

of the role of $n\pi^*$ states in the magnetic mixing throughout our qualitative discussion as well as in the PPP calculations seems to have no untoward effect on the agreement with experiment. As discussed in more detail in part 2,⁵ $n\pi^*$ states apparently play a secondary role as far as signs of B terms of $\pi\pi^*$ transitions are concerned.

Conclusions

The simple theory of parts 1–3^{4–6} rationalizes the response of the MCD spectrum of **1** to E substitution, and its predictions for other azines are to be taken seriously. The full PPP calculation produces very similar results, and the neglect of $n\pi^*$ states appears to have no serious effect on the discussion of signs of B terms of $\pi\pi^*$ transitions.³⁰

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Magnetic Circular Dichroism of Cyclic π -Electron Systems. 6.¹ Pyridones and Related Heterocycles

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Abstract: Magnetic circular dichroism of seven pyridones, pyrimidones, and hydroxypyridones is reported. The plus, minus sign pattern of the B terms of the L bands observed for all of these compounds, and previously also observed for uracil, agrees with expectations based on the qualitative theory of parts 1–3, permitting extrapolation to other heterocycles of this type. The first MCD sign of cytosine is also interpreted. Finally, the theory permits some general statements concerning the utility of MCD spectroscopy for study of tautomeric equilibria of the pyridone–hydroxypyridine type.

Introduction

The simple qualitative theory of MCD signs of bands related to L and B transitions of the perimeter, described in parts 1,² 2,³ and 3⁴ has been found to work well for the even-soft chromophores, pyridine and the diazines,⁵ as well as their derivatives carrying simple mesomeric (E) substituents.^{1b} Cyclic lactams of the pyridone type can be formally derived from protonated azines by introduction of the very strong –E substituent –O[–] and thus can be viewed as –E-substituted derivatives of an even-soft chromophore, isoelectronic with the amino derivatives of the azines investigated in part 5.^{1b} General similarities between the cation of an amino-*N*-heteroaromatic compound and the neutral species of the corresponding oxo analogue are well-known from absorption spectroscopy.^{6–8} In

order to assess the scope and limitations of the simple model described in parts 1–3, we presently investigate a series of pyridones. The compounds are of intrinsic interest as cornerstones of a large part of heterocyclic chemistry and because of their widespread occurrence in nature.

We shall refer to γ -pyridone as **1**, and α -pyridone as **2**, and we shall indicate the location of methyl, hydroxy, and aza replacement by symbols such as 1-CH₃-**2**. The MCD spectra of two related compounds, uracil (**3**) and cytosine (**4**), have been published.⁹

Excited singlet states of **1**, of **2**, and of their simple derivatives in their various tautomeric forms have been the subject of considerable attention. Most of the spectroscopic work was of an analytical nature and was concerned with elucidation of the various possible tautomeric equilibria. It will not be re-

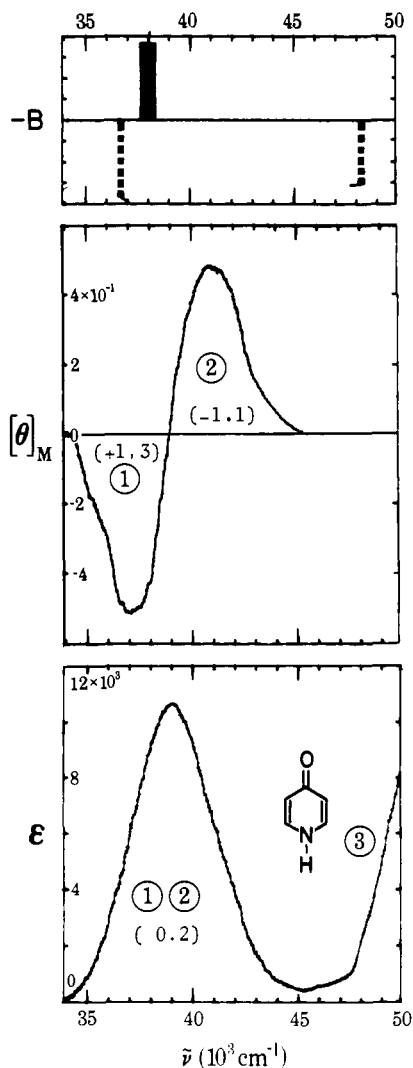


Figure 1. 4-Pyridone: bottom, absorption (oscillator strengths given); center, MCD (B terms given in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$); top, calculation [a broken (full) bar indicates horizontal (vertical) polarization with respect to the formula given; the thickness of the bar indicates intensity, and its direction and length the sign and magnitude of the B term].

viewed here, since a recent summary is available.¹⁰ The energies, intensities, and polarizations of electronic transitions in the pyridones and their N -methyl derivatives were analyzed in qualitative terms¹¹ and calculated by π -electron^{6,12,13} and all-valence electron (CNDO)¹⁴ semiempirical methods. Both approaches yield similar results for $\pi\pi^*$ transitions, in good agreement with experiments. On the basis of these calculations, the lowest absorption band of **1** was postulated to contain two $\pi\pi^*$ transitions, the lower of which is quite weak, and we shall show below that two transitions are indeed present. The $n\pi^*$ transitions calculated by the CNDO method¹⁴ appear at much too low energies. There is no experimental evidence for any such transition below the first $\pi\pi^*$ band, and in the case of 1-CH₃-**2**, there is good evidence against it, based on polarized fluorescence,¹⁵ which also shows that the first two $\pi\pi^*$ transitions of this molecule are polarized approximately perpendicular to each other, as demanded by theory. Also, the transition energies, intensities, and polarizations for 3-N-**2**, 5-N-**2**, 3-OH-**2**, and 4-OH-**2** have been computed in the π -electron approximation and found to compare well with absorption curves.^{6,16-18}

To summarize, compounds related to **1** and **2** generally exhibit two $\pi\pi^*$ transitions in the wavelength region accessible to us in MCD measurements, and these are distantly related

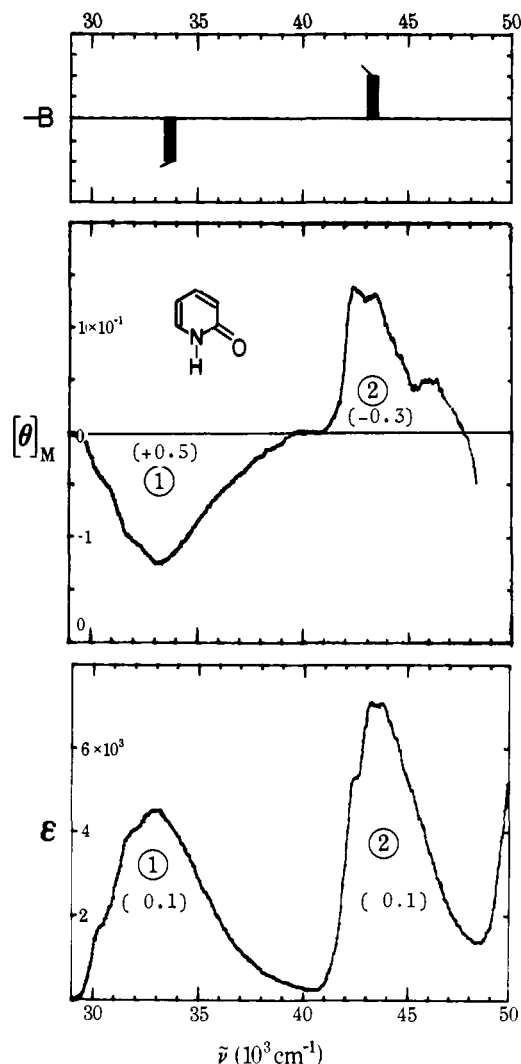
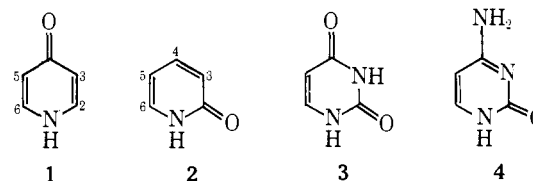


Figure 2. 2-Pyridone. See caption to Figure 1. Flags at the ends of bars representing calculated transitions indicate calculated polarization directions with respect to the formula shown.

to the two L states of benzene, with varying degrees of charge transfer from the $-E$ substituent. Transitions of $n\pi^*$ character may be present in this region, but their existence has not been proven.



Experimental Section and Calculations

The samples were commercial and were purified by sublimation except for 4-OH-**2**, which was crystallized twice from ethanol, and 1-CH₃-**2**, which was distilled. Details of the measurements were given in part 4.⁵ The solvent was acetonitrile. 1-CH₃-**2** was remeasured in cyclohexane but did not show a significantly increased amount of fine structure in the MCD spectrum. The calculations were of the PPP type and were performed as described in part 4⁵ except that C-C bond lengths and resonance integrals were not all assumed to be equal. Instead, they were obtained in a self-consistent manner from calculated ground-state bond orders using the formulas $\beta_{\mu\nu} = -2.318 \exp[0.335(p_{\mu\nu} - 2/3)]$ and $r_{\mu\nu} = 1.517 - 0.18 p_{\mu\nu}$. The one-center parameter for the amino nitrogen was $A_{N+} = 10.15$ eV. Use of the value 9.1 eV did not change MCD signs but gave poorer agreement with excitation energies. The resonance integral of the C=O bond

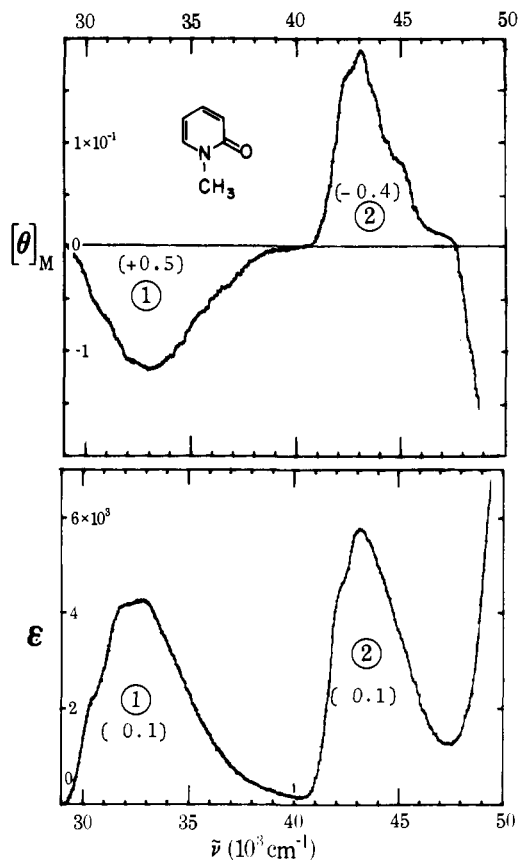


Figure 3. 1-Methyl-2-pyridone: bottom, absorption (oscillator strengths given); top, MCD (B terms given in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$).

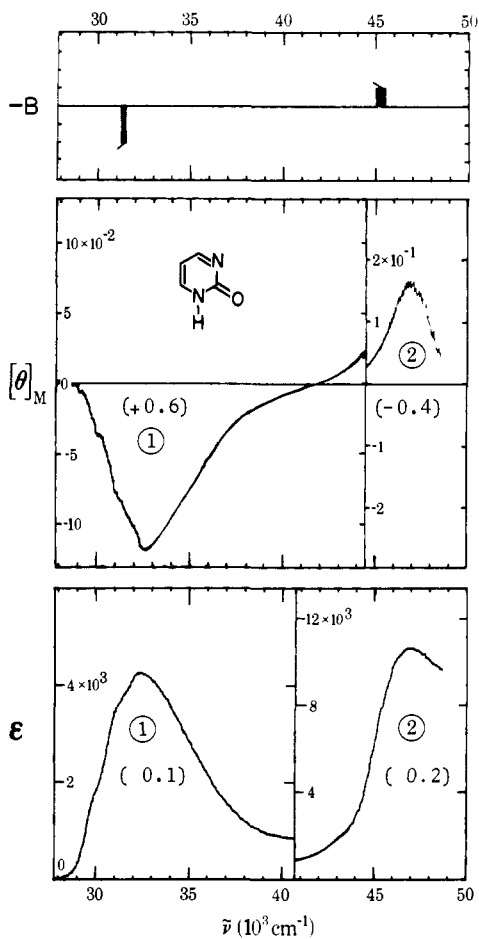


Figure 4. 2-Pyridone. See captions to Figures 1 and 2.

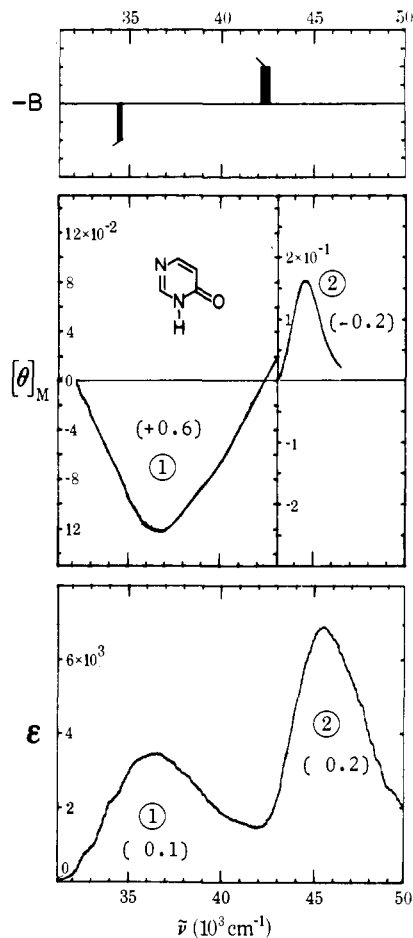


Figure 5. 4-Pyrimidone. See captions to Figures 1 and 2.

was -2.8 eV and once again, the MCD results were insensitive to the exact value of this parameter.

Results

The results are shown in Figures 1–7. The assignment of two $\pi\pi^*$ transitions proposed is based on spectral shapes, similarities to amino derivatives of azines, and previous work on these molecules, cited in the introduction. In **1**, the two transitions are clearly seen in MCD but not in the absorption spectrum. The MCD spectra provide no evidence for the presence of additional transitions of $\pi\pi^*$ or $n\pi^*$ type. Transition 1 is identified with the lower of the two L states, L_1 , and transition 2 with the higher one, L_2 , on the basis of similarity to substituted azines and inspection of the PPP wave functions. The MCD signs are the same throughout: $B(L_1) > 0$ and $B(L_2) < 0$. The formulas shown in the figures are those of the predominant tautomers,¹⁰ to which the calculations also refer. In water, 3-H and 1-H tautomers of 4-pyrimidone (5-N-2 and 3-N-1) are believed to coexist in an approximately 1:1 ratio,¹⁰ and this may be true in acetonitrile as well. The calculated results shown in Figure 5 refer to 5-N-2; those calculated for 3-N-1 are almost identical and would fit the experimental observations just as well. Hydrogen-bonded dimer formation appears not to be reflected in the MCD spectra (compare Figures 2 and 3).

Discussion

Substituent Effects on MCD of Protonated Pyridine. Since we are proposing to view the pyridones and their derivatives as formally derived from pyridinium by attachment of the $-E$ substituent $-O^-$, and possibly additional perturbations, it is appropriate to briefly summarize the expectations provided

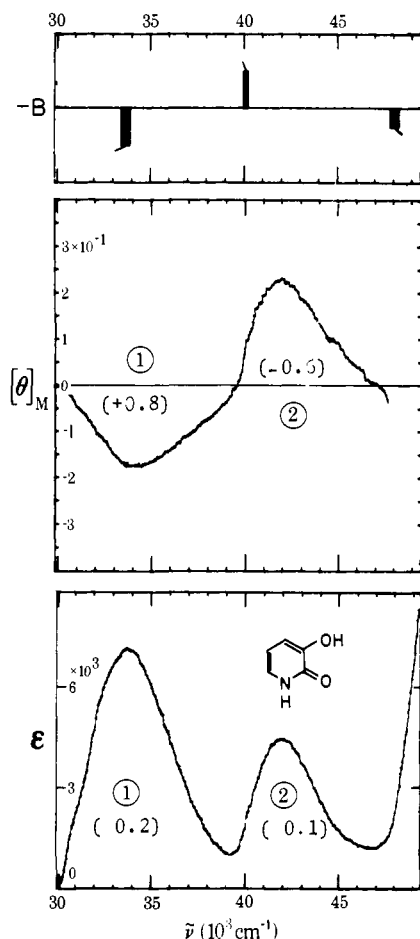


Figure 6. 3-Hydroxy-2-pyridone. See captions to Figures 1 and 2.

by the simple theory of part 3⁴ for the effect of $-E$ substitution on an even-soft chromophore such as pyridinium.

There are two types of positions in an even-soft chromophore, differing in the effect which E substitution has on the sign of $\Delta HOMO - \Delta LUMO$, which in turn determines the signs contributed to B terms ($\Delta HOMO = |E(\mathbf{a}) - E(\mathbf{s})|$ and $\Delta LUMO = |E(-\mathbf{a}) - E(-\mathbf{s})|$, where the orbital labels \mathbf{a} , \mathbf{s} , $-\mathbf{a}$, and $-\mathbf{s}$ have the meanings defined in part 1²). In positions of type DS ($+E$ dominant, $-E$ subdominant), e.g., position 4 in pyridinium, the contribution of a $+E$ substituent to $B(L_1)$ is negative and the sign of the contribution of a $-E$ substituent to $B(L_1)$ depends on its strength. A weak $-E$ substituent will provide a negative contribution, an intermediate one will be without effect, and a strong one will produce a positive contribution. In the case of protonated pyridines, results of part 5^{1b} show that the strength of an NH_2 group is sufficient to produce a positive contribution, while that of the OH group is not. In positions of type SD ($+E$ subdominant, $-E$ dominant), e.g., position 2 and 3 in pyridinium, the contribution of a $-E$ substituent to $B(L_1)$ is positive and the sign of the contribution of a $+E$ substituent depends on its strength. A weak $+E$ substituent will provide a positive contribution, an intermediate one will be without effect, and a strong one will produce a negative contribution. In all of these cases, the sign of the substituent effect on $B(L_2)$ will be just the opposite of that for $B(L_1)$.

These substituent effects, due to the μ^+ magnetic moment and originating in L_1-L_2 mixing, are to be added to the small intrinsic B terms which are due to the μ^- magnetic moment and originate in $L-B$ mixing; for both L bands these are positive (or zero).

MCD Spectra of Pyridones and Related Heterocycles. Since

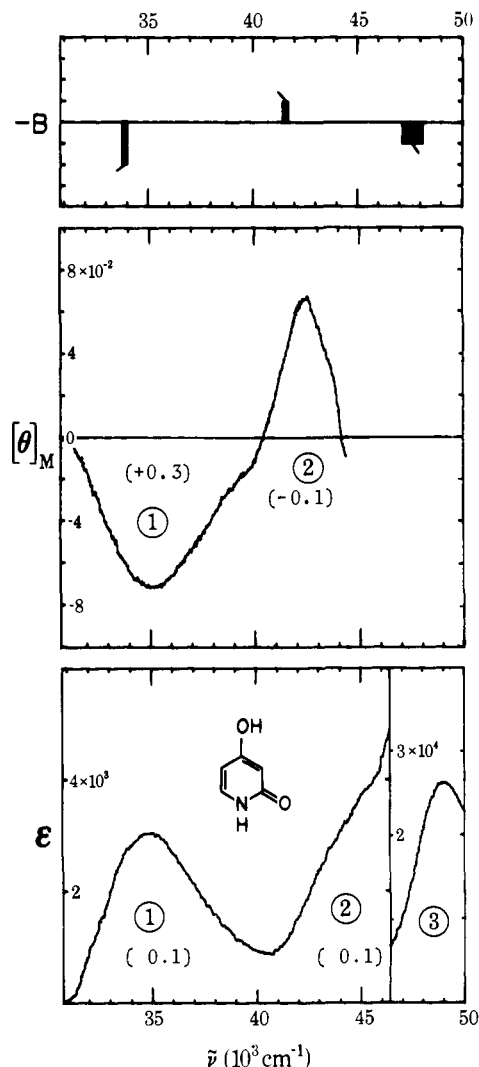


Figure 7. 4-Hydroxy-2-pyridone. See captions to Figures 1 and 2.

the $-O^-$ substituent has an even somewhat stronger $-E$ effect than NH_2 ,^{19,20} it should provide a positive μ^+ contribution to $B(L_1)$ in a protonated azine regardless of its position of attachment and a similar but negative contribution to $B(L_2)$.

The effect of additional $-E$ substitution, such as hydroxy, can be estimated roughly by inspection of the MO's of benzene, using PMO-type arguments (cf. Figure 5 in ref 5). In **1**, the orbital \mathbf{s} should lie above \mathbf{a} , and both 2-OH and 3-OH substitution should therefore decrease the $\Delta HOMO - \Delta LUMO$ difference, reducing the magnitude of the μ^+ contributions. In **2**, the orbital \mathbf{a} should lie above \mathbf{s} , so that OH substitution in any position but 4 should increase the $\Delta HOMO - \Delta LUMO$ difference, increasing the μ^+ contributions, whereas 4-OH substitution should decrease them. At a higher level of sophistication, the MO coefficients of **1** and **2** obtained from a PPP calculation can be used instead of those of benzene; this does not change the results qualitatively. The theoretical expectations are in excellent agreement with the available experimental data (Figures 1-7). The qualitative arguments are also in agreement with results of full PPP calculations shown in the figures.

The MCD signs previously published for uracil (**3**)⁹ are now understandable, considering its formal construction from a doubly protonated pyrimidine and two $-O^-$ substituents. The reduced intensity of its first MCD band relative to 3-N-**2** and 5-N-**2** is understandable since in uracil the effects of the two $-O^-$ substituents on $\Delta HOMO$ are opposed: 2- O^- substitution raises the energy of the \mathbf{s} orbital of a doubly protonated py-

rimidine, and 4-O⁻ substitution raises its α orbital, but to a lesser degree. In the published spectrum of cytosine (**4**)⁹ the first transition (37 600 cm⁻¹) has the expected positive B term. The next transition occurs near 42 500 cm⁻¹, 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.⁹

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⁻ 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 π -Electron Systems. 7.^{1,2} Aza Analogues of Naphthalene

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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 π -electron systems which can be related to the L and B states of the perimeter, described in parts 1-3,⁴⁻⁶ polycyclic benzenoid hydro-

carbons without a threefold or higher axis of symmetry are odd-soft chromophores. Some very definite predictions were reached in part 3⁶ 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