

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 8.^{1,2} Derivatives of Naphthalene

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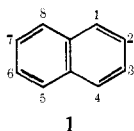
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Abstract: Magnetic circular dichroism of naphthalene and 17 of its derivatives is reported and interpreted. The signs of $B(L_b)$ and $B(L_a)$ are sensitive to the location and nature of the substituents, and that of $B(B_b)$ is positive. The signs are in excellent agreement with the general qualitative theory of parts 1–3 for an odd-soft chromophore and its response to mesomeric effects of substituents.

Introduction

According to the general qualitative theory of MCD of transitions related to the L and B states of the perimeter, outlined in parts 1–3,^{4–6} naphthalene (**1**), like other polycyclic benzenoid hydrocarbons without a threefold or higher symmetry axis, is an odd-soft MCD chromophore and the theory makes some very definite predictions⁶ for its MCD signs and substituent effects on them. In part 7,² the effect of inductive (I) substitution (aza replacement) was investigated. The present paper deals with the effect of attaching a substituent with an I or E (mesomeric) effect or both. We report the MCD spectra of **1** substituted in the 1 or 2 position with the following groups: CH₃, F, OH, NH₂ (–E substituents), CN, CHO (+E substituents), NH₃⁺. Also the 2-OCOCF₃, 2-NHCOCF₃, and 2,3-diamino derivatives have been measured. In part 9,⁷ we examine simultaneous substitution of **1** with a +I (aza) and a –E (amino) substituent. In part 10,⁸ we discuss the MCD spectra of more severely perturbed heterocyclic analogues of **1** related to quinolone and isoquinolone. Investigations of substituent effects on the MCD spectra of other odd-soft chromophores are also being reported, as noted in part 1.⁴

Much attention has been paid to the excited singlet states of **1**. The experimental evidence⁹ can be summarized as follows: a very weak long-axis-polarized transition near 32 000 cm⁻¹ (L_b) is followed by a medium-intensity short-axis-polarized transition near 35 000 cm⁻¹ (L_a) and by a very intense long-axis-polarized transition near 45 000 cm⁻¹ (B_b). The B_a transition and several others have been identified at energies above 50 000 cm⁻¹. The labels of these states go back to Klevens and Platt.¹⁰ These results are in good agreement with calculations,¹¹ which also predict two or three additional symmetry-forbidden transitions to occur in the vicinity of the B_b band. Evidence for the presence of two such transitions at 42 500 and 44 500 cm⁻¹ has been obtained recently from two-photon excitation spectra.¹⁴



Derivatives of **1** have also been studied in detail. Some of the recent theoretical work, which also summarized experimental data, is found in ref 12, 13, and 15–18. In substituted naphthalenes, the principal bands of **1**, L_b , L_a , and B_b , can often still be recognized, but they are sometimes heavily mixed. In some cases, the previously forbidden additional bands in the region of the B_b band acquire sufficient intensity to stand out clearly in the absorption spectra. By far most experimental^{19–23} and theoretical^{12,13,15–18} attention has concentrated on the curious behavior of polarization directions of the two L bands. These are perpendicular to each other in the parent **1** and remain little

affected by 1-substitution, but in 2-substituted derivatives of **1**, the L_b and L_a states mix strongly and the transition moment of the lower of this pair of states (L_1) is rotated close to the short axis of the molecule and is then nearly parallel to the L_a (L_2) transition moment. The only reliable experimental transition directions are those of the 0–0 component of the L_1 band of naphthalenes carrying a F, OH, or NH₂ substituent in positions 1 or 2, obtained from rotational band contour analysis.²⁰ In our opinion, the angles reported from analysis of linear dichroism in stretched polymer sheets for L and B bands of substituted naphthalenes^{21–23} are not quantitatively reliable, since unphysical assumptions were made about the nature of the orientation distribution function (a single orientational parameter; cf. the criticism of this approximation in ref 24), but qualitatively, they leave no doubt about the great difference between substitution in positions 1 and 2 and about the near parallelism of the L_1 and L_2 transition moments in the latter case, which is also clear from polarized emission studies.¹⁹ The calculated transition moment directions cannot be considered accurately reliable either, in view of the great sensitivity of this property to the extent of configuration interaction,²⁵ but once again, the gross features of the results probably can be trusted. A general interpretation of the sensitivity of the L_1 transition moment direction as a function of the position of substitution in a variety of benzenoid hydrocarbons has been offered some time ago by Koutecký;¹⁸ it is based on properties of Hückel coefficients of the highest and second highest occupied MO's. Similar insight can be obtained using the perimeter model: the angles $\arg a$ and $\arg b$ defined in part 2⁵ are related to the matrix elements of the perimeter-perturbing operator between the orbitals **a** and **s** and between the orbitals $-\mathbf{a}$ and $-\mathbf{s}$; these matrix elements vanish if the substituent is attached at a node of either **a** ($-\mathbf{a}$) or **s** ($-\mathbf{s}$), e.g., in position 1 of naphthalene.

MCD of naphthalene, 1,4,5,8-tetrachloronaphthalene, and acenaphthene have been reported,²⁶ and MCD of the L_b band of **1** has been calculated²⁷ previously. A newly remeasured and extended spectrum of **1** appeared in the immediately preceding part 7.² MCD spectra of other substituted naphthalenes had not been described prior to our preliminary reports.^{1,28} Recently, a group of substituted naphthalenes was measured by Eyring et al.,²⁹ and a report of similar work has appeared in a Japanese journal.³⁰

Experimental Section and Calculations

The samples were purified by preparative GLC or by gradient sublimation as appropriate. They were commercial except for 2-CF₃CONH-**1** and 2-CF₃COO-**1**, which were prepared following the general procedure of ref 31. The measurements and calculations were performed as described in part 4.³² The protonated 1-NH₃⁺-**1** and 2-NH₃⁺-**1** were measured in 1 M H₂SO₄ in methanol, and 2,3-NH₂-**1** was measured in acetonitrile.

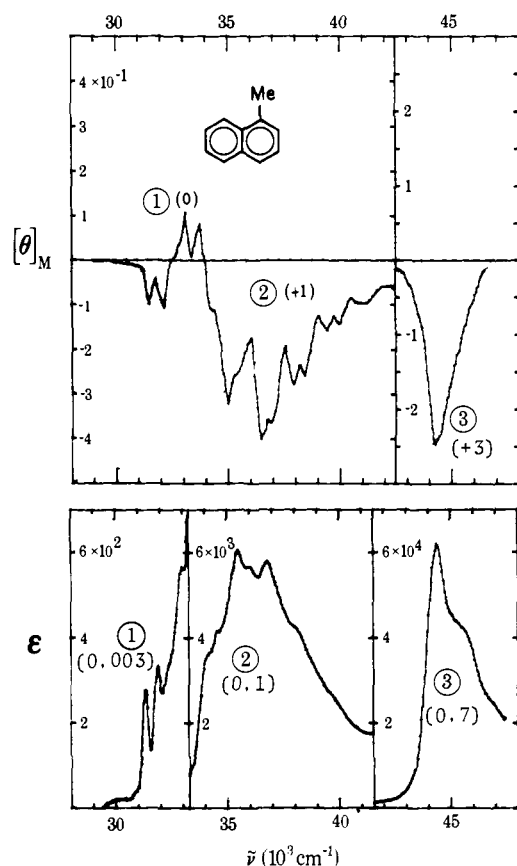


Figure 1. 1-Methylnaphthalene: bottom, absorption (oscillator strength given); top, MCD (B terms in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$).

Results

The results are shown in Figures 1–17. A tentative identification of individual electronic transitions is proposed. There is little problem with the identification of the L_1 , L_2 , and B_b (B_1) bands in the spectra. In several instances additional transitions in the region of the B_b band are clearly present, in agreement with the calculations. The B terms of the L bands depend on the nature and location of the substituent, as expected for an odd-soft chromophore, $B(B_b)$ is positive. As in other papers in this series, the calculations are of the standard PPP type without any adjustments for the use in MCD, and qualitative arguments⁵ suggest that they are best viewed as approximating the differences in the B terms of a substituted **1** with respect to those of **1** itself.

No $n\pi^*$ or similar bands are observed in any of the MCD spectra. Vibronic interactions are clearly present in several instances of nearly vanishing B terms and promise much interesting information once a high-resolution study is performed.

Discussion

Naphthalene As an Odd-Soft Chromophore. As described in some detail in part 2,⁵ μ^+ contributions to the MCD of an odd-soft chromophore vanish, and μ^- contributions yield $B(L_b) = 0$, $B(L_a)$ small and positive (due to L_a – B_b mixing), and $B(B_b)$ larger and positive (due to B_b – B_a mixing), in agreement with the observed spectrum of **1** shown in part 7.² The potentially strong μ^+ contributions will appear as soon as a perturbation produces $\Delta\text{HOMO} \neq \Delta\text{LUMO}$ ($\Delta\text{HOMO} = |E(\mathbf{a}) - E(\mathbf{s})|$, $\Delta\text{LUMO} = |E(-\mathbf{a}) - E(-\mathbf{s})|$). The contributions to $B(L_1)$ and $B(B_1)$ will be positive if $\Delta\text{HOMO} > \Delta\text{LUMO}$ and negative if $\Delta\text{HOMO} < \Delta\text{LUMO}$, and the contribution to $B(L_2)$ will have the opposite sign. Their magnitudes will de-

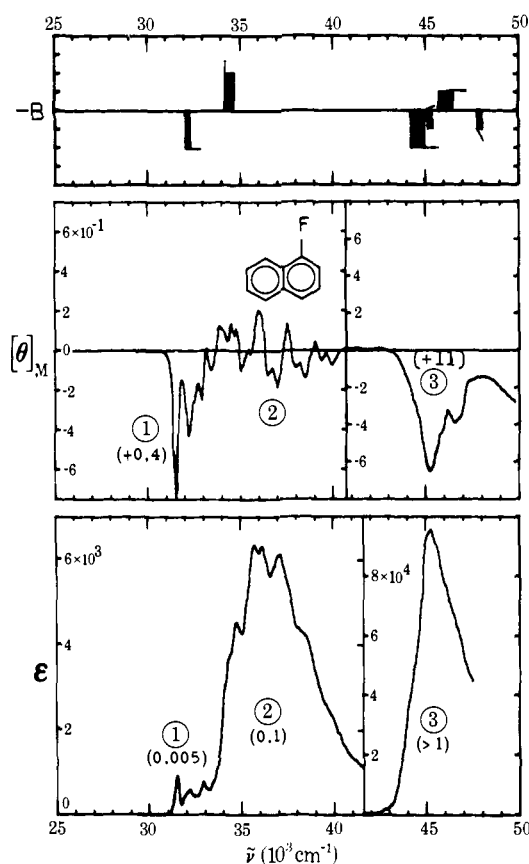


Figure 2. 1-Fluoronaphthalene: bottom, absorption (oscillator strength given); center, MCD (B terms in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$); top, calculation. Calculated $-B$ values are indicated by the length of the bars (shortest, below 1; next, 1–3; next, 3–10; longest, over 10; in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$), calculated oscillator strengths by their three grades of thickness (less than 0.2, 0.2–0.5, over 0.5), and calculated polarizations by directions of the flags at the end with respect to the formula shown.

pend on the absolute value of $|\Delta\text{HOMO} - \Delta\text{LUMO}|$. This dependence is not linear, and the B terms will gradually level off to limiting values.⁵

1-Substitution. Position 1 is dominant (D) since the Hückel coefficient of orbitals \mathbf{a} and $-\mathbf{a}$ (HOMO and LUMO) of naphthalene is large ($c_{1,1}^2 = 0.18$), whereas that of the next orbitals \mathbf{s} and $-\mathbf{s}$ vanishes ($c_{1,2}^2 = 0$). Thus, for +E substitution, we expect $\Delta\text{HOMO} < \Delta\text{LUMO}$ and for –E substitution, we expect $\Delta\text{HOMO} > \Delta\text{LUMO}$. If the inductive effect of the substituent is considered as well, it is seen that the I and E effect reinforce each other if they have the same sign. If they are opposed, the stronger effect wins. However, the I effect is already known to be rather ineffective since even the strong effect of aza replacement² leads to rather small B terms. In the halogens, the –E effect prevails. Clearly, however, a more quantitative treatment will require a consideration of both E and I effects of the substituent.

Comparison with experiment reveals excellent agreement with the simple theory. The weak –E effect of the methyl substituent barely modifies the MCD spectrum of naphthalene given in part 7.² It does, however, make the origin of the L_b band distinctly negative in the MCD curve (Figure 1) as expected for a positive $B(L_b)$. The somewhat stronger –E effect of fluorine, undoubtedly somewhat attenuated by its +I effect, makes $B(L_b)$ distinctly positive and apparently just compensates the inherent positive μ^- contribution to $B(L_a)$, so that $B(L_a)$ now is almost exactly zero and the MCD curve is dominated by vibronic interactions (Figure 2). The even stronger –E effects of hydroxy (Figure 3) and, particularly, amino (Figure 4) substituents continue this trend and lead to

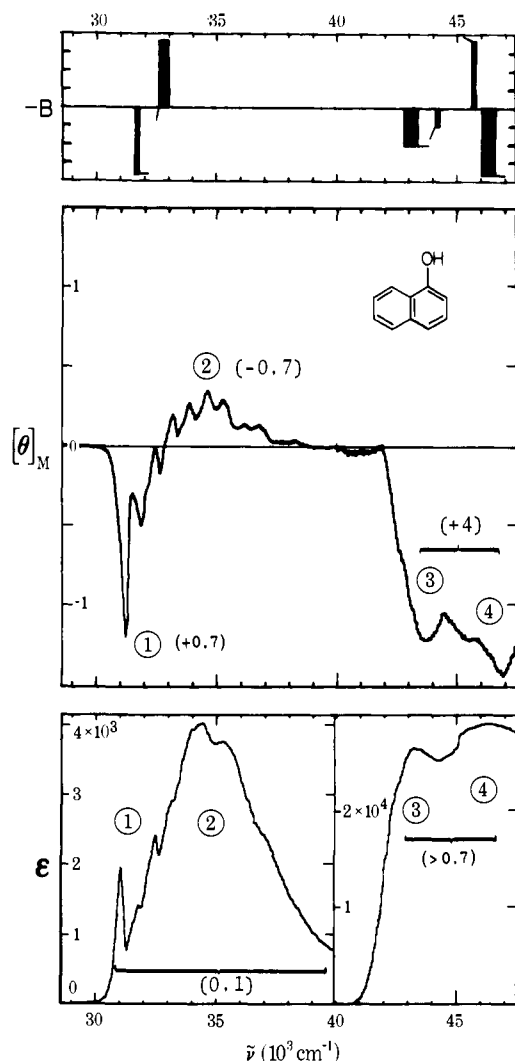


Figure 3. 1-Naphthol. See caption to Figure 2.

increasingly more positive $B(L_b)$ and more negative $B(L_a)$, just as expected. Also, the published²⁶ positive $B(L_b)$ and negative $B(L_a)$ values of 1,4,5,8-tetrachloronaphthalene and acenaphthene are now understandable. On the other hand, the strong +E substituents, CHO (Figure 5) and CN (Figure 6), produced the predicted large negative $B(L_b)$ and large positive $B(L_a)$ terms. The value of $B(B_b)$ remains positive throughout, indicating that the inherent μ^- contribution predominates even where opposed by the substituent-induced μ^+ contribution. In 1-CHO-1 and 1-CN-1 the region of B_b transition is confused by the presence of additional transitions. It will be noted that the substituent-induced contributions to the B terms have the same signs as they would in a $[4N + 2]$ annulene. Thus, removal of the 9-10 cross-link would make no qualitative difference to MCD signs; there is no clash between the influences of the cross-link and of the substituent located in a dominant position.

2-Substitution. Position 2 is subdominant (S) ($c_{2,1}^2 = 0.07$, $c_{2,2}^2 = 0.17$). Now, we expect⁵ $\Delta HOMO > \Delta LUMO$ for weak +E substituents and for very strong -E substituents, and we expect $\Delta HOMO < \Delta LUMO$ for weak -E substituents and for very strong +E substituents. Somewhere between the two extremes of substituent strength, $\Delta HOMO = \Delta LUMO$, and the substituent-induced μ^+ contributions to B terms are expected to go through zero. At that point, the π system is a zero-soft MCD chromophore, and the μ^- contributions to both of its L bands should be positive.

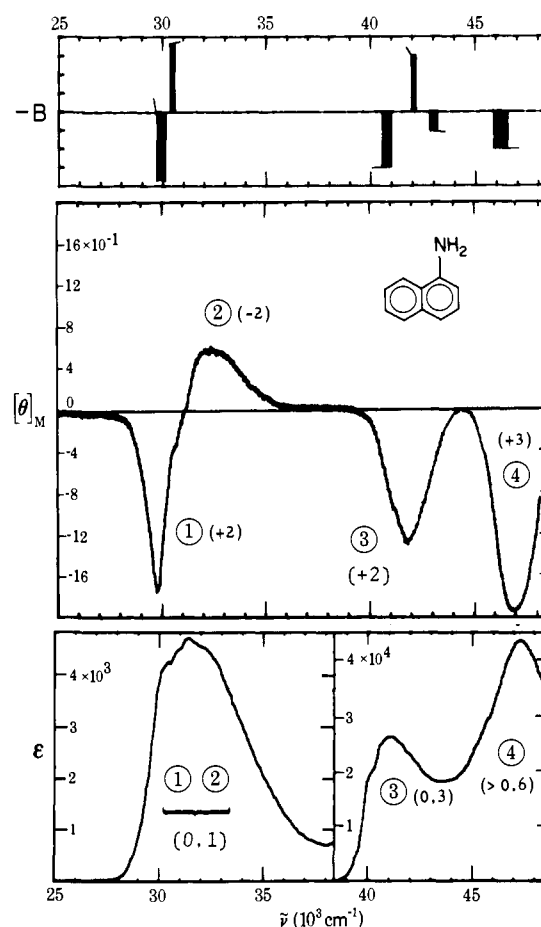


Figure 4. 1-Naphthylamine. See caption to Figure 2.

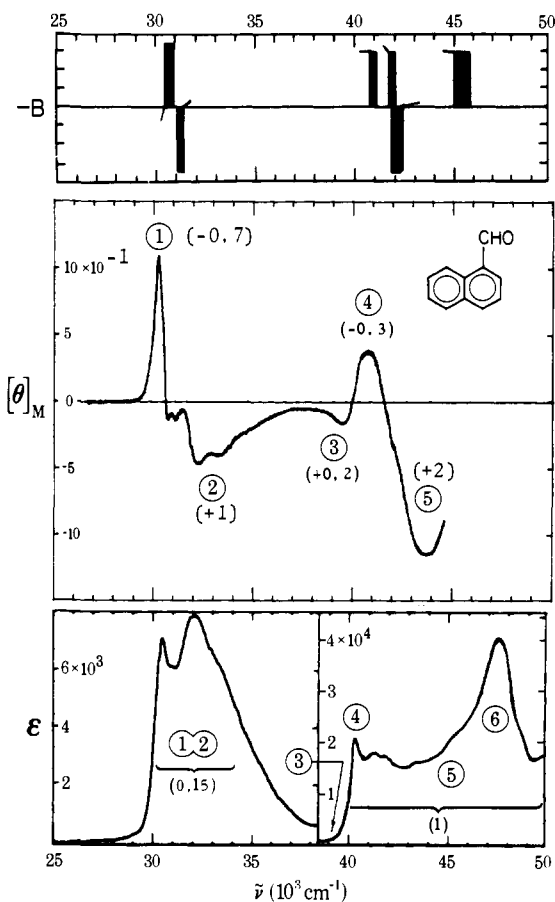


Figure 5. 1-Naphthaldehyde. See caption to Figure 2.

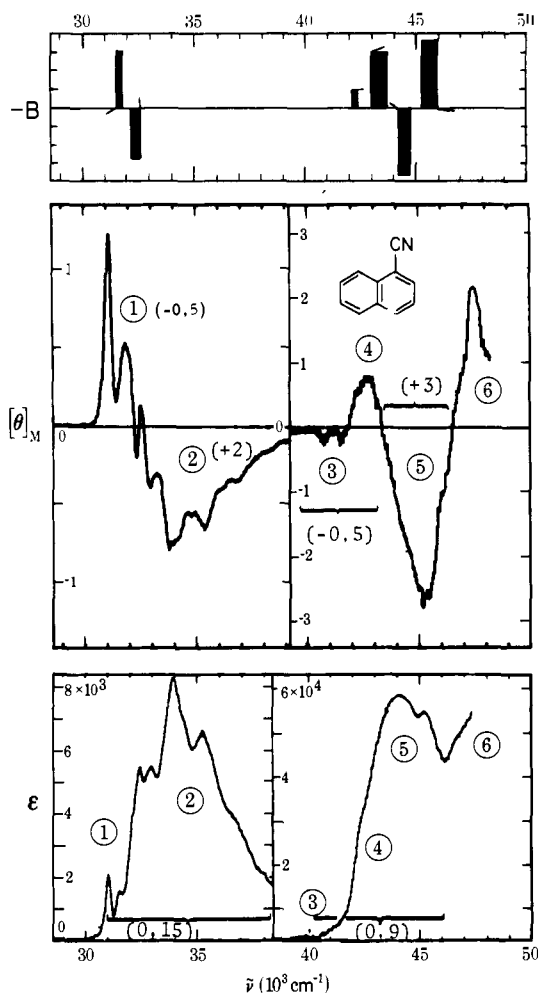


Figure 6. 1-Naphthonitrile. See caption to Figure 2.

Clearly, for E substitution in a subdominant position, there is a clash between the preferences imposed on the MO's by the 9-10 cross-link and by the substituent; one orbital ordering results if the substituent is removed; another if the cross-link

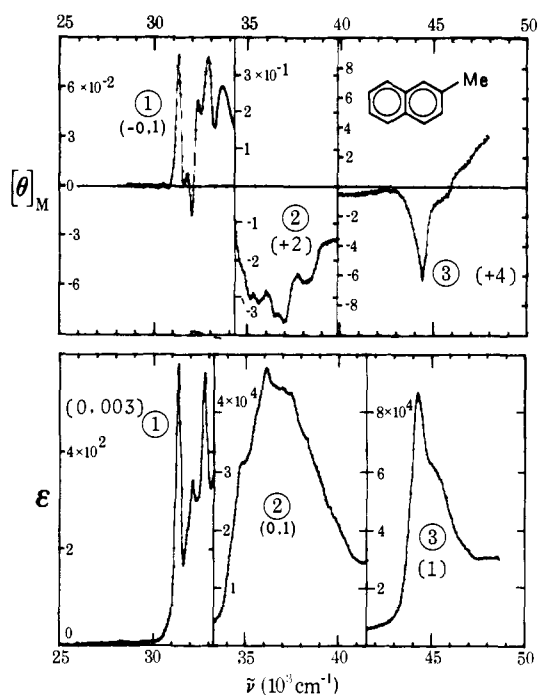


Figure 7. 2-Methylnaphthalene. See caption to Figure 1.

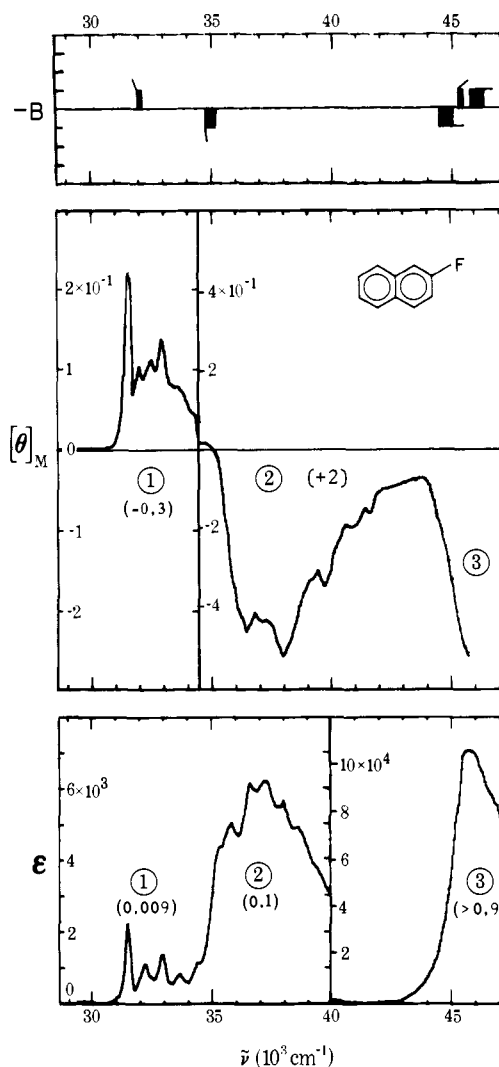


Figure 8. 2-Fluoronaphthalene. See caption to Figure 2.

is removed. It will be useful to consider this more generally for any substituent (E or I) in a qualitative fashion. Attachment of the substituent to a $[4N + 2]$ annulene forces an arrangement of the previously degenerate and arbitrarily selectable \mathbf{a} , \mathbf{s} and $-\mathbf{a}$, $-\mathbf{s}$ orbital pairs, such that two of the orbitals have a node at the position of substitution, and two orbitals an antinode. As a result, it forces L_b and B_b polarizations to be perpendicular to the substituent-ring bond and L_a and B_a polarizations to be parallel to it. On the other hand, the arrangement forced by the cross-link on the previously degenerate orbital pairs of the annulene is described by the Hückel MO's of the polycyclic hydrocarbon. In the case of naphthalene, the cross-link causes \mathbf{s} and $-\mathbf{s}$ to have a node in position 1 and \mathbf{a} and $-\mathbf{a}$ to have an antinode very close to it. On the other hand, both orbitals have significant coefficients in position 2. Therefore, a 1-substituent can be said to be satisfied with the orbital choice and polarization directions already imposed by the 9-10 cross-link, but a 2-substituent attempts to adapt them to its own preferences. Since the 9-10 cross-link alone does not provide the L_b transition with any intensity, whereas the substituent alone does, it is not surprising that the easiest change for the substituent in position 2 to effect is to rotate the L_b polarization direction toward the position it favors, i.e., perpendicular to the substituent-ring bond.¹⁹⁻²³ The L_a band, which also had no intensity in the parent [10]annulene, has been provided considerable intensity already by the 9-10 cross-linking, and one can expect that it will require a much stronger substituent effect to rotate it parallel to the

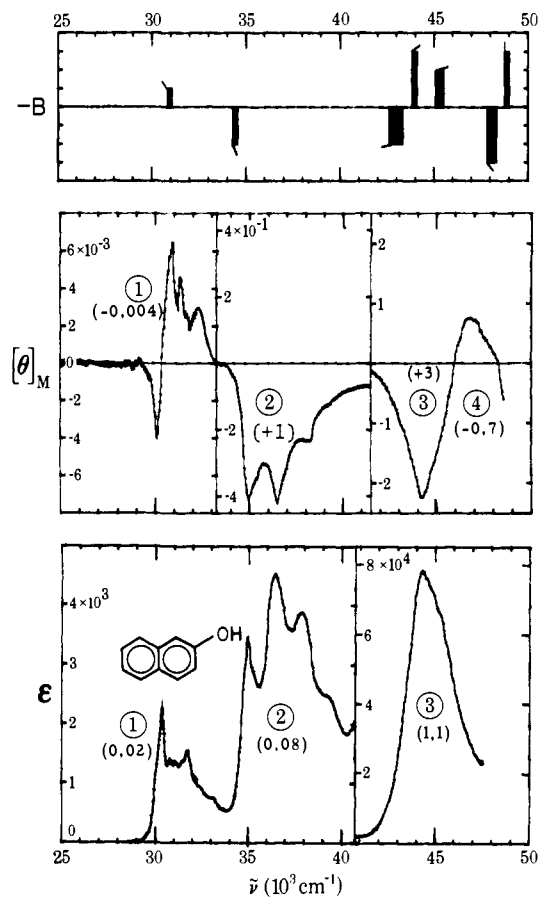


Figure 9. 2-Naphthol. See caption to Figure 2.

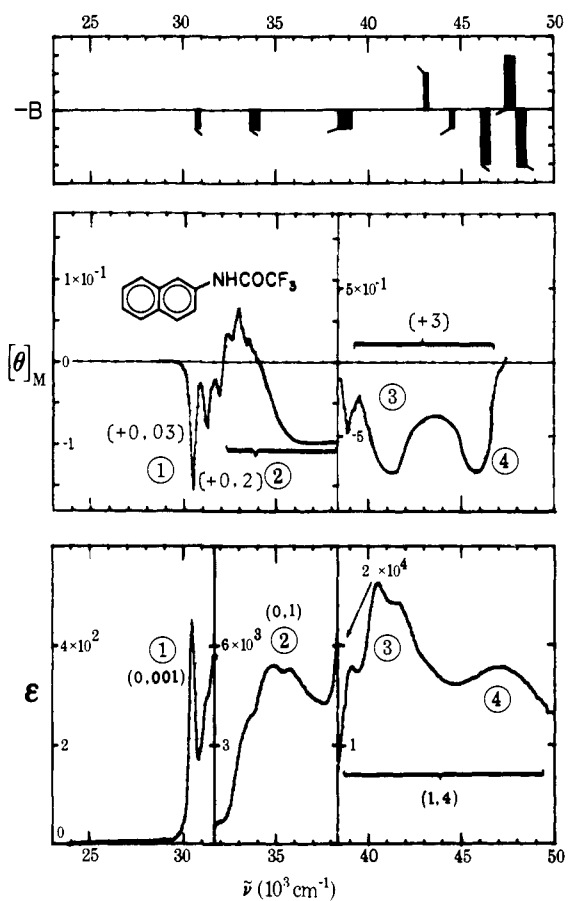


Figure 11. 2-Trifluoroacetamidonaphthalene. See caption to Figure 2.

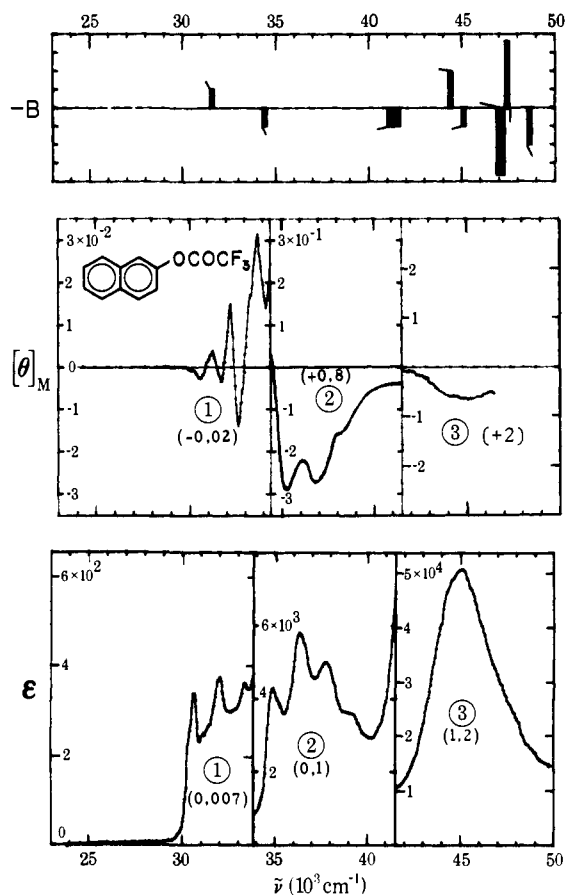


Figure 10. 2-Trifluoroacetoxynaphthalene. See caption to Figure 2.

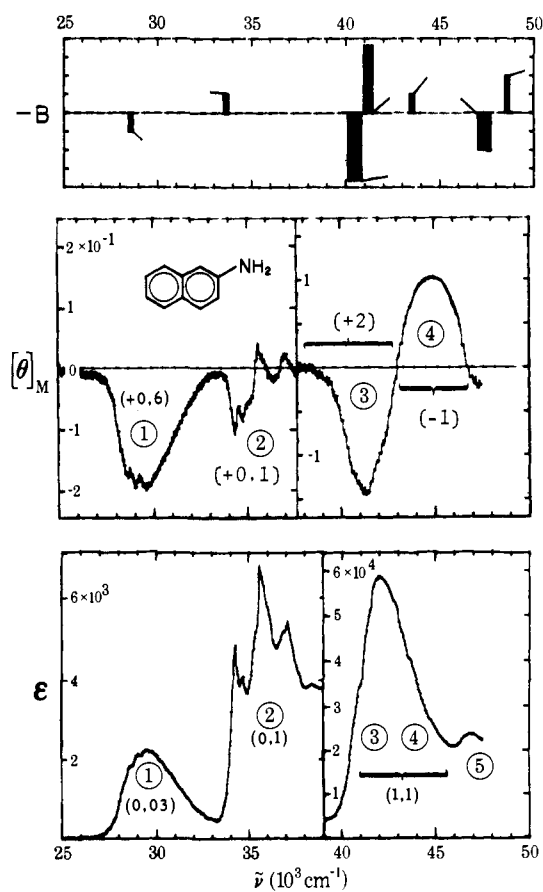


Figure 12. 2-Naphthylamine. See caption to Figure 2.

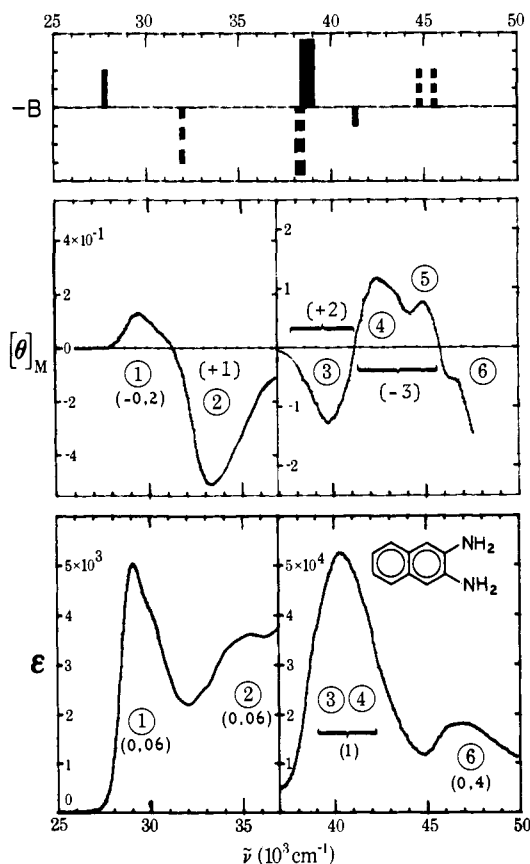


Figure 13. 2,3-Diaminonaphthalene. See caption to Figure 2. Solid bars indicate horizontal polarization and broken bars vertical polarization with respect to the formula shown.

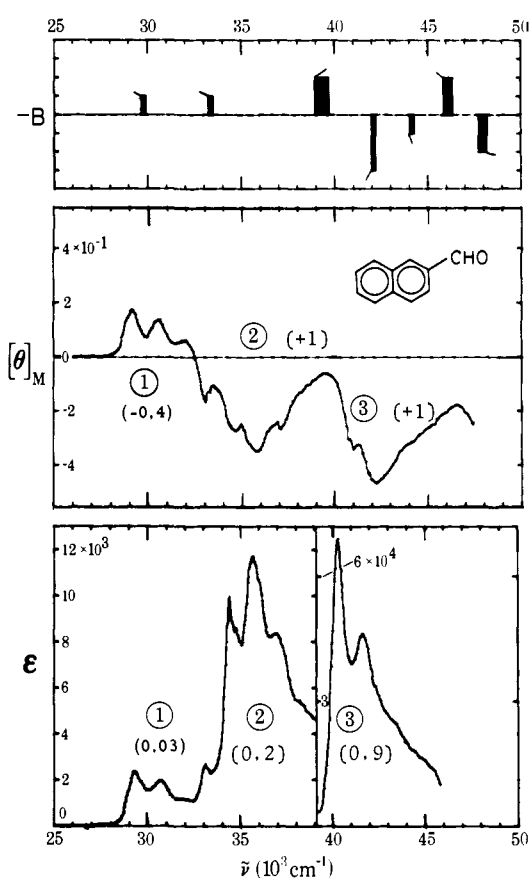


Figure 15. 2-Naphthaldehyde. See caption to Figure 2.

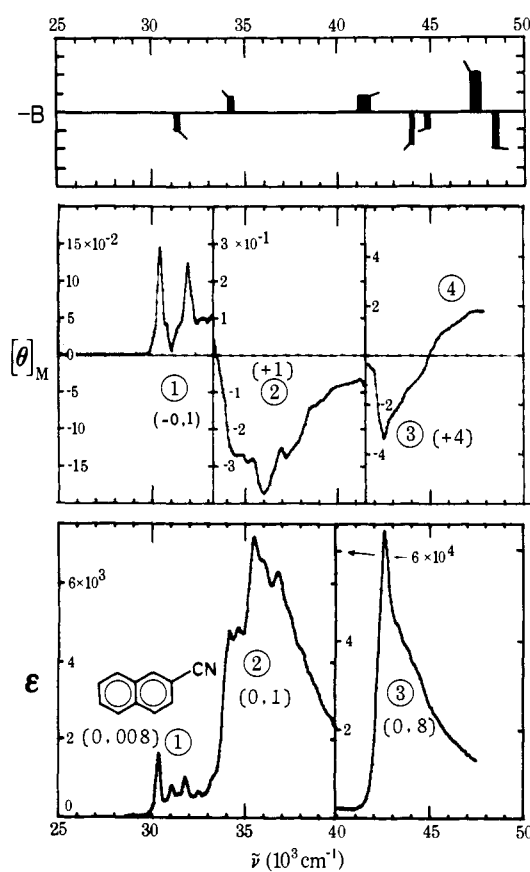


Figure 14. 2-Naphthonitrile. See caption to Figure 2.

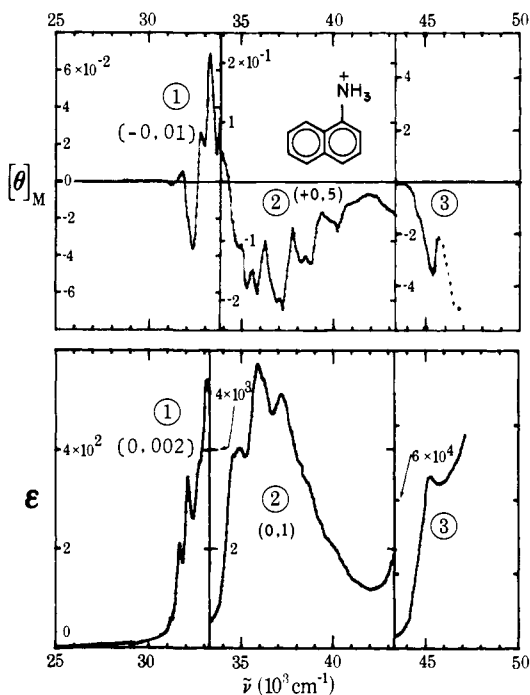


Figure 16. Protonated 1-naphthylamine. See caption to Figure 1.

substituent-ring bond. This simple intuitive rationalization for the curious behavior of the polarization directions agrees with the analysis of Koutecký¹⁸ in that the latter predicts little polarization rotation if the substituent is attached to a position where the *s* or the *a* orbital already has a node. The substituent will also cause orbital energies to approach an arrangement

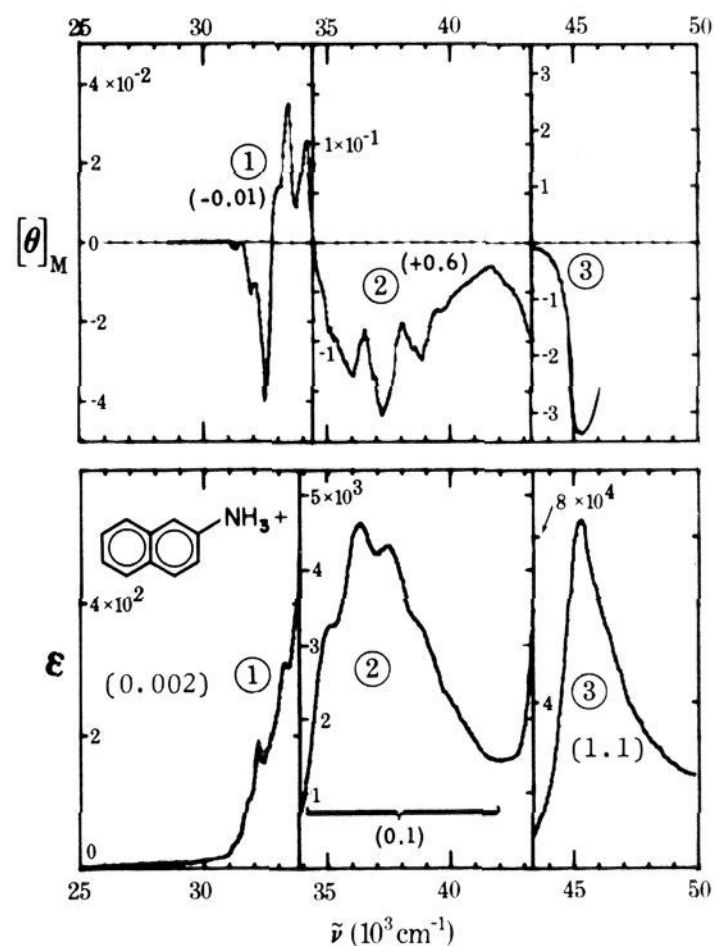


Figure 17. Protonated 2-naphthylamine. See caption to Figure 1.

avored by it in $[4N + 2]$ annulene. E substitution forces $\Delta\text{HOMO} \neq \Delta\text{LUMO}$, and, if the substituent is sufficiently strong, it will overrule the effects of the cross-link and dictate the same MCD signs as would be expected for a substituted annulene.

These qualitative arguments are illustrated by model calculations for **1**, -E substituted either in positions 2 and 3 (Figure 18) or in position 2 (Figure 19), using the method described in part 5.³³ The disubstituted derivative, which has C_{2v} symmetry and permits no mixing of the L_b and L_a states, is easier to discuss first. The orbital energies clearly reflect the expected much larger substituent effect on the bonding than the antibonding orbitals and also the larger effect on the lower orbital (s) compared with a, as expected for a subdominant position. Initial decrease of ΔHOMO to zero followed by an increase, compared with the absence of any drastic change in ΔLUMO , leads to $\Delta\text{HOMO} < \Delta\text{LUMO}$ except for the very strongest -E substitution, for which the eventual trend to $\Delta\text{HOMO} > \Delta\text{LUMO}$ is clearly apparent. Configuration energies follow orbital energy differences quite faithfully and show the expected crossing of the $a \rightarrow -a$ and $s \rightarrow -s$ configuration energies for very strong substituents. The configuration mixing scheme, in turn, follows predictably the course of configuration energies. For the purpose of Figure 18, we write it in a way used in part 5,³³ which is simply related to that used in part 2⁵ (β is about 15° for **1**):

$$|L_b\rangle = |s \rightarrow -a\rangle \cdot \sin \alpha - |a \rightarrow -s\rangle \cdot \cos \alpha$$

$$|L_a\rangle = |s \rightarrow -s\rangle \cdot \sin \beta + |a \rightarrow -a\rangle \cdot \cos \beta$$

In this formulation, the signs of the μ^+ contributions are ruled by the sign of $\cos 2\alpha \cos 2\beta$. The lower energy $s \rightarrow -a$ configuration dominates the wave function of the L_b state, which contains also an admixture of $a \rightarrow -s$ ($\alpha > 45^\circ$). The wave function of the L_a state is dominated by the $a \rightarrow -a$ configuration if the substituent effect is weak, but for the strongest substituents it acquires predominant $s \rightarrow -s$ character. Thus, $\beta < 45^\circ$ for most substituents, but $\beta > 45^\circ$ for the very strongest ones. This illustrates graphically the effect of the sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$ on the sign of $\cos 2\alpha \cos 2\beta$. The calculated transition moment directions are displayed with a

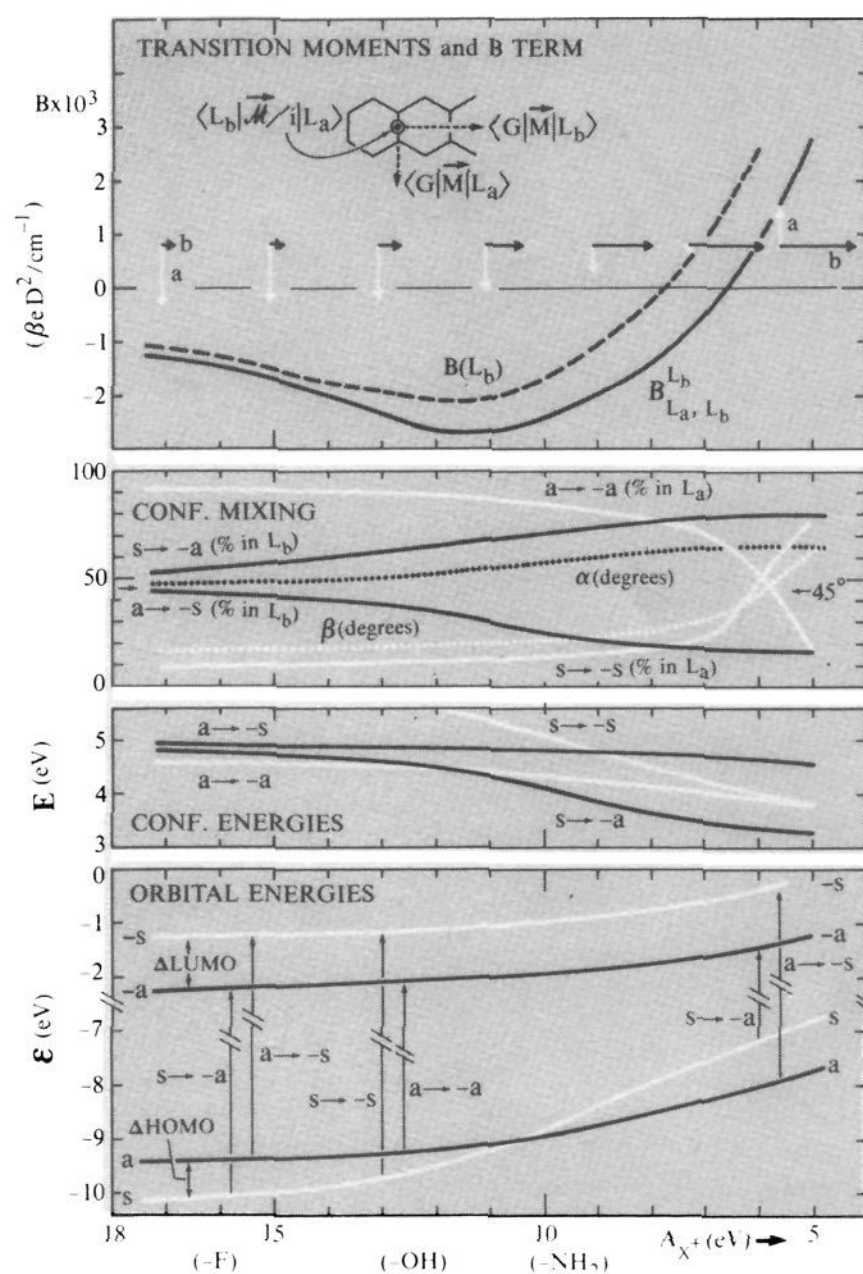


Figure 18. Reversal of the sign of $B(L_b)$ of a 2,3-disubstituted naphthalene with increasing substituent -E effect.

choice of phase such that the magnetic moment $\langle L_b | \hat{M} / i | L_a \rangle$ points to the reader. That of the L_b transition is seen to point to the right and to gradually acquire intensity as the substituent becomes stronger and $s \rightarrow -a$ begins to prevail over $a \rightarrow -s$. This is qualitatively understandable since the contributions from $s \rightarrow -a$ and $a \rightarrow -s$ to the transition moment oppose each other and cancel exactly in **1** itself (odd-soft chromophore). The transition moment of the L_a transition at first points down and is quite strong. As the substituent becomes stronger, however, and the weight of the $s \rightarrow -s$ configuration in the wave function gradually increases, this transition moment decreases in magnitude. Again, this is easily understood since the contribution of $s \rightarrow -s$ to the transition moment is opposed to that of $a \rightarrow -a$, and they cancel exactly in the double-soft [10]annulene. Figure 18 shows that they also cancel exactly when the 2,3-disubstitution becomes sufficiently strong, at which point the π system is an even-soft chromophore, and thereafter the moment points up. The sign of the triple vector product $\langle F | \hat{M} / i | I \rangle \cdot \langle F | \hat{M} | G \rangle \times \langle G | \hat{M} | I \rangle$ changes at that point also, and a simultaneous reversal of the sign of the calculated $B_{L_a, L_b}^{L_b}$ contribution to $B(L_b)$ is expected. This is indeed observed; moreover, the total value of $B(L_b)$ shows the same trend. It is somewhat more positive because of a contribution from L_b - B_a mixing which grows with increasing substituent strength and with the concurrent decrease in L_b - B_a energy separation. Thus, Figure 18 clearly shows the mechanism by which a sign of the $\Delta\text{HOMO} - \Delta\text{LUMO}$ difference propagates to eventually appear in the signs of $B(L_b)$. It will be difficult to find real substituents strong enough to actually effect the predicted sign reversal. However, the trend to first increasingly

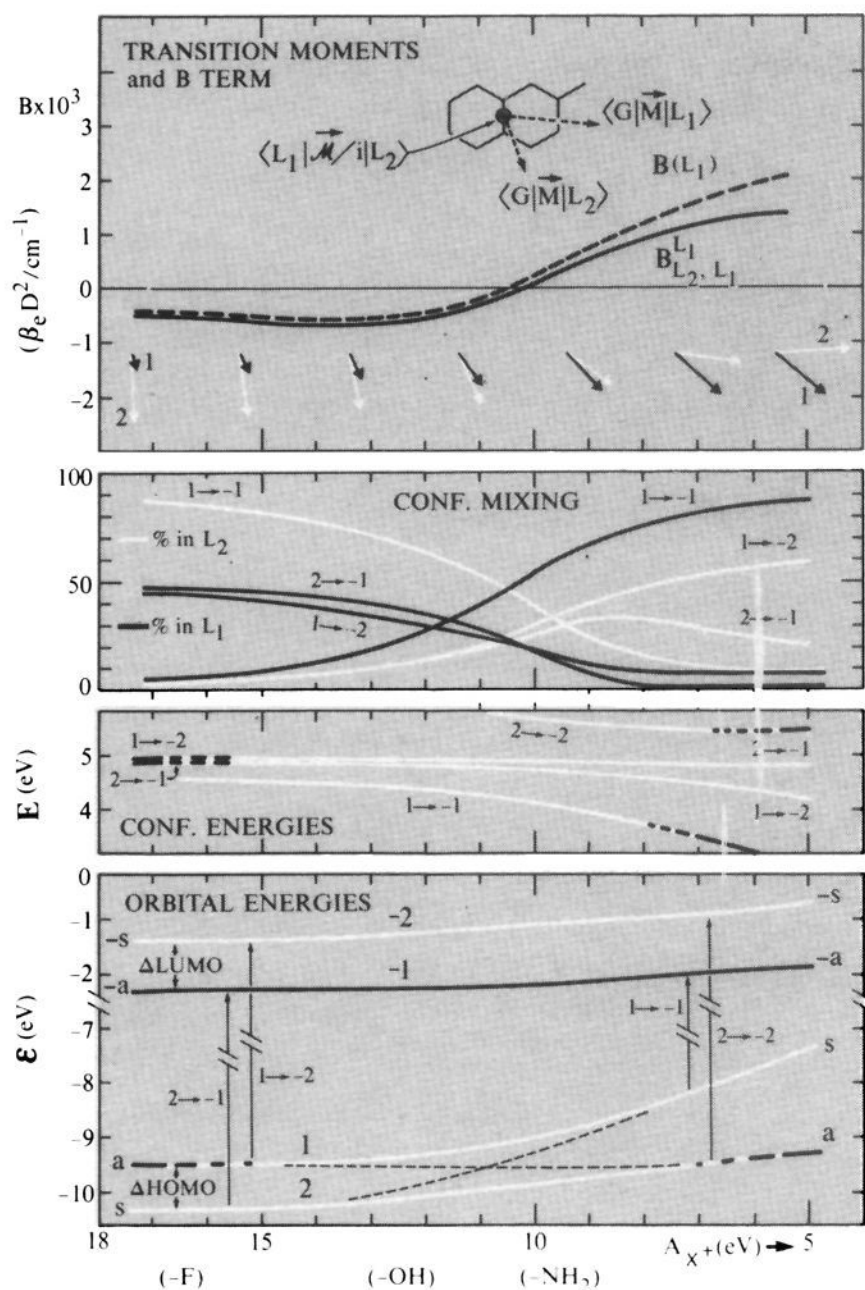


Figure 19. Reversal of the sign of $B(L_1)$ of a 2-substituted naphthalene with increasing substituent $-E$ effect.

negative and then decreasingly negative $B(L_b)$ with increasing substituent strength should be observable.

In 2-substituted **1**, the situation is complicated by the lower symmetry. In general, Figure 19 results from Figure 18 when crossings are avoided as indicated. The transition moment vectors behave similarly as in Figure 18 in that they reverse the sign of the triple vector product as the substituent becomes stronger. This is accomplished no longer by causing one of the moments to become zero and then change sign but by the rotation of both, which is now allowed by the lower symmetry. At the point where the two moments become parallel, the π system is zero-soft as defined in part 2:⁵ both L_1 and L_2 carry intensity, but all μ^+ contributions to B terms vanish. The figure clearly shows the gradual rotation of the moments into the positions favored by the substituent, L_1 nearly perpendicular to the substituent–ring bond and L_2 nearly parallel to it.

Figures 18 and 19 do not show μ^- contributions to B terms and therefore represent only an approximation to substituent effects; on the other hand, they incorporate the effects of the two-electron part of the operator which perturbs the perimeter states, which was ignored in the derivation in part 2,⁵ but this does not lead to any qualitative differences. Also, real substituents generally have I as well as E effects, which would have to be considered in a more quantitative argument (we assume that the E effect prevails). Comparison with experiment is straightforward for the weak $-E$ substituents methyl and fluorine. Both make a feeble but distinct negative contribution to $B(L_b)$ and add little to $B(L_a)$ which is already weakly positive in the parent. The effect of methyl (Figure 7) is weaker than that of fluorine (Figure 8). All of this is as expected. The

stronger hydroxy substituent (Figure 9) has a much weaker negative $B(L_b)$ with vibronic structure (hot band?) and the usual weakly positive $B(L_a)$ inherent to naphthalene. When its $-E$ effect is reduced by trifluoro acetylation (Figure 10), $B(L_b)$ becomes more negative but is still quite weak and shows vibronic interactions. These results make sense if the $OCOCF_3$ and, particularly, OH substituents are close to the zero-soft chromophore border line at which 2-substituent-induced effects operating by L_b – L_a mixing vanish. Since the L_b polarization direction in β -naphthol^{21–23} is undoubtedly rotated with respect to its direction in **1**, the reduced magnitude of $B(L_b)$ in these two compounds can be viewed as a result of the near parallelism of the L_b and L_a transition directions; this is clearly the mechanism by which the border line is approached (Figure 19). Full PPP calculations of substituent effects using standard parameters shown in Figures 9 and 10 gives weak $B(L_b)$ and $B(L_a)$ terms with the correct signs.

The results for the $NHCOCF_3$ (Figure 11) and NH_2 (Figure 12) substituents indicate that their $-E$ effect is sufficiently strong to place them just on the other side of the border line for which the system is zero-soft. At the border line, μ^- contributions to both L bands will be positive, and μ^+ contributions will vanish. Both of these substituents cause a positive $B(L_b)$ and reduce the positive magnitude of $B(L_a)$ found in naphthalene. In accord with Figure 19, we interpret this as implying that the substituents cause a positive μ^+ contribution to $B(L_b)$ and a negative one to $B(L_a)$, NH_2 with its stronger $-E$ effect being more effective than $NHCOCF_3$. In 2- NH_2 -**1**, $B(L_a)$ is almost exactly compensated to zero and is dominated by vibronic effects; in the $NHCOCF_3$ derivative the compensation is less complete but a sign reversal through the band still occurs (L_1 – L_2 mixing is apparently more important for the lower vibronic levels where it is favored by a small energy difference). The full PPP calculation of substituted effects also places both compounds on the other side of the border line and correctly predicts the signs of most of the substituent-induced μ^+ contributions to $B(L_b)$ and $B(L_a)$ (except for the latter in the trifluoroacetamide). In agreement with the results shown in Figures 18 and 19, in 2,3- NH_2 -**1** (Figure 13) the border line has not yet been reached, $B(L_b) < 0$, $B(L_a) > 0$, while in 2- NH_2 -**1** (Figure 12), it has. It is also interesting to note the quite weak intensity of the L_a band in 2,3- NH_2 -**1** relative to L_a in 2- NH_2 -**1**, which is in agreement with the discussion of Figure 18 and indicates that the border line is not far away.

Both of the $+E$ derivatives investigated, the 2-CN (Figure 14) and 2-CHO (Figure 15) compounds, appear to be strong enough to find themselves just beyond the border line. Thus, weak negative $B(L_b)$ and positive $B(L_a)$ are observed, the latter undoubtedly mostly due to the inherent μ^- contribution (in the preliminary communications²⁸ it was implied incorrectly that $B(L_b)$ and $B(L_a)$ were of the same sign). The full PPP calculation of substituent effects apparently underestimates the strength of the $+E$ effect of the cyano group somewhat, with the unoptimized parameters chosen. It correctly predicts very weak B terms but gives the wrong signs. The aldehyde is correctly placed on the other side of the border line (the weak negative contribution to $B(L_a)$ which it also predicts is hard to verify). As in the case of 1-substituents, 2-substituents also appear unable to change the inherently positive sign of $B(L_b)$ which we assign to the μ^- contribution.

On the whole, the simple theory is in excellent qualitative agreement with the observed experimental trends, but a reliable prediction of signs will require a better knowledge of the details of substituent properties than is presently available, and in particular, a careful consideration of both E and I effects which was not done in our PPP calculations. By the same token, it appears likely that much will be learned about substituents from MCD measurements on naphthalene derivatives. It appears that 2- NH_2 -**1** and 2- $NHCOCF_3$ -**1** are probably closer

to the ideal zero-soft MCD chromophore than any other molecule which we have studied so far. In part 9,⁷ we shall see the approximately zero-soft nature of 2-NH₂-1 documented further in an investigation of the effect of aza replacement on its MCD spectrum.

The NH₃⁺ Substituent. The purely electrostatic action of a monopole such as NH₃⁺ is well-known to have a negligible effect on electronic spectra of conjugated hydrocarbons, even nonalternant ones such as azulene, which readily respond to inductive perturbations.³⁴ It has been suggested³⁵ that this is due to the slow falloff of their electrostatic potential with distance, so that atomic orbitals on neighbors of the carbon which carries the substituent are affected almost as much as the one located on that carbon itself. Figures 16 and 17 show the MCD spectra of the protonated forms of the naphthylamines. Both are almost identical with the spectrum of parent **1** shown in part 7.² Thus, even the more sensitive MCD probe fails to detect much effect, and this can be again rationalized by the slow falloff of the electrostatic potential, and by the generally lower sensitivity of *B* terms to effects which act equally on two mutually paired orbitals.

Conclusion

Since the simple theory performs so well for the naphthalene derivatives investigated here, its qualitative predictions for other substituted naphthalenes should be taken seriously. A closer examination of 2-substituted naphthalenes and, in particular, of the details of the way in which E and I effects both contribute to the induced *B* terms remains for the future and promises to enhance the understanding of substituent effects in general.

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References and Notes

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- (3) Swiss National Foundation Fellow, 1975–1977.
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