Pure & Appl. Chem., Vol.52, pp.1549-1563.
Pergamon Press Ltd. 1980. Printed in Great Britain.

ELECTRONIC STRUCTURE OF AROMATIC π-ELECTRON SYSTEMS AS REFLECTED IN THEIR MCD SPECTRA

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Abstract - The physical origin of the MCD effect in aromatic molecules is described in simple terms, and the rules for the effect of substituents and heteroatoms on their MCD signs are reviewed. Three examples of their application are presented: the effect of -E substituents in a subdominant position of an even-soft chromophore (γ-substituted pyridinium), the effect of +I, +E, and -E substitution in different positions of an odd-soft chromophore (the three positions of pyrene), and the effect of the introduction of heteroatoms into a single-soft chromophore (conversion of the indenide anion into indole and similar heterocycles).

INTRODUCTION

Circular dichroism (CD) is measured as differential absorption of left-handed and right-handed circularly polarized light propagating through a sample ($\varepsilon_L - \varepsilon_R$). When such measurements are performed on isotropic solutions, only very special molecules produce a non-zero CD spectrum, i.e., are optically active. The condition for natural optical activity in solution, molecular chirality, is well known to organic chemists who have been using CD spectra for the assignment of absolute configurations for some time. It is perhaps less well known that in the presence of a magnetic field parallel to the light-propagating direction, solutions of all molecules will exhibit the CD effect. This magnetically induced circular dichroism is referred to as magnetic circular dichroism (MCD)[1] and has a quite different physical origin from natural circular dichroism, although it is measured in very much the same way. It will be the object of the present lecture to show the relation between MCD spectra and electronic structure of a particular class of molecules which I shall refer to as aromatic for the present purpose, namely those which can be derived from a (4N+2)-electron [n]annulene perimeter by perturbations such as cross-linking, bridging, and introduction of heteroatoms and substituents. For instance, naphthalene and azulene can be thus derived from the 10-electron [10]annulene by cross-linking; pyrene can be obtained from the 14-electron [14] annulene by bridging with a 2-carbon bridge; pyrrole can be obtained from the 6-electron [5]annulenide anion by replacement of the CH^- group with the NH group; and tropone can be derived from the 6-electron [7]annulenylium (tropylium) cation by substitution with a $-O^-$ substituent. Admittedly, some compounds which might at times be considered aromatic, such as anthraquinone or biphenylene, cannot be derived in the prescribed fashion from a (4N+2)-electron perimeter and will not be covered presently.

According to the perimeter model, those cyclic π-electron systems which we refer to as aromatic are characterized by four low-energy electronic excitations which we shall refer to as L_1, L_2, B_1, and B_2 in the order of increasing energy. We shall be concerned with the MCD activity of these four low-energy transitions, as reflected in the sign and the magnitude of the corresponding peaks in the MCD spectrum. A quantitative measure of this activity for a given transition is provided by defining its so called A term and so called B term:

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

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

Here, $\tilde{\nu}$ is wavenumber and $\tilde{\nu}_0$ is the center of the absorption band, and $[\Theta]_M$ is the molar ellipticity per unit magnetic field. The A term is zero unless the excited state of the transition is degenerate, and thus is always zero except possibly in molecules of high symmetry. Its presence is revealed in the spectrum by a pair of peaks, one positive, the other negative, i.e., by an S-shaped contribution to the MCD curve. The B term is always non-zero unless the transition is forbidden in

absorption, and it has a shape generally similar to the peak in absorption. It should be noted that a positive A term is expressed in the MCD spectrum by a negative dip followed by a positive peak as one proceeds to higher photon energies. The opposite sign sequence would be found for a negative A term. A positive B term is reflected in the MCD curve as a negative peak and a negative B term as a positive peak. Finally, it should be mentioned that molecules with degenerate ground states exhibit also C terms, but are not of interest to us presently.

THE PHYSICAL ORIGIN OF THE MCD EFFECT

A reasonable first question which an organic chemist is apt to pose when confronted with a new physical method is, is there a simple way to understand the physical origin of the observed effect? We shall now proceed with such a simple and intuitive description of how the effect originates, but shall limit our attention to the A terms. Very similar but slightly more complicated arguments[2] can be made in order to understand the physical origin of B terms.

The description will be based on the perimeter model whose application to the MCD of aromatic molecules has been discussed in detail elsewhere[2-4]. We shall concentrate on the unperturbed perimeter of a (4N+2)-electron [n]annulene possessing an n-fold axis of symmetry perpendicular to the molecular plane and we shall further assume that N is different from zero and that n is different from 2(N+1). In such a case the highest occupied molecular orbitals (HOMOs) as well as the lowest unoccupied molecular orbitals (LUMOs) of the ground state of the cyclic π-electron perimeter are both degenerate. To provide a simple physical picture of the MCD effect, it is useful to choose these orbitals in their complex form (Figure 1). This is less familiar than the usual real form and will actually not be needed for any further concrete applications and predictions of MCD spectra, but it does permit a simple derivation of the physical origin of the MCD effect. This is so because complex wavefunctions permit a description of net electron circulation which real wavefunctions do not. Thus, in one of the two complex HOMOs, ψ_N, two electrons circulate counterclockwise in the plane of the perimeter.

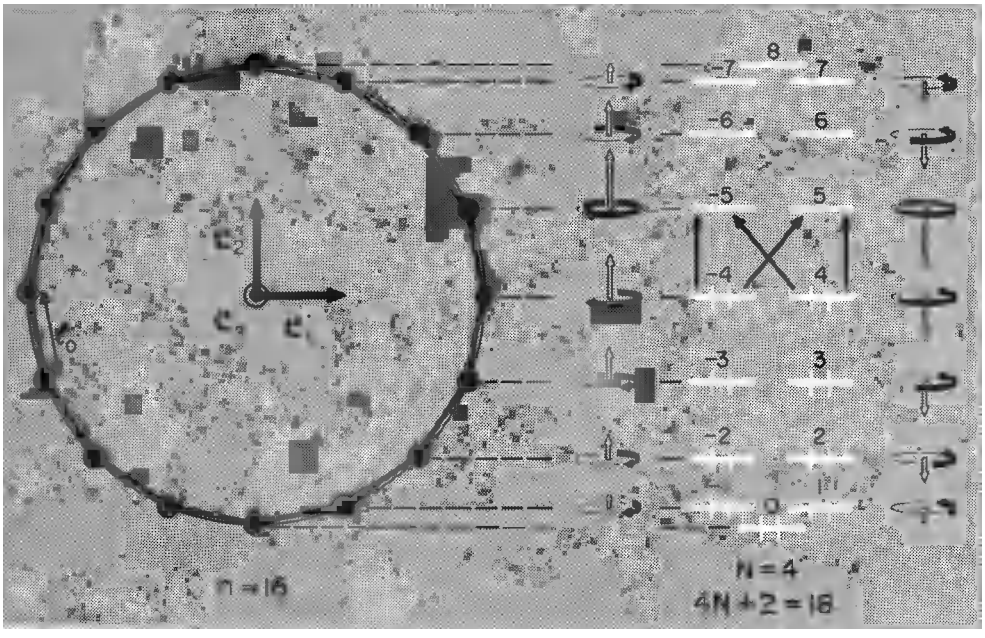

Figure 1. Geometry and MO occupancy for a (4N+2)-electron [n]annulene, $C_{16}H_{16}^{2-}$. For each MO, the angular momentum quantum number k is given and the sense and amount of electron circulation and of the resulting orbital magnetic moment are shown schematically. The MO's ψ_0 and ψ_8 have no net electron circulation and no magnetic moment.

In the other, ψ_{-N}, two electrons circulate clockwise along the perimeter. We use the convention that the viewer is looking into the light source and the molecular plane is perpendicular to the light beam. Four low-energy excitations can promote

an electron from either ψ_N or ψ_{-N} into one of the two LUMOs. In one of these, ψ_{N+1}, the excited electron circulates counterclockwise, in the other, ψ_{-N-1}, it circulates clockwise. Thus, in the transitions $\psi_N \rightarrow \psi_{N+1}$ and $\psi_{-N} \rightarrow \psi_{-N-1}$, the sense of circulation of the excited electron around the perimeter is preserved. Both of these transitions are electric dipole allowed. The former requires absorption of left-handed circular polarized light (CPL); the latter requires absorption of right-handed CPL. By symmetry, the two transitions occur at the same energy which is relatively high (e.g., 185 nm in benzene), and produce the two components of a doubly degenerate excited state which has been labeled B by Platt[5]. In distinction to the ground state, they can possess a non-vanishing magnetic moment. In the ground state, the moment due to the circulation of an electron in ψ_N was exactly cancelled by that due to the circulation of an electron in ψ_{-N}. After excitation, the promoted electron is in ψ_{N+1} and its net rate of circulation along the perimeter may well be different from what it was in ψ_N so that the compensation with the electron which remained in ψ_{-N} is no longer perfect. If the net circulation is larger in the excited orbital, the excited molecule possesses a loop of current due to a negative particle circulating counterclockwise if left-handed CPL was absorbed and clockwise if right-handed CPL was absorbed. If the net circulation in the excited orbital is smaller, the cancellation is incomplete in the opposite direction, and the molecule now effectively finds itself with a loop of current due to a positive hole circulating counterclockwise if left-handed CPL was absorbed, and clockwise if right-handed CPL was absorbed. In either case, circulation of a charged particle in a loop will produce a magnetic moment. If the particle is positive, i.e., if the net circulation of the promoted electron decreased upon excitation, the molecular magnetic moment due to orbital motion ($\bar{\mu}$) will be directed along the light propagation direction and thus also along the magnetic field direction in the MCD experiment. If the circulating particle is negative, i.e., if the circulation of the excited electron increased upon promotion, the molecular magnetic moment will be directed against the light propagation direction, and thus also against the magnetic field direction. For most usual combinations of n and N, $\bar{\mu}$ is weakly negative, of the order of several tenths of a bohr magneton.

In summary, in either of the two components of the degenerate excited B state which can be reached by circularly polarized light, the molecule will behave as a small magnet and the direction of its magnetic moment will be determined by the nature of the light absorbed, left-handed or right-handed. (If linearly polarized light or natural light were used in the experiment instead of circularly polarized light, the excited molecule would find itself in a non-magnetic linear combination of the above two states, since both directions of magnetic moment would be equally likely). The magnetic moment of the molecule will interact with the outside magnetic field as is well known from the Zeeman effect. This interaction is very similar to that observed in ESR or NMR spectroscopy, except that the molecular magnetic moment is now due to an electron motion around the perimeter rather than to electron or nuclear spin. The application of the magnetic field will change the energy of the state reached by left-handed CPL by an amount equal to $-\bar{\mu} \cdot B$, and that of the state reached by right-handed CPL by $-(-\bar{\mu}).B$. If $\bar{\mu}$ is a negative quantity, as happens for most perimeters[3], the energy of the state reached by right-handed CPL will then be a little lower than that of the state reached by left-handed CPL. In those rare instances in which $\bar{\mu}$ is positive, the opposite will be true. In the former case, scanning the photon energy to higher values (shorter wavelengths), and plotting $\varepsilon_L - \varepsilon_R$ will therefore first lead to a negative peak and then to a positive peak as one and then the other state of the originally degenerate pair come into resonance with the photon energy in the magnetic field. In other words, the shape referred to above as the positive A term will be produced in the MCD spectrum. It is readily seen that the latter case similarly leads to the shape of a negative A term.

There are two other HOMO → LUMO transitions, $\psi_{-N} \rightarrow \psi_{N+1}$ and $\psi_N \rightarrow \psi_{-N-1}$. In these, the excitation reverses the sense of circulation of the promoted electron around the perimeter. Unless symmetry-breaking vibrations are considered, these transitions have zero intensity. They are referred to as the L states by Platt[5] and occur at lower energies than the B states. If the perimeter is charged ($n \neq 4N+2$), these two transitions produce the two degenerate components of a single excited L state (e.g., 320 nm in $C_9H_9^-$). If the perimeter is uncharged ($n=4N+2$), the two excited states combine into a lower (L_b) and upper (L_a) state (e.g., 270 nm and 205 nm in benzene, respectively). Although forbidden, these transitions are observed in reality due to vibronic interactions. We shall not consider such interactions here, but even without them, the two L transitions play a very important role as soon as symmetry is lowered by one of the structural perturbations mentioned above which produce the real molecule of interest from the parent perimeter. The configurations reached by the two sense-reversing transitions have

large magnetic moments. In the transition $\psi_{-N} \rightarrow \psi_{N+1}$, the promoted electron no longer compensates the negative magnetic moment due to an electron in ψ_N as it did before it was excited, but actually adds another large magnetic moment, μ^+. As a result, the magnetic moment of this excited state is large and negative (μ^+). For similar reasons, the magnetic moment of the state reached by the $\psi_N \rightarrow \psi_{-N-1}$ transition is large and positive ($-\mu^+$). The values of μ^+ are typically an order of magnitude larger than the values of μ^-.[3]

In constructing the actual molecule of interest from the parent (4N+2)-electron [n]annulene perimeter by introduction of cross-links, bridges, substituents, heteroatoms, etc., symmetry is usually lowered and three or all four transitions become electronically allowed. In the case of an uncharged perimeter, it is often possible to distinguish the L_b and L_a parentage of the two L states. Either of these can be lower in energy.[2] A detailed analysis of the mixing of the four configurations by the perturbation which produces the actual molecule from the perimeter permits an explicit prediction of its effect on transition intensities and MCD behavior[2,3]. The sense-preserving character and thus the intensity is now distributed over all four transitions, although most of it still remains in the B transitions. Similarly, the small magnetic moment μ^- of the sense-preserving excitations is now shared by all four transitions but remains largely in the B bands, while the large magnetic moment μ^+ of the sense-reversing excitations is also shared but resides predominantly in the L transitions. In the absence of magnetic field, the intensity-providing configurations $\psi_N \rightarrow \psi_{N+1}$ and $\psi_{-N} \rightarrow \psi_{-N-1}$ are strictly degenerate, and therefore both enter always with the same weight into any final state. As a result, the probability of absorption of left-handed and right-handed CPL is the same at all wavelengths, and there is no CD effect. In the presence of a magnetic field, however, the energies of these two configurations are split by the above described Zeeman effect and this exact balance is destroyed. One of these excitations mixes more into some of the four transitions, while the other contributes more to the others. Then, $\varepsilon_L - \varepsilon_R$ no longer vanishes and the MCD spectrum appears. The detailed analysis shows that the B term of each of the four transitions is composed of two contributions. One of these is proportional to μ^-, the other to μ^+. The former is small, particularly for the L bands, and is largely independent of the molecular structure. For the two L transitions, its contribution to the B term is weakly positive or vanishes altogether, depending on the details of the structure. For the lower of the two B transitions it is more strongly positive and for the upper B transitions it is more strongly negative. The latter contribution, due to μ^+, is potentially large, but enters with a weight that depends upon the degree to which the splitting of the HOMOs of the original [n]annulene perimeter differs from the splitting of its LUMOs, once the perturbation is introduced. These splittings shall be referred to as ΔHOMO and ΔLUMO. Qualitatively, they can be viewed as posing a hindrance to the circulation of particles along the perimeter. The larger the splitting, the larger the hindrance and the smaller the moment which results from the circular motion in magnetic field. The hindrance to the circulation of the positive hole which the promoted electron left behind in a HOMO is related to the size of ΔHOMO. Similarly, the hindrance to the circulation of the promoted negative electron in LUMO is reflected in ΔLUMO. If the two are equal, ΔHOMO = ΔLUMO, the contribution proportional to μ^+ vanishes. If ΔHOMO > ΔLUMO, electron circulation dominates and the μ^+ contributions to the B terms of the four transitions are +, -, +, -, in the order of increasing energy (L_1, L_2, B_1, B_2). If ΔHOMO < ΔLUMO, hole circulation dominates, and the μ^+ contributions to the B terms are just the opposite, -, +, -, +. The hindrance to electron circulation in the magnetic field by the non-vanishing values of ΔHOMO and ΔLUMO is related to the fact that the real and not the complex description of the four orbitals is now appropriate, since the symmetry is low. The real description will be used in the discussion of specific examples in the rest of this paper. The simplified description outlined above shows that the MCD of aromatic molecules can be understood in terms of the energies of four frontier molecular orbitals. In this respect, MCD is complementary to photoelectron spectroscopy, which provides a measure of occupied orbital energies and to electron transmission spectroscopy, which, in favorable cases, provides a measure of the unoccupied orbital energies.

Obviously, the orbital energy differences derived from any one of these methods are only meaningful within a model. The numerous simplifying assumptions which go into the MCD derivations briefly outlined above, based on the perimeter model, have been discussed in references 2 and 3. The assignment of orbital energies from photoelectron and electron transmission spectra is based on a different model assumption (Koopmans' theorem). In spite of their limitations, the MO models used have already proven very useful.

The value of MCD spectroscopy of aromatic molecules can thus be seen primarily in

the insight it provides into their electronic structure. However, there may be a more practical aspect to it: since the relative size of ΔHOMO and ΔLUMO can be usually readily derived from qualitative notions of orbital interactions, and since it is quite sensitive to molecular structure, for instance, in positional isomers, MCD spectroscopy of aromatic molecules could conceivably be of interest as a complementary means of structure determination. In this respect, MCD is far more powerful than ordinary UV-visible spectroscopy, with which it shares the advantage of requiring only minute amounts of material. Its disadvantage is the requirement for more complex instrumentation. With a modern CD instrument, however, only a relatively inexpensive electromagnet is required to obtain quite acceptable MCD spectra.

SUBSTITUENT AND HETEROATOM EFFECTS IN MCD SPECTROSCOPY OF AROMATIC MOLECULES

Molecules in which ΔHOMO = ΔLUMO provide a particularly interesting class of MCD chromophores. Since already weak perturbation can destroy the equality of ΔHOMO and ΔLUMO in one or the other direction, and thus induce one or another set of signs for the potentially large μ^+ contributions to the B terms of the four low-energy transitions, their MCD signs are quite sensitive to changes in molecular structure. We refer to chromophores of this type as soft MCD chromophores. Several types of such chromophores exist, depending on the details of molecular structure, and these are discussed in more detail elsewhere[4] (double-soft, odd-soft, even-soft and zero-soft). It is possible to formulate general rules for substituent effects on the MCD signs of these various types of chromophores as a function of the position of substitution. Those chromophores in which ΔHOMO > ΔLUMO or ΔHOMO < ΔLUMO are referred to as positive-hard and negative-hard, respectively, and their MCD signs are far less likely to be affected by small changes in molecular structure, such as substitution or introduction of heteroatoms.

Since the μ^- contributions to the B terms of the four low-energy transitions are almost structure-independent, and the size and magnitudes of the potentially large μ^+ contributions are simply related to the sign and magnitude of the difference ΔHOMO - ΔLUMO, the task of deriving rules for substituent and heteroatom effects is essentially reduced to finding rules for their effects on the value of ΔHOMO - ΔLUMO. As long as the perturbations are sufficiently weak for simple perturbation theory to be applicable, this is a very simple task. An inductive effect of a substituent or a heteroatom is represented by an increase in the electronegativity at the center μ where attachment or replacement occured, $\Delta\alpha_\chi$. Its effect on the energy of orbital i is then given by the product $c^2_{i\mu} \cdot \Delta\alpha_\mu$, where $c_{i\mu}$ is the expansion coefficient of i-th MO on the substitution center μ. Therefore, the inductive effect is in principle equally likely to affect ΔHOMO and ΔLUMO. This is not true of mesomeric effects. An electron-donating (-E) mesomeric substituent acts by introducing a relatively high energy orbital occupied by two electrons, which can interact with the orbitals already present in the chromophore. Such interaction is again proportional to the square of the expansion coefficient at the position of attachment, but now also depends inversely on the energy separation between the newly introduced orbital and the orbitals of the perimeter. For this reason, a -E substituent primarily affects the occupied orbitals of the parent chromophore and thus ΔHOMO, and its interaction with the unoccupied orbitals can be frequently neglected (notice that this is not true when considering total energies). Similarly, an electron-withdrawing (+E) substituent provides a relatively low-lying empty orbital interacting with the orbitals of the parent chromophore and acts primarily on ΔLUMO.

In a double-soft chromophore, ΔHOMO and ΔLUMO both vanish. Examples of these chromophores are the parent perimeters and other high-symmetry molecules such as triphenylene. In this type of chromophore, mesomeric substituents can only increase ΔHOMO or ΔLUMO, which are zero to start with. Thus, a -E substituent, which acts on ΔHOMO, will cause ΔHOMO to be larger than ΔLUMO, and a +E substituent will similarly cause ΔLUMO to be larger than ΔHOMO. We see that the natural tendency of an electron-donating substituent when introduced onto a conjugated perimeter is to convert it into a positive-hard MCD chromophore. Similarly, the natural tendency of an electron-withdrawing mesomeric substituent is to produce a negative-hard MCD chromophore. Such domination of the sign of the value of ΔHOMO - ΔLUMO by a mesomeric substituent is unopposed if the MCD chromophore is simply the original unperturbed perimeter. In a more general case, however, this can be a cross-linked or bridged perimeter, in which ΔHOMO and ΔLUMO, though still equal or approximately equal, no longer vanish (Figure 2). Whether a given mesomeric substituent, say -E, then has a tendency to reduce or increase the orbital energy gap, in this case ΔHOMO, depends on the relative size of the squares

of the expansion coefficients of the two orbitals in question at the position of attachment. If the uppermost occupied orbital has the larger coefficient, and thus

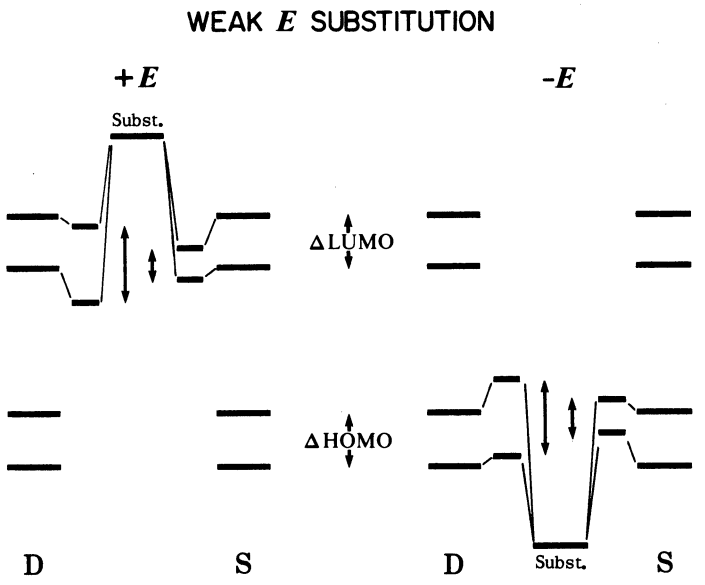

Figure 2. Effects of weak mesomeric substituents on ΔHOMO and ΔLUMO in a dominant (D) and subdominant (S) position.

interacts more strongly with the donor substituent, ΔHOMO will be increased upon introduction of the substituent. As the strength of the substituent increases, ΔHOMO continues to increase. In such a case, the natural desire of a -E substituent for a positive value for ΔHOMO - ΔLUMO is satisfied from the beginning and such a position of substitution is referred to as dominant (i.e., substituent-dominated). On the other hand, if the cross-links or bridges in the original chromophore were such that the uppermost occupied orbital has the smaller value of the square of the expansion coefficient at the position of substitution, the initial effect of a weak -E mesomeric electron donor will be to decrease the ΔHOMO gap. In such a case, the natural tendency of a -E substituent is perverted by the cross-links or bridges present in the parent chromophore, and the induced sign ΔHOMO - ΔLUMO as well as the resulting MCD signs are the reverse of what the substituent would induce on the parent perimeter alone. However, as shown in Figure 3, increasing

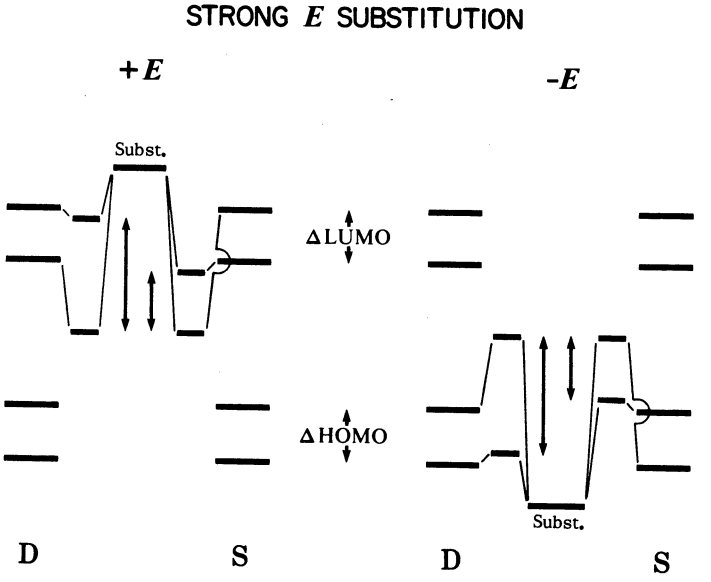

Figure 3. Effects of very strong mesomeric substituents on ΔHOMO and ΔLUMO in a dominant (D) and subdominant (S) position.

strength of the substituent will induce a crossing of the two highest occupied orbitals and thereafter any further increase in the substituent strength will cause an increase in ΔHOMO, so that eventually the sign of ΔHOMO - ΔLUMO will become positive. In such a limit the substituent again dominates the sign of the ΔHOMO - ΔLUMO value as if the additional cross-links or bridges were not present. Positions of this second type are referred to as subdominant (i.e., only latently substituent-dominated). An entirely analogous situation exists with respect to +E substituents (Figures 2,3). Now, positions can be classified as +E-dominant or +E-subdominant. For both -E and +E substituents, positions in which the squares of the coefficients of both orbitals are approximately equal are referred to as neutral and relatively little effect is expected for substitution in these.

In MCD chromophores derived from an uncharged perimeter, which play an important role in practice, orbital pairing properties permit considerable simplifications. Soft chromophores of this type which possess at least one plane of symmetry other than the molecular plane are classified as odd-soft or even-soft, depending on the ordering of the four frontier orbitals. In odd-soft chromophores[4], the uppermost occupied orbital is paired or approximately paired with the lowermost unoccupied orbital and the second highest occupied orbital is paired with the second lowest unoccupied orbital. Such pairing implies identical values for squares of the coefficients of the two paired molecular orbitals in a given position of substitution. Alternant benzenoid hydrocarbons are an example of this type of soft chromophore. In even-soft chromophores[4], the orbital ordering is such that the uppermost occupied MO is paired with the second lowest unoccupied MO, and the second highest occupied MO with the lowest unoccupied MO. Here, pairing is usually only approximate and examples are azulene and pyridine. Because of the pairing properties in odd and even-soft chromophores, the number of possibilities for MCD substituent effects is restricted. In an odd-soft chromophore, a position which is dominant (subdominant) with respect to a -E substituent is also dominant (subdominant) with respect to a +E substituent. Thus, all positions fall into one of three classes: dominant (D), neutral (N), and subdominant (S). In an even-soft chromophore, a position of substitution which is dominant (subdominant) with respect to the -E effect is of necessity subdominant (dominant) with respect to the +E effect. Stating the responses of a given position in the order +E, -E, there are then again only three possibilities: DS, N, and SD. The effects of inductively donating (-I) and withdrawing (+I) substituents follow from simple addition of the effects on ΔHOMO and on ΔLUMO. It is readily seen that I-substitution in any position of an even-soft chromophore is without effect to the first order in the perturbation, since the effects on ΔHOMO and ΔLUMO are the same. In an odd-soft chromophore, the -I effect (+I effect) will make the value of ΔHOMO - ΔLUMO positive (negative) in a position of type D, and it will have the opposite effect in a position of type S; it will have little or no effect in a position of type N. The introduction of a heteroatom can be viewed as a special case of inductive substitution.

In chromophores of other types, and in particular in those derived from a charged perimeter, the number of possibilities is considerably wider. Not only can all four principal combinations, DD, DS, SD, and SS occur, but the sensitivity of ΔHOMO and ΔLUMO to the substituent effect do not need to be the same. This is indicated by using lower case letters (d,s) to indicate positions of low sensitivity, where the difference of the two squared coefficients is small. To completely specify the response of a given position of such a general MCD chromophore to substituent effects, it is therefore necessary to indicate both the responseto +E and -E substitution, such as Ds, but independently also the response to +I substitution such as d. A summary of the various possibilities is given in Table 1.

The magnitudes of MO expansion coefficients can be obtained from standard tables or calculated using simple π-electron methods as the need arises. Frequently it is possible to understand qualitative trends in the size of these coefficients without resorting to any calculations whatever[6] and this is illustrated on several examples in the following.

EXAMPLES OF THE EFFECTS OF SUBSTITUENTS AND HETEROATOMS ON MCD SPECTRA OF AROMATIC CHROMOPHORES

The general principles outlined in the preceding section have been tested on a wide variety of cases, many already published, some in the process of publication. Here we shall illustrate their use on several selected examples.

TABLE 1

SUBSTITUENT EFFECTS ON (ΔHOMO - ΔLUMO)

Type of Substituent	Type of Position[a] Dominant (D)	Neutral (N)	Subdominant (S)[b]
+E	$c_{-1}^2 > c_{-2}^2$	$c_{-1}^2 \tilde{} c_{-2}^2$	$c_{-1}^2 < c_{-2}^2$
Action	Increases ΔLUMO	Little	Decreases ΔLUMO
-E	$c_1^2 > c_2^2$	$c_1^2 \tilde{} c_2^2$	$c_1^2 < c_2^2$
Action	Increases ΔHOMO	Little	Decreases ΔLUMO
+I	$(c_2^2 - c_1^2 + c_{-2}^2 - c_{-1}^2)^b < 0$	$(c_2^2 - c_1^2 + c_{-2}^2 - c_{-1}^2) \tilde{} 0$	$(c_2^2 - c_1^2 + c_{-2}^2 - c_1^2) > 0$
Action	Decreases (ΔHOMO-ΔLUMO)	Little	Increases (ΔHOMO-ΔLUMO)
-I	$(c_2^2 - c_1^2 + c_{-2}^2 - c_1^2) < 0$	$(c_2^2 - c_1^2 + c_{-2}^2 - c_1^2) \tilde{} 0$	$(c_2^2 - c_1^2 + c_{-2}^2 - c_1^2) > 0$
Action	Increases (ΔHOMO-ΔLUMO)	Little	Decreases (ΔHOMO-ΔLUMO)

[a] A lower case letter indicates a weak S or D character and thus a weaker response to substituent effects.

The quantity $c_2^2 - c_1^2 + c_{-2}^2 - c_{-1}^2$ is equivalent to $\Delta(\Delta HOMO-\Delta LUMO)/(-\Delta\alpha)$ to first-order in perturbation theory.

[b] The action stated applies to weak substituent effects. Very strong E substituents will act in all positions as if they were of type D.

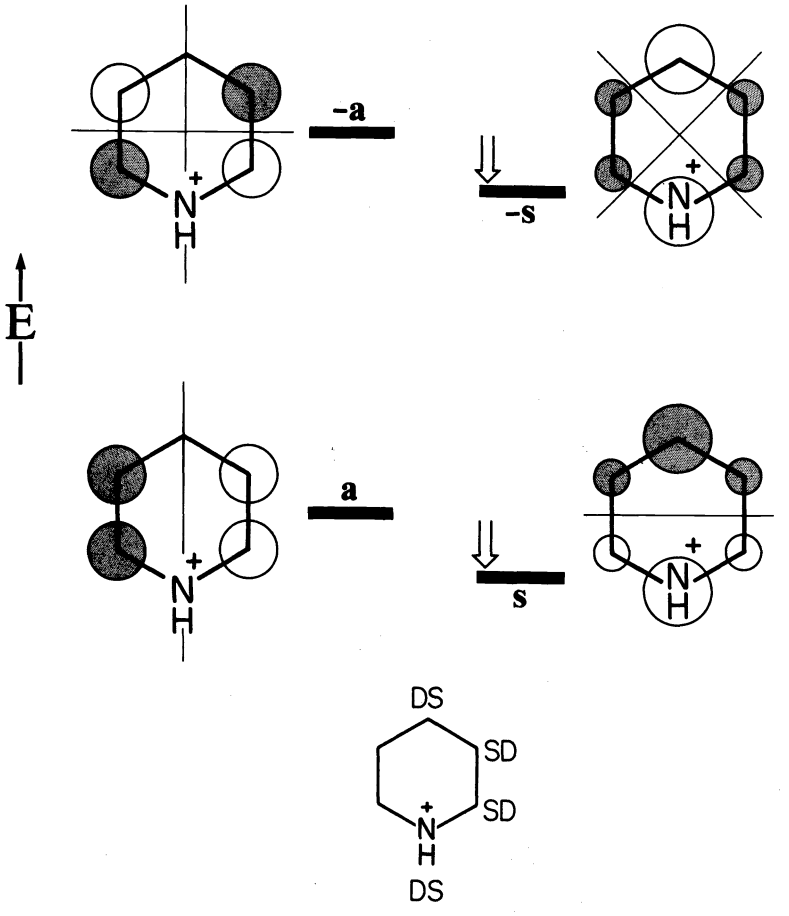

Figure 4. The frontier orbitals of the pyridinium cation derived from those of the parent perimeter (benzene).

The first of these, the pyridinium cation, is chosen as an example of the effect of mesomeric electron donor substituents of gradually increasing strength, attached in a subdominant position. In the first approximation, the frontier orbitals of the pyridinium cation can be derived from those of benzene (Figure 4). Introduction of the more electronegative NH^+ substituent in one of the benzene positions lowers the energy of the two orbitals which have a large coefficient at the position of substitution (s, -s). This results in an orbital ordering s, a, -s, -a. ΔHOMO and ΔLUMO are approximately equal, since two orbitals of benzene are paired. If it is now assumed that the coefficients of the MOs of pyridinium are approximately the same as in benzene, it is straightforward to label the positions in pyridinium as DS or SD, according to whether the antisymmetric or the symmetric orbital in each pair has the larger coefficient in a given position. The result is given in Figure 4, and shows that positions α and β in the pyridine nucleus are dominant with respect to -E substitution, whereas position γ is subdominant. Therefore, introduction of a weak -E substituent in position γ should induce a negative μ^+ contribution to the B term of the lowest transition, L_1, and a positive μ^+ contribution to the B term of the next transition, L_2, the signs being just the opposite of what one would expect upon introduction of the same substituent into the unperturbed perimeter, benzene. As the -E effect of the substituent increases in strength, the signs are expected to reverse and eventually be the same as would be the case for substitution in benzene itself. The spectra shown in Figure 5

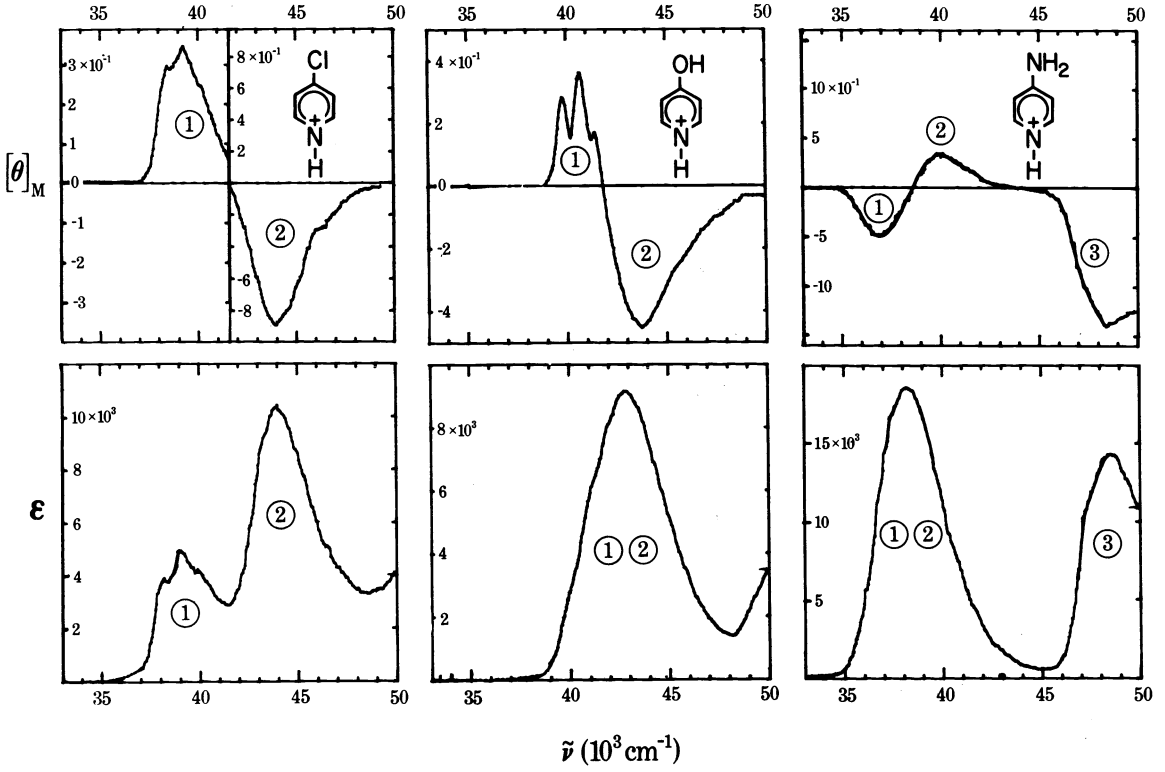

Figure 5. Magnetic circular dichroism (top) and u.v. absorption (bottom)[7].

demonstrate that this reversal actually occurs. Like pyridinium, pyridine itself is an approximately even-soft chromophore and substituent effects on its MCD spectrum follow the expected pattern[7]. In particular, a weak electron donor and a weak electron acceptor induce the same sign in a given position. Our second example is pyrene, which is an odd-soft chromophore. We use it not only to demonstrate how the S, D nature of a position varies along the perimeter, but also to demonstrate the striking difference in the response of a given position to electron-withdrawing +E versus electron-donating -E substituents. The important qualitative features of the frontier molecular orbitals of pyrene are derived from the nodal properties of the [14]annulene perimeter in Figure 6. Here again, we use the real representation of the perimeter orbitals, which does not permit an easy visualization of electron circulation, but is ideal for the derivation of the relative size of ΔHOMO and ΔLUMO splittings. The HOMO pair, being the fourth π level from the bottom, has three nodes perpendicular to the molecular plane in

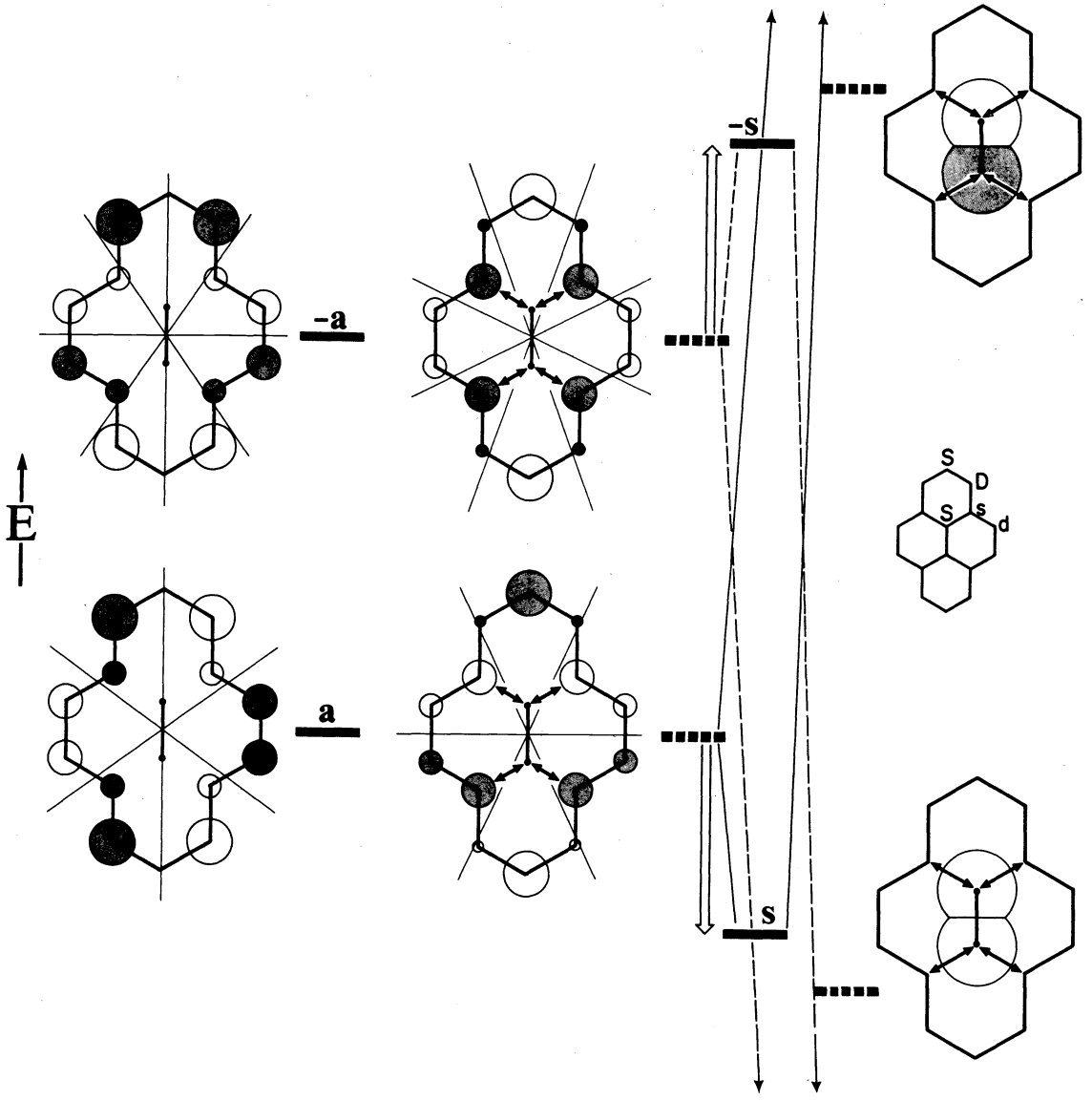

Figure 6. The frontier orbitals of pyrene derived from those of the parent perimeter.

each orbital. They cut the perimeter at regular intervals, as shown in Figure 6 (each interval is equal to 7/3 of the bond length). The LUMO pair is the fifth π level and therefore has four such nodes in each orbital, arranged in a similar regular pattern (each interval between two nodal points is 7/4 of the bond length). The size of the MO coefficient on each atom is determined by the sinusoidal nature of the wavefunction along the perimeter: the closer an atom lies to a nodal point on the perimeter, the smaller the MO coefficient of its orbital. Thus, the relative sizes shown can actually be drawn without calculation. In order to convert the [14]annulene perimeter into pyrene, interaction with the orbitals of an inside ethylene bridge must be considered. The bonding and antibonding orbital of this bridge is shown on the right-hand side of Figure 6. It is obvious from symmetry considerations that the former interacts with the symmetric LUMO of the perimeter ($\tilde{-s}$), the latter with the symmetric HOMO of the perimeter ($\tilde{s}$), while neither interacts with the antisymmetric $\tilde{a}$ and $\tilde{-a}$ orbitals of the perimeter. The net result of these interactions is that the order of pyrene orbitals is $\tilde{s}$, $\tilde{a}$, $\tilde{-a}$, $\tilde{-s}$ in the order of increasing energy, and that ΔHOMO and ΔLUMO are equal, as they must be at this level of approximation, because of orbital pairing. The highest occupied MO is paired with the lowest unoccupied MO and the second highest occupied MO is paired with the second lowest unoccupied MO. This arrangement is characteristic of an odd-soft chromophore and can be contrasted with the arrangement found above for the pyridinium cation, an even-soft chromophore (Figure 4). Assuming

now that the qualitative features of the molecular orbitals of the perimeter are retained upon transition to pyrene, and evaluating the relative sizes in the orbital pairs $\underset{\sim}{a}$, $\underset{\sim}{s}$, and $-\underset{\sim}{a}$, $-\underset{\sim}{s}$, we deduce the position labeling shown in Figure 6: the pyrene position 1 should be strongly dominant, position 4 weakly dominant, and position 2 subdominant. Table 2 summarizes the observed signs of B terms of the L bands in azapyrenes[8] (+I effect), aminopyrenes[9] (-E effect), and pyrenecarboxylic esters[9] (+E effect). They agree perfectly with expectations based on our simple model and suggest that MCD spectroscopy might well be of use in the determination of the position of substitution in polynuclear aromatic hydrocarbons, particularly if only small amounts of the sample are available. Even substituents as weak as methyl show pronounced effects of this kind[10].

TABLE 2

SUBSTITUTION IN PYRENE: OBSERVED SIGNS OF B TERMS[8,9]

Substituent	Position	Type	B (L_1)	B (L_2)
N (AZA)	1	D	-	+
	2,7	S	+	-
	4	d	-	+
NH_2	1	D	+	-
	2	S	-	+
	4	d	+	-
$COOC_2H_5$	1	D	-	+
	2	S	+	-
	4	d	-	+

It is interesting to note that the sensitivity of the MCD signs to position and nature of substitution is not a universal property and is limited to soft chromophores. This is illustrated nicely by comparison of the results for pyrene with those for its isomer, fluoranthene, which is a negative-hard MCD chromophore. Amino and carboxy substitution on fluoranthene has been investigated[11] and shows none of the variability associated with pyrene.

Our third and last example deals with a group of heterocycles of considerable biological interest. These are derived from the indenide anion by introduction of a heteroatom which contributes two π-electrons to the conjugated system, such as NH, O, or S, and possibly of additional heteroatoms such as aza nitrogens. Indoles and purines are perhaps the best known examples of this type of heterocycle. Once again, qualitative trends can be predicted without any calculations. Figure 7 shows the MO coefficients of the parent perimeter, $C_9H_9^-$. The HOMO pair, being the third π level from the bottom, has two nodes perpendicular to the molecular plane in each orbital. These lie at right angles to each other as shown. The LUMO pair is the fourth π level and therefore has three such nodes in each orbital, intersecting at 60° angles. The size of the MO coefficient on each atom is again determined by its proximity to a nodal point: the closer an atom lies to a node, the smaller its MO coefficient in a given orbital. The introduction of a cross-link which converts the [9]annulenide anion into the indenide anion is indicated by double-headed arrows in Figure 7. Its expected first-order effect on the four orbital energies follows from the signs and magnitudes of the orbital coefficients shown and is indicated by vertical arrows. The cross-linking splits the degenerate pairs but preserves the equality of ΔHOMO and ΔLUMO to first order. If one now again assumes that the orbital coefficients themselves do not change at all as a result of the cross-linking, that is that first-order perturbation theory is exact, and compares their sizes within the bonding MO pair and within the antibonding MO pair, one derives the D and S labels for the individual positions of the indenide anion as shown in Figure 7. In reality, of course, an inspection of the Hückel orbitals of the indenide anion shows that the first-order approximation is not quite correct. However, the nodal properties of the four orbitals are still preserved perfectly, as are their relative magnitudes. Only the response of position 1 to +E effect, expected to be subdominant from the argument presented here, turns out to be almost exactly neutral when the actual Hückel MO's are used. The S, D characterization of the various positions in the 10 π-electron indenide anion is interesting to compare with those of the 10 π-electron odd-soft naphthalene and the even-soft azulene chromophores. Indenide positions 3a, 4 and 5 resemble the positions 8a (S), 1 (DD), and 2 (SS), of naphthalene, respectively, while indenide positions 1 and 2 are reminiscent of the positions 1 (SD) and 2 (dS) of azulene. The greater complexity of a chromophore derived from a charged perimeter is thus apparent.

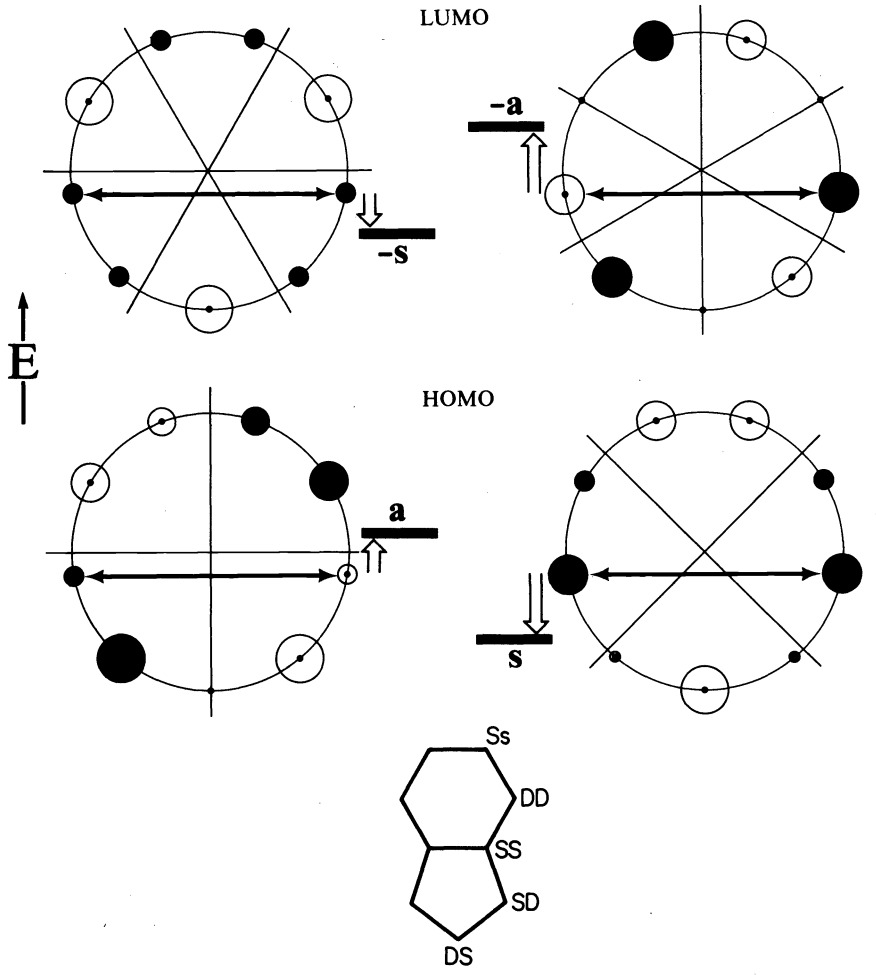

Figure 7. The frontier orbitals of the indenide anion derived from those of the parent perimeter.

The squares of the Hückel coefficients for the indenide anion and the expected effects of the introduction of an electronegative heteroatom on ΔHOMO - ΔLUMO are shown in Table 3. The resulting predictions of the signs of μ^+ contributions to the B terms of L_1 and L_2 transitions in various heterocycles isoelectronic with the indenide anion are presented in Figure 8. Most of these predictions cannot yet be verified by comparison with experiment, but those comparisons which can be made exhibit perfect agreement. Figure 9 shows the spectrum of benzothiophene, displaying the expected sign sequence. It is now possible to proceed further, viewing heterocycles such as indole as the parent MCD chromophore and evaluating the MO coefficients in its various positions in order to predict the effect of further substitution or additional heteroatoms[12]. In indole itself, ΔHOMO is smaller than ΔLUMO, but the difference is relatively small, and can be reversed by a strong perturbation. Inspection of the indole MOs shows that this difference will be increased and the negative μ^+ contribution to the B terms of transition L_1 and the positive μ^+ contribution to that of transition L_2 will be augmented if an additional aza nitrogen is introduced into any of the dominant positions, 2,3,4, or 7. Aza replacement in the neutral position 6 should have little effect, and only in the subdominant position 5 of indole will aza substitution tend to decrease the magnitude or perhaps even reverse the sign of the ΔHOMO - ΔLUMO difference. Thus we expect monoazaindoles to have at least as strong a negative B term for the L_1 transition and positive B term for the L_2 transition as indole itself, with the only exception of 5-azaindole. It is possible to proceed further along these lines all the way to the purines and to use MCD measurements to assign, for instance, the position of protonation in various isomeric N-methylpurines[12].

TABLE 3

SQUARES OF HMO COEFFICIENTS IN THE INDENIDE ANION AND EXPECTED EFFECTS OF ELECTRONEGATIVE HETEROATOMS ON ΔHOMO - ΔLUMO

	Position				
Orbital	1 = 3	2	3a = 7a	4 = 7	5 = 6
c^2_{-2}	0.067	0.000	0.113	0.026	0.295
c^2_{-1} (LUMO)	0.024	0.118	0.042	0.294	0.081
Δ	0.043	-0.118	0.071	-0.268	0,214
c^2_1 (HOMO)	0.295	0.000	0.026	0.113	0.067
c^2_2	0.042	0.317	0.171	0.009	0.119
Δ	0.253	-0.317	-0.145	0.104	-0,052
Δ(ΔHOMO-ΔLUMO)/(-Δα)	-0.210	0.199	0.216	-0.372	0.266
Position type	ND	dS	sS	Dd	Ss
Type of response to I effect	D	S	S	D	S

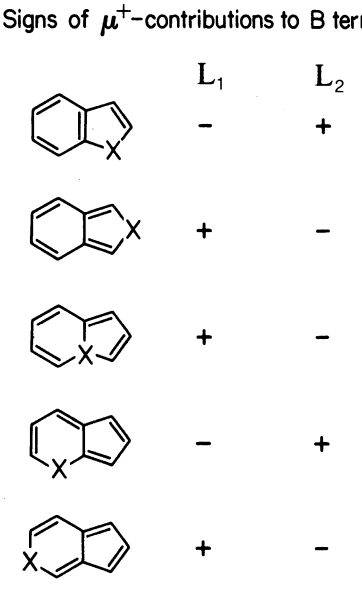

Figure 8. Predictions based on Table 3,

The effects of mesomeric substituents on heterocycles isoelectronic with the indenide anion can be analyzed along similar lines. Without going into detail, let us only mention that this permits an understanding of the MCD signs of molecules such as serotonin and adenine, as well as an understanding of changes in the MCD spectra upon protonation[13].

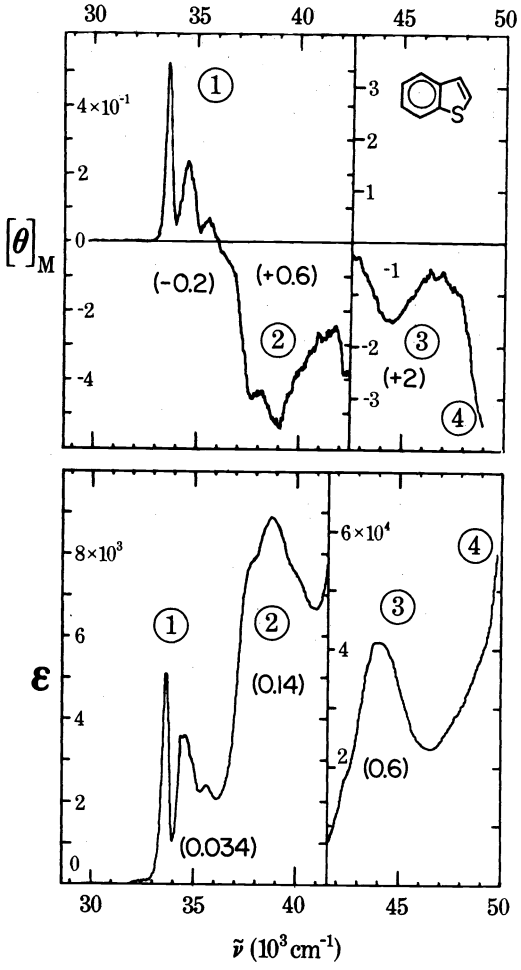

Figure 9. Magnetic circular dichroism (top) and u.v. absorption (bottom)[12]

CONCLUSIONS

It has been the purpose of this presentation to demonstrate that the MCD effect in aromatic molecules has a simply understandable physical origin, and that the observed signs are related to orbital energy differences which can frequently be simply estimated from molecular structure. Thus, in the hands of the organic chemist interested in aromatic molecules, MCD is likely to turn into a useful tool for the investigation of electronic structure and possibly even for structure determination, for instance for investigations of protonation sites or tautomerism in heterocycles and of the positions of substitution in polynuclear aromatics.

It must be emphasized that the theory used for the derivations outlined here is only approximate and is suitable for an investigation of trends and qualitative features rather than for a quantitative evaluation of the magnitude of MCD B terms. Perhaps the most obvious neglect in the procedure has to do with the π-electron approximation: mutual magnetic mixing of ππ* states is considered, but magnetic mixing with other states such as σπ*, nπ*, etc., is ignored. Fortunately, all experimental evidence available so far indicates that this is quite justified in qualitative and semiquantitative applications. Another potentially serious neglect is the inclusion of only four excited states in the model. As a result, only the predictions for the L transitions and usually also the lower of the B transitions are meaningful and predictions for higher energy ππ* transitions would require numerical calculations. These higher energy states are usually of little concern to the organic chemist, however. A more detailed discussion of the approximations involved in the use of the perimeter model is found in reference 2.

Acknowledgement - I thank the Editor of the Journal of the American Chemical Society for kind permission to reproduce Figure 1, reprinted from reference 3 (copyright of

the American Chemical Society). I am grateful to the U.S. Public Health Service for research grant support (GM 21153) and to Professor Henry Eyring for the use of his MCD instrument. I am further deeply indebted to my collaborators who performed the experimental work reviewed here: A. Berg, Alain Castellan, Genomarta P. Dalgaard, John W. Downing, Danielle Muller, Dale Otteson, Mark A. Souto, Richard P. Steiner, Erik W. Thulstrup, Milan Vašák, Susan L. Wallace, and Michael R. Whipple.

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