7776 J. Phys. Chem. A **2000,** *104,* 7776–7784

MCD of Nonaromatic Cyclic π-Electron Systems. 4.[1] Explicit Relations between Molecular Structure and Spectra

Jörg Fleischhauer[†] **and Josef Michl***[,‡]

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

Received: January 7, 2000; In Final Form: May 2, 2000

The relation of molecular structure to the six perturbation parameters h_D, s_D, l_D, h, s, and l of the theory of MCD (magnetic circular dichroism) spectra of π systems derived from 4*N*-electron perimeters (parts 1−3) is developed explicitly. The MCD spectra of acenaphthylene and pleiadiene are interpreted in the way of illustration. Simple PMO arguments are used to derive general rules for the response of the MCD spectra of nonaromatic cyclic π chromophores to inductive and mesomeric effects of substituents.

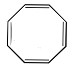
The purpose of this paper is to work out the consequences of the general theory of the MCD (magnetic circular dichroism) and polarized electronic spectra of nonaromatic[2] molecules derived from 4*N*-electron perimeters, such as **1**−**12**, developed in parts 1,[2] 2,[3] and 3[1] using the 4*N*-electron *n*-center perimeter model and to point out similarities and differences relative to the spectra of aromatic molecules, derived from a (4*N* + 2)-electron *n*-center perimeter.[4,5] We distinguish three categories of nonaromatic molecules: (i) antiaromatic biradicals with a very small energy gap (less than about 2 eV) between the orbitals that are occupied and those that are unoccupied in the lowest energy configuration and closed-shell, (ii) unaromatic and (iii) ambiaromatic, molecules in which this energy gap is sizable. The difference between unaromatic and ambiaromatic molecules is that the latter can also equally well be derived from a (4*N* + 2)-electron perimeter. All results of the present paper apply equally to unaromatic and ambiaromatic molecules.

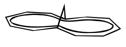
In parts 2[3] and 3,[1] we showed that qualitative information about absorption intensities and polarizations, and about the signs of the MCD *B* terms, can be deduced simply for six low-lying $\pi\pi^*$ excited states of unaromatic and ambiaromatic molecules with a plane of symmetry σ_v perpendicular to the molecular plane. This information is obtained from the knowledge of the relative size and signs of six quantities. Three are derived from orbital energy differences, ΔHSL, ΔHL, and ΣHL, and three are the phase angles, η, σ, and λ. For molecules with a plane of symmetry σ_v or σ_d, the phase angles are dictated by the energy order of orbital symmetries relative to this plane.[1]

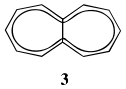
These six quantities can be obtained from the six parameters h_D, s_D, l_D, h, s, and l that describe in terms of degenerate perturbation theory how the perturbation converts the degenerate complex frontier orbitals of the perimeter, $\psi_{\pm(N-1)}$, $\psi_{\pm N}$, and $\psi_{\pm(N+1)}$, into the six frontier orbitals of the resulting molecule, $h_\pm$, $s_\pm$, and $l_\pm$. Next, the six important perturbation parameters h_D, s_D, l_D, h, s, and l need to be related to molecular structure. The arguments are similar to those more[4,5] or less[6] implicitly contained in the earlier work on the (4*N* + 2)-electron perimeter model.

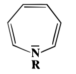
Second, we illustrate the use of the model by showing how it accounts for the low-energy transitions of acenaphthylene (**9**) and pleiadiene (**10**). These are ambiaromatic molecules and their low-lying electronic states have been already interpreted in terms of the ordinary (4*N* + 2)-electron perimeter model for aromatics.[7] The present alternative description permits us to contrast the 4*N*- and (4*N* + 2)-electron perimeter models. The two yield different state labels but predict the same MCD signs, and these are in agreement with experiment. In subsequent papers of this series, we plan to report and interpret the MCD spectra of several families of unaromatic compounds.

Third, we use first- and second-order perturbation theory to formulate general rules for the effect of substituents on the MCD of the first two allowed bands of soft unaromatic and ambiaromatic chromophores. Although reminiscent of the rules for aromatics,[5,6] they are distinctly different.

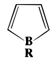

1


2

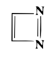

3



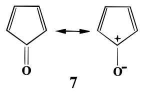
4



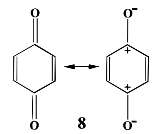
5



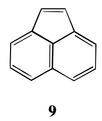
6

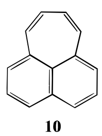


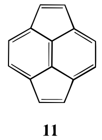
7

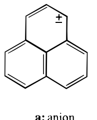


8


9


10


11



12 **a:** anion **b:** cation

Results and Discussion

Perturbation of the Perimeter. Earlier, we presented the results for spectroscopic properties of high-symmetry (threefold or higher order rotational axis, part 2[3]) and low-symmetry (part 3[1]) unaromatic and ambiaromatic molecules in terms of quantities describing their parent perimeter, i.e., the number of centers *n* and the number of electrons 4*N*, and in terms of quantities describing the perturbation that formally converts the perimeter into the molecule in question. These were three off-diagonal and three diagonal matrix elements of the one-electron operator $\hat{a}$ that provides an approximate description of the perturbation,

---

[†] Permanent address: Institut für Organische Chemie, RWTH Aachen, Prof.-Pirlet-Str. 1, D-52056 Aachen, Germany.

[‡] This project was initiated at the University of Utah.

10.1021/jp000117+ CCC: $19.00

$$h = (\Delta H/2)\ \mathrm{e}^{i\eta} = \langle \psi_{N-1}|\hat{a}|\psi_{-N+1}\rangle \tag{1}$$

$$s = (\Delta S/2)\ \mathrm{e}^{i\sigma} = \langle \psi_{N}|\hat{a}|\psi_{-N}\rangle \tag{2}$$

$$l = (\Delta L/2)\ \mathrm{e}^{i\lambda} = \langle \psi_{N+1}|\hat{a}|\psi_{-N-1}\rangle \tag{3}$$

$$h_{\mathrm{D}} = \langle \psi_{N-1}|\hat{a}|\psi_{N-1}\rangle \tag{4}$$

$$s_{\mathrm{D}} = \langle \psi_{N}|\hat{a}|\psi_{N}\rangle \tag{5}$$

$$l_{\mathrm{D}} = \langle \psi_{N+1}|\hat{a}|\psi_{N+1}\rangle \tag{6}$$

where ψ_k and ψ_{-k} are the complex perimeter MOs with "magnetic quantum numbers" $\pm k$ ($k \geq 0$) that belong to the irreducible representations ϵ_k and ϵ_{-k} in C_n, respectively (in this convention basis vectors rather than functions are subjected to symmetry operations). In terms of the Löwdin-orthogonalized AOs χ_ν, labeled counterclockwise $\nu = 0, 1, 2, ..., n - 1$ modulo n ($0 = n$, $1 = n + 1$, etc.):

$$\psi_{\pm k} = n^{-1/2} \sum_{\nu=0}^{n-1} \chi_\nu \exp(\pm 2\pi i k \nu / n) \tag{7}$$

The description of the structural perturbation by a one-electron operator is compatible with the use of first-order perturbation theory. Since the orbitals themselves are assumed not to change as a result of the perturbation (except for mixing within degenerate pairs that have equal two-electron contributions to their Hartree−Fock orbital energies), the two-electron contributions to HF orbital energies do not change, either. Changes in relative energies of configuration state functions, which determine the resulting MCD patterns, then originate only in the effects of the perturbation on the one-electron parts of orbital energies. Throughout the present paper, we shall therefore mean the one-electron part of an orbital energy when we refer to the energy E of an orbital.

The off-diagonal perturbation parameters h, s, and l are complex numbers. Their absolute values, $\Delta H/2$, $\Delta S/2$, and $\Delta L/2$, respectively, and their complex arguments, η, σ, and λ, respectively, combined with the three real diagonal elements, h_{D}, s_{D}, and l_{D}, represent quantities that are adequate for a complete characterization of the perturbation for the purposes of the perimeter model description of low-lying electronic states. In the following, we use the general symbol k_{D} to represent any one of h_{D}, s_{D}, or l_{D}, κ to represent any one of h, s, or l, the symbol ΔK for ΔH, ΔS, or ΔL, and $\varkappa$ for η, σ, or λ. The analogy of these quantities to those that describe the effect of a one-electron perturbation on an aromatic ($4N + 2$)-electron perimeter,[4,5] richer by two π electrons, is obvious: ΔS and ΔL correspond to ΔHOMO and ΔLUMO, respectively, and σ and λ to π + arg a and -arg b, respectively. The simple explicit rules derived in the following for obtaining these quantities by inspection of molecular structure will therefore be equally useful for all cyclic π systems.

The quantities needed in parts 2[3] and 3[1] for the prediction of spectral properties were

$$\begin{aligned} \Delta H &= E(h_+) - E(h_-) \geq 0 \\ \Delta S &= E(s_+) - E(s_-) \geq 0 \\ \Delta L &= E(l_+) - E(l_-) \geq 0 \end{aligned} \tag{8}$$

$$\begin{aligned} \Delta HL &= \Delta H - \Delta L \\ \Sigma HL &= \Delta H + \Delta L \\ \Delta HSL = 2(\Delta HS - \Delta LS) &= 2[2E(\mathrm{SO}) - E(\mathrm{HO}) - E(\mathrm{LO}) + 2s_{\mathrm{D}} - h_{\mathrm{D}} - l_{\mathrm{D}}] \\ \Delta HS &= [E(s_+) + E(s_-) - E(h_+) - E(h_-)]/2 \\ \Delta LS &= [E(1_+) + E(1_-) - E(s_+) - E(s_-)]/2 \end{aligned} \tag{9}$$

The overall conversion of an ideal $4N$-electron perimeter into a molecule of interest is described by the operator $\hat{A}$, approximated as a sum of one-electron operators, $\hat{A} = \sum_i \hat{a}_i$, where the sum runs over all electrons in π orbitals. In the following, we list the important classes of simple perturbations and define the associated elementary operators $\hat{a}$. Their matrix elements are specified in the basis of the AOs of the perimeter or in the basis of its complex MOs, ψ_k and ψ_{-k} [$k = 0, +1, +2, ..., +(n/2 - 1)$, $n/2$ if n is even, with $\psi_{n/2} \equiv \psi_{-n/2}$, and $k = 0, +1, ..., +(n - 1)/2$ if n is odd]. We assume that the effects of composite perturbations are additive. In defining the operators $\hat{a}$, we rely heavily on the description of organic π-electron structures in terms of perturbation theory (PMO) as summarized in the book by Dewar and Dougherty.[8] The elementary perturbations are of two kinds: size-conserving and size-expanding. The matrix elements of the former are defined simply in the AO basis and are handled using first-order perturbation theory; those of the latter can be written in a simple approximate way in the MO basis and are handled using second-order perturbation theory, in a fashion that avoids an actual expansion of the size of the n-dimensional one-electron function space (this can be done more formally by partitioning theory).

Note that perturbations that are of purely two-electron nature in the model used, such as a geometrical distortion of the perimeter from the shape of a regular polygon without a significant modification of bonding interactions, do not affect the wave functions of the perimeter model states in the present approximation. It is still possible to incorporate the effects of such geometrical distortions on the matrix elements of electric dipole or magnetic dipole operators in a very straightforward way since atomic coordinates enter into their definition.[4]

After perturbation, each perimeter orbital pair ψ_k, ψ_{-k} will in general yield a pair of real orbitals, κ_- at a lower one-electron energy, $E(\psi_k) + k_{\mathrm{D}} - \Delta K/2$, and κ_+ at a higher energy, $E(\psi_k) + k_{\mathrm{D}} + \Delta K/2$, where $E(\psi_k)$ is the energy of the unperturbed orbital ψ_k. Their separation will be ΔK, and their average energy will be $E(\psi_k) + k_{\mathrm{D}}$. For systems derived from $4N$-electron perimeters, the knowledge of both ΔK and k_{D} is essential, while for those derived from ($4N + 2$)-electron perimeters, only ΔK values were needed to predict signs in MCD spectra.[4,5]

In practice, the relative orbital energies can be estimated in a variety of ways, starting with PMO theory, through Hückel, PPP, DFT or ab initio theories. The values of ΔK, with the exception of ΔS, can in principle also be derived from experimental data using Koopmans' theorem. The PMO estimate is most in keeping with the spirit of the perimeter model, which keeps all the essential physics for a qualitative understanding but expends the smallest possible computational effort.

The PMO approximation defines the action of the perturbation as combining the complex MOs of the perimeter pairwise into real MOs and changing their energies, but permits no mixing of members of different degenerate pairs. The pairwise combination of a general orbital pair ψ_k and ψ_{-k} proceeds in a way dictated by the complex phase $\varkappa$, and we introduce the definitions

$$\kappa_+ = [\mathrm{e}^{i\varkappa/2}\psi_k + \mathrm{e}^{-i\varkappa/2}\psi_{-k}]/\sqrt{2} = (2/n)^{1/2}\sum_\nu \chi_\nu \cos(2\pi k\nu/n + \varkappa/2) \quad (10)$$

$$\kappa_- = [\mathrm{e}^{i\varkappa/2}\psi_k - \mathrm{e}^{-i\varkappa/2}\psi_{-k}]/i\sqrt{2} = (2/n)^{1/2}\sum_\nu \chi_\nu \sin(2\pi k\nu/n + \varkappa/2)$$

where the energy of κ_- is not above that of κ_+.

The specific three phase angles of interest now, η, σ, and λ, ultimately determine the phase factors $\rho^\pm = \sigma \pm (\eta + \lambda)/2$ of part 3[1] as well as the directions of spectroscopic transition moments, and thus affect the signs of B terms. The factor ρ^+ only occurs if the parent perimeter is uncharged. The analogy to the aromatic $(4N + 2)$-electron perimeter is also obvious. There, the specific phase angles arg a and arg b dictated the phase factors γ and ϕ and thus transition moment directions, and, in the case of uncharged perimeters $(4N + 2 = n)$, also affected the magnitudes of the B terms.[4,5]

The center of the perimeter is located at the center of the coordinate system. If the symmetry plane σ_v perpendicular to the molecular plane passes through an atom, we let the x axis pass through this atom (i.e., give it the label $\nu = 0$), and only the values $\varkappa = 0$ or $\varkappa = \pi$ are possible. The former applies if κ_- is antisymmetric and the latter if κ_- is symmetric. If the symmetry plane passes only through bond midpoints, the label $\nu = 0$ is assigned to one of the atoms located counterclockwise next to a midpoint, and only the angles $\varkappa = 2\pi k/n$ or $\varkappa = 2\pi k/n - \pi$ are possible. The former applies if κ_- is antisymmetric and the latter if κ_- is symmetric. A general way to visualize the location of the nodal points in κ_- is to first place one of them at the initial atom $\mu = 0$ and others at intervals of $n/2k$ bond lengths apart, and then move the positions of all of them clockwise by an amount equal to $\varkappa/2\pi$ times the internodal separation. Conversely, if the location of the nodal points in a particular orbital κ_- is known, it permits the value of $\varkappa$ to be deduced.

Size-Conserving Elementary Perturbations. These do not change the size of the π system. The most important are (i) bond torsion, extension, or compression (e.g., **1**); (ii) cross-linking, either by introduction of transannular overlap between nonneighboring AOs of the π perimeter (e.g., between $2p_z$ orbitals on carbon atoms 1 and 7 in **2**) or by introduction of sigma bonds (e.g., **3**); (iii) introduction of an inductive effect by heteroatom replacement (e.g., **4**, **5**, **6**) or by inductive substituents with negligible conjugative and hyperconjugative effects.

A change in the strength of the valence interaction between the AOs ρ and τ as in (i), or an introduction of a new one as in (ii) are represented by an operator with matrix elements $a_{\rho\tau} = a_{\tau\rho}$ in the AO basis set. In the Hückel approximation, they are a change in the resonance integral $\beta_{\rho\tau}$.

In the same basis, an inductive effect of a substituent or a heteroatom located at atom ρ is described by the matrix element $a_{\rho\rho}$. In the Hückel approximation, this corresponds to a change in the Coulomb integral α_ρ of the AO ρ. For atoms more electronegative than carbon, $\alpha_\rho < 0$ (+I effect), for those less electronegative, $\alpha_\rho > 0$ (−I effect).

Expressions for k_D, given by $\langle\psi_k|\hat{a}|\psi_k\rangle$, follow by direct substitution from eq 7. For a change in the valence interaction between AOs ρ and τ, such as an introduction of a cross-link

$$k_\mathrm{D} = (2/n)a_{\tau\rho}\cos[2\pi k(\rho - \tau)/n] \quad (11)$$

and for an inductive effect by a heteroatom or a substituent in position ρ

$$k_\mathrm{D} = a_{\rho\rho}/n \quad (12)$$

Expressions for ΔK and $\varkappa$ follow from their definition, $\kappa = (\Delta K/2)\mathrm{e}^{i\varkappa}$, by substitution from eq 7 into $\kappa = \langle\psi_k|\hat{a}|\psi_{-k}\rangle$. Modification of a valence interaction between AOs ρ and τ yields

$$\kappa = 2(a_{\rho\tau}/n)\exp[-i(4k/n)(\pi/2)(\tau + \rho)] \quad (13)$$

$$\Delta K = 4|a_{\rho\tau}|/n \quad (14)$$

Inductive effect of a substituent or a heteroatom in position ρ yields

$$\kappa = (a_{\rho\rho}/n)\exp[-i(4k/n)\pi\rho] \quad (15)$$

$$\Delta K = 2|a_{\rho\rho}|/n \quad (16)$$

For a cross-link $(\rho \neq \tau, \tau \pm 1)$, a bond compression $(\rho = \tau \pm 1)$, or a +I effect $(\rho = \tau)$, we have $a_{\rho\tau} < 0$, and the complex phase $\varkappa$ for these elementary perturbations therefore is

$$\varkappa = -(2\pi/n)[(\tau + \rho)k - n/2] \quad (17)$$

while for bond stretching or twisting $(\rho = \tau \pm 1)$ and for a −I effect $(\rho = \tau)$, $a_{\rho\tau} > 0$, and the phase is

$$\varkappa = -(2\pi/n)(\tau + \rho)k \quad (18)$$

In uncharged perimeters $(n = 4N)$, the equations for σ $(k = N)$ simplify. If $a_{\rho\tau} < 0$, the expression for σ $(k = N)$ becomes

$$\sigma = -(\pi/2)[\tau + \rho - 2] \quad (17')$$

If $a_{\rho\tau} > 0$, we obtain

$$\sigma = -(\pi/2)(\tau + \rho) \quad (18')$$

According to Moffitt,[9] "even" elementary perturbations are those for which $\tau + \rho$ is even. For these, eqs 17′ and 18′ show that σ is a multiple of π and $\rho^+ = \rho^- = 0$. Examples are +I and −I effects and cross-links forming odd-membered rings. In this case, the nodal planes in s_+ and s_- pass through atoms. For "odd" elementary perturbations, $\tau + \rho$ is odd, eqs 17′ and 18′ show that σ is an odd multiple of $\pi/2$, and $\rho^- = 0$, $\rho^+ = \pi$. An example are cross-links forming even-membered rings. Then, the nodal planes in s_+ and s_- pass through midpoints of bonds.

Size-Expanding Elementary Perturbations. These are associated with an increase in the size of the π system. Two kinds are important: (i) introduction of mesomeric substituents (e.g., **7** and **8**); (ii) bridging (e.g., **9**−**12**). Such perturbations are properly described by direct addition of a one-electron space of dimensionality m equal to the number of π-symmetry orbitals ψ_j $(j = n, n + 1, ..., n + m - 1)$ on the substituent or the bridge, to the space defined by the perimeter orbitals. The matrix elements of $\hat{a}$ in the expanded AO basis are like those for cross-linking (Hückel resonance integrals) but connect the substituent AO in the exocyclic position to a single perimeter AO, or a bridge AO or AOs to two or more perimeter AOs. In the order to characterize this type of perturbation through the quantities h, s, l, h_D, s_D, and l_D, we need to express the effect of these interactions within the original n-dimensional perimeter space. Since we are treating symmetrical molecules, it is easy to do this approximately, using degenerate second-order perturbation

CHART 1

$$\begin{array}{c|ccccccccccc}
 & \psi_0 & \cdots & \psi_{-k} & \psi_k & \cdots & \psi_n & \cdots & \psi_j & \cdots & \psi_{n+m-1} \\
\hline
\psi_0 & E(\psi_0) & & & & & & & & & \\
\vdots & & \ddots & & & & & & & & \\
\psi_{-k} & & & E(\psi_k) & 0 & & \langle -k|\hat{a}|n\rangle & \cdots & \langle -k|\hat{a}|j\rangle & \cdots & \langle -k|\hat{a}|n+m-1\rangle \\
\psi_k & & & 0 & E(\psi_k) & & \langle k|\hat{a}|n\rangle & \cdots & \langle k|\hat{a}|j\rangle & \cdots & \langle k|\hat{a}|n+m-1\rangle \\
\vdots & & & & & \ddots & & & & & \\
\psi_n & & & \langle n|\hat{a}|-k\rangle & \langle n|\hat{a}|k\rangle & & E(\psi_n) & & & & \\
\vdots & & & \vdots & \vdots & & & \ddots & & & \\
\psi_j & & & \langle j|\hat{a}|-k\rangle & \langle j|\hat{a}|k\rangle & & & & E(\psi_j) & & \\
\vdots & & & \vdots & \vdots & & & & & \ddots & \\
\psi_{n+m-1} & & & \langle n+m-1|\hat{a}|-k\rangle & \langle n+m-1|\hat{a}|k\rangle & & & & & & E(\psi_{n+m-1})
\end{array} \qquad (20)$$

theory within the spirit of the PMO model[8] to derive the energies and nodal properties of the perturbed perimeter orbitals.

Let the substituent or bridge carry m AOs of π symmetry, combined into a set of m delocalized orbitals

$$\psi_j = \sum_{\nu=n}^{n+m-1} c_{\nu j}\chi_\nu \qquad (19)$$

with one-electron energies $E(\psi_j)$, and let its AOs $\sigma_1, \sigma_2, ..., \sigma_l, ...$ be attached to perimeter atoms $\rho_1, \rho_2, ..., \rho_l, ...$, respectively. We consider the effect of the perturbation on one degenerate perimeter orbital pair ψ_k, ψ_{-k} at a time and ignore substituent-induced mixing of the members of different pairs.

In the MO basis, the Hamiltonian matrix of the expanded system takes the form of eq 20 shown in Chart 1 (only those off-diagonal elements that are pertinent to the behavior of orbitals Ψ_{-k} and Ψ_k are shown).

For the matrix elements $\langle \pm k|\hat{a}|j\rangle$, substitution from eq 7 yields

$$\langle \pm k|\hat{a}|j\rangle = n^{-1/2}\sum_l c_{\sigma(l)j}\exp(\mp 2\pi i k\rho_l/n)a_l \qquad (21)$$

where $a_l = \langle \sigma_l|\hat{a}|\rho_l\rangle$. Here and in the following, we use σ_l and $\sigma(l)$ interchangeably in order to avoid subscripts on subscripts.

If the complex phase of the elements $\langle \pm k|\hat{a}|j\rangle$ is the same for all values of the index j (or differs by π), a simple result is obtained. We specify the complex phase as $\varkappa'/2$ by writing

$$\langle \pm k|\hat{a}|j\rangle = |\langle \pm k|\hat{a}|j\rangle| \mathrm{e}^{\pm i\varkappa'/2} \qquad (22)$$

The condition that $\varkappa'_j$ be the same for all j, or at most different by π, permitting us to drop the subscript j, is satisfied for many important structural classes of perturbations. In particular, it holds if at least one of the following conditions holds: (i) The perturbing group is a substituent and not a bridge, i.e., is attached by its AO χ_σ to a single perimeter AO χ_ρ, as in **7**. (ii) The substituent or bridge has only one orbital $\psi_j = \psi_n$ (others are absent or their effects can be ignored). An example is **12**. (iii) The perturbed molecule has one or more planes of symmetry σ_ν perpendicular to the plane of the perimeter, which is the case considered here. Examples are **7**−**12**. This instance is particularly important for multiply perturbed perimeters such as **8** and will be discussed below.

We now define real orbitals κ_1 and κ_2 in the same way as κ_+ and κ_-, respectively, were defined in eq 10, using the angle $\varkappa'$ instead of $\varkappa$. From eq 21, we then obtain

$$\langle \kappa_1|\hat{a}|j\rangle = (2/n)^{1/2}\, |\sum_l c_{\sigma(l)j}\exp(-2\pi i k\rho_l/n)a_l| \qquad (23)$$

$$\langle \kappa_2|\hat{a}|j\rangle = 0$$

Next, we treat the effect of the substituent or bridge to second order in perturbation theory, assuming that its orbitals are not degenerate with the ψ_k, ψ_{-k} pair. We obtain for the one-electron energies of the perturbed perimeter orbitals

$$E(\kappa_1) = E(\psi_k) + (2/n)\sum_j |\sum_l c_{\sigma(l)j} \exp(-2\pi i k\rho_l/n)a_l|^2/ [E(\psi_k) - E(\psi_j)] \quad (24)$$

$$E(\kappa_2) = E(\psi_k)$$

Since by definition $E(\psi_k) + k_D = [E(\kappa_1) + E(\kappa_2)]/2$ and $\Delta K = |E(\kappa_1) - E(\kappa_2)|$, we obtain

$$k_D = n^{-1}\sum_j \{\sum_{l,l'} c_{\sigma(l)j}c_{\sigma(l')j}a_l a_{l'} \cos[2\pi k(\rho_{l'} - \rho_l)/n]\}/ [E(\psi_k) - E(\psi_j)] \quad (25)$$

$$\Delta K = 2|k_D|$$

and

$$\exp(i\varkappa'/2) = \sum_l c_{\sigma(l)j} \exp(-2\pi i k\rho_l/n)a_l/ \{\sum_{l,l'} c_{\sigma(l)j}c_{\sigma(l')j}a_l a_{l'} \cos[2\pi k(\rho_{l'} - \rho_l)/n]\}^{1/2} \quad (26)$$

While in eq 24 the numerator is positive for each j, the denominator can be positive (donor orbitals j) or negative (acceptor orbitals j). If the one-electron energy of the perturbed orbital κ_1 lies above $E(\psi_k)$, the perturber acts as a net donor, and we introduce the notation

$$k_+ = \kappa_1$$

$$k_- = \kappa_2 \quad (27)$$

$$\varkappa = \varkappa'$$

If the one-electron energy of the perturbed orbital κ_1 lies below $E(\psi_k)$, the perturber acts as a net acceptor, and we introduce the notation

$$k_+ = \kappa_2$$

$$k_- = \kappa_1 \quad (28)$$

$$\varkappa = \varkappa' - \pi$$

With eqs 24−26 and either eq 27 or 28 we can now effectively replace the size-expanding elementary perturbation $\hat{a}$ by a size-conserving one and proceed with the application of the perimeter model. This perturbation behaves in a manner very similar to a true size-conserving inductive perturbation, except that its effect on the orbital pair ψ_k, ψ_{-k} depends on the orbital energy $E(\psi_k)$ through the factor $E(\psi_k) - E(\psi_j)$.

Because of the presence of the energy denominators, a transformation of the Hamiltonian matrix containing the diagonal shifts k_D given by eq 12 from the MO basis back to the AO basis yields a complicated matrix with many off-diagonal elements containing energy differences. Thus, while the size-expanding mesomeric effect of a perturbation can formally be expressed in the n-dimensional one-electron space of the perimeter also in the AO basis, like those of size-conserving perturbations given above, this is not particularly useful in practice.

Simple results are obtained for special cases. Throughout, we have $\Delta K = 2|k_D|$.

A. If only a single substituent orbital, ψ_n, needs to be considered, the results simplify to

$$k_D = n^{-1}\sum_{l,l'} c_{\sigma(l)n}c_{\sigma(l')n}a_l a_{l'} \cos[2\pi k(\rho_{l'} - \rho_l)/n]/[E(\psi_k) - E(\psi_n)] \quad (29)$$

$$\tan(\varkappa/2) = -\sum_l c_{\sigma(l)n}a_l \sin(2\pi k\rho_l/n)/ \sum_l c_{\sigma(l)n}a_l \cos(2\pi k\rho_l/n), \quad \text{if } k_D > 0 \quad (30)$$

$$\tan[(\varkappa + \pi)/2] = -\sum_l c_{\sigma(l)n}a_l \sin(2\pi k\rho_l/n)/ \sum_l c_{\sigma(l)n}a_l \cos(2\pi k\rho_l/n), \quad \text{if } k_D < 0$$

(i) The substituent is only attached to atom ρ of the perimeter:

$$k_D = c_{\sigma n}^2\, a_{\rho\sigma}^2/n[E(\psi_k) - E(\psi_n)] \quad (31)$$

$$\varkappa = -(2\pi/n)2\rho k, \quad \text{if } k_D > 0 \text{ (donor)} \quad (32)$$

$$\varkappa = -(2\pi/n)[2\rho k + n/2], \quad \text{if } k_D < 0 \text{ (acceptor)}$$

These results for mesomeric (E) substituents thus are very similar to those given in eqs 12, 17, and 18 for a purely inductive (I) substituent ($\rho = \tau$), with $c_{\sigma j}^2\, a_{\rho\sigma}^2$ playing the role of $a_{\rho\rho}$, except that the contribution of the mesomeric effect is attenuated by division by the orbital energy difference $E(\psi_k) - E(\psi_j)$. The phase factors are the same for both types of donor (−I and −E) substituents, and also for both types of acceptor (+I and +E) substituents.

(ii) The substituent (bridge) is attached to two atoms of the perimeter, through σ_1 to ρ_1 and through σ_2 to ρ_2, and the resonance integrals are equal, $a = a_{\rho(1)\sigma(1)} = a_{\rho(2)\sigma(2)}$.

Then, if the coefficients in ψ_n at the position of attachment are equal, or the same position of the substituent is attached to both ρ_1 and ρ_2, $c_{\sigma(1)n} = c_{\sigma(2)n} = c_{\sigma n}$ (if the substituent consists of a single atom, $c_{\sigma n} = 1$):

$$k_D = 4a_{\rho\sigma}^2\, c_{\sigma m}^2 \cos^2[\pi k(\rho_1 - \rho_2)/n]/n[E(\psi_k) - E(\psi_n)] \quad (33)$$

$$\varkappa = -(2\pi/n)(\rho_1 + \rho_2)k, \quad \text{if } k_D > 0 \quad (34)$$

$$\varkappa = -(2\pi/n)[(\rho_1 + \rho_2)k + n/2], \quad \text{if } k_D < 0$$

If the coefficients in ψ_m are equal in size and opposite in sign, $c_{\sigma(1)n} = -c_{\sigma(2)n} = c_{\sigma n}$,

$$k_D = 4a_{\rho\sigma}^2\, c_{\sigma n}^2 \sin^2[\pi k(\rho_1 - \rho_2)/n]/n[E(\psi_k) - E(\psi_n)] \quad (35)$$

$$\varkappa = -(2\pi/n)[(\rho_1 + \rho_2)k + n/2], \quad \text{if } k_D > 0 \quad (36)$$

$$\varkappa = -(2\pi/n)(\rho_1 + \rho_2)k, \quad \text{if } k_D < 0$$

B. If the substituent is attached in a single position ρ of the perimeter, through its AO σ, we obtain

$$k_D = \sum_j c_{\sigma j}^2\, a_{\sigma\rho}^2/n[E(\psi_k) - E(\psi_j)] \quad (37)$$

$$\varkappa = -(2\pi/n)2\rho k, \quad \text{if } k_D > 0 \tag{38}$$

$$\varkappa = -(2\pi/n)[2\rho k + n/2], \quad \text{if } k_D < 0$$

Intruder Orbitals and Intruder States. When the perturbing orbitals ψ_j of the substituent or bridge are empty and lie well above or are occupied and lie well below the orbital pair ψ_k, ψ_{-k} in energy, size-expanding elementary perturbations can be adequately handled by the above procedure. In the case of very strong mesomeric perturbations by substituents and, particularly, by bridges, this condition need not be satisfied and two difficulties arise.

First, the second-order approximation to k_D and to ΔK diverges as $E(\psi_j)$ approaches $E(\psi_k)$. This can be handled as usual in PMO theory:[8] Whenever one of the energies $E(\psi_j)$ is approximately or exactly equal to the energy $E(\psi_k)$, one sets them exactly equal, describes the effect of ψ_j by first-order theory, and ignores the other orbitals of the perturber. The orbital energy splitting that results from the perturbation is then approximated by $2\langle\kappa_1|\hat{a}|\psi_j\rangle$, and the two new orbitals are $(\kappa_1 \pm \psi_j)/\sqrt{2}$.

The nature of the second difficulty is thus brought into focus. Which one of the two new orbitals is to be taken for "perturbed perimeter MO" and which one is to be ignored is determined by orbital occupancies in the ground state. If $E(\psi_j)$ lies between $E(\kappa_1)$ and $E(\kappa_2)$, one needs to interchange the role of $E(\psi_k)$ and $E(\psi_j)$ in the expression 21 for $E(\kappa_1)$, $[E(\psi_j) - E(\psi_k)]/2$ needs to be added to the expression 25 for k_D, and the sum over j in both expressions becomes a single term.

In the size-expanded system, it is clearly not always possible to ignore the existence of the other orbital or orbitals that result from the perturbing interaction. As long as the mesomeric perturbation was weak, the existence of those energetically distant new orbitals that contained only a small admixture of κ_1 did not cause the appearance of any configurations with energies close to those considered in the perimeter model. However, if the initial energies $E(\psi_k)$ and $E(\psi_j)$ are close, both resulting orbitals may have energies comparable with those of the three orbital pairs treated by the perimeter model. They then give rise to low-energy configurations that are likely to contribute to low-energy states of the perturbed system. We speak of "intruder" orbitals and intruder configurations. The resulting states that are in excess of those expected from the simple perimeter model are called intruder states.

This situation usually reduces the number of spectroscopic transitions whose MCD can be interpreted using the perimeter model, and each case requires a separate analysis, as illustrated below on the examples of acenaphthylene (**9**) and pleiadiene (**10**). It may appear surprising that the simple model can be used at all; it is very helpful that in the evaluation of the matrix elements of the electric ($\hat{\boldsymbol{m}}$) and magnetic ($\hat{\boldsymbol{\mu}}$) dipole operators between a mixed perturber−perimeter orbital $c_1\kappa_1 + c_2\psi_j$ and a pure perimeter orbital $\psi_{K'}$, only the perimeter part of the former contributes, $c_1\langle\kappa_1|\hat{\boldsymbol{o}}|\psi_{K'}\rangle$, where $\hat{\boldsymbol{o}} = \hat{\boldsymbol{m}}$ or $\hat{\boldsymbol{\mu}}$. The contribution is reduced by the factor c_1 relative to an otherwise analogous contribution of a pure perimeter orbital, but for qualitative interpretations this can often be ignored.

Multiple Elementary Perturbations. The Effect of Symmetry. The effects of the elementary perturbations, summarized in Table 1, are additive at our level of approximation. Since k_D is real, simple scalar addition is required. In contrast, for $\varkappa$, vector addition in the complex plane is necessary, in a manner known from the classical investigations of the effect of inductive substituents on the intensity of the L_b band of benzene[10] and from the original development of the perimeter model for aromatics.[9,11] Simplifications occur in our case because the composite perturbation is assumed to possess symmetry.

MCD Spectra of Acenaphthylene (9) and Pleiadiene (10). We shall use these hydrocarbons as examples to illustrate the use of the general results and to test them. The MCD spectra of both **9**[12] and **10**,[13] and of a series of their simple derivatives,[7,13] have already been reported and analyzed.[7] The MCD signs were found to agree with expectations based on the aromatic $(4N + 2)$-electron perimeter, but certain transitions, in particular the weak first band, had to be treated as intruder transitions not related simply to those of the parent perimeter, and their existence and MCD signs could not be predicted by inspection (the correct signs were computed[12,13] in the PPP approximation). It has also been pointed out that the MCD spectra of **9** and **10** exhibit an approximate mirror symmetry, and the reasons for this were analyzed in simple terms.[7,14]

We now take an alternative look at the MCD spectra of these ambiaromatic hydrocarbons, using the $4N$-electron perimeter as the starting point. This will result in an alternative set of labels for the electronic states, an alternative view of the origin of the approximate mirror symmetry of their MCD spectra, and an alternative derivation of the absolute signs in these spectra.

MCD Spectrum of Acenaphthylene[12] (9). The π system of **9** is viewed formally as a union of the antiaromatic 12-electron [11]annulenide anion with the methyl cation. The resultant MO ordering is dominated by the interactions of the symmetric orbitals of the perimeter with the empty $2p_z$ orbital at the central carbon atom, which shall be labeled ϕ (Figure 1). The antibonding combination of the symmetric orbital of the SO level with ϕ is strongly shifted to higher energies. The bonding combination is strongly stabilized and forms the HOMO (s_-) of **9**. The interaction of ϕ with the symmetric orbitals of the HO and LO levels is much weaker since the energy gaps are larger. These interactions cause h_- and l_+ to be symmetric. The antisymmetric orbitals of the perimeters are not perturbed in the first approximation, and the antisymmetric member of the SO level of the perimeter represents the LUMO (s_+) of **9**. Since h_- and l_- have different symmetry, the perturbation of the perimeter is of the S type ($\rho_- = \pi/2$) in the nomenclature of part 3.[1]

It is clear from Figure 1 that these interactions yield a ΔLS value larger than the ΔHS value. Since ΔHSL is then negative, the HO → SO excitations are expected to lie at considerably lower energies than the SO → LO excitations. Moreover, the splittings ΔH and ΔL are small, since ϕ is far in energy from HO and LO, and $\sum HL$ is much smaller than ΔHSL. The chromophore should be "negative hard", and according to Figure 4 of part 3[1] a −+ B term sign sequence is expected for the low-energy pair of transitions to the N states in the order of increasing energy, which should be N_α below N_β (Figure 2 of part 3[1]). The higher lying transitions to the P states should show a +− pattern.

The first three transitions in **9** are indeed known[12] to correspond to single-electron excitations of the $s_- \rightarrow s_+$, $h_+ \rightarrow s_+$, and $h_- \rightarrow s_+$ types in the order of increasing energy, and correspond to the G → S, G → N_α and G → N_β transitions in the present nomenclature, respectively. Since $\sigma = \eta$, transitions into the α states should be polarized along the x axis, which passes through a perimeter atom.[1] This is the axis that lies in the symmetry plane, vertical in formula **9**. Transitions into the β states should be polarized in the perpendicular direction. Both results agree with the observed[12] polarization directions. In terms

TABLE 1: Characteristics of the Elementary Perturbations of an [*n*]Annulene Perimeter

perturbation	type	k_D	$\Delta K/2$	$\varkappa$
		Size-Conserving		
bond interaction of AOs ρ, τ	reduced	$(2/n)\lvert a_{\tau\rho}\rvert \cos[2\pi k(\rho - \tau)/n]$	$(2/n)\lvert a_{\rho\tau}\rvert$	$-2k\pi(\tau + \rho)/n$
	increased	$-(2/n)\lvert a_{\tau\rho}\rvert \cos[2\pi k(\rho - \tau)/n]$	$(2/n)\lvert a_{\rho\tau}\rvert$	$\pi - 2k\pi(\tau + \rho)/n$
inductive effect at ρ	−I	$\lvert a_{\rho\rho}\rvert/n$	$\lvert a_{\rho\rho}\rvert/n$	$-4k\pi\rho/n$
	+I	$-\lvert a_{\rho\rho}\rvert/n$	$\lvert a_{\rho\rho}\rvert/n$	$\pi - 4k\pi\rho/n$
		Size-Expanding		
mesomeric effect at ρ	−E	$(a_{\rho\sigma}^2/n)\lvert\sum_j c_{\sigma j}^2/[E(\psi_k) - E(\psi_j)]\rvert$	$(a_{\rho\sigma}^2/n)\lvert\sum_j c_{\sigma j}^2/[E(\psi_k) - E(\psi_j)]\rvert$	$-4\pi k\rho/n$
	+E	$(a_{\rho\sigma}^2/n)\lvert\sum_j c_{\sigma j}^2/[E(\psi_k) - E(\psi_j)]\rvert$	$(a_{\rho\sigma}^2/n)\lvert\sum_j c_{\sigma j}^2/[E(\psi_k) - E(\psi_j)]\rvert$	$\pi - 4\pi k\rho/n$

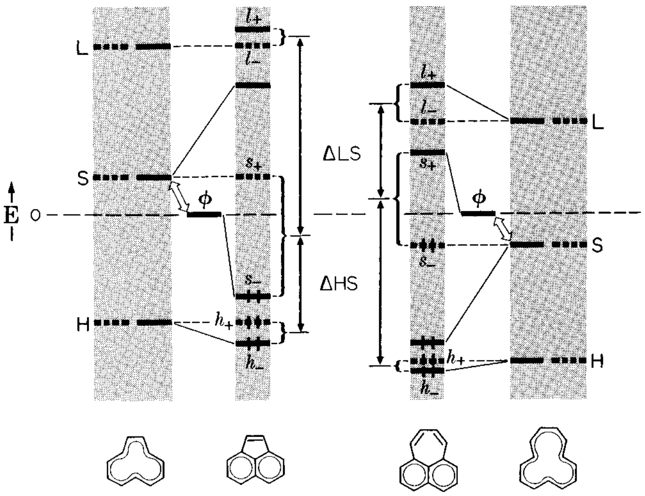


Figure 1. Derivation of the MO energy diagrams of acenaphthylene (left, **9**) and pleiadiene (right, **10**) by perimeter perturbation. The HO, SO, and LO orbital levels of the perimeter are indicated by H, L, and S, respectively.

of the spectroscopic labels proposed in part 3,[1] we have $N_\alpha = N_a$ and $N_\beta = N_b$, and the state order is S, N_a, N_b.

The observed signs of the MCD *B* terms are S, negative and very weak, N_a, strongly negative, and N_b, strongly positive. The −+ sign sequence for the N_a and N_b *B* terms is just that expected from $\Delta HSL < 0$. In the previous derivation from an aromatic perimeter,[7] these were the L_1 and L_2 bands, and their signs followed from ΔHOMO < ΔLUMO. According to the nomenclature proposed in part 3,[1] they are the L_a and L_b bands, respectively.

The S band is weak both in absorption and in MCD. The present treatment predicts its existence but yields zero intensities for both and thus makes no claims concerning the MCD sign. The observed very weak negative *B* term therefore presently has no simple interpretation, but at least the presence of a weak transition is anticipated. The previous derivation from an aromatic perimeter[7] could not relate this first weak transition to the states of the perimeter at all and did not provide a Platt label.

Beyond the first three excited states, the presence of intruder states makes it difficult to assign the states of **9** to the states of either the 4*N*-electron or the (4*N* + 2)-electron perimeter and to make simple predictions of MCD signs.

MCD Spectrum of Pleiadiene[13] (10). The π system of **10** is constructed formally as a union of the antiaromatic 12-electron [13]annulenyl cation with the methyl anion. Arguments similar to those given for **9** lead to the orbital scheme shown in Figure 1. The HOMO (s_-) is the antisymmetric member of the SO pair of the perimeter, and the LUMO (s_+) is the antibonding combination of the symmetric member of this pair with the central orbital ϕ.

According to Figure 1, **10** has an ΔLS value smaller than the ΔHS value, and ΔHSL is positive and again much larger than $\sum HL$. The SO → LO excitations should lie at much lower energies than the HO → SO excitations, and the chromophore should be "positive hard". Since h_- and l_- have opposite symmetries, the perimeter perturbation is again of the S type ($\rho^- = \pi/2$) and the state order should be N_β below N_α (Figure 2 of part 3[1]). Since s_- is antisymmetric, $\sigma = 0$, while h_- is symmetric, $\eta = \pi$, and the β transitions should be polarized along the symmetry axis *x*. This again agrees with observations.[13] According to the proposal made in part 3,[1] $N_\beta = N_a$ and $N_\alpha = N_b$, and the state order is S, N_a, N_b.

The +− *B* term sign sequence is expected (Figure 4 of part 3[1]) for the low-energy transitions into the N_a and N_b states. The higher lying transitions to P states should show a −+ pattern. The first three transitions are known[13] to be well represented as the single-electron excitations of the $s_- \rightarrow s_+$, $s_- \rightarrow l_-$, and $s_- \rightarrow l_+$ types and correspond to G → S, G → N_a, and G → N_b.

The observed signs of the *B* terms of the S, N_β, and N_α states are ++−. Once again, the +− sign sequence for the *B* terms of the N_a and N_b transitions agrees with that expected from $\Delta HS > \Delta LS$. When derived from an aromatic perimeter,[7] these were the L_1 and L_2 bands (now we would call them L_a and L_b, respectively), and their signs followed from ΔHOMO > ΔLUMO.

The S band is weak both in absorption and in MCD, as expected. Thus, while its presence follows from the 4*N*-electron perimeter model, the sign of its *B* term does not. The (4*N* + 2)-electron perimeter viewpoint[7] did not relate this excited state to the states of the perimeter at all.

Higher excited states are not simply related to perimeter states.

Acenaphthylene (9), Pleiadiene (10), Their Double Ions, and Phenalenyl (12) Ions. A Comparison. In summary, the perimeter labels of the lower states of the ambiaromatic systems **9** and **10** are G, S, $N_a = L_a$, and $N_b = L_b$. Either perimeter choice correctly accounts for the absolute signs of the *B* terms of the second and third transitions, but only the 4*N*-electron perimeter has a transition that is simply related to the weak lowest energy transition. We believe that the present results represent a deeper level of insight and provide a theoretically better justified nomenclature than the K, L, M transition labels that we proposed for these and related hydrocarbons some time ago.[15]

The mirror image symmetry in the signs of the *B* terms of the system is due to the approximate mirror image symmetry between the orbital energies of **9** and **10** (approximate alternant pairing[14]), which yields ΔHSL values with opposite signs in **9** and in **10**, and to the dominance of the ΔHSL contribution in dictating the MCD behavior.

The MO level schemes for **9** and **10** are very similar, with three MO levels located between the weakly split HO and LO pairs. As far as the content of perimeter contributions is concerned, the bottom and the top among these three orbitals are similar. Either one could be used as a member of the SO pair, and the other one would remain unlabeled as an intruder orbital. Which one needs to be used is determined by the occupancy of these three central levels, which determines the sign of ΔHSL and thus the MCD sign pattern. In **9**, only the lowest of the three MOs is occupied, and therefore the bottom two represent the perturbed SO pair. In **10**, only the highest of the three MOs is empty, and therefore the top two represent the SO pair.

Therefore, the sign pattern in the MCD spectrum of the dianion of **9** should be the same as that in the spectrum of neutral **10**, and the MCD sign sequence for the dication of **10** should be identical with that for neutral **9**. The spectra of these doubly charged ions have not been measured.

There is a clear relation to other peri-condensed systems as well. For instance, the union of the uncharged antiaromatic [12]annulene perimeter with a methyl anion or cation can lead to the highly symmetrical phenalenyl ions **12**. Similar MO schemes are expected for all of these, except that the HO and LU degeneracy is not removed at all. The MCD signs should again be dictated by the occupancy of the central three MOs. In this respect, the anion **12a** should be positive-hard like **10** or the dianion of **9**, and the cation **12b** negative-hard like **9** or the dication of **10**.

Substituent and Heteroatom Effects on Soft Unaromatic Chromophores. The best candidates for soft MCD chromophores are those derived from uncharged perimeters. In the Hückel and PPP approximations, alternant pairing guarantees $\Delta HSL = 0$ and $\Delta H = \Delta L$ and thus "double softness" if the perturbation of the perimeter is of odd parity and only even-membered rings are present. There is reason to believe that the alternant pairing property does not hold well in the presence of four-membered rings,[16] but it might hold somewhat better in π systems with eight-membered rings. For alternant hydrocarbons of this type, simple predictions of substituent and heteroatom effects on MCD signs,[5] based on PMO theory,[8] are possible. Such predictions have been very successful for aromatic alternant hydrocarbons derived from $(4N + 2)$-electron perimeters. They were used, e.g., for analytical purposes,[17] for separation of inductive and mesomeric effects of substituents,[18] and for study of transannular interaction.[19]

We shall now outline the application of the same principles to unaromatic alternant hydrocarbons. In these, the orbitals h_- and l_+, h_+ and l_-, and s_- and s_+ are paired in the sense of alternant symmetry, such that $c^2_{\mu h(-)} = c^2_{\mu l(+)}$, $c^2_{\mu h(+)} = c^2_{\mu l(-)}$, and $c^2_{\mu s} = c^2_{\mu s(+)}$.

Inductive Effects of Heteroatoms and Substituents. When the effect of the position of replacement or attachment is characterized by the change in the effective electronegativity $a_{\rho\rho}$ ($\Delta\alpha$ in Hückel theory), first-order perturbation theory yields

$$\Delta(\Delta HSL - \Delta HL) = 4a_{\rho\rho}(c^2_{\rho s(+)} - c^2_{\rho h(+)}) \qquad (39)$$

$$\Delta[\Delta HSL - \sum HL(\mathrm{sgn}\Delta HL)] = 4a_{\rho\rho}[c^2_{\rho s(+)} - (c^2_{\rho h(+)} + c^2_{\rho h(-)})/2]$$

Thus, for an electronegative heteroatom such as an aza nitrogen, $a_{\rho\rho} < 0$, and in a C-type system $\Delta HSL - \Delta HL$ ought to increase in replacement positions at which h_+ (and l_-) has a particularly large amplitude and s_+ (and s_-) a particularly small one (note that the coefficients of the orbitals h_- and l_+ do not matter). In an S-type system one needs to use the average of the coefficients in h_+ and h_- instead of the coefficient in h_+. Such substitution should make the B term of the lower N transition more positive or less negative, and it should have the reverse effect on the B term of the upper N transition.

The opposite effect is expected for replacement positions at which h_+ has a particularly small and s_+ a particularly large amplitude. For electropositive heteroatoms ($a_{\rho\rho} > 0$), the rules are reversed.

Mesomeric Effects of Substituents. Since unaromatic alternant hydrocarbons derived by an odd perturbation of the perimeter have nodes cutting bond midpoints as we have seen above, mesomeric monosubstitution lowers symmetry and is generally characterized by η and λ values different from multiples of $\pi/2$ even when the parent hydrocarbon is symmetrical, and we do not have an algebraic solution for the perturbed system. In multiply substituted systems, symmetry may be restored. We shall assume in the following that we are dealing with a monosubstituted hydrocarbon and that the solution obtained by setting η and λ equal to multiples of $\pi/2$ is still approximately correct. In using second-order perturbation theory, we assume in the first approximation $[E(l_+) - E(\psi_j)]^{-1} = [E(l_-) - E(\psi_j)]^{-1} = 0$ and $[E(s_+) - E(\psi_j)]^{-1} = [E(s_-) - E(\psi_j)]^{-1} = [E(h_+) - E(\psi_j)]^{-1} = [E(h_-) - E(\psi_j)]^{-1} = \Delta E^{-1} > 0$ for a mesomeric -E substituent with a donor orbital at energy $E(\psi_j)$. For a +E substituent with an acceptor orbital of energy E_j, we use $[E(l_+) - E(\psi_j)]^{-1} = [E(l_-) - E(\psi_j)]^{-1} = [E(s_+) - E(\psi_j)]^{-1} = [E(s_-) - E(\psi_j)]^{-1} = \Delta E^{-1} < 0$, $[E(h_+) - E(\psi_j)]^{-1} = [E(h_-) - E(\psi_j)]^{-1} = 0$. With this extremely crude approach, we obtain

$$\Delta(\Delta HSL - \Delta HL) = (2a^2_{\rho\tau}\Delta \mathrm{E}^{-1})(2c^2_{\rho s(+)} - c^2_{\rho h(+)})$$

$$\Delta[\Delta HSL - \sum HL\cdot(\mathrm{sgn}\Delta HL)] = (2a^2_{\rho\tau}\Delta \mathrm{E}^{-1})(2c^2_{\rho s(+)} - c^2_{\rho h(+)}) \quad \text{if } -\mathrm{E}, \Delta HL > 0 \text{ or } +\mathrm{E}, \Delta HL < 0 \qquad (40)$$

$$\Delta[\Delta HSL - \sum HL\cdot(\mathrm{sgn}\Delta HL)] = (2a^2_{\rho\tau}\Delta \mathrm{E}^{-1})(2c^2_{\rho s(+)} - c^2_{\rho h(-)}) \quad \text{if } +\mathrm{E}, \Delta HL > 0 \text{ or } -\mathrm{E}, \Delta HL < 0$$

In a more realistic description, the factor 2 at $c^2_{\rho s(+)}$ would be reduced, making the formulas even more similar to those given in eq 25. Clearly, not much more than an expectation of a trend can be derived at this level of approximation. We conclude that weak mesomeric donors and acceptors should have qualitatively similar effects on the B terms of the N transitions as inductive donors and acceptors, respectively. If the mesomeric effect is strong, i.e., when the energy of the substituent orbital lies closer in energy to the SO perimeter pair than either the HO or the LO orbitals, simple predictions become difficult.

With results given in eqs 39 and 40 in hand, it is now possible to label positions in any unaromatic alternant hydrocarbon with respect to expected donor and acceptor heteroatom and substituent effects on the B terms of the N transitions, using only tables of Hückel orbital coefficients. The rules for the B term signs are quite different from those derived earlier[4,5] for aromatic alternant hydrocarbons, and it remains to be seen if they work anywhere near as well in practice. The first indications for aza analogues of biphenylene[20] are encouraging.

Conclusion

We have provided an explicit link of the orbital energy difference and orbital phase angle parameters that dictate spectral observables in the perimeter model for unaromatic and ambiaromatic molecules to the perturbations in molecular structure that produce these molecules from their parent 4*N*-electron perimeters. Elementary perturbations can be of the size-conserving type (bond torsion, extension, or compression, cross-linking, and substituents or heteroatoms with an inductive effect) or the size-expanding type (bridging and substituents with a mesomeric effect). Simple expressions have been presented for both, and general rules for substituent and heteroatom effects in this class of compounds have been formulated. Although they are reminiscent of the rules for aromatics, they are distinctly different.

In the way of illustration, the spectra of acenaphthylene, pleiadiene, their double ions, and the phenalenyl ions have been interpreted. In future publications of this series, we plan to report similar treatments for several classes of unaromatic molecules.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9819179). J.F. is grateful to the Deutsche Forschungsgemeinschaft for a scholarship and acknowledges support by the Fonds der Chemischen Industrie.

References and Notes

(1) Part 3: Fleischhauer, J.; Höweler, U.; Michl, J. *J. Phys. Chem. A* **2000**, 7762.

(2) Höweler, U.; Downing, J. W.; Fleischhauer, J.; Michl, J. *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1101, 2323.

(3) Fleischhauer, J.; Höweler, U.; Michl, J. *Spectrochim. Acta* **1999**, *55A*, 585.

(4) Michl, J. *J. Am. Chem. Soc*. **1978**, *100*, 6801.

(5) Michl, J. *J. Am. Chem. Soc*. **1978**, *100*, 6812, 6819.

(6) Michl, J. *Tetrahedron* **1984**, *40*, 3845.

(7) Kenney, J. W., III; Herold, D. A.; Michl, J. *J. Am. Chem. Soc*. **1978**, *100*, 6884.

(8) Dewar, M. J. S.; Dougherty, R. C. In *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

(9) Moffitt, W. *J. Chem. Phys*. **1954**, *22*, 320, 1820.

(10) Petruska, J. *J. Chem. Phys*. **1961**, *34*, 1111, 1120 and references therein.

(11) Platt, J. R. *J. Chem. Phys*. **1949**, *17*, 484.

(12) Thulstrup, E. W.; Michl, J. *J. Am. Chem. Soc*. **1976**, *98*, 4533.

(13) Kolc, J.; Michl, J. *J. Am. Chem. Soc*. **1976**, *98*, 4540.

(14) Michl, J. *J. Am. Chem. Soc*. **1976**, *98*, 4546.

(15) Michl, J.; Muller, J. F. *J. Am. Chem. Soc*. **1976**, *98*, 4550.

(16) Jorgensen, N. H.; Pedersen, P. B.; Thulstrup, E. W.; Michl, J. *Int. J. Quantum Chem*. **1978**, *S12*, 419.

(17) Michl, J.; Weeks, G. H. In *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry*; Sixth International Symposium, Battelle Press: Columbus, OH, 1982; p 501. Waluk, J. W.; Michl, J. *Anal. Chem*. **1981**, *53*, 236.

(18) Weeks, G. H.; Adcock, W.; Klingensmith, K. A.; Waluk, J. W.; West, R.; Vasak, M.; Downing, J.; Michl, J. *Pure Appl. Chem*. **1986**, *58*, 39.

(19) Klingensmith, K. A.; Püttmann, W.; Vogel, E.; Michl, J. *J. Am. Chem. Soc*. **1983**, *105*, 3375.

(20) Höweler, U.; Spanget-Larsen, J.; Michl, J. Unpublished results.