

rimidine, and 4-O<sup>-</sup> substitution raises its  $\alpha$  orbital, but to a lesser degree. In the published spectrum of cytosine (**4**)<sup>9</sup> the first transition (37 600 cm<sup>-1</sup>) has the expected positive  $B$  term. The next transition occurs near 42 500 cm<sup>-1</sup>, has a positive  $B$  term, and appears only as a shoulder in absorption. It has been assigned as  $n\pi^*$ , since it is not present in the absorption of the protonated form and is at best indistinct in its MCD spectrum.<sup>9</sup>

**MCD and Pyridone-Hydroxypyridine Tautomerism.** MCD spectroscopy would be particularly helpful for studies of tautomeric equilibria if the two tautomers differed in the MCD signs of their bands or at least greatly differed in their intensities; otherwise, it is likely to be no more useful but more expensive than ordinary UV spectroscopy. The general discussion of substituent effects on MCD signs of an even-soft chromophore given above shows that a sign difference can only be hoped for if the oxygen is attached in one of the positions of type DS, and even then, only if the strength of the -OH substituent is sufficiently small to place it on the "weak" side of the expected borderline, so that it produces  $\Delta\text{HOMO} < \Delta\text{LUMO}$  in the parent azine (the strength of the -O<sup>-</sup> substituent is sufficiently large to produce  $\Delta\text{HOMO} > \Delta\text{LUMO}$  in the protonated azine). According to standard PPP calculations with the usual unoptimized parameter values, the latter condition should be fulfilled for the 4-hydroxypyridine tautomer of **1**, which is predicted to have the -, + sign sequence for  $B$  terms, unlike **1** itself. The same calculations predict the same sign sequence (+, -) for 4-hydroxypyrimidine and 5-N-2 but opposite sequences for 4,6-dihydroxypyrimidine (-, +) and 4-OH-5-N-2. Unfortunately, positions of type DS are relatively rare, so that MCD spectroscopy is likely to be of only limited usefulness in studies of tautomerism of the pyridone-hydroxypyridine type.

### Conclusion

The presence of two nearly degenerate transitions in the first absorption band of **1**, postulated previously on the basis of

calculations, has now been demonstrated. The MCD signs of the first two bands in pyridones and their aza and hydroxy derivatives follow readily from the qualitative theory of parts 1-3.

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## Magnetic Circular Dichroism of Cyclic $\pi$ -Electron Systems. 7.<sup>1,2</sup> Aza Analogues of Naphthalene

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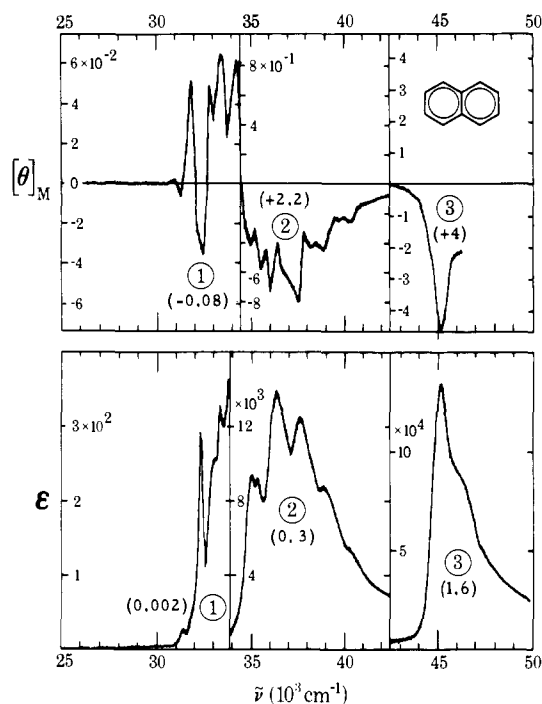
Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received January 5, 1978

**Abstract:** Magnetic circular dichroism of naphthalene, seven of its aza analogues, and the protonated forms of quinoline and isoquinoline is reported and interpreted. The  $B$  terms of the  $n\pi^*$  transitions are very weak; evidence for the presence of two low-energy  $n\pi^*$  transitions in phthalazine is obtained. Among the  $\pi\pi^*$  transitions, the signs of  $B(L_b)$  and  $B(L_a)$  are sensitive to the location of the heteroatoms and that of  $B(B_b)$  is positive. These signs are in excellent agreement with the general qualitative theory of parts 1-3 for an odd-soft chromophore and its response to inductive substitution. Magnetic mixing of  $n\pi^*$  with  $\pi\pi^*$  states appears to play a subordinate role as far as the signs of the  $B$  terms of the latter are concerned.

### Introduction

According to the general qualitative theory of the MCD signs of those transitions in cyclic conjugated  $\pi$ -electron systems which can be related to the L and B states of the perimeter, described in parts 1-3,<sup>4-6</sup> polycyclic benzenoid hydro-

carbons without a threefold or higher axis of symmetry are odd-soft chromophores. Some very definite predictions were reached in part 3<sup>6</sup> for effects of inductive (I) and mesomeric (E) substitutions on their MCD signs. In the present paper, we investigate the effect of I substitution, exemplified by the aza "substituent", on the MCD spectrum of naphthalene (**1**) and

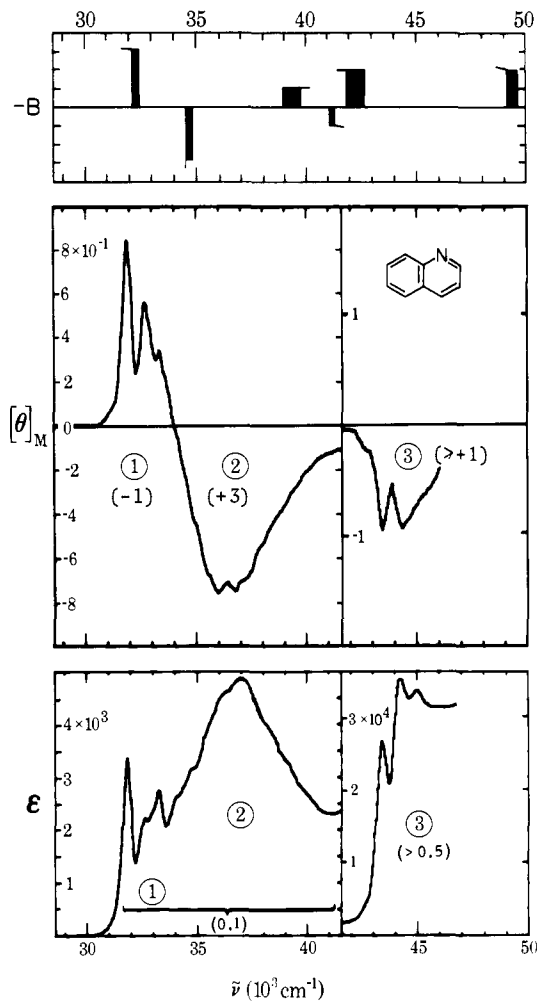


**Figure 1.** Naphthalene spectra: bottom, absorption (oscillator strength given); top, MCD ( $B$  terms in units of  $10^{-3}\beta_e D^2/\text{cm}^{-1}$ ).

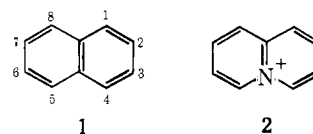
report the spectra of quinoline (1-N-1), isoquinoline (2-N-1), cinnoline (1,2-N-1), quinazoline (1,3-N-1), quinoxaline (1,4-N-1), phthalazine (2,3-N-1), and *as*-benzotriazine (1,2,4-N-1). The protonated forms of 1-N-1 and 2-N-1 have also been measured and will be referred to *as*-1-NH<sup>+</sup>-1 and 2-NH<sup>+</sup>-1, respectively. In part 8<sup>7</sup> we examine the effect of E substitution, and in parts 9<sup>8</sup> and 10,<sup>9</sup> the effect of simultaneous E and I substitution on the MCD of 1. As noted in part 1,<sup>4</sup> studies of substituent and aza-replacement effects on other odd-soft chromophores, anthracene, phenanthrene, and pyrene, are also being reported.

Singlet excited states of most of the above aza heterocycles have been analyzed in considerable detail by methods of UV spectroscopy as well as by calculations. Most of the experimental evidence is summarized in several recent theoretical studies,<sup>10-14</sup> which also give references to previous theoretical work. It is generally agreed that the long-wavelength weak absorption observed in most of these heterocycles is due to an  $n\pi^*$  transition (22 000–32 000  $\text{cm}^{-1}$ ), and in the case of 2,3-N-1 there has been some discussion as to whether two  $n\pi^*$  transitions are present in this region, as suggested by calculations.<sup>11,14</sup> For assignments of the  $n$  levels involved in the  $n\pi^*$  transitions, see ref 15 and 16. The three best characterized  $\pi\pi^*$  transitions are  $L_b$  (near 32 000  $\text{cm}^{-1}$ ),  $L_a$  (near 36 000  $\text{cm}^{-1}$ ), and  $B_b$  (near 45 000  $\text{cm}^{-1}$ ), similar to the analogous transitions in 1 which are discussed in more detail in part 8.<sup>7</sup> Calculations predict the presence of several additional weak transitions in the region of the  $B_b$  band, but experimental evidence for these is very limited. At somewhat higher energies ( $\sim 50\,000\text{ cm}^{-1}$ ), the  $B_a$  band is found, but this generally lies beyond our instrumental limit for MCD work.

MCD of 1 has been reported<sup>17,18</sup> and the sign of its  $B(L_b)$  calculated<sup>19</sup> previously. We have extended the MCD curve to higher energies (Figure 1) and use it for comparison. The MCD spectra of the heterocycles have not appeared in print previously, except for a brief description in our preliminary communications.<sup>20,21</sup> Very recently, Professor M. Hatano (Sendai) has informed us of his study of the azanaphthalenes, in which similar experimental data were obtained and a rather different method was used for their interpretation.<sup>26</sup>



**Figure 2.** Quinoline spectra: bottom, absorption (oscillator strength 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 (short, below 1; medium, 1–3; long, over 3; in units of  $10^{-3}\beta_e D^2/\text{cm}^{-1}$ ), calculated oscillator strengths by their three grades of thickness (less than 0.02; 0.2–0.5; over 0.5), and calculated polarizations by directions of the flags at the end with respect to the formula shown.



## Experimental Section and Calculations

The samples were purified by preparative GLC or by gradient sublimation as appropriate. They were commercial except for *as*-benzotriazine which was donated by Dr. P. Iversen from the Aarhus University, Denmark. Details of the measurements and PPP calculations were given in part 4.<sup>22</sup> The protonated forms 1-NH<sup>+</sup>-1 and 2-NH<sup>+</sup>-1 were measured in 1 M H<sub>2</sub>SO<sub>4</sub> in methanol.

For over a dozen aza analogues of 1, the PPP calculations were repeated using the finite-perturbation London-orbital method of Seamans and Linderberg.<sup>23</sup> The same signs but smaller magnitudes resulted for the several lowest  $B$  terms.

## Results

The results for 1 and its aza analogues are shown in Figures 1–8 and those for the protonated heterocycles 1-NH<sup>+</sup>-1 and 2-NH<sup>+</sup>-1 in Figures 9 and 10. An assignment of electronic transitions is indicated by consecutive numbering. As in aza analogues of benzene<sup>22</sup> and phenanthrene,<sup>24</sup> the MCD effect is much weaker for the  $n\pi^*$  bands than for the  $\pi\pi^*$  bands. The  $B$  term of the  $n\pi^*$  band is always negative, as it was in the az-

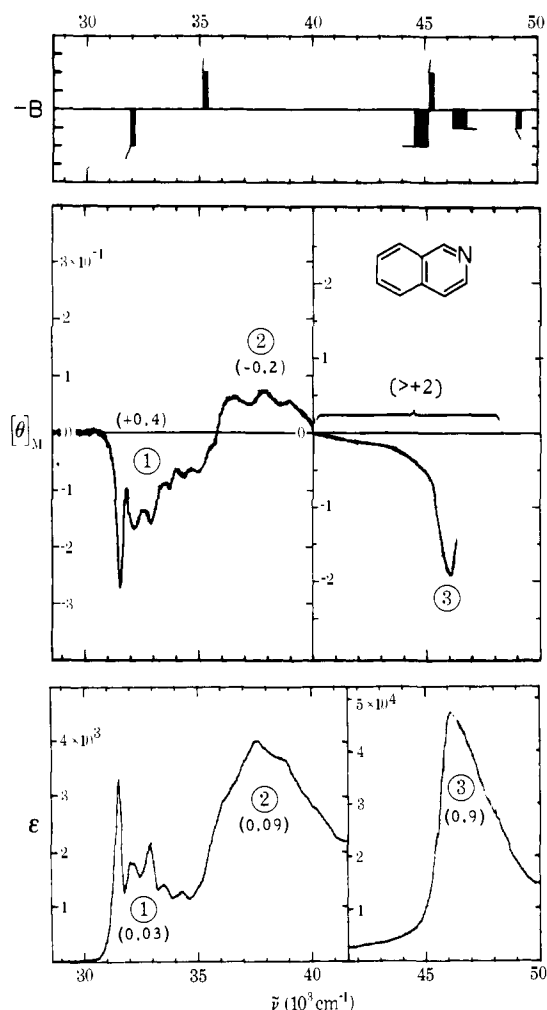


Figure 3. Isoquinoline. See caption to Figure 2.

ines,<sup>22</sup> except in 2,3-N-1 where one negative and one positive  $n\pi^*$  band appear to be present or, less likely, one  $n\pi^*$  band is present whose MCD shows strong vibronic effects. The signs of  $B(L_b)$  and  $B(L_a)$  are a sensitive function of the location of the heteroatom, and  $B(B_b)$  is positive, as expected for aza analogues of an odd-soft chromophore. There is little evidence for vibronic interactions except perhaps in the very weak MCD of the  $L_a$  band of 2,3-N-1 and possibly in its  $n\pi^*$  band as already mentioned. In 1,4-N-1, 1,2,4-N-1, and 1-NH<sup>+</sup>-1, the MCD spectra reveal the presence of two distinct transitions  $L_b$  and  $L_a$  where ordinary absorption curves suggest one.

### Discussion

**Naphthalene As an Odd-Soft Chromophore.** In **1** and other polycyclic benzenoid hydrocarbons,  $\Delta HOMO = \Delta LUMO$  to a good approximation as a result of alternant pairing, and general theory of parts 1-3<sup>4-6</sup> predicts that such  $\pi$  systems are odd-soft chromophores unless they possess a threefold or higher axis of symmetry ( $\Delta HOMO = |E(\mathbf{a}) - E(\mathbf{s})|$  and  $\Delta LUMO = |E(-\mathbf{a}) - E(-\mathbf{s})|$ , using the notation of part 1;<sup>3</sup> the perimeter orbital sequence is  $\mathbf{s}, \mathbf{a}, -\mathbf{a}, -\mathbf{s}$  in **1** and the same, or possibly  $\mathbf{a}, \mathbf{s}, -\mathbf{s}, -\mathbf{a}$ , in other polycyclic benzenoid hydrocarbons). In this type of chromophore,  $\mu^+$  contributions to the  $B$  terms of the  $L$  and  $B$  bands vanish, as does the  $\mu^-$  contribution to that of the  $L_b$  band, while the  $\mu^-$  contribution is small and positive for  $B(L_a)$  ( $L_a$ - $B_b$  mixing) and larger and positive for  $B(B_b)$  ( $B_b$ - $B_a$  mixing). The  $B_a$  band is not observed on the equipment used. These expectations are in good agreement with the MCD spectrum of **1** shown in Figure 1. The MCD

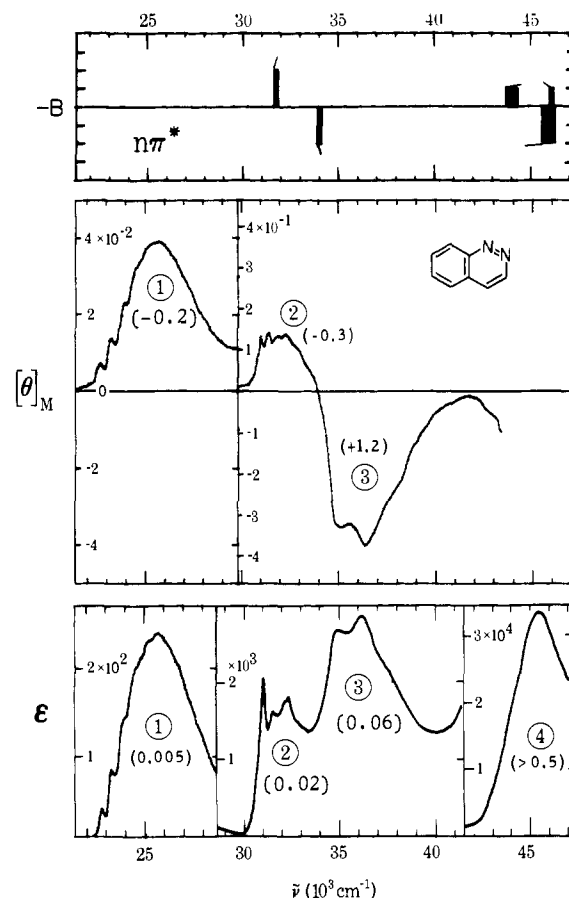


Figure 4. Cinnoline. See caption to Figure 2.

effect of the  $L_b$  band, predicted to vanish, is very weak and dominated by vibronic effects, not considered in the simple theory,  $B(L_a)$  is weakly positive, and  $B(B_b)$  is more strongly positive. In a better approximation, a small deviation from the equality  $\Delta HOMO = \Delta LUMO$  will occur and its sense will then determine the sign contributed by the no longer vanishing  $L_a$ - $L_b$  mixing (cf. ref 19).

**Effect of I Substituents.** For Hückel orbitals of **1**,  $c_{1,1}^2 \approx 0.18$ ,  $c_{1,2}^2 = 0.0$ ,  $c_{2,1}^2 = 0.07$ , and  $c_{2,2}^2 = 0.17$ . We conclude that position 1 is dominant (D) and position 2 subdominant (S). This is obvious when the inductive effect of the aza nitrogen on the adjacent carbons is neglected, but it also holds when it is considered, using numerical values deduced<sup>16</sup> from photoelectron spectra ( $\Delta\alpha = -3.3$  eV,  $\Delta\alpha' = -1.0$  eV). As discussed in part 3,<sup>6</sup> the +I aza replacement in a dominant position leads to  $\Delta HOMO < \Delta LUMO$  and in a subdominant one to  $\Delta HOMO > \Delta LUMO$ . Thus, we expect 1-aza replacement to make  $B(L_b)$  and  $B(B_b)$  more negative and  $B(L_a)$  more positive and 2-aza replacement to have just the opposite effect. Effects of multiple aza replacement on the  $\Delta HOMO$ - $\Delta LUMO$  difference are additive in the first approximation. Using Hückel orbitals and the above values of  $\Delta\alpha$  and  $\Delta\alpha'$ , the magnitudes of the contributions of 1-aza and 2-aza replacement to this difference are in the ratio -1.3:1. With increasing  $\Delta HOMO$ - $\Delta LUMO$  difference, the substituent-induced contributions to the  $B$  terms increase and the  $B$  terms gradually approach their limiting values given by the formulas of part 2.<sup>5</sup>

Agreement of the simple theory with our experimental results is excellent. In all cases dominated by 1-aza replacement,  $B(L_b) < 0$ ,  $B(L_a) > 0$ , and  $|B(L_a)| > |B(L_b)|$  as expected since both  $\mu^-$  and  $\mu^+$  terms contribute positively to  $B(L_a)$ . In 2-N-1 and 2,3-N-1, 2-aza replacement dominates, and we observe  $B(L_b) > 0$ ,  $B(L_a) < 0$ , and  $|B(L_a)| < |B(L_b)|$ , again

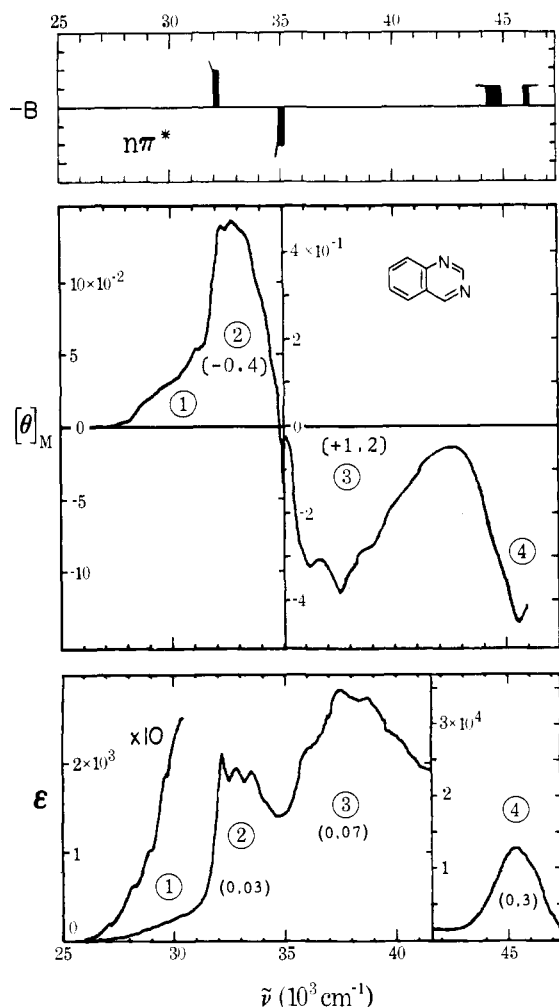


Figure 5. Quinazoline. See caption to Figure 2.

as expected, since now, the negative  $\mu^+$  and positive  $\mu^-$  contributions to  $B(L_a)$  counteract each other. A more quantitative treatment of  $B(L_b)$  and  $B(L_a)$  as a function of the number and location of the aza substituents is hampered by the strong overlap of the two oppositely signed bands which makes reliable estimates of the two  $B$  terms impossible. The positive  $\mu^-$  contribution to  $B(B_b)$  is apparently sufficiently large, compared with the substituent-induced  $\mu^+$  contribution to this term, that it always safely dominates.

As elaborated in more detail in part 2,<sup>5</sup> the purpose of the simple PPP calculations shown in the figures is to evaluate the performance of the simple  $\pi$ -electron theory without any adjustment for MCD purposes; these calculations show only the  $\mu^+$  contributions and should therefore be interpreted as indicating the difference between the aza heterocycles and parent **1**; in this, they are very successful for the two L bands. They predict consistently that several transitions are present in the region of the  $B_b$  band, but our MCD curves for azanaphthalenes are noisy and not very reliable in this region.

The excellent agreement between the signs predicted from our PPP calculations using the standard formulation and those obtained using the Seamans-Lindberg program based on finite perturbation theory and London orbitals and thus avoiding origin dependence<sup>23</sup> is reassuring.

**Azonia Substitution.** In the 1 position, azonia replacement has almost exactly the same effect as aza replacement, only somewhat stronger (Figure 9), but a quantitative comparison is impossible because of the strong overlap of the  $L_b$  and  $L_a$  transitions in 1-NH<sup>+</sup>-**1**; indeed, they cannot be discerned

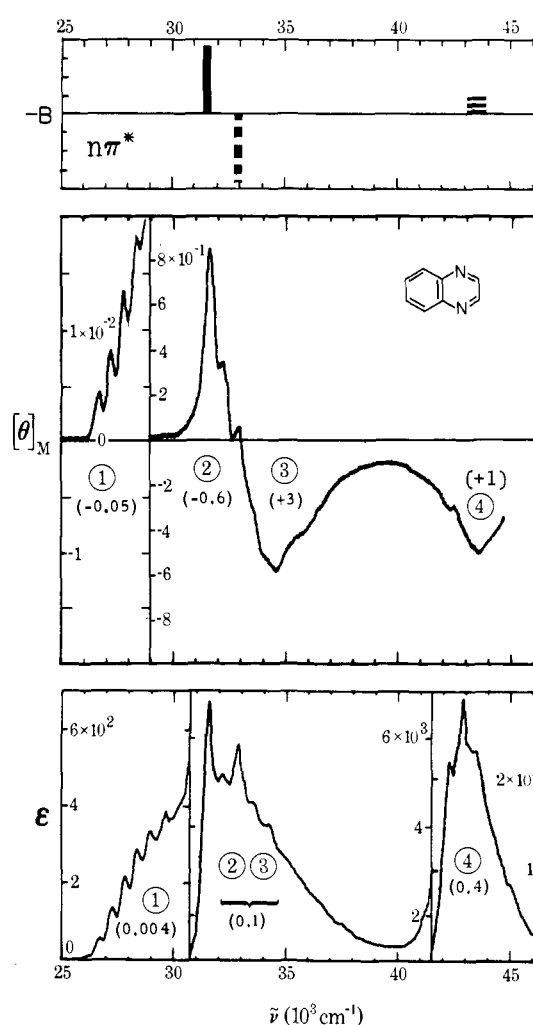


Figure 6. Quinoxaline. See caption to Figure 2. Solid bars indicate horizontal polarization and broken bars vertical polarization with respect to the formula shown.

separately in the absorption curve. The situation is different for replacement in the 2 position. While in 2-NH<sup>+</sup>-**1** a fairly strong positive  $B(B_b)$  is present as in all other naphthalene analogues, presumably due to a  $\mu^-$  contribution ( $B_b$ - $B_a$  mixing),  $B(L_b)$ , though positive as expected, is very small, and  $B(L_a)$  is small and positive as in naphthalene (Figure 10). Certainly, the  $\mu^+$  contribution due to substituent-induced mutual mixing of  $L_b$  and  $L_a$  states does not dominate the  $B$  terms of both of these states as it does in 2-N-**1**, and it may even be vanishingly small, although NH<sup>+</sup> has a stronger +I effect than N. It is tempting to say that the transition moments of the  $L_b$  and  $L_a$  transitions, which are known to be sensitive to 2-substitution for reasons which are now well understood,<sup>25</sup> have been rotated so close to each other in 2-NH<sup>+</sup>-**1** that the effect of their mutual mixing has been greatly reduced. This suggests that in this molecule, a first-order description of the perturbing effect of NH<sup>+</sup> is not adequate and that  $\Delta HOMO \approx \Delta LUMO$ , so that 2-NH<sup>+</sup>-**1** is approximately a zero-soft MCD chromophore in the sense of part 2.<sup>5</sup> This is not reflected in our PPP calculations which incorrectly predict little difference between 2-N-**1** and 2-NH<sup>+</sup>-**1** for the parameters used, and it will be interesting to employ an all-valence electron method.

In the case of symmetrical azonia substitution these difficulties will not occur. For instance, one can confidently expect the lower of the L bands of quinolizium **2** to have a strong positive  $B$  term and the higher one to have a strong negative  $B$  term.

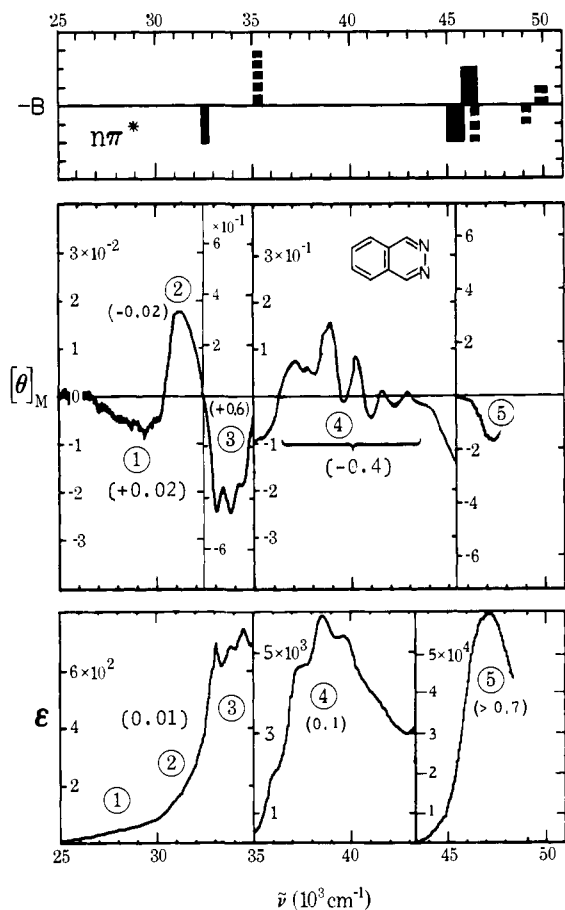


Figure 7. Phthalazine. See caption to Figures 2 and 6.

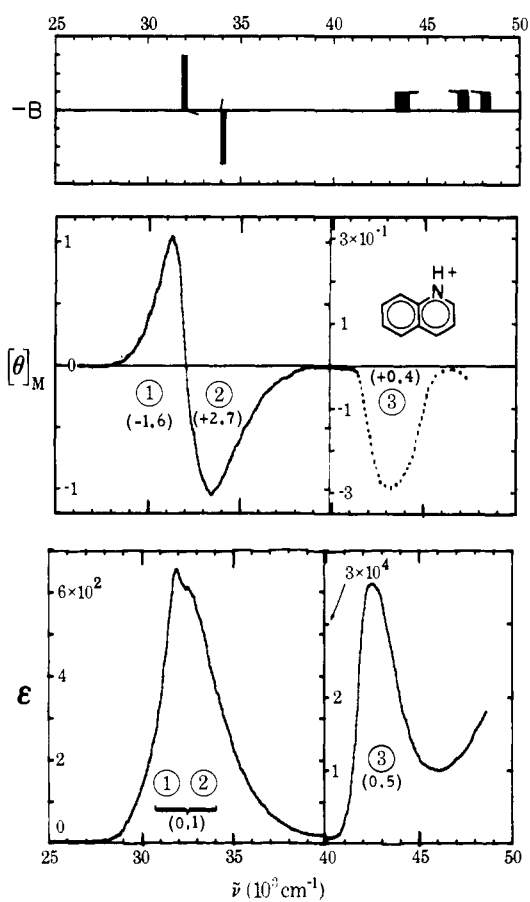


Figure 9. Protonated quinoline. See caption to Figure 2.

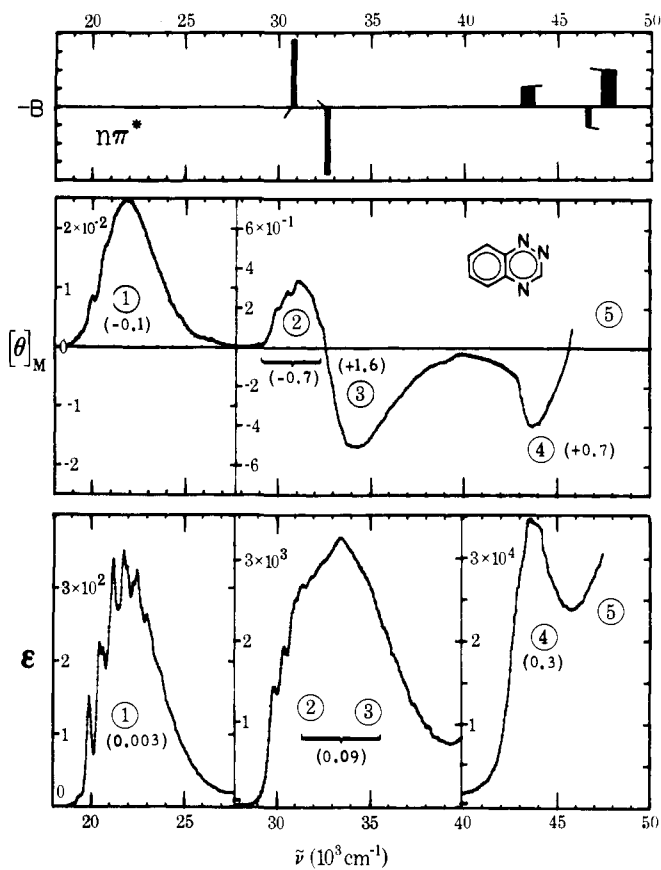
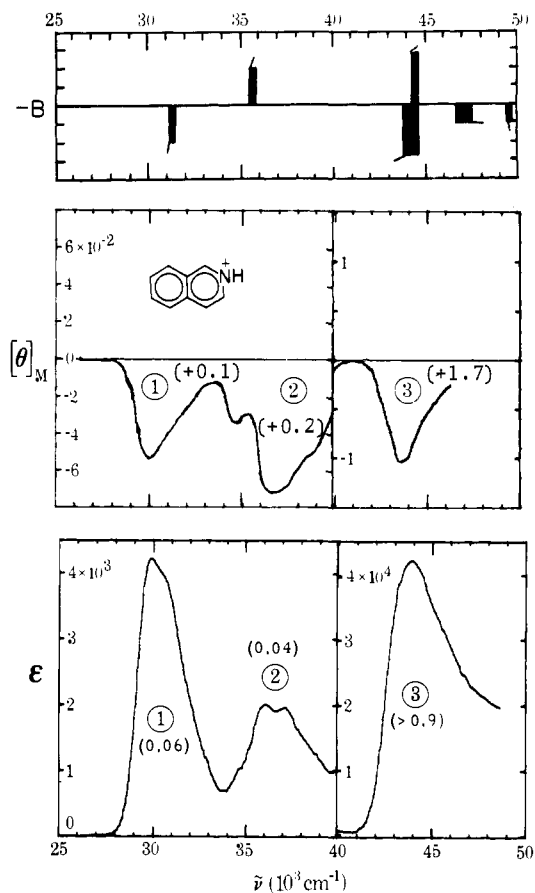
Figure 8. *as*-Benzotriazine. See caption to Figure 2.

Figure 10. Protonated isoquinoline. See caption to Figure 2.

**Role of the  $n\pi^*$  States.** Similarly as in the case of the azines discussed in part 4,<sup>22</sup> it appears that the  $B$  terms of the  $\pi\pi^*$  transitions can be accounted for without any reference to  $n\pi^*-\pi\pi^*$  mixing. Again, there are additional reasons to believe that the contributions of such mixing to the  $B$  terms of either the  $\pi\pi^*$  or the  $n\pi^*$  transitions are relatively small and do not dominate the signs of the  $B$  terms of  $\pi\pi^*$  transitions. The observed  $B$  terms of  $n\pi^*$  transitions are very small, and removal of these transitions by protonation of 1-N-1 and 2-N-1 has no profound effect on the  $B$  terms of  $\pi\pi^*$  transitions. The spectra of 1-N-1 and 1-NH<sup>+</sup>-1 are very similar, and the differences between  $B(L_a)$  in 2-N-1 and in 2-NH<sup>+</sup>-1 can be accounted for by consideration of  $\pi$  electrons alone as already discussed. Some reasons for the smallness of the effect of  $n\pi^*-\pi\pi^*$  mixing have been suggested in part 2.<sup>5</sup>

It is interesting to note the shape of the MCD curve for 2,3-N-1 in the  $n\pi^*$  region. Although the sign reversal from negative to positive could be assigned to vibronic effects, the shape of the curve does not make such an explanation very likely, and no analogy exists in any of the other  $n\pi^*$  bands which we have measured. On the other hand, published calculations<sup>11,14</sup> predict the presence of two  $n\pi^*$  transitions below the onset of  $\pi\pi^*$  absorption in 2,3-N-1 but not in the other azanaphthalenes studied here and discuss some previous tentative experimental evidence. We propose that the MCD curve of 2,3-N-1 provides experimental support for the existence of the two predicted  $n\pi^*$  transitions. A high-resolution study would be quite interesting, but lies beyond the capabilities of the equipment presently available to us.

## Conclusions

The simple theory of parts 1-3<sup>4-6</sup> accounts very well for the MCD signs and, qualitatively, even for intensities of MCD peaks of the aza analogues of 1 investigated here. Thus, its predictions for other azanaphthalenes probably are quite reliable. Full PPP calculations by a standard nonadjusted method provide very similar results for the azanaphthalenes but work less well for the azonia derivatives.

Additional support is also obtained for the presence of two  $n\pi^*$  transitions in phthalazine below the onset of  $\pi\pi^*$  absorption. The  $B$  terms of  $n\pi^*$  transitions are very small. The existence of low-energy  $n\pi^*$  states seems to have no effect on the applicability of the  $\pi$ -electron theory approach to the  $B$  terms of  $\pi\pi^*$  transitions, although this ignores magnetic  $n\pi^*-\pi\pi^*$  mixing.

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