# Magnetic Circular Dichroism of Cyclic π-Electron Systems. 9.[1,2] Aminoquinolines and Aminoisoquinolines

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**Abstract.** Magnetic circular dichroism of eight aminoazanaphthalenes is reported. The MCD signs of the L bands and the lower B band are rationalized in terms of the qualitative theory of parts 1–3. 2-Aminonaphthalene is found to represent a nice example of a nearly zero-soft chromophore.

## Introduction

In the preceding papers of this series, we have tested the predictions of the qualitative theory[3] of substituent effects on MCD signs of bands related to L and B transitions in polycyclic benzenoid hydrocarbons in the case of aza analogues of naphthalene[4] and substituted derivatives of naphthalene[2] and found excellent agreement. Also, the results for simple analogues and derivatives of anthracene[5] and pyrene[6] are very well accounted for by the theory, while somewhat less perfect agreement is found for aza analogues of phenanthrene.[7] On the whole, it appears that the simple model works very well for simple derivatives of odd-soft chromophores in general. Since we are interested in eventual application to more complex π systems containing several different substituents and/or heteroatoms, such as pteridines and flavines, it appeared important to investigate the simultaneous effect of two substituent effects of different types. Presently, we report the spectra of eight aminoquinolines and aminoisoquinolines which can be derived from naphthalene by simultaneous introduction of the +I (inductive) aza replacement and −E (mesomeric) amino substituent.

In spite of numerous reports of solution absorption curves and interest in fluorescence spectra of this class of naphthalene analogues,[8] very few detailed spectroscopic assignments have appeared. Relative transition polarization directions have been estimated in 2- and 3-aminoquinolines from measured linear dichroism in a stretched poly(vinyl alcohol) sheet, in good agreement with PPP calculations,[9] which have also been shown to account for excitation energies and relative intensities of low-energy excitations in these and other aminoquinolines.[10,11]

In the following, we shall refer to these amines as derivatives of 1-aminonaphthalene (**1**) and 2-aminonaphthalene (**2**), indicating the position of the aza nitrogen: 1-N-**2**, etc.



**1**          **2**
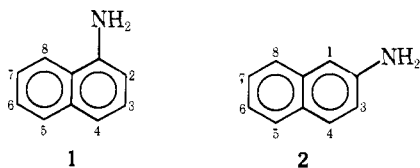
## Experimental Section and Calculations

The samples were obtained from commercial sources. 6-N-**1** was crystallized from hexane–chloroform, and the hydrochloride of 5-N-**2** was crystallized from aqueous ethanol before conversion to the free base. The final purification of all samples was by gradient sublimation. The techniques of measurements and calculations were described in part 4.[12] Two different values for the amino nitrogen parameter $A_{N^+}$, both suggested in the literature,[13,14] were used (9.1 eV, 10.15 eV) with very similar results. The results shown were obtained with $A_{N^+}$ = 10.15 eV.

## Results

The results are presented in Figures 1–8. The PPP calculations are of the standard type considering only nearest-neighbor interactions ($\mu^+$ contributions). The assignment of electronic transitions indicated is based on analogy to **1** and **2**. It is quite possible that additional transitions are present in the spectra above 40 000 cm$^{-1}$. We can identify transition no. 1 with $L_1$, no. 2 with $L_2$, and no. 3 with $B_1$. The spectra are to be compared with those of **1** and **2** shown in part 8.[2] The aza replacement is seen to modify the MCD intensities but not signs of the first few transitions, except for 3-CH$_3$-4-N-**1**, where vibronic effects come to light in the very weak first band. There is no evidence for nπ* transitions in any of the spectra. On the other hand, the MCD curve clearly reveals the presence of separate transitions 1 and 2 in the derivatives of **1**, where it is usually not at all apparent from the absorption curve.

## Discussion

**Substituent Effects on MCD of Naphthalene.** The general qualitative theory of parts 1–3[3] predicts that $B(L_b) = 0$, $B(L_a) > 0$ (weak), and $B(B_b) > 0$ originate from the small magnetic moment $\mu^-$ in an odd-soft chromophore such as naphthalene and suggests that substituent effects involving the large magnetic moment $\mu^+$ ought to be added to these intrinsic contributions. The signs of the contributions from substituents, which are mostly due to mutual mixing of the two L states and to that of the two B states, should be given by the sign of ΔHOMO − ΔLUMO, defined as in parts 1–3[3] by differences of orbital energies: ΔHOMO = $|E(\mathbf{a}) − E(\mathbf{s})|$ and ΔLUMO = $|E(−\mathbf{a}) − E(−\mathbf{s})|$, where $\mathbf{s}$, $\mathbf{a}$, $−\mathbf{a}$, and $−\mathbf{s}$ are the four frontier orbitals of a perturbed naphthalene which correlate with the two HOMO's and the two LUMO's of [10]annulene. If ΔHOMO > ΔLUMO, the substituent contributes positively to $B(L_1)$ and $B(B_1)$ and negatively to $B(L_2)$. If ΔHOMO < ΔLUMO, the reverse holds. In parts 1–3[3] we have illustrated the use of first-order perturbation theory for derivation of the sign of ΔHOMO − ΔLUMO without any computations, and the reader is referred there for details. Inequality of ΔHOMO and ΔLUMO also modifies the $\mu^-$ contributions: due to L–B mixing, they provide positive amounts both to $B(L_1)$ and $B(L_2)$, and due to L–L mixing, they provide an additional positive amount to $B(L_1)$ and negative amount to $B(L_2)$. These effects are usually negligible next to the $\mu^+$ contributions.

The simplest way to estimate orbital energy differences required for the evaluation of the sign of ΔHOMO − ΔLUMO for N-**1**'s and N-**2**'s would be to add up the perturbation of the naphthalene orbital energies by the aza nitrogen and the perturbation by the amino substituent. Since position 1 is of type D (dominant) ($c_{1,1}^2 = c_{1,-1}^2 > c_{1,2}^2 = c_{1,-2}^2$), the +I effect of a 1-aza nitrogen provides a negative contribution to ΔHOMO − ΔLUMO,[4] and the −E effect of a 1-NH$_2$ group provides a positive contribution.[2] The latter is considerably
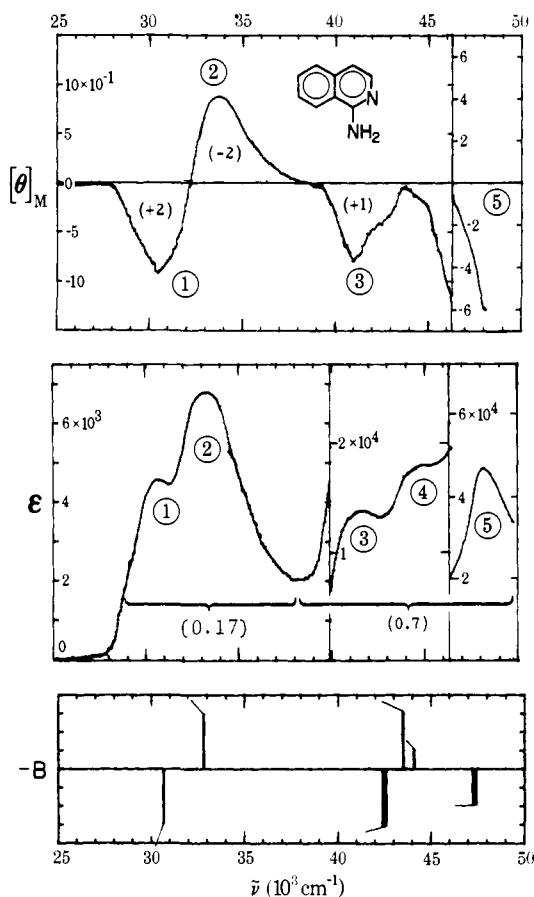
**Figure 1.** 1-Aminoisoquinoline (2-N-1) spectra: bottom, calculated; center, absorption; top, MCD. The calculated $B$ term (units of $10^{-3}\beta_e\ D^2/cm^{-1}$) is indicated by the length of the bar ($|B| < 1$, short; $1 < |B| < 5$, medium; $|B| > 5$, long), the calculated oscillator strength by its thickness ($f < 0.3$, thin; $f > 0.3$, thick), and the calculated polarization by the direction of the flag at the end with respect to the formula shown.

larger, as shown by comparison of the spectra of quinoline[4] and 1.[2] The energy difference between the two L bands is not exactly the same in the two compounds, so that in this comparison one is not looking at the magnitude of $\Delta$HOMO $-$ $\Delta$LUMO alone. However, the domination of the amino group over an opposed effect of the aza nitrogen is also clearly seen in the spectrum of 4-aminopyridine,[15] where no such objection arises. Position 2 is of type S (subdominant) ($c_{2,1}{}^2 = c_{2,-1}{}^2 < c_{2,2}{}^2 = c_{2,-2}{}^2$), so that the aza nitrogen provides a positive contribution to $\Delta$HOMO $-$ $\Delta$LUMO.[3] The $-E$ effect of the amino group is too strong to induce a negative contribution as a weaker $-E$ substituent in this position would. Instead, as elaborated in detail in parts 3[3] and 8[2] (in particular, Figure 19 in ref 2), the amino group lies close to the border line at which the sign induced by a $-E$ substituent in position 2 changes, so that its effect on $\Delta$HOMO $-$ $\Delta$LUMO is almost zero and **2** is very nearly a zero-soft chromophore. One thus expects its MCD spectrum to be dominated by $\mu^-$ contributions, which yield the sign sequence $+,+,+,-$ in order of increasing energy. Note that none of these vanish, in contrast to all other types of soft chromophores: as implied in its name, a zero-soft chromophore should exhibit decreased sensitivity to additional perturbations which remove the equality of $\Delta$HOMO and $\Delta$LUMO, such as aza replacement; we shall see in the following that this expectation is fulfilled.

Simply adding up the $\mu^+$ contributions due to the introduction of $NH_2$ and N, we obtain for the sign of $\Delta$HOMO $-$ $\Delta$LUMO, and thus for the sign of $B(L_1)$, which has no intrinsic $\mu^-$ component to the first approximation:



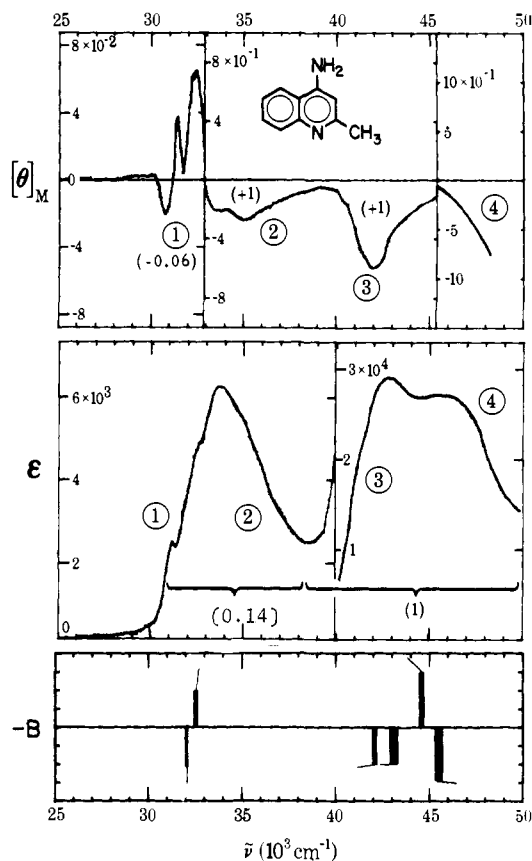**Figure 2.** 4-Aminoquinoline (3-$CH_3$-4-N-1). See caption to Figure 1. The calculations are for 4-N-1 ($|B| < 5$, short lines, $|B| > 5$, long lines; $f < 0.1$, thin; $0.1 < f < 0.5$, medium; $f > 0.5$, thick).
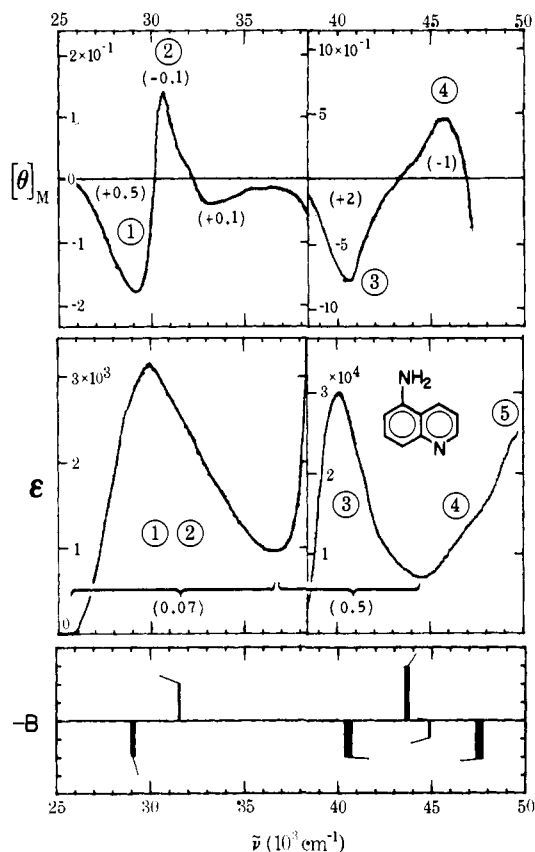


**Figure 3.** 5-Aminoquinoline (5-N-1). See caption to Figure 1 ($|B| < 5$, short lines; $|B| > 5$, long lines; $f < 0.05$ thin; $0.05 < f < 0.5$, medium; $f > 0.5$, thick).

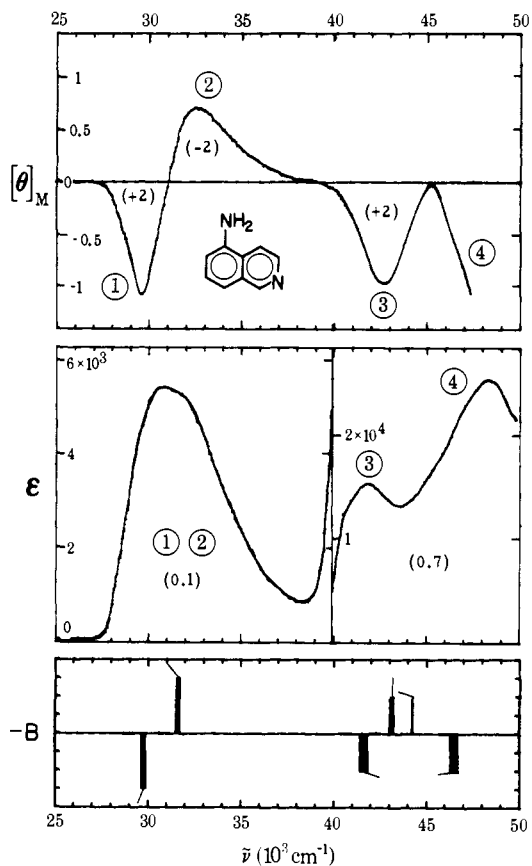**Figure 4.** 5-Aminoisoquinoline (6-N·1). See caption to Figure 1 ($f < 0.1$, thin; $0.1 < f < 0.5$, medium; $f > 0.5$, thick).



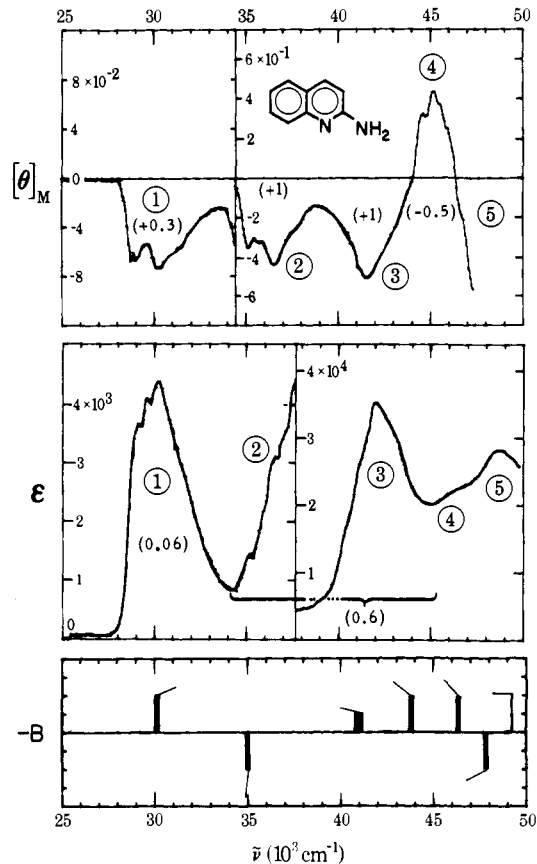**Figure 6.** 2-Aminoquinoline (1-N-2). See caption to Figure 1 ($|B| < 1$, short; $|B| > 1$, long; $f < 0.1$, thin; $0.1 < f < 1.0$, medium; $f > 1$, thick).



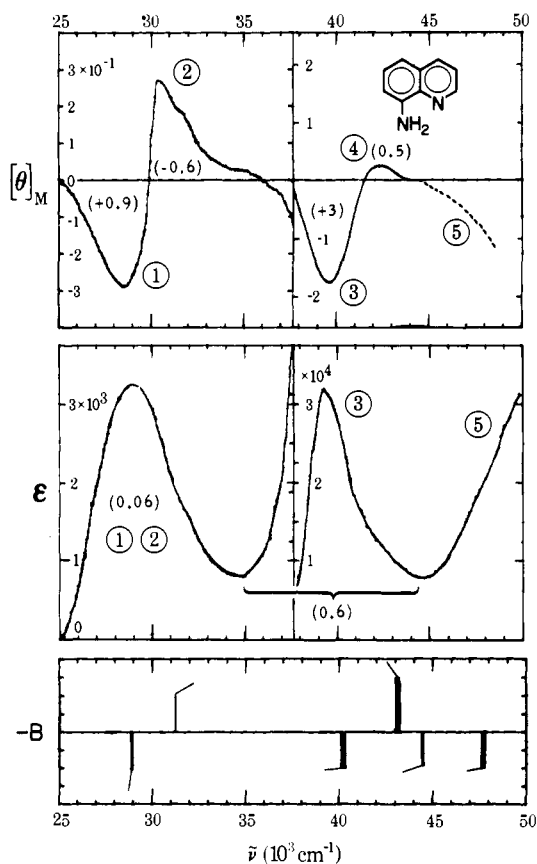**Figure 5.** 8-Aminoquinoline (8-N-1). See caption to Figure 1 ($|B| < 5$, short; $|B| > 5$, long; $f < 0.01$, thin; $0.01 < f < 0.1$, medium; $f > 0.1$, thick).



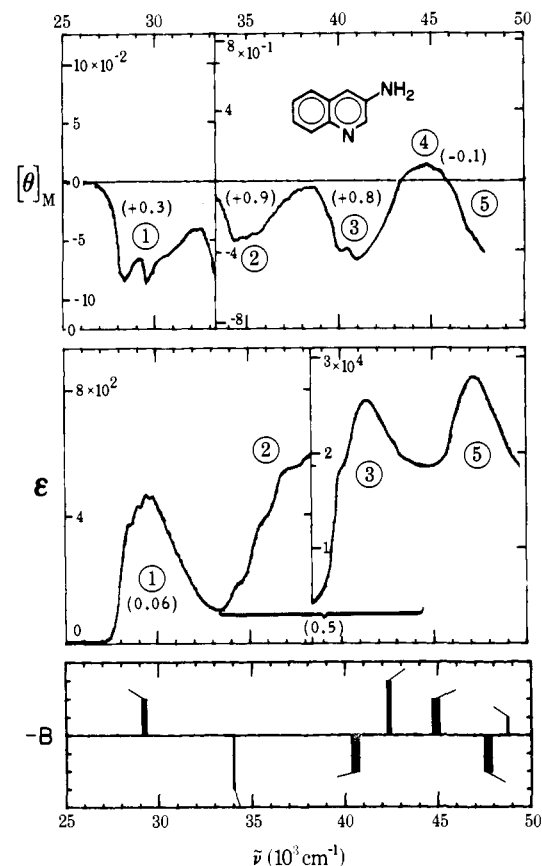**Figure 7.** 3-Aminoquinoline (4-N-2). See caption to Figure 1 ($|B| < 0.2$, short; $0.2 < |B| < 2$, medium; $|B| > 2$, long; $f < 0.1$, thin; $0.1 < f < 0.5$, medium; $f > 0.5$, thick).

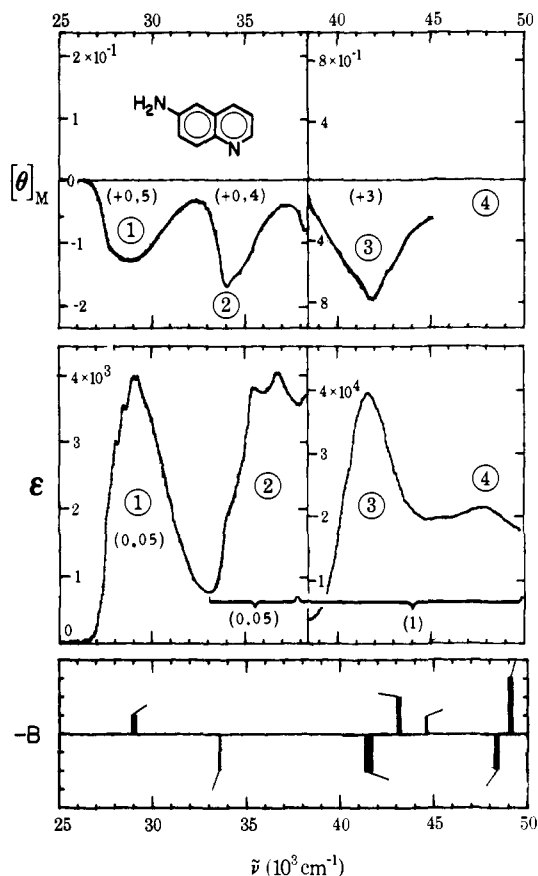**Figure 8.** 6-Aminoquinoline (5-N-2). See caption to Figure 1 ($f < 0.1$, thin; $0.1 < f < 1$, medium; $f > 1$, thick).

| | | |
|---|---|---|
| I | 2-N-1, 3-N-1, 6-N-1, 7-N-1 | ++ |
| II | 4-N-1, 5-N-1, 8-N-1 | + |
| III | 1-N-2, 4-N-2, 5-N-2, 8-N-2 | ~0 |
| IV | 3-N-2, 6-N-2, 7-N-2 | ~0 |

$\mu^+$ contributions to $B(L_2)$ would then be roughly equal in magnitude and opposite in sign. In group I, $\Delta$HOMO −

$\Delta$LUMO is large and the $\mu^-$ contributions should be inconsequential, but in the other three groups, $\Delta$HOMO − $\Delta$LUMO could be quite small and the positive $\mu^-$ contributions to both L bands should then be important.

Comparison with the experimental data indicates that this crude procedure correctly reproduces general trends but not the details. Among the amines measured, $B(L_1)$ is indeed most positive for compounds of the above group I (2-N-1, Figure 1; 6-N-1, Figure 4) and less so for those of group II (4-N-1, Figure 2; 5-N-1, Figure 3; 8-N-1, Figure 5). For group III, $B(L_1)$ is weakly positive as in **2** itself, undoubtedly due to the $\mu^-$ contribution, demonstrating the expected decreased sensitivity of a zero-soft chromophore to perturbations which make $\Delta$HOMO and $\Delta$LUMO different (1-N-2, Figure 6; 4-N-2, Figure 7; 5-N-2, Figure 8). It will be noted that the numerical PPP calculation, in which $\mu^-$ contributions are neglected, produces mostly the signs which the simple argument predicts for $\mu^+$ contributions alone and as a result predicts incorrect signs for $B(L_1)$ of compounds of group III but otherwise gives correct answers (except for 4-N-1).

A shortcoming of the simplest approach is the lack of differentiation within the groups. For instance, while $B(L_1)$ is distinctly positive for 5-N-1, it is actually very weakly negative for 4-N-1. At the next level of sophistication, it is recognized that the amino group is a much stronger substituent than the aza nitrogen and one may then view the presence of the latter as a perturbation on the electronic structure of **1** and **2**. The requisite squares of SCF MO coefficients obtained from our MO calculation using $A_{N^+} = 9.1$ eV are collected in Table I, and they are seen to account for most of the differences in the magnitude of $B(L_1)$ among compounds of the groups I and II. In particular, $\Delta$HOMO − $\Delta$LUMO is predicted to decrease in the order **1**, 8-N-1, 5-N-1, 4-N-1, so that one expects a decrease in the positive value of $B(L_1)$ along this series, and this is observed (ref 2 and Figures 5, 3, and 2). For 4-N-1, $\Delta$HOMO − $\Delta$LUMO already is weakly negative, so that the L–L mixing contributes negatively to $B(L_1)$ and positively to $B(L_2)$ (for the parameter chosen in Table 1, $A_{N^+} = 9.1$ eV, $\Delta$HOMO − $\Delta$LUMO is calculated to be slightly positive so that it is understandable that the PPP signs shown in Figure 2 are incorrect; this could be corrected by a minor adjustment of parameters). The L–L mixing appears to dominate the MCD sign of the higher vibrational levels of the $L_1$ band, which

**Table I.** Effect of Aza Replacement on the $\Delta$HOMO − $\Delta$LUMO Difference in Aminonaphthalenes[a]

| | **1, 1-Aminonaphthalene position** | | | | | | |
|---|---|---|---|---|---|---|---|
| | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| $c_{-2}^2$ | 0.15 | 0.15 | 0.00 | 0.00 | 0.16 | 0.16 | 0.00 |
| $c_{-1}^2$ | 0.04 | 0.07 | 0.13 | 0.21 | 0.08 | 0.07 | 0.21 |
| $\Delta$ | 0.11 | 0.08 | −0.13 | −0.21 | 0.08 | 0.09 | −0.21 |
| $c_1^2$ | 0.16 | 0.03 | 0.21 | 0.08 | 0.02 | 0.05 | 0.05 |
| $c_2^2$ | 0.18 | 0.17 | 0.00 | 0.00 | 0.13 | 0.16 | 0.00 |
| $\Delta$ | −0.02 | −0.14 | 0.21 | 0.08 | −0.11 | −0.11 | −0.05 |
| $\Delta(\Delta$HOMO − $\Delta$LUMO$)/\Delta\alpha_N$ | +0.13 | +0.22 | −0.34 | −0.29 | +0.19 | +0.20 | −0.26 |
| $\Delta(\Delta$HOMO − $\Delta$LUMO$)/$eV | +0.14 | +0.25 | −0.90 | −0.45 | +0.13 | +0.15 | −0.38 |

| | **2, 2-Aminonaphthalene position** | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 3 | 4 | 5 | 6 | 7 | 8 |
| $c_{-2}^2$ | 0.00 | 0.11 | 0.00 | 0.00 | 0.19 | 0.14 | 0.00 |
| $c_{-1}^2$ | 0.14 | 0.11 | 0.19 | 0.19 | 0.05 | 0.08 | 0.17 |
| $\Delta$ | −0.14 | 0.00 | −0.19 | −0.19 | 0.14 | 0.06 | −0.17 |
| $c_1^2$ | 0.31 | 0.01 | 0.06 | 0.04 | 0.09 | 0.00 | 0.10 |
| $c_2^2$ | 0.02 | 0.26 | 0.10 | 0.13 | 0.00 | 0.16 | 0.09 |
| $\Delta$ | 0.29 | −0.25 | −0.04 | −0.09 | 0.09 | −0.16 | 0.01 |
| $\Delta(\Delta$HOMO − $\Delta$LUMO$)/\Delta\alpha_N$ | −0.43 | +0.25 | −0.15 | −0.10 | +0.05 | +0.22 | −0.16 |
| $\Delta(\Delta$HOMO − $\Delta$LUMO$)/$eV | −0.53 | +0.39 | −0.35 | −0.21 | −0.01 | +0.25 | −0.32 |

[a] $\Delta$HOMO − $\Delta$LUMO as estimated from first-order perturbation theory in units of $\Delta\alpha_N$ and as given by a full SCF PPP calculation in units of eV (using $A_{N^+} = 10.15$ eV, $\Delta$HOMO − $\Delta$LUMO is 0.77 eV in **1** and −0.18 eV in **2**; using $A_{N^+} = 9.1$ eV, the values are 0.97 eV in **1** and −0.08 eV in **2**).

are closest to $L_2$ in energy. The origin of the $L_1$ band has the opposite sign, most likely originating from the opposing $\mu^-$ and $\mu^+$ 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 $\Delta$HOMO − $\Delta$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 $\Delta$HOMO-$\Delta$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 $\mu^-$ 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 $\mu^+$ contribution. Since the positive amount due to the $\mu^-$ contribution is allocated between $B(L_1)$ and $B(L_2)$ in a way which depends not only on $\Delta$HOMO − $\Delta$LUMO but also on $\phi$ (in the notation of part 2[3]), 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 $\Delta$HOMO − $\Delta$LUMO alone.

The value of $B(B_1)$ is positive for all of the compounds investigated here, similarly as for all aza naphthalenes[4] and substituted naphthalenes, as well as naphthalene itself.[2] This is presumably again due to the next-nearest-neighbor contribution of the $\mu^-$ 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.

**References and Notes**

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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 naphthalene[4] and its substituted derivatives,[5] for amino-azanaphthalenes,[2] for substituted and aza derivatives of anthracene[6] and pyrene,[7] and for azaphenanthrenes.[8] It also accounts well for MCD spectra of derivatives[9] and heterocyclic analogues[10] 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