

are closest to L_2 in energy. The origin of the L_1 band has the opposite sign, most likely originating from the opposing μ^- and μ^+ contributions due to L-B mixing. Overall, the two contributions nearly cancel for $B(L_1)$ but they add up for $B(L_2)$.

Similarly, large values of $\Delta\text{HOMO} - \Delta\text{LUMO}$ are predicted for 2-N-1 and 6-N-1, and a corresponding large positive value of $B(L_1)$ similar to that in 1 is indeed observed (ref 2 and Figures 1 and 4). Not surprisingly, the relative magnitudes of $B(L_1)$ within the "zero-soft" group III are not very sensitive to the $\Delta\text{HOMO} - \Delta\text{LUMO}$ difference, which should decrease in the order 2, 5-N-2, 4-N-2, 1-N-2, so that the positive value of $B(L_1)$ should decrease in the same order. Some indication of this is observed (ref 2 and Figures 8, 7, and 6), but the bulk of $B(L_1)$ is probably dominated by the μ^- contribution. On the other hand, the expected corresponding increase in the positive value of $B(L_2)$ is large and grows along the series in the order expected for the μ^+ contribution. Since the positive amount due to the μ^- contribution is allocated between $B(L_1)$ and $B(L_2)$ in a way which depends not only on $\Delta\text{HOMO} - \Delta\text{LUMO}$ but also on ϕ (in the notation of part 2³), it is perhaps not surprising that the relative intensities within group III are not as readily understood in a qualitative fashion from the magnitude of $\Delta\text{HOMO} - \Delta\text{LUMO}$ alone.

The value of $B(B_1)$ is positive for all of the compounds investigated here, similarly as for all aza naphthalenes⁴ and substituted naphthalenes, as well as naphthalene itself.² This is presumably again due to the next-nearest-neighbor contribution of the μ^- type ($B_b - B_a$ mixing) inherent to the basic chromophore.

Conclusion

The effect of aza substitution on the B terms of both L bands and the lower B band of 1 and 2 can be rationalized qualitatively on the basis of very simple arguments. While it is believed

that the basics are well understood, there clearly is considerable room for quantitative developments, and these compounds are likely to provide a good test case for more sophisticated theories.

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM 21153. We thank Dr. Henry Eyring for kind permission to use his MCD instrument. Helium gas was provided by a departmental grant from the Office of Naval Research.

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Magnetic Circular Dichroism of Cyclic π -Electron Systems. 10.^{1,2} Quinolones, Isoquinolones, and Related Heterocycles

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Abstract. Magnetic circular dichroism is reported for seven heterocycles of quinolone and isoquinolone types. The arrangement of the NH and CO groups dictates the MCD signs of the L bands in a way expected from the properties of orbitals of naphthalene and the qualitative theory of parts 1-3. Also, the effects of further aza replacement and hydroxy substitution are accounted for by simple qualitative arguments. The results are reproduced correctly by numerical PPP calculations.

Introduction

The simple qualitative theory of substituent effects on MCD signs of bands related to L and B transitions of the perimeter, described in parts 1-3,² has been found to work well for the derivatives of many odd-soft chromophores: for aza analogues of naphthalene⁴ and its substituted derivatives,⁵ for amino-azanaphthalenes,² for substituted and aza derivatives of anthracene⁶ and pyrene,⁷ and for azaphenanthrenes.⁸ It also accounts well for MCD spectra of derivatives⁹ and heterocyclic analogues¹⁰ of the even-soft chromophores, the azines,¹¹ and since we are interested in eventual applications to molecules

such as pteridines and flavines, it is desirable to test it on heterocyclic analogues of naphthalene.

In the present paper, we report the MCD spectra of seven heterocyclic analogues of naphthalene containing the combination of carbonyl and NH groups in the ring system. Some contain also an aza nitrogen, a hydroxy, or a methyl group. Formally, such compounds can be derived from naphthalene by simultaneous replacement of one CH group by the NH⁺ group in the ring and attachment of an O⁻ group to another position in the ring. While such an operation certainly represents a serious perturbation of the parent system, one can hope to understand the resulting ordering of orbitals and their nodal

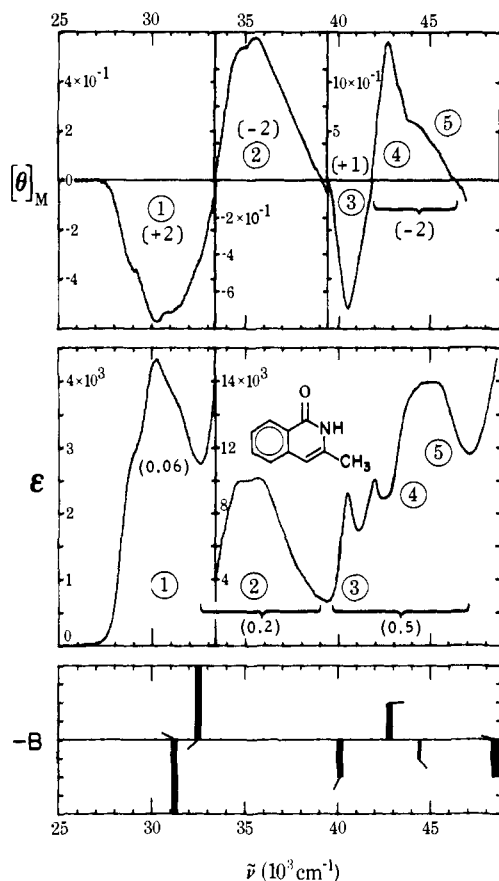


Figure 1. 3-Methyl-1-isoquinolone: top, MCD (B terms given in units of $10^{-3} \beta_e D^2/\text{cm}^{-1}$); center, absorption (oscillator strengths given); bottom, calculation (the thickness of the bar indicates intensity, its direction and length show the sign and magnitude of the B term, and the flag at the end indicates the polarization direction with respect to the formula shown).

properties by considering the perturbation to consist of a strong +I substitution in one position (NH^+) and simultaneous very strong $-E$ substitution in another ($-\text{O}^-$). In this sense, the naphthalene chromophore is perturbed in exactly the same manner as upon the simultaneous introduction of an aza and an amino substituent investigated in part 9,² only more strongly.

We shall refer to these heterocycles by indicating the location of the NH group on the ring of naphthalene, referring to $=\text{O}$ in position 1 as **1** and in position 2 as **2**. For instance, 2-quinolone is 1-NH-2 and 1-isoquinolone is 2-NH-1, and they are isoelectronic with the compounds which carried the analogous labels in part 9,² 2-aminoquinoline and 1-aminoisoquinoline, respectively. In many cases, the compounds which were actually measured also contained aza nitrogens and/or methyl groups, whose position will be shown in the same way. The possibility that minor amounts of other tautomers may be present must be kept in mind. Our assignment of the predominant tautomers present is based on ref 12.

Only a very limited amount of attention has been paid to the excited states of this group of compounds. The spectrum of 1-NH-2 has been briefly discussed and compared with π -electron calculations in ref 13, and calculations for several **1**'s and **2**'s have been found to agree with reported absorption curves.¹⁴

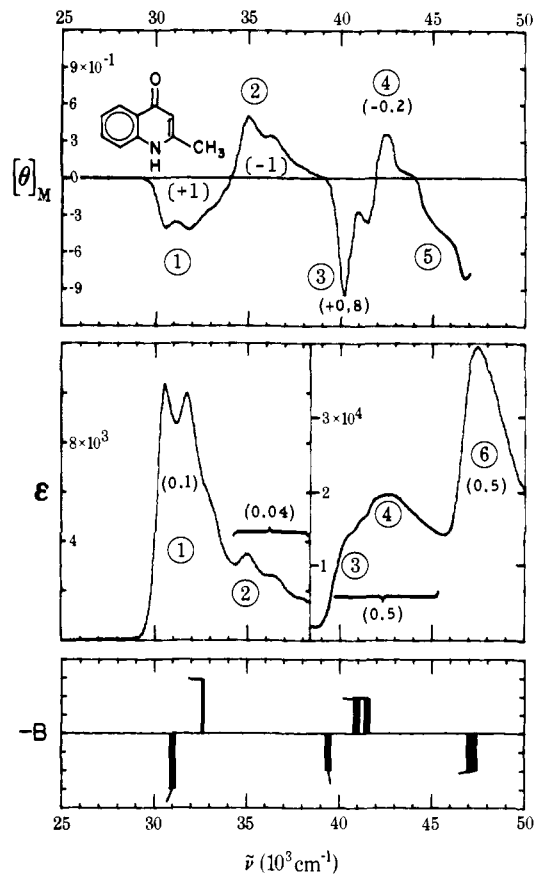
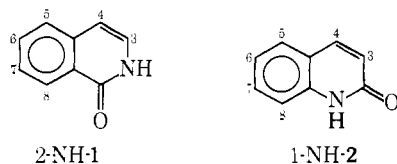


Figure 2. 2-Methyl-4-quinolone. See caption to Figure 1. The spectra of 4-quinolone were also measured and are similar.

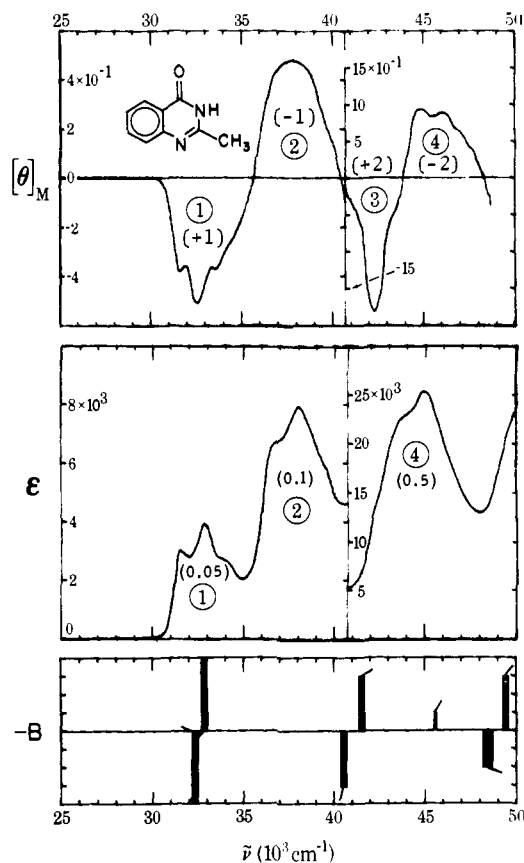


Figure 3. 2-Methyl-4-quinazolone. See caption to Figure 1.

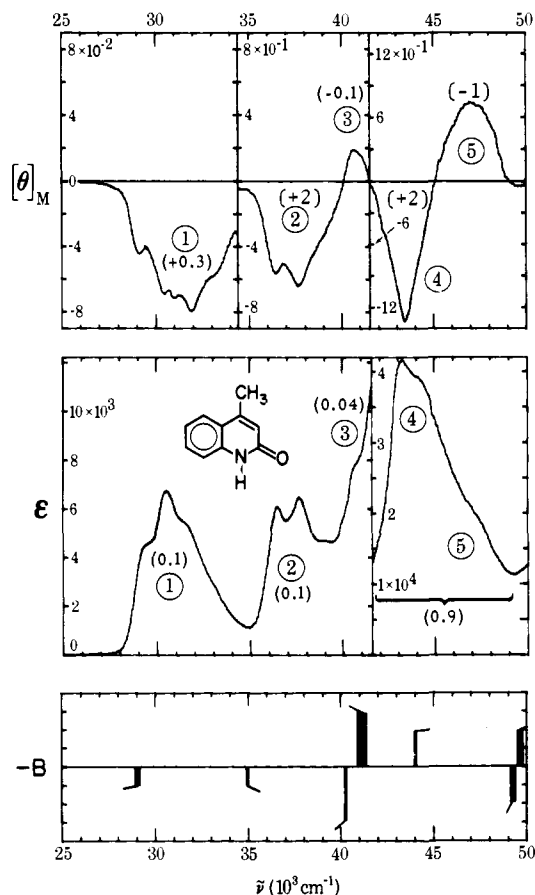


Figure 4. 4-Methyl-2-quinolone. See caption to Figure 1.

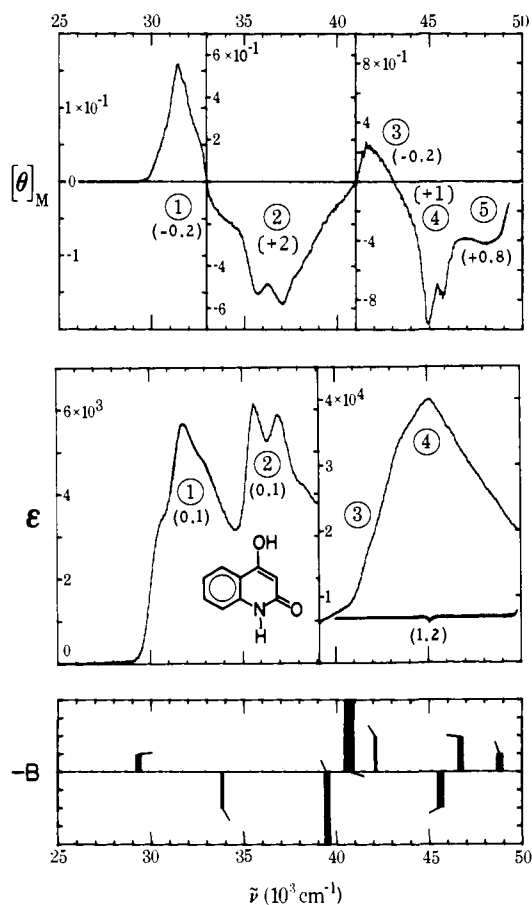


Figure 5. 4-Hydroxy-2-quinolone. See caption to Figure 1.

Experimental Section and Calculations

The samples were commercial and were purified by gradient sublimation except for 4-OH-(1-NH-2), which was crystallized from acetic acid. Details of the measurements and PPP calculations were given in part 4.¹¹ The solvent was acetonitrile except for 4-OH-(1-NH-2) which was measured in ethanol.

Results

The results are shown in Figures 1–7. As noted in part 4,¹¹ the calculations are of the standard type considering only nearest-neighbor interactions and describe only the μ^+ contribution to the B terms, i.e., approximately the difference with respect to naphthalene. An assignment of electronic transitions is proposed, based on shapes of the absorption and MCD spectra. The low-energy portions of several of the spectra are strikingly similar to the corresponding regions in the spectra of the isoelectronic aminoazaphthalenes described in part 9.²

Transition 1 is identified with L_1 and transition 2 with L_2 , based on similarity to spectra of substituted naphthalenes and on inspection of PPP wave functions. These criteria suggest the assignment of transition 3 to B_1 and transition 4 to B_2 , but in several of the molecules, an additional transition is present in this region. The PPP wave functions indicate that its presence is due to the configuration $3 \rightarrow -1$, which mixes with those normally present in the B states, so that the additional transition shares the B character with the two already present. At 40 000 cm^{-1} and higher, the MCD spectra reveal the presence of transitions which are not obvious in the absorption curves.

Discussion

Substituent Effects on MCD of Naphthalene. According to the general qualitative theory of parts 1–3,³ the inherent B terms of the naphthalene chromophore, due to the μ^- magnetic moment which results from next-nearest-neighbor interactions, are $B(L_b) = 0$, $B(L_a) > 0$ (weak), and $B(B_b) > 0$. They are modified in the presence of substituents, primarily by addition of terms originating in the μ^+ magnetic moment, which results from nearest-neighbor contributions. The signs of the contributions due to substituents are given by the sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$, defined by orbital energies of the four orbitals which correlate with the frontier orbitals in the parent [10]-annulene, s , a , $-a$, and $-s$: $\Delta\text{HOMO} = |E(a) - E(s)|$, $\Delta\text{LUMO} = |E(-a) - E(-s)|$. The contributions to $B(L_1)$ and $B(B_1)$ have the same sign as the $\Delta\text{HOMO} - \Delta\text{LUMO}$ difference, and that to $B(L_2)$ has the opposite sign (the transitions are labeled L_1 , L_2 , B_1 , and B_2 in the order of increasing energy). The sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$ can be usually estimated by use of simple notions of orbital interactions.

In the most primitive application of these notions to the lactams investigated presently, one can add up the perturbations of the naphthalene orbitals due to the NH^+ substituent, the $-\text{O}^-$ substituent, and any other substituents present such as aza nitrogen. Since position 1 of naphthalene is of type D ($c_{1,1}^2 = c_{1,-1}^2 > c_{1,2}^2 = c_{1,-2}^2$), the +I effect of 1- NH^+ provides a negative contribution to $\Delta\text{HOMO} - \Delta\text{LUMO}$ and the +I effect of N a weaker one,^{3,4} and the -E effect of 1- O^- provides a positive contribution.^{3,5} Results of parts 5⁹ and 6¹⁰ show that the +I effect of NH^+ predominates over an opposed -E effect of OH but that it is considerably weaker than the -E effect of the much stronger electron donor, $-\text{O}^-$. Naphthalene position 2 is of type S ($c_{2,1}^2 = c_{2,-1}^2 < c_{2,2}^2 = c_{2,-2}^2$), so that 2- NH^+ and 2-N provide a positive contribution to $\Delta\text{HOMO} - \Delta\text{LUMO}$. The -E effect of $-\text{O}^-$ is comparable to that of NH_2 or somewhat stronger,^{15,16} so that the 2- O^- substituent should lie a little past the “zero-soft” border line at which the effect of 2-substitution on $\Delta\text{HOMO} - \Delta\text{LUMO}$ vanishes and it should provide a positive contribution but not nearly as strong

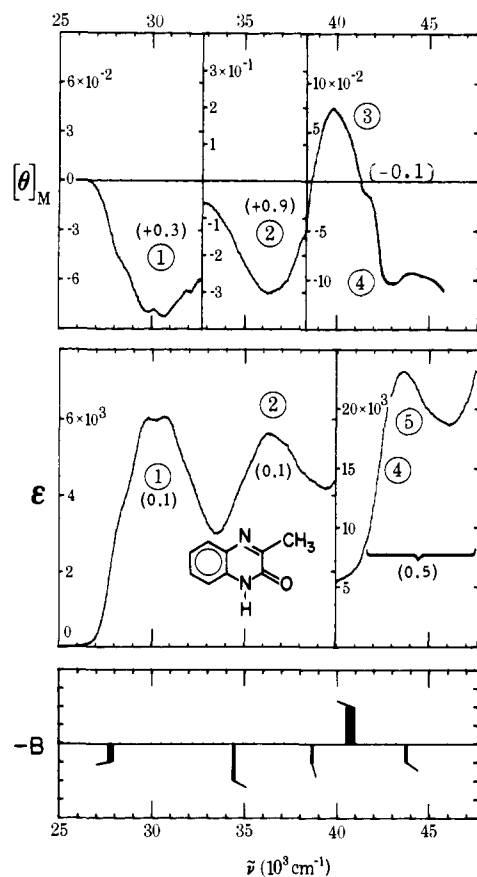


Figure 6. 3-Methyl-2-quinoxalone. See caption to Figure 1.

as in position 1 (note that the $-E$ effect of $-OH$ in the lactim tautomer is much weaker so that it should provide a negative contribution, partly canceling or perhaps even overwhelming the positive contribution of the aza nitrogen in position 1, so that one expects the MCD spectra of the two tautomers to differ considerably).

If we now simply add up the contributions from the perturbations, we obtain a positive sign for $\Delta HOMO - \Delta LUMO$ in the four basic isomers of interest here, and a magnitude decreasing in the order $2-NH-1 > 4-NH-1 \gg 3-NH-2 > 1-NH-2$. Assuming comparable energy separations of the two L bands in all four compounds, this translates into a positive $B(L_1)$ decreasing in roughly the same order (this B term contains a positive μ^- contribution except in naphthalene itself). This result is in qualitative agreement with experiment. To estimate $B(L_2)$ very roughly, we add $-B(L_1)$ to the positive inherent μ^- contribution observed in naphthalene. Once again, qualitative agreement with experiment is excellent. In $2-NH-1$ and $4-NH-1$, whose $B(L_1)$ is relatively large, $B(L_2)$ is negative (Figures 1-3); in $1-NH-2$, in which it is very small (and at least partly due to a μ^- contribution), $B(L_2)$ is positive as in naphthalene (Figures 4-6). If carbonyls are present in both the 1 and 2 positions (Figure 7), $B(L_1)$ is a little larger again, and $B(L_2)$ is almost exactly zero.

Effects of additional aza replacement and substitution are again easy to interpret in a qualitative fashion based on naphthalene orbitals. In $2-NH-1$, the orbital ordering is $s, a, -a, -s$ as in naphthalene, and $\Delta HOMO - \Delta LUMO > 0$. +I substitution in position 4 should decrease the difference $\Delta HOMO - \Delta LUMO$ similarly as in naphthalene itself,⁴ and this is observed (Figures 1 and 3). In $1-NH-2$, the strong $-E$ substituent in a subdominant position 2 has taken the system beyond the "zero-soft" border line so that the orbital ordering now is $a, s, -a, -s$, and I substitution should have little effect

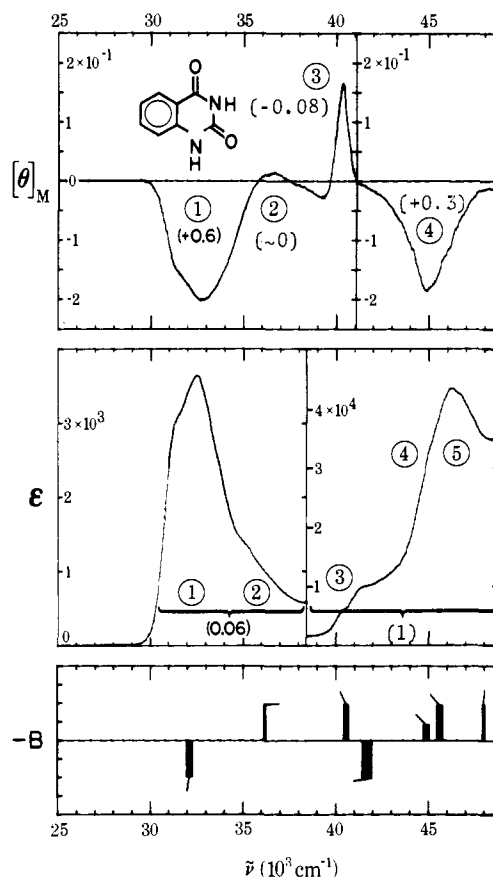


Figure 7. Benzoyleneurea. See caption to Figure 1.

(compare Figures 4 and 6), while $-E$ substitution in position 4 should decrease $\Delta HOMO - \Delta LUMO$, i.e., should have the opposite effect than in naphthalene itself because the order of a and s is now reversed. This finds a striking confirmation in the comparison of Figures 4 and 5, which shows that in $4-OH-1-NH-2$, $\Delta HOMO < \Delta LUMO$.

The signs of the higher energy bands $B(B_1)$ and $B(B_2)$ are positive and negative, respectively, in lactams of type 1, as expected from inherent effects in naphthalene itself, but their signs are just the opposite in lactams of type 2, and this is not accounted for by the simplest qualitative theory.

Full PPP calculations account well for the signs and even relative magnitudes of $B(L_1)$ and $B(L_2)$, and correctly describe the effect of 4-hydroxy substitution in $1-NH-2$. In lactams of type 1, they also yield correct signs for the B bands, but in lactams of type 2, they fail in this higher energy region.

Conclusion

The MCD signs of the first two bands of lactams of types 1 and 2, as well as effects of further structural perturbations, are understood readily from properties of naphthalene orbitals. Signs of higher energy transitions are not accounted for in this simple manner but mostly agree with standard PPP calculations.

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM 21153. We are grateful to Professor Henry Eyring (University of Utah) for kind permission to use his MCD instrument. Helium gas was provided by a departmental grant from the Office of Naval Research.

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

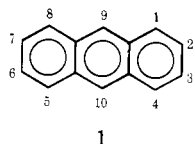
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Abstract: Magnetic circular dichroism of anthracene, nine of its derivatives, acridine, and phenazine is reported and interpreted. Evidence for the assignment of the controversial L_b transition and for some other weak transitions is obtained. The 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).



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-