present no experimental data for derivatives of soft chromophores with a charged perimeter. However, as noted in part 1,<sup>2</sup> publication of such evidence for several structural types of compounds is currently under preparation.

**5. Summary of Results and Conclusions.** Consideration of the predicted MCD behavior provides a unified view of all cyclic  $\pi$ -electron chromophores which possess a  $(4N + 2)$ -electron [ $n$ ]annulene perimeter and leads to the comprehensive classification of such chromophores given in Tables I and II. This classification also systematizes transition intensities and polarizations, but this has not been discussed in detail here. General rules for the response of MCD signs to substituent effects which were derived for chromophores with an uncharged perimeter are summarized in Chart III. No such sweeping generalizations appear possible for chromophores with a charged perimeter, which present a much wider variety of structural types and of possible responses.

It remains to be seen whether any of this predictability will find use in organic structural problems, since so many structural tools already exist. An advantage of the MCD technique is the very small amount of material required; for fluorescent materials this advantage could be pressed several orders of magnitude farther by using fluorescence-detected MCD.<sup>16</sup>

On the other hand, it is already quite clear that MCD measurements will be useful for separation of the I and E ef-

**Chart III.** Sign of  $(\Delta \text{HOMO} - \Delta \text{LUMO})^a$  for Uncharged-Perimeter Soft Chromophores

chromophore	position	substituent effects				example
		+I	-I	+E <sup>b</sup>	-E <sup>b</sup>	
double-soft		0	0	-	+	
even-soft	DS	~0	~0	-	-, then 0, then +	
	N	0	0	~0, then -	~0, then +	
	SD	~0	~0	+, then 0, then -	+	
odd-soft	D	-	+	-	+	
	N	0	0	~0, then -	~0, then +	
	S	+	-	+, then 0, then -	-, then 0, then +	

<sup>a</sup> A positive sign implies a +, -, +, - sign sequence for substituent-induced  $\mu^+$  contributions to  $B$  terms of the L and B bands in the order of increasing energy; a negative sign implies the -, +, -, + sign sequence. <sup>b</sup> Changes which occur as the E effect gradually becomes stronger are noted.

fects of substituents, and we are presently pursuing this line of investigation.

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# Magnetic Circular Dichroism of Cyclic $\pi$ -Electron Systems. 4.<sup>1</sup> Aza Analogues of Benzene

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**Abstract:** Magnetic circular dichroism of pyridine and the three diazines is analyzed. The  $B$  terms of the  $n\pi^*$  transition are very small and negative. Those of the  $L_b \pi\pi^*$  transition are small and positive and thus opposite to those one might expect from a simple extension of the empirical rule for substituted benzenes to the aza "substituent", but they are in excellent agreement with the general qualitative theory of parts 1-3 for even-soft MCD chromophores. The results indicate that MCD will be generally useful for the separation of inductive and mesomeric effects of substituents.

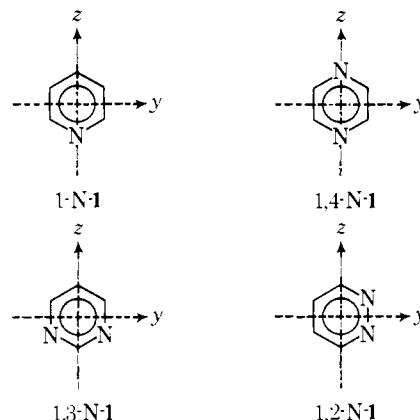
## Introduction

The first three papers of this series<sup>1,3,4</sup> presented an analysis of the consequences of a simple  $\pi$ -perimeter model for MCD signs of transitions in cyclic conjugated  $\pi$  systems which can be related to the two  $L$  and two  $B$  states of the  $(4N + 2)$ -electron perimeter. In this and the following papers, we attempt to determine the scope of validity of the results by comparison with experimental data. Presently, we report results for four aza analogues of benzene (1): pyridine (1-N-1), pyrazine (1,4-N-1), pyrimidine (1,3-N-1), and pyridazine (1,2-N-1). These can be viewed as benzene with one or two +I substituents and, according to the simple theory,<sup>3,4</sup> should represent even-soft MCD chromophores. A study of the effect of E substitution on azines, confirming this conclusion, appears as part 5.<sup>5</sup>

Singlet excited states of the azines have been analyzed in considerable detail. Electronic spectroscopy,<sup>6</sup> photoelectron spectroscopy,<sup>7</sup> and calculations<sup>8</sup> show that the weak first singlet-singlet absorption band near 30-35 000  $\text{cm}^{-1}$  is due to an  $n\pi^*$  transition ( $1\text{-N-1}$ ,  $n \rightarrow -s$ ;  $1,4\text{-N-1}$ ,  $n_+ \rightarrow -s$ ;  $1,3\text{-N-1}$ ,  $n_- \rightarrow -a$ ;  $1,2\text{-N-1}$ ,  $n_- \rightarrow -a$ , using the nomenclature of ref 1 for labeling  $\pi$  orbitals of a perturbed annulene with respect to mirroring in the  $xz$  plane implied in the formulas). The next band near 40 000  $\text{cm}^{-1}$  is of  $\pi\pi^*$  nature and corresponds to the  $L_b$  transition ( $B_{2u}$  state) of benzene. A stronger  $\pi\pi^*$  band near 50 000  $\text{cm}^{-1}$  corresponds to the  $L_a$  transition ( $B_{1u}$  state of benzene). Higher energy states lie outside the experimental region accessible to us presently.

Magnetic circular dichroism of the azines was briefly mentioned in our preliminary communication.<sup>9a</sup> Professors Hezemans (Utrecht) and Hatano (Sendai) have informed us recently of their respective independent studies of the MCD of these compounds; the latter has just appeared in print.<sup>9b</sup>

Their interest centers on the  $n\pi^*$  transitions in the free-base azines and on numerical calculations of the  $B$  terms in the spectra, both of which are of secondary importance in the present paper, so that a very small degree of overlap results.



## Experimental Section and Calculations

Absorption and MCD spectra were recorded at room temperature in spectral-grade cyclohexane (Eastman). Protonated 1-N-1 was run in 0.5 N aqueous HCl. Standard volumetric techniques were used for sample preparation. The measurements were done on Cary 17 and modified Cary 60 instruments. The latter was equipped with a 45-kG superconducting magnet and was calibrated using *d*-camphorsulfonic acid. The accuracy of the measured MCD intensities is estimated at about 10% and was double-checked by comparison with published data for several organic and inorganic compounds. The spectra were digitized and plotted using a PDP-11/10 minicomputer, which also calculated  $B$  terms ( $\beta_e D^2/\text{cm}^{-1}$ ) from the formula<sup>10</sup>  $B = (1/33.53) \cdot \int [\theta]_M \bar{\nu}^{-1} d\bar{\nu}$ , where  $[\theta]_M$  is molar ellipticity in  $\text{deg L m}^{-1} \text{mol}^{-1} \text{G}^{-1}$  and  $\bar{\nu}$  is wavenumber, and oscillator strengths  $f$  from the formula  $f$