

- Workshop on Molecular Optical Dichroism and Chemical Applications of Polarized Spectroscopy, University of Lund, Oct 25–27, 1976 [J. Michl, *Spectrosc. Lett.*, **10**, 509–517 (1977)].
- (2) Part 9: M. A. Souto and J. Michl, *J. Am. Chem. Soc.*, preceding paper in this issue.
 - (3) J. Michl, *J. Am. Chem. Soc.*, companion papers in this issue (parts 1–3).
 - (4) M. Vašák, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 7).
 - (5) M. R. Whipple, M. Vašák, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 8).
 - (6) R. P. Steiner and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 11).
 - (7) E. W. Thulstrup, J. W. Downing, and J. Michl, *Chem. Phys.*, **23**, 307–319 (1977); M. Vašák, M. R. Whipple, A. Berg, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 13).
 - (8) M. Vašák, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 12).
 - (9) S. L. Wallace, A. Castellan, D. Muller, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 5).
 - (10) I. Jonáš and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 6).
 - (11) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).
 - (12) J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, "The Tautomerism of Heterocycles", Academic Press, New York, N.Y., 1976.
 - (13) W. Seiffert and H. H. Mantsch, *Tetrahedron*, **25**, 4569–4578 (1969).
 - (14) K. Nishimoto and L. S. Forster, *J. Phys. Chem.*, **71**, 409–413 (1967).
 - (15) M. Tichý and R. Zahradník, *J. Phys. Chem.*, **73**, 534–544 (1969).
 - (16) M. Berndt and J. S. Kwiatkowski, *Theor. Chim. Acta*, **17**, 35–48 (1970).

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 11.¹ Derivatives and Aza Analogues of Anthracene

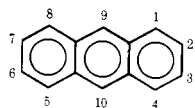
Richard P. Steiner and Josef Michl*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received February 14, 1978

Abstract: Magnetic circular dichroism of anthracene, nine of its derivatives, acridine, and phenazine is reported and interpreted. Evidence for the assignment of the controversial L_b transition and for some other weak transitions is obtained. The signs of $B(L_a)$ and $B(L_b)$ are sensitive to the location and nature of substituents; $B(B_b)$ is positive, and $B(B_a)$ is negative. The signs are in excellent agreement with the general qualitative theory of parts 1–3 for the response of an odd-soft chromophore to substituent effects.

Introduction

According to the general qualitative theory described in parts 1–3 of this series,² anthracene (**1**), like other polycyclic benzenoid hydrocarbons without a threefold or higher symmetry axis, should be an odd-soft MCD chromophore. The theory makes definite predictions for substituent effects on the MCD signs of the L and B transitions of **1**. We now report the MCD spectra of anthracene and nine of its derivatives, as well as the aza analogues, acridine and phenazine. In addition to confirming the predictive value of the simple theory, the results also secure a firmer assignment of the elusive L_b band of anthracene and help to identify some higher energy transitions. Studies of substituent and aza nitrogen effects on other odd-soft chromophores appear in parts 7,³ 8,⁴ 9,⁵ 10⁶ (naphthalene), 12⁷ (phenanthrene), and 13⁸ and in ref 9 (pyrene).



1

The MCD spectrum of **1** itself has been reported^{10–12} and the sign of its L_b band calculated¹¹ previously; a correction of the spectrum of ref 11 has appeared subsequently.¹³ We have remeasured the spectrum and include it here for comparison. No MCD spectra of the other compounds studied here have been reported previously except for a mention in our preliminary reports.^{1,14}

1 is one of the most thoroughly studied π -electron chromophores. The presently available information on its excited singlet states has been recently summarized.^{15–17} The assignment of the lowest excited singlet state of **1** near 26 500 cm^{-1} as L_a (short-axis polarized, negative in MCD) is well established. On the other hand, although there is little doubt

that the L_b band must lie nearby, just as in other benzenoid hydrocarbons, and although both bands are clearly seen in the spectra of many anthracene derivatives, two groups of workers^{15,16} have recently concluded independently that there is as yet no compelling evidence that any one of the various proposed assignments of L_b in **1** itself is correct. In what is considered by both groups to be the most plausible assignment among the various suggestions, the origin of the band is identified with the onset of long-axis-polarized absorption near 27 800 cm^{-1} , identical with the first positive peak in the MCD spectrum. However, it has so far not been possible to exclude the possibility that this absorption is a vibronic component of the L_a band due to borrowing from the intense B_b band. Such an alternative assignment is supported, but not proven, by the near constancy¹⁵ of the separation between the origin of the L_a band and the suspected origin of the L_b band in a variety of weakly perturbed derivatives of **1**. The assignments of two bands of higher energy are beyond doubt; these are the intense long-axis-polarized B_b band near 39 000 cm^{-1} , negative in MCD, and the short-axis-polarized B_a band near 45 500 cm^{-1} .

Results of π -electron calculations, summarized in ref 15, are in good agreement with the location, intensity, and polarization of the L_a , B_b , and B_a bands and predict unequivocally that an L_b band must lie near L_a . In addition, they predict several symmetry-forbidden transitions in the vicinity of the B_b band and higher. Evidence for the existence of these bands has been discussed in ref 15 and is still fairly incomplete.

The excited states of many of the simple derivatives of **1**^{15,16,18–24} and of its aza analogues acridine (9-N-**1**)^{25–37} and phenazine (9,10-N-**1**)^{33,37–40} have also received much attention. Much of the experimental evidence for 9-N-**1** and 9,10-N-**1** is summarized in a recent theoretical study.⁴¹ In most instances, correspondence to the excited states of **1** is fairly clear-cut. Frequently, additional transitions which are sym-

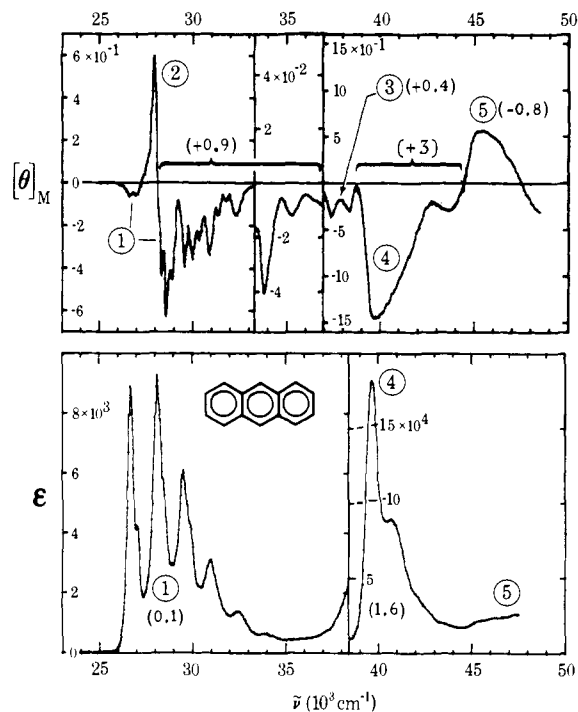


Figure 1. Anthracene spectra: bottom, absorption (oscillator strengths given); top: MCD (B terms in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$).

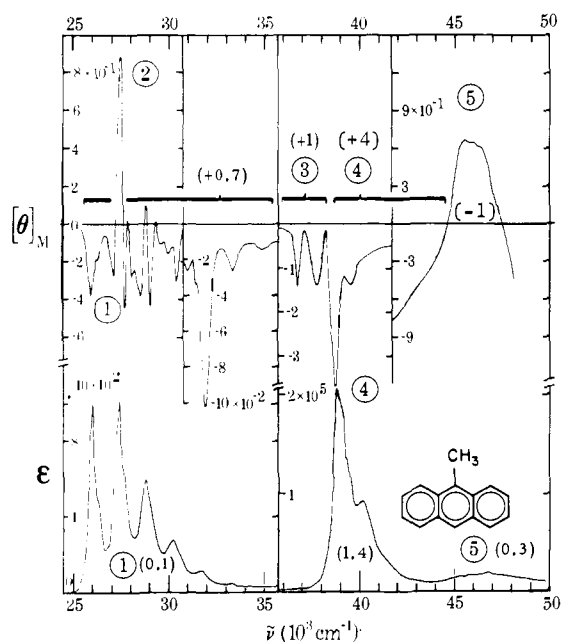


Figure 2. 9-Methylantracene. See caption to Figure 1.

metry forbidden in **1** itself are revealed in the spectra of the derivatives and aza analogues. Similarly as in the case of naphthalene, some attention has been paid to the behavior of the polarization direction of the L bands upon substitution in position 2, and semiquantitatively reliable calculated^{15,42,43} as well as experimental¹⁵ values for transition moment directions in all three aminoanthracenes are available.

Experimental Section and Calculations

The samples were commercial or available from previous work⁴⁴ and were purified by gradient sublimation. The measurements and calculations were performed as in part 4.⁴⁵

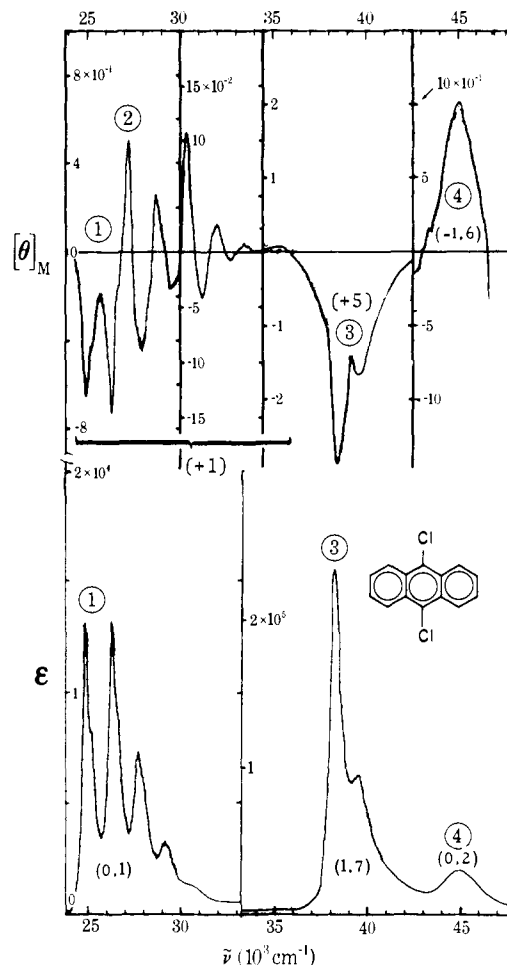


Figure 3. 9,10-Dichloroanthracene. See caption to Figure 1.

Results

The results are shown in Figures 1-12. A tentative identification of individual electronic transitions is proposed. In many instances several bands are revealed in addition to the readily identified L and B bands; their existence is in agreement with the calculations as shown. The signs of $B(L_a)$ and $B(L_b)$ are sensitive to the nature and location of substituents as expected for an odd-soft chromophore. In general, $B(B_b) > 0$ and $B(B_a) < 0$. As in the other papers in this series, the calculations shown are of the standard PPP variety without any adjustment for MCD purposes and are best viewed² as a calculation of the difference between the spectra of the substituted **1** and the parent **1**.

Discussion

Anthracene as an Odd-Soft Chromophore. Like other low-symmetry benzenoid hydrocarbons, anthracene is an odd-soft chromophore in terms of the theory of parts 1-3² (it is derived from the perimeter by an odd perturbation, and $\Delta\text{HOMO} = \Delta\text{LUMO}$ because of alternant orbital pairing). In soft chromophores, the potentially large μ^+ contribution to the B terms of L and B transitions is absent, and their MCD is dominated by the smaller μ^- contribution. In chromophores derived from an uncharged perimeter, such as **1**, the latter originates solely in next-nearest-neighbor interactions. In odd-soft chromophores, the μ^- contribution to $B(L_b)$ is zero (the transition has vanishing intensity), that to $B(L_a)$ is very small and positive, that to the B term of the lower of the two B bands is larger and positive, and that to the B term of the higher one is larger and negative. Any deviation from the exact equality of ΔHOMO and ΔLUMO provides the L_b band with nonvanishing inten-

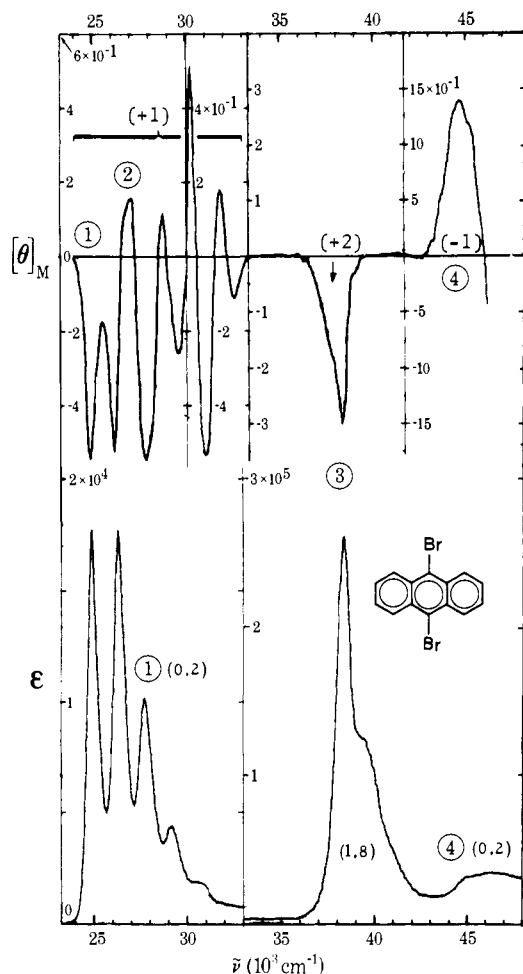


Figure 4. 9,10-Dibromoanthracene. See caption to Figure 1.

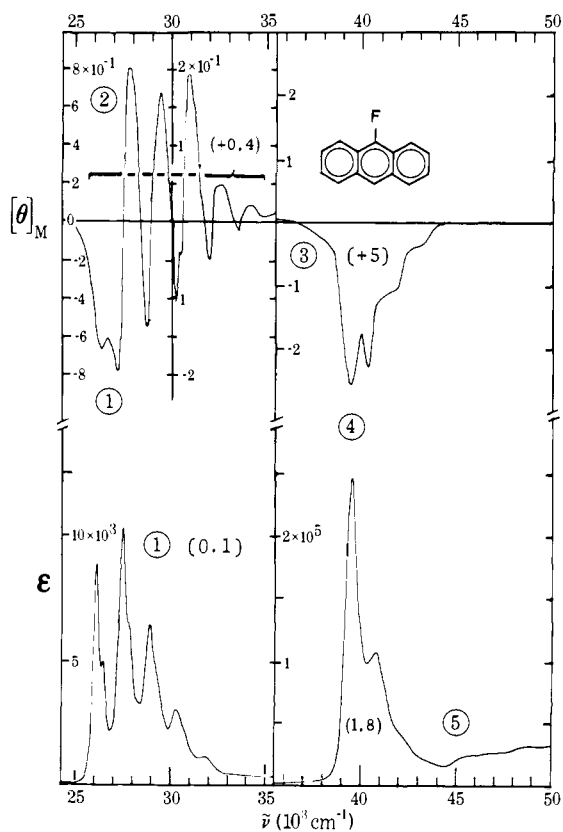


Figure 5. 9-Fluoroanthracene. See caption to Figure 1.

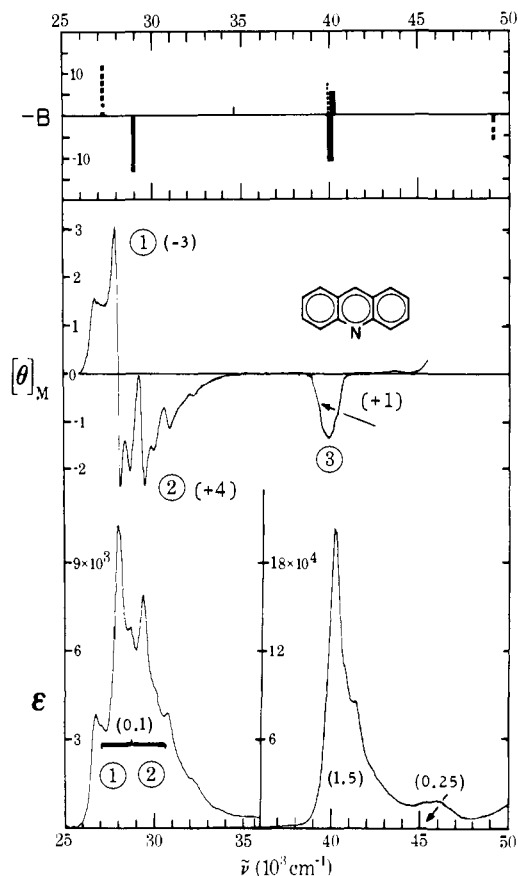


Figure 6. Acridine spectra: bottom, absorption (oscillator strengths given); center, MCD (B terms in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$); top, calculated. Calculated $-B$ values are indicated by the length of the bars and calculated oscillator strengths by their thickness. Solid bars indicate horizontal polarization with respect to the formula given and broken bars vertical polarization with respect to the formula given.

sity, and the μ^- contribution to $B(L_b)$ then consists of two opposed parts: if L_b lies between L_a and the B states, L-L mixing contributes negatively and L-B mixing positively. In reality, MO pairing in **1** is undoubtedly only approximate, so that this situation should obtain already in the parent, but since the L_b state is imbedded in the vibrational structure of the L_a band, a vibronic treatment appears mandatory from the start. Small deviations from the equality of $\Delta HOMO$ and $\Delta LUMO$ have only limited effect on the μ^- contributions to the other three bands.

Comparison with the MCD spectrum of **1** (Figure 1) is seen to give signs in good agreement with experiment for $B(B_b)$ and $B(B_a)$, but the region of the L bands is unclear. The sum of $B(L_a) + B(L_b)$ is clearly positive as expected, and the origin of the L_a band, although extremely weak, also has the predicted sign, as do some of its other vibrational components. Others, however, have the opposite sign. The peaks which apparently belong to the L_b transition have negative MCD, and there appears to be strong vibronic interaction. A high-resolution analysis of this region would undoubtedly be most rewarding.

A perturbation which removes the equality of $\Delta HOMO$ and $\Delta LUMO$ also permits the large magnetic moment μ^+ , which results from nearest-neighbor interactions, to contribute to the MCD effect. If $\Delta HOMO > \Delta LUMO$, the μ^+ contributions to the B terms of the lower of the two L bands and the lower of the two B bands are positive and those to the upper two are negative; if $\Delta HOMO < \Delta LUMO$, the opposite is true. Simple PMO arguments were used in parts 1–3² to derive the sign of $\Delta HOMO - \Delta LUMO$ in a perturbed odd-soft chromophore.

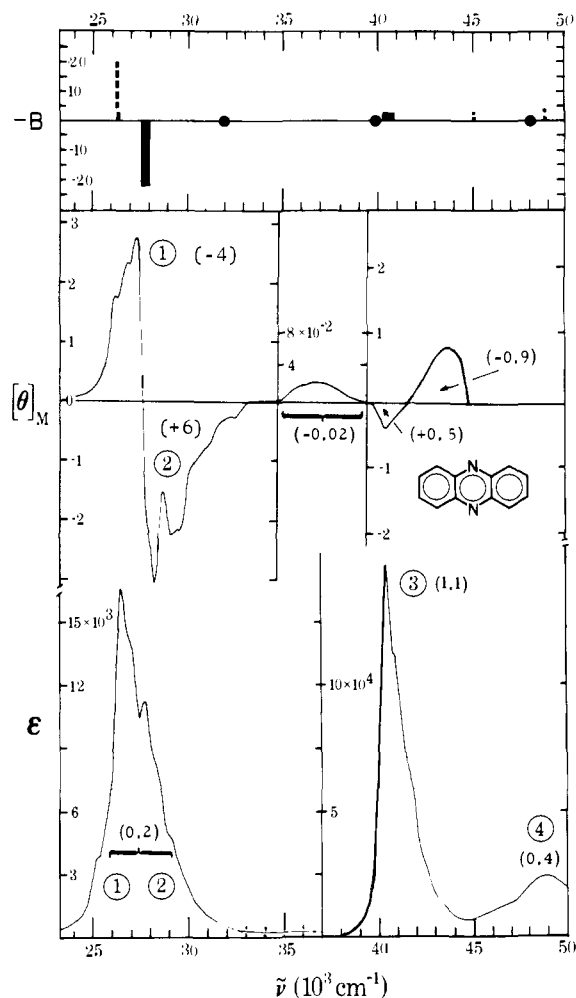


Figure 7. Phenazine. See caption to Figure 6. Calculated forbidden transitions are shown as dots.

In dominant (D) positions (Hückel coefficients $c_{\kappa,1}^2 > c_{\kappa,2}^2$) a +I or +E (electron-withdrawing) substituent induces $\Delta\text{HOMO} < \Delta\text{LUMO}$ and a -I or -E (electron-donating) substituent induces $\Delta\text{HOMO} > \Delta\text{LUMO}$; as the strength of the substituent effect and the difference $c_{\kappa,1}^2 - c_{\kappa,2}^2$ increase, the induced difference $|\Delta\text{HOMO} - \Delta\text{LUMO}|$ increases in magnitude, and the values of the B terms will be closer to their limiting values (excessively large substituent effects will tend to reduce the B terms again). In subdominant (S) positions ($c_{\kappa,1}^2 < c_{\kappa,2}^2$), a +I or +E substituent induces $\Delta\text{HOMO} > \Delta\text{LUMO}$ and a -I or -E substituent induces $\Delta\text{HOMO} < \Delta\text{LUMO}$, again more so as the magnitude of the difference $c_{\kappa,2}^2 - c_{\kappa,1}^2$ increases. As a function of the strength of the E effect of the substituent, $|\Delta\text{HOMO} - \Delta\text{LUMO}|$ first increases, but then decreases, goes through zero (at which point the molecule is a zero-soft chromophore or an even-soft chromophore, depending on its symmetry), and changes sign, since in the limit of extremely strong E substitution the orbital energy arrangement resembles that of a substituted $[4N + 2]$ -annulene in which +E substitution induces $\Delta\text{HOMO} < \Delta\text{LUMO}$ and -E substitution induces $\Delta\text{HOMO} > \Delta\text{LUMO}$. Since such strong substituents are needed for this, the B terms will probably never reach their limiting values. Such a reversal has actually been observed for 2-substituted naphthalene derivatives.⁴ In anthracene, it should be harder to effect, since the orbitals s (HOMO) and a have a very different energy to start with (the Hückel energies are 0.414β and 1.0β , respectively, compared with 0.618β and 1.0β in naphthalene). This large difference is also reflected in the relatively low energy

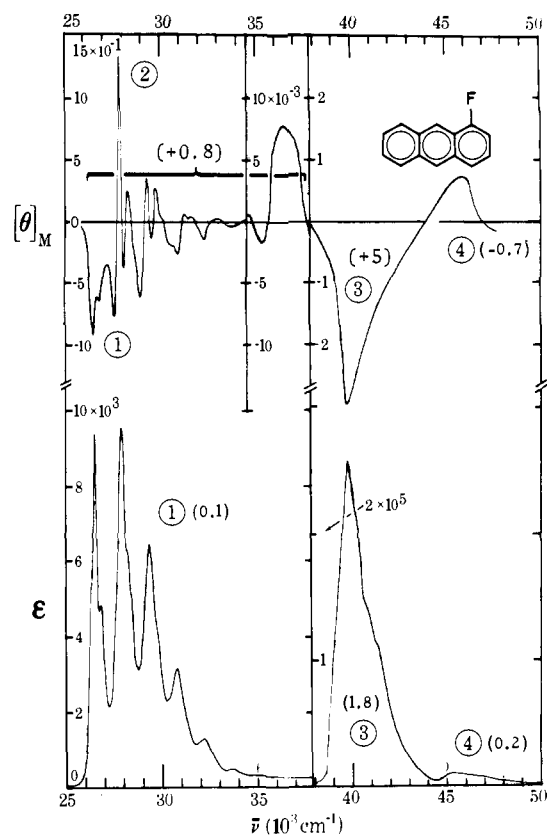


Figure 8. 1-Fluoroanthracene. See caption to Figure 1.

of the L_a band compared with L_b ; their order is reversed from naphthalene. Other things being equal, it should then take a stronger E substituent than was needed in naphthalene to reach the borderline point at which $\Delta\text{HOMO} = \Delta\text{LUMO}$. In naphthalene, this point lies somewhere between OH and NHCOCF_3 for a single substituent in position 2; it will be interesting to identify it for position 2 in **1**.

The analysis of the effects of substitution in a subdominant position is clearly much more demanding than that for a dominant position, and more complete theory may well be necessary to interpret any but the most qualitative aspects. In particular, since the form of the MO's changes significantly from that of the parent **1** upon such strong perturbation, it may be necessary to work explicitly with configuration energies rather than orbital energy differences. Also, the interplay of I and E effects calls for a closer examination.

For comparison with experimental results, we recall that the L_a band lies below L_b in energy, wherever the latter may be, and therefore, $\Delta\text{HOMO} > \Delta\text{LUMO}$ implies $B(L_a) > 0$ and $B(L_b) < 0$, and $\Delta\text{HOMO} < \Delta\text{LUMO}$ implies the opposite.

9-Substitution. Since its squared Hückel coefficients are $c_{9,1}^2 = 0.19$ and $c_{9,2}^2 = 0.0$, the 9 position in **1** is very definitely of the dominant type and strong substituent effects can be expected. The experimental MCD spectra are in excellent agreement with expectations if the series of long-axis polarized bands of **1** starting near $27\,800\text{ cm}^{-1}$ is accepted as the L_b band. In 9- CH_3 -**1** (Figure 2), 9,10- Cl -**1** (Figure 3), 9,10- Br -**1** (Figure 4), and 9- F -**1** (Figure 5), $B(L_a) > 0$ and $B(L_b) < 0$, while in 9- N -**1** (Figure 6) and 9,10- N -**1** (Figure 7), $B(L_a) < 0$ and $B(L_b) > 0$. In all instances in which the B bands were observed, $B(B_b) > 0$ and $B(B_a) < 0$, as demanded by the simple theory in **1** itself. As in naphthalene,^{3,4} the substituent effects are apparently unable to override the relatively strong inherent μ^- contributions from second-nearest-neighbor terms.

1-Substitution. Since $c_{1,1}^2 = 0.097$ and $c_{1,2}^2 = 0.0$, the 1

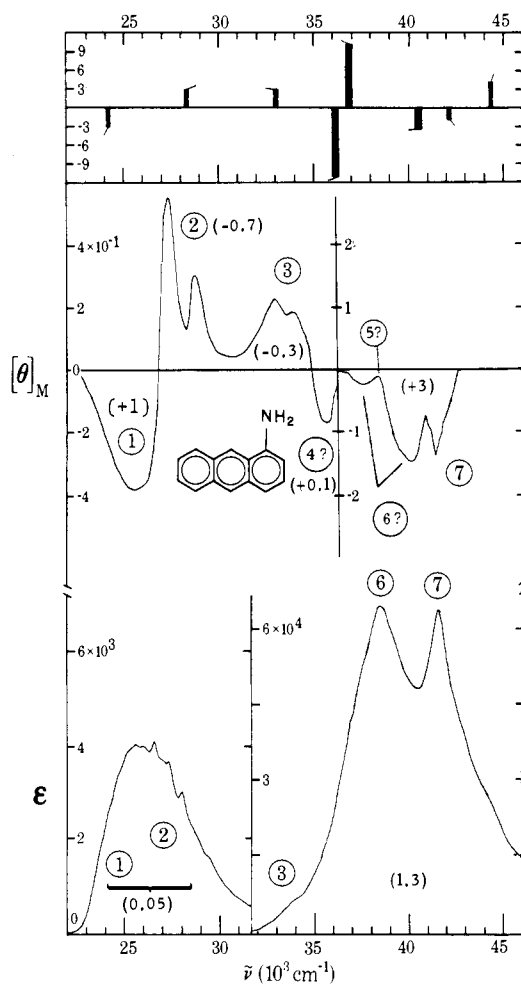


Figure 9. 1-Aminoanthracene. See caption to Figure 6. Calculated polarization directions are given with respect to the formula shown by directions of the flags at the end of bars.

position of **1** is also dominant, though somewhat less strongly than the 9 position. Once again, the experimental spectra show the expected signs. In 1-F-**1** (Figure 8) and 1-NH₂-**1** (Figure 9), $B(L_a) > 0$ and $B(L_b) < 0$. As before, $B(B_b) > 0$ and $B(B_a) < 0$ (in 1-NH₂-**1**, the B_b character is distributed between two transitions¹⁹ and the L_a and L_b character may be shared somewhat by both L bands;²¹ it is more appropriate to state $B(L_1) > 0$, $B(L_2) < 0$).

2-Substitution. Now, $c_{2,1}^2 = 0.048$ and $c_{2,2}^2 = 0.125$, and the 2 position is of the subdominant type, similarly as the 2 position of naphthalene where the difference $c_{2,1}^2 - c_{2,2}^2$ was 0.097. This is reflected in the MCD spectra in a dramatic fashion. Using the above assignment for L_b , for the weak -E substituents methyl and fluoro, $B(L_a) < 0$ and $B(L_b) > 0$ as is seen in Figure 10 for 2,3-Me-**1** and in Figure 11 for 2-F-**1**. In both instances, $B(B_b) > 0$ and $B(B_a) < 0$. The spectrum of 2-NH₂-**1** (Figure 12) shows $B(L_2) > 0$ as expected, but the B term is weaker than in 2-F-**1** or even 2,3-CH₃-**1** and may be largely of the inherent type due to a μ^- contribution rather than substituent induced, if the molecule is near the zero-soft-chromophore borderline case as happened in 2-amino-naphthalene.⁴ In this case, the L_b and L_a states of **1** are mixed efficiently²¹ and it is advisable to use the labels L_1 for the lower and L_2 for the higher of the two L states. The MCD effect of L_1 is very weak and appears to be dominated by vibronic effects. In the region of band origin, the curve is weakly negative; close to the L_2 band, it is weakly positive. Overall, $B(L_1)$ is almost exactly zero. This suggests that 2-NH₂-**1** is indeed very nearly a zero-soft chromophore, and that in this derivative

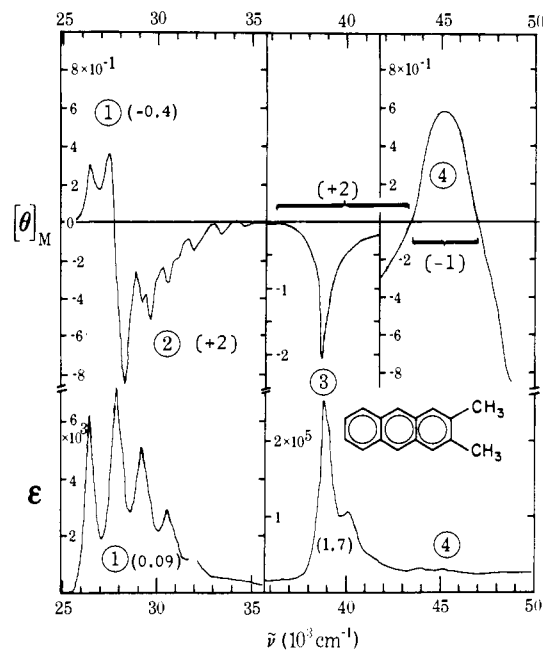


Figure 10. 2,3-Dimethylanthracene. See caption to Figure 1.

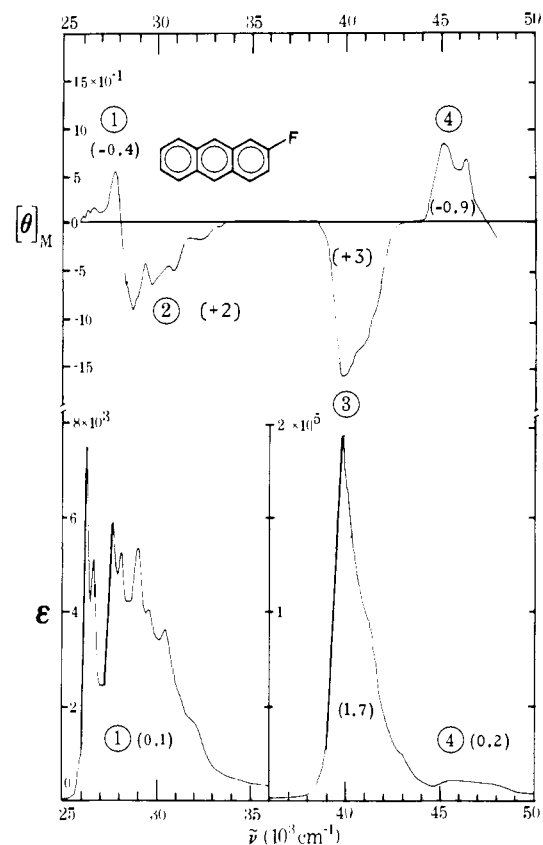


Figure 11. 2-Fluoroanthracene. See caption to Figure 1.

cross-link domination is about to be overruled by substituent domination. The shape of the MCD curve of L_1 indicates that the mixing of L_1 with L_2 contributes negatively to the B term of the former and positively to the B term of the latter and that this mixing prevails for high vibrational levels of L_1 for which the energy separation from L_2 is the smallest. It is not clear which of the several possible types of mixing produces the positive contribution to $B(L_1)$ which appear near its origin, but a prime suspect is substituent-induced L-B mixing which is expected to oppose the effects of L-L mixing. Similar sign

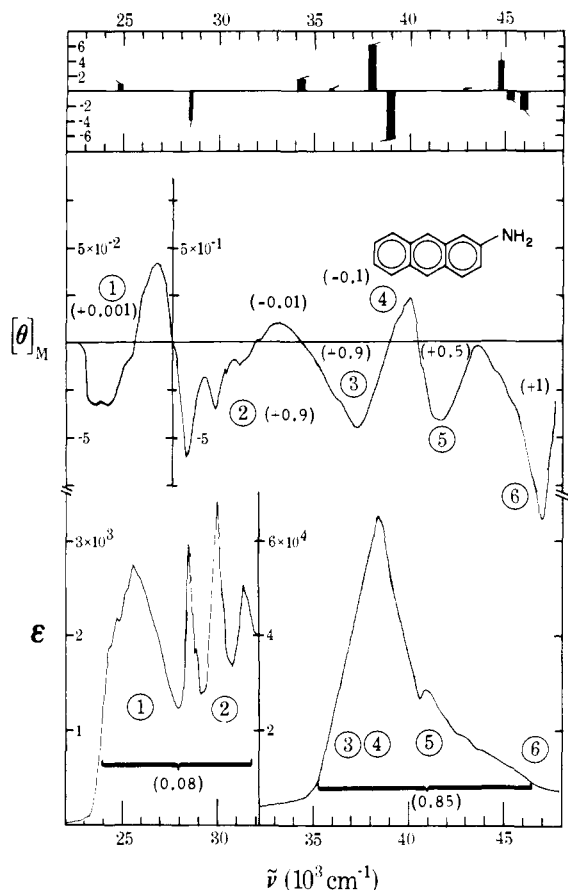


Figure 12. 2-Aminoanthracene. See caption to Figure 9.

reversals within a band for which there are two opposing contributions, one from a nearby state and one from a more distant state, have been noticed earlier.⁴⁶ The B bands are not easily recognized, and it is difficult to verify the expected signs.

In summary, it appears that 2-NH₂-1, like 2-aminonaphthalene, is close to the border line, but, unlike 2-aminonaphthalene, does not yet lie past it. This difference is accounted for qualitatively by the above discussion of the ease with which substituents in subdominant positions can take a parent system past the border line.

The L_b Transition of Anthracene. We propose that the perfect agreement between the MCD response of the series of long-axis polarized bands starting near 27 800 cm⁻¹ and that expected for the L₂ transition provides definitive evidence that these bands contain a large amount of L_b character. Obviously, the vibronic states may be mixed: containing terms of the types L_a × (b_{1g}), L_b × (a_{1g}), B_b × (a_{1g}), and others, but to the first approximation, it appears reasonable to refer to these bands as L_b. Thus, the new evidence causes us to reverse our earlier reserved stand¹⁵ on this assignment.

Other Transitions. The MCD spectra of 9-N-1 and 9,10-N-1 (Figures 6 and 7) show no distinct features attributable to their nπ* transitions. This is not surprising considering how weak the MCD effect is for nπ* transitions in aza analogues of benzene,⁴⁵ naphthalene,³ and phenanthrene.⁷ In general, MCD does not appear to be a useful method for detecting weak nπ* transitions buried under ππ* absorption.

On the other hand, in several instances weak ππ* transitions are revealed by the MCD spectra. In particular, the transition to a state of g parity near 37 000 cm⁻¹, forbidden by symmetry in 1 itself but allowed and presumably causing a short-axis-polarized transition in 9-substituted derivatives of C_{2v} symmetry as detected in polarized stretched-sheet spectra of 9-CH₃-1,³³ is quite distinct in the MCD spectrum of 9-CH₃-1

(Figure 2) and its presence is also indicated by a shoulder in MCD of 9-F-1 (Figure 5).

In the aminoanthracenes, previous assignments of individual electronic transitions¹⁵ are now complemented by MCD evidence (Figures 9 and 12). The results of the two methods lead to similar conclusions, except that MCD suggests the presence of one additional transition at high energies in each amine, as shown in the figures.

Conclusion

Since the simple theory performs so well once the newly reconfirmed assignment of the L_b transition is accepted, its predictions for other anthracenes are likely to be useful. A closer examination of 2-substituted anthracenes, of the interplay of substituent I and E effects, and of vibronic interactions remains for the future.

Note Added in Proof. Margulies and Yogev⁴⁷ propose that the well-known¹⁶ mixed polarization of anthracene fluorescence is not due to vibronic mixing, but instead to simultaneous emission from almost degenerate L_b and L_a levels with comparable rate constants. Their arguments appear unconvincing to us; certainly our spectra provide no support for such an assignment of the L_b origin.

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM 21153. We are indebted to Ms. Lise Flindt-Pedersen for recording two of the MCD spectra and to Professor Henry Eyring for kind permission to use his MCD instrument. Helium gas was provided by a departmental grant from the Office of Naval Research.

References and Notes

- (1) Presented at the First Chemical Congress of the North American Continent, Mexico City, Mexico, Nov 30–Dec 5, 1975; International Symposium on Atomic, Molecular, and Solid-State Theory, Sanibel Island, Fla., Jan 18–24, 1976; the 2nd International Congress of Quantum Chemistry, New Orleans, La., Apr 19–24, 1976; the Nobel Workshop on Molecular Optical Dichroism and Chemical Applications of Polarized Spectroscopy, Lund, Sweden, Oct 25–27, 1976; and the Third International Symposium on Novel Aromatic Compounds, San Francisco, Calif., Aug 22–26, 1977; for part 10, see ref 6.
- (2) J. Michl, *J. Am. Chem. Soc.*, companion papers in this issue (parts 1–3).
- (3) M. Vašák, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 7).
- (4) M. R. Whipple, M. Vašák, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 8).
- (5) M. A. Souto and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 9).
- (6) D. Otteson and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 10).
- (7) M. Vašák, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 12).
- (8) M. Vašák, M. R. Whipple, A. Berg, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 13).
- (9) E. W. Thulstrup, J. W. Downing, and J. Michl, *Chem. Phys.*, **23**, 307–319 (1977).
- (10) D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 1377–1382 (1966).
- (11) J. P. Larkindale and D. J. Simkin, *J. Chem. Phys.*, **55**, 5668–5674 (1971).
- (12) J. G. Foss and M. E. McCarville, *J. Chem. Phys.*, **44**, 4350–4351 (1966).
- (13) S. F. Mason and R. D. Peacock, *Chem. Phys. Lett.*, **21**, 406–408 (1973).
- (14) J. Michl, *Chem. Phys. Lett.*, **39**, 386–390 (1976); *Int. J. Quant. Chem.*, **10S**, 107–117 (1976).
- (15) J. Michl, E. W. Thulstrup, and J. H. Eggers, *Ber. Bunsenges. Phys. Chem.*, **78**, 575–586 (1974).
- (16) D. M. Friedrich, R. Mathies, and A. C. Albrecht, *J. Mol. Spectrosc.*, **51**, 166–188 (1974).
- (17) E. E. Koch, A. Otto, and K. Radler, *Chem. Phys. Lett.*, **21**, 501–504 (1973).
- (18) I. Ohno and K. Iguchi, *Bull. Chem. Soc. Jpn.*, **41**, 2264–2269 (1968).
- (19) S. Suzuki and H. Baba, *Bull. Chem. Soc. Jpn.*, **37**, 519–524 (1964).
- (20) M. Tichý and R. Zahradník, *J. Phys. Chem.*, **73**, 534–544 (1969).
- (21) K. Rotkiewicz and Z. R. Grabowski, *Trans. Faraday Soc.*, **65**, 3263–3278 (1969).
- (22) E. Döller, Th. Förster, and H. Renner, *Z. Phys. Chem. (Frankfurt am Main)*, **15**, 34–47 (1958).
- (23) A. Kowski and J. Kukielski, *Z. Naturforsch., A*, **25**, 653–656 (1970).
- (24) A. Kowski and B. Pasztor, *Acta Phys. Pol.*, **31**, 357–370 (1967).

- (25) G. Leroy, C. Aussems, and F. Van Remoortere, *Bull. Soc. Chim. Belg.*, **77**, 181–190 (1968).
 (26) J. Nasielski and E. Vander Donckt, *Bull. Soc. Chim. Belg.*, **72**, 725–739 (1963).
 (27) V. Zanker and W. Schmid, *Chem. Ber.*, **90**, 2253–2265 (1957).
 (28) V. Zanker and W. Schmid, *Chem. Ber.*, **92**, 615–626 (1959).
 (29) W. Seiffert, V. Zanker, and H. Mantsch, *Tetrahedron Lett.*, 3437–3442 (1968).
 (30) A. Wittwer and V. Zander, *Z. Phys. Chem. (Frankfurt am Main)*, **22**, 417–439 (1959).
 (31) W. Seiffert, V. Zanker, and H. Mantsch, *Tetrahedron*, **25**, 1001–1012 (1969).
 (32) W. Seiffert, H. Limbach, V. Zanker, and H. H. Mantsch, *Tetrahedron*, **26**, 2663–2675 (1970).
 (33) H. Inoue, T. Hoshi, T. Masamoto, J. Shiraishi, and Y. Tanizaki, *Ber. Bunsenges. Phys. Chem.*, **75**, 441–446 (1971).
 (34) R. Williams, *J. Chem. Phys.*, **26**, 1186–1188 (1957).
 (35) A. Weller, *Z. Elektrochem.*, **61**, 956–961 (1957).
 (36) R. M. MacNab and K. Sauer, *J. Chem. Phys.*, **53**, 2805–2817 (1970).
 (37) H.-H. Perkampus and K. Kortüm, *Z. Phys. Chem. (Frankfurt am Main)*, **56**, 73–94 (1967).
 (38) N. Mataga and K. Nishimoto, *Z. Phys. Chem. (Frankfurt am Main)*, **13**, 140–157 (1957).
 (39) N. Mikami, *J. Mol. Spectrosc.*, **37**, 147–158 (1971).
 (40) F. Kummer and H. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, **71**, 1119–1126 (1967).
 (41) R. W. Wagner, P. Hochmann, and M. A. Al-Bayoumi, *J. Mol. Spectrosc.*, **54**, 167–181 (1975).
 (42) J. Kouřtecký, *J. Chem. Phys.*, **47**, 1501–1511 (1967).
 (43) P. Jørgensen, *J. Chem. Phys.*, **56**, 1839–1841 (1972).
 (44) M. J. S. Dewar and J. Michl, *Tetrahedron*, **26**, 375–384 (1970).
 (45) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).
 (46) J. Kolc, E. W. Thulstrup, and J. Michl, *J. Am. Chem. Soc.*, **96**, 7188–7202 (1974).
 (47) L. Margulies and A. Yogev, *Chem. Phys.*, **27**, 89 (1978).

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 12.^{1,2} Aza Analogues of Phenanthrene

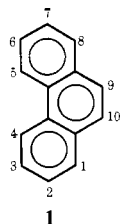
Milan Vašák,³ Michael R. Whipple, and Josef Michl*

Contribution from the Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112. Received February 14, 1978

Abstract: Magnetic circular dichroism of phenanthrene and seven of its aza analogues is reported and interpreted. An improved characterization of $\pi\pi^*$ transitions is achieved, evidence for a new low-lying $\pi\pi^*$ state in phenanthrene is presented, and a reassignment of the $\pi\pi^*$ states of the azaphenanthrenes is proposed. The perimeter model of parts 1–3 combined with the PMO approximation accounts for most of the observed signs of the lowest two bands but, with the exception of phenanthrene itself, not for those of higher energy transitions. Simple PPP calculations account well for the MCD signs of the four lowest $\pi\pi^*$ bands. Only in the case of benzo[*c*]cinnoline has an $n\pi^*$ transition been observed; its *B* term is weakly negative.

Introduction

According to the qualitative theory of the MCD signs of transitions of the L and B types in cyclic π -electron systems described in parts 1–3,^{4–6} phenanthrene and other polycyclic benzenoid hydrocarbons without a threefold or higher symmetry axis are odd-soft chromophores. Some simple consequences follow for their MCD spectra and for the effect of I and E substituents on these spectra. As noted in part 1,⁴ elsewhere in the present series we investigate the case of naphthalene, anthracene, and pyrene. In the present paper, we examine the effects of I substitution, represented by aza replacement, on MCD of phenanthrene (**1**). The MCD spectrum of **1** has been reported previously,^{7,8} and the sign of its first *B*



term has been calculated.⁸ A remeasured spectrum is included here for comparison. The MCD spectra of azaphenanthrenes have not been reported previously except for a mention in our preliminary communications.^{1,9,10} Presently, we report the spectra of three azaphenanthrenes (1-N-**1**, 4-N-**1**, 9-N-**1**) and four diazaphenanthrenes (1,8-N-**1**, 1,5-N-**1**, 4,5-N-**1**, 9,10-N-**1**).

Singlet excited states of **1** are now understood in considerable detail. The presently accepted assignment of the L and B bands was proposed by Dörr et al.,¹¹ arguing on basis of

polarized fluorescence spectra. These authors discussed in detail the relation to earlier experimental and theoretical work, such as the classical papers of Kleven and Platt¹² and of Pariser.¹³ The assignment, in particular the identification of the *B_b* band, is in agreement with measurements of linear dichroism in stretched polymer sheets.^{14–16} Theoretical and experimental work on assignment of electronic transitions was summarized in ref 14; the more recent theoretical work^{17–19} has brought no substantial changes. Well-established bands of interest here are *L_b* (short-axis polarized) near 29 000 cm^{-1} , *L_a* (long-axis polarized) near 34 000 cm^{-1} , *B_b* (short-axis) near 38 000 cm^{-1} , and *B_a* (long-axis) near 40 000 cm^{-1} . The B bands are so close to each other that the weaker *B_b* band is hidden in ordinary absorption spectra, but its presence is obvious in stretched-sheet spectra^{14–16} and also in the MCD spectrum.^{7,8} The former also show that the next higher region of absorption contains two intense transitions near 45 000 cm^{-1} (short-axis polarized) and 47 000 cm^{-1} (long-axis polarized), assigned as *C_b* and *C_a*, respectively. In addition to these six transitions, most calculations also predict the presence of about three or four very weak transitions at energies about 40 000–50 000 cm^{-1} . No definitive experimental evidence appears to exist for these.

The experimental^{11,15,20–22} and calculated^{11,15,21–27} absorption and polarization spectra of various aza analogues of **1** generally are in good mutual agreement. As noted in ref 22, the $\pi\pi^*$ transition energies in azaphenanthrenes are quite close to those of the parent **1**, but intensities and, if symmetry is *C_s*, also polarization directions are modified. Since the aza nitrogen breaks the alternant pairing symmetry, it is not surprising that the *L_b* transition is more intense in the heterocycles. Intensities and polarizations in diazaphenanthrenes have been discussed