

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 5.^{1,2} Derivatives of Pyridine

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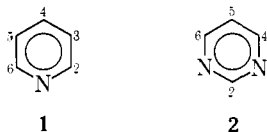
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Abstract: Magnetic circular dichroism of 16 fluoro, chloro, hydroxy, amino, and cyano derivatives of pyridine, pyrimidine, or their protonated forms is reported and interpreted. The B terms of the $n\pi^*$ transitions, where observed, are extremely weak with the single exception of 4-cyanopyridine. As for $\pi\pi^*$ transitions, the signs of $B(L_b)$ and $B(L_a)$ are sensitive to the location and nature of substituents and are in excellent agreement with the general qualitative theory of parts 1-3 for even-soft chromophores and their response to mesomeric 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 simple theory of MCD signs of transitions of L and B types in cyclic π -electron systems described in parts 1-3,⁴⁻⁶ the azines should be, to a good approximation, even-soft chromophores. Thus, the signs of their two L bands, and possibly their B bands, should be sensitive to substituent effects in a simply predictable way, and the nature of their response to substitution should be distinctly different from that shown by double-soft or odd-soft chromophores.⁶

In the present paper, we compare the theoretical expectations with MCD spectra for 14 fluoro, chloro, hydroxy, amino, and cyano derivatives of pyridine (**1**) and two derivatives of pyrimidine (**2**), including some protonated on ring nitrogen. In part 6,⁷ we apply the same principles to a class of more severely perturbed azines, the pyridones, and their analogues and derivatives.



Excited singlet states of substituted derivatives of **1** have been investigated repeatedly.⁸⁻²⁸ The spectra of fluoro and chloro derivatives reveal the presence of both a $n\pi^*$ and a $\pi\pi^*$ transition near 36 000 cm^{-1} in the case of 3-substitution, but only the much stronger $\pi\pi^*$ transition is apparent in the 2- and 4-substituted compounds.⁸ These bands are analogous to those of **1**.²⁹ A recent study of the cyanopyridines²² provides safe assignments also in this case; in the 3 and 4 isomers both transitions were observed. The spectra of the amino derivatives differ more from those of parent **1** (the 2- and 4-hydroxy derivatives normally occur in the carbonyl tautomer form). Much earlier work^{14,27,28} and some recent work²⁶ assigns the $n\pi^*$ state below the lower of the $\pi\pi^*$ states in this case, too. However, rotational band contour analysis has been performed on the 2-amino compound and showed clearly that the $\pi\pi^*$ transition is lowest.²⁴ This appears likely also for the other isomers because of the observed great similarity in the fine vibrational structure of vapor-phase spectra of the three aminopyridines and of aniline.²⁵ At any rate, the bulk of the two absorption bands observed near 36 000 and 43 000 cm^{-1} is undoubtedly due to two transitions of $\pi\pi^*$ character, the former being analogous to the lowest $\pi\pi^*$ transition in **1** and to the $B_{2u}(L_b)$ band of benzene and the latter to the second $\pi\pi^*$ transition in **1** and to the $B_{1u}(L_a)$ band of benzene. In some derivatives, one or the other band may be very weak and difficult to observe in absorption, and this is accounted for by theory (see below). Obviously, however, even in the hydroxy and amino compounds, an $n\pi^*$ transition should be present

somewhere in the general vicinity of 35 000 cm^{-1} , where it occurs in **1**, or somewhat higher, and should contribute a small part of the intensity of the observed first band. This is also indicated by CNDO calculations.¹⁶ It has been suggested on the basis of calculations but without experimental evidence that the lower of the two bands of aminopyridines is actually composed of several $\pi\pi^*$ transitions,¹⁸ but this claim appears unconvincing to us.

Experimental Section and Calculations

The samples were commercial and were purified by preparative GLC or by gradient sublimation as appropriate. 2-OH-2-HCl was crystallized from ethanol twice. Details of the measurements and PPP calculations were given in part 4.² The spectrum of 2-OH-2-HCl was taken in acetonitrile solvent, the spectra of the protonated forms of 4-Cl-1 and 4-NH₂-1 were taken in 0.1 N aqueous HCl, and the spectrum of 4-OH-1 was taken in 0.5 N aqueous HCl.

Results

The spectra are shown in Figures 1-16. All of the MCD effects are relatively weak. An assignment of individual electronic transitions is indicated and follows previous work. This holds particularly for the assignment of $n\pi^*$ transitions^{8,22} which are extremely weak both in absorption and, with the exception of 4-CN-1, in MCD, so that they generally appear in our spectra only as very indistinct shoulders, indicated by arrows in the figures. The $n\pi^*$ transitions are not at the center of our interest at the present time; they need to be remeasured with a higher resolution instrument.

The signs of the $\pi\pi^*$ bands are a sensitive function of the position and nature of substitution as expected for an even-soft chromophore. There is little evidence for vibronic interactions. The MCD spectra do not reveal the presence of any new electronic transitions; however, for the protonated forms of 4-NH₂-1 and 4-OH-1, they clearly resolve the first two $\pi\pi^*$ transitions which overlap completely in the absorption curves.

Discussion

Azines as Even-Soft Chromophores. As described in detail in parts 2-4,^{2,5,6} simple theory predicts that the azines are even-soft chromophores so that the μ^+ contributions to the B terms of their L and B bands vanish ($\Delta\text{HOMO} = \Delta\text{LUMO}$, where $\Delta\text{HOMO} = |E(\mathbf{a}) - E(\mathbf{s})|$ and $\Delta\text{LUMO} = |E(-\mathbf{a}) - E(-\mathbf{s})|$; orbital labels are as in part 1⁴). In a better approximation, $\Delta\text{HOMO} \approx \Delta\text{LUMO}$, and extremely weak μ^+ contributions to the B terms of **1** and somewhat larger ones to those of **2** appear (L_a - L_b mixing). Their signs are $B(L_b) > 0$ and $B(L_a) < 0$ for both **1** and **2**. The μ^- contribution to $B(L_a)$ vanishes almost exactly in all cases, and the contributions to $B(L_b)$, due to L_b - B_a mixing, are positive and small. The feeble

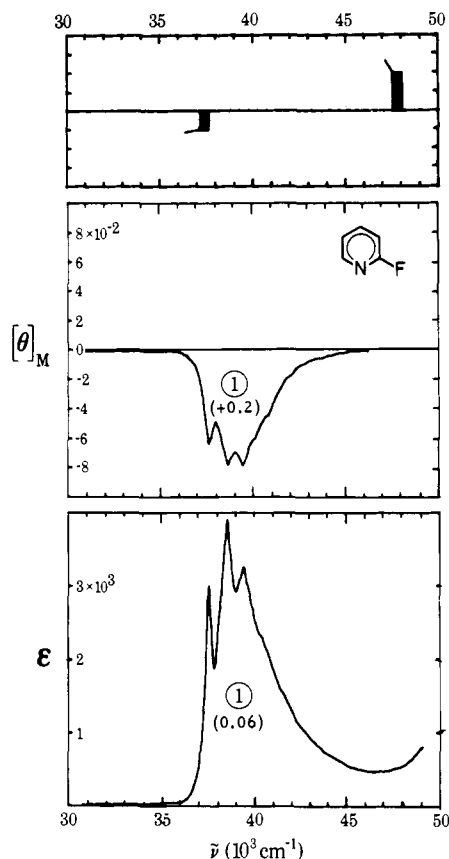


Figure 1. 2-Fluoropyridine: absorption (oscillator strength given), MCD (B term in units of $10^{-3}\beta_c D^2/\text{cm}^{-1}$), and calculation for $\pi\pi^*$ only; transition energies, intensities (bar thickness), polarizations (flags), and signs and magnitudes (bar length) of $-B$ terms are given.

preferences for the sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$ inherent in the parent azines are easily overruled by substituent effects. A nonvanishing $\Delta\text{HOMO} - \Delta\text{LUMO}$ difference brings in nonvanishing μ^+ contributions, and these then easily dominate the signs of the B terms of the L bands.

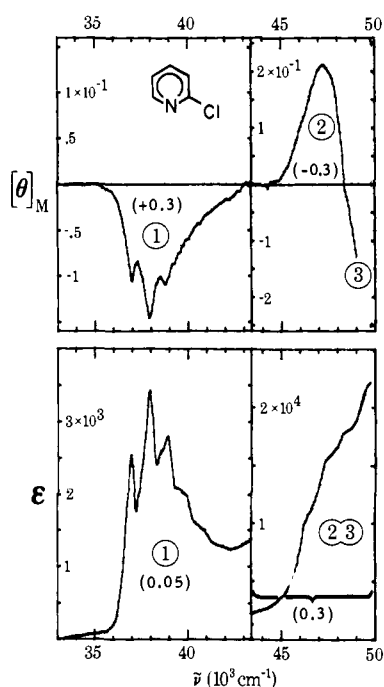


Figure 2. 2-Chloropyridine. See caption to Figure 1.

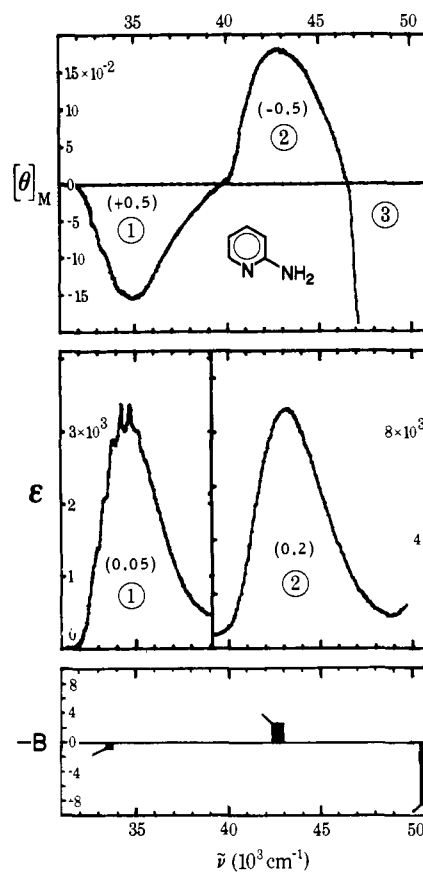


Figure 3. 2-Aminopyridine. See caption to Figure 1.

E Substitution in 1. Positions 2 and 3. Inspection of benzene or pyridine orbitals shows that these positions are +E subdominant and -E dominant (SD).⁵ For -E substitution, one expects $\Delta\text{HOMO} > \Delta\text{LUMO}$ and thus a positive μ^+ contri-

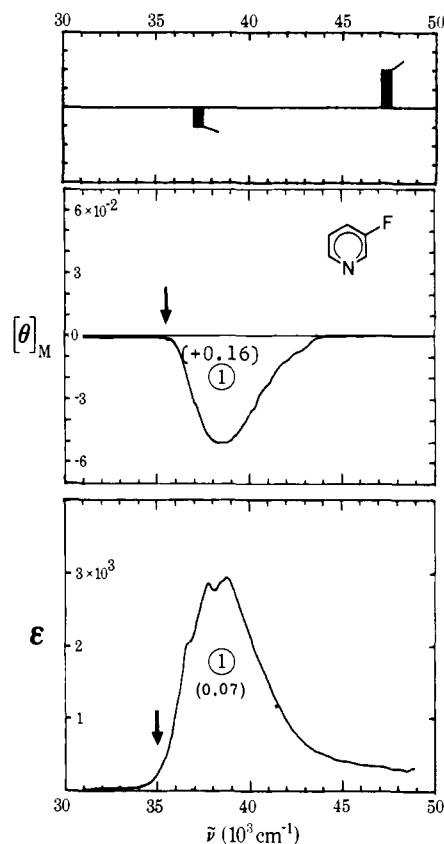


Figure 4. 3-Fluoropyridine. See caption to Figure 1.

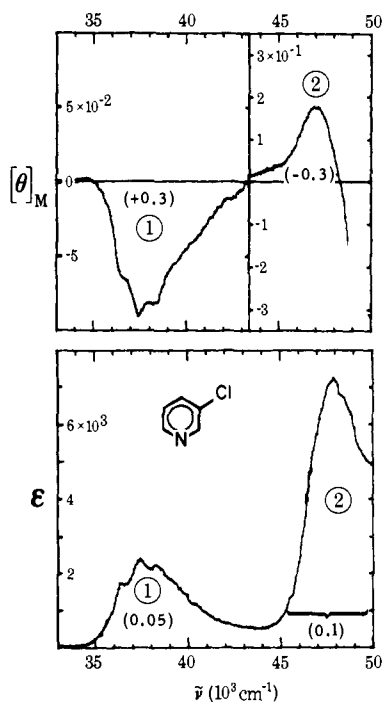


Figure 5. 3-Chloropyridine. See caption to Figure 1.

tribution to the B term of the lower of the two $G \rightarrow L$ transitions, $B(L_1)$, and a negative one to the B term of the higher one, $B(L_2)$, due to the mutual mixing of the two L states. This is indeed observed both in position 2 (Figures 1–3) and position 3 (Figures 4–6), and the effect of the amino group is stronger than that of a halogen. For weak +E substitution, one again expects $\Delta HOMO > \Delta LUMO$ and μ^+ contributions of the same signs as above. For stronger +E substitution, the system

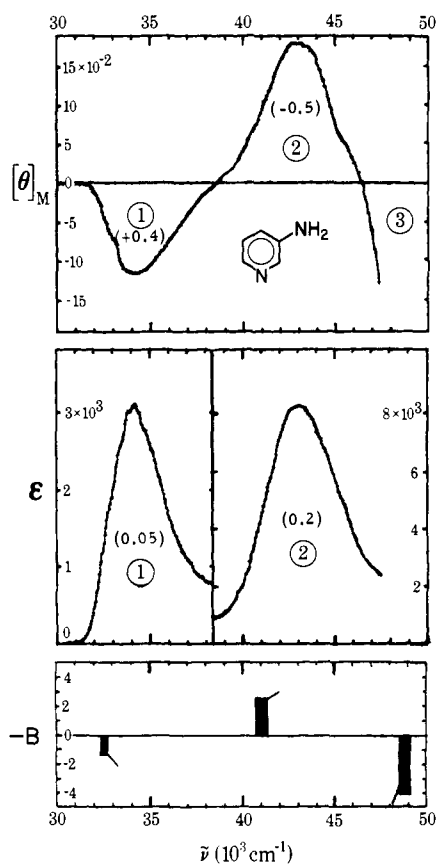


Figure 6. 3-Aminopyridine. See caption to Figure 1.

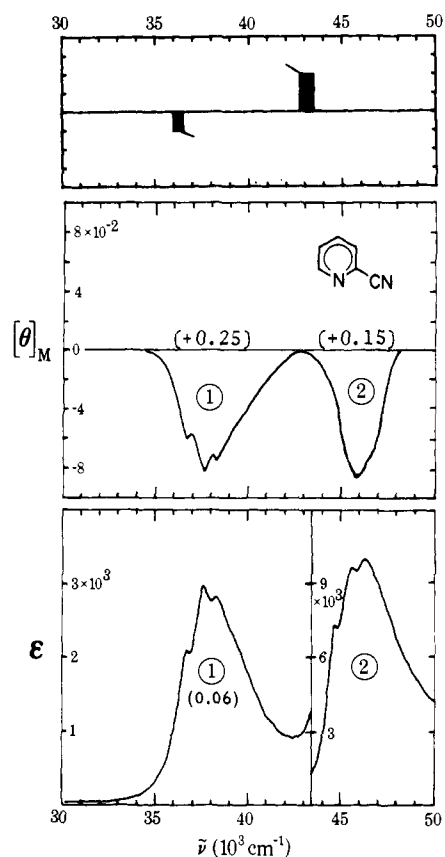


Figure 7. 2-Cyanopyridine. See caption to Figure 1.

will become a zero-soft chromophore and the μ^+ contributions will vanish ($\Delta HOMO = \Delta LUMO$), and for even stronger +E substitution, we expect $\Delta HOMO < \Delta LUMO$, a negative μ^+ contribution to $B(L_1)$, and a positive μ^+ contribution to $B(L_2)$.

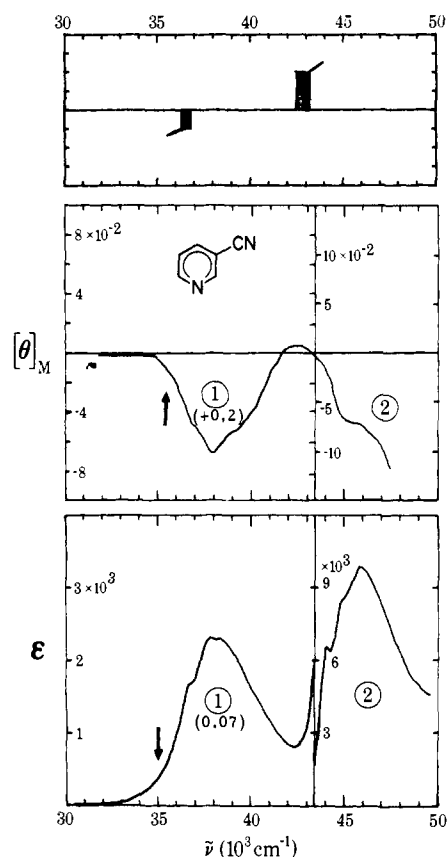


Figure 8. 3-Cyanopyridine. See caption to Figure 1.

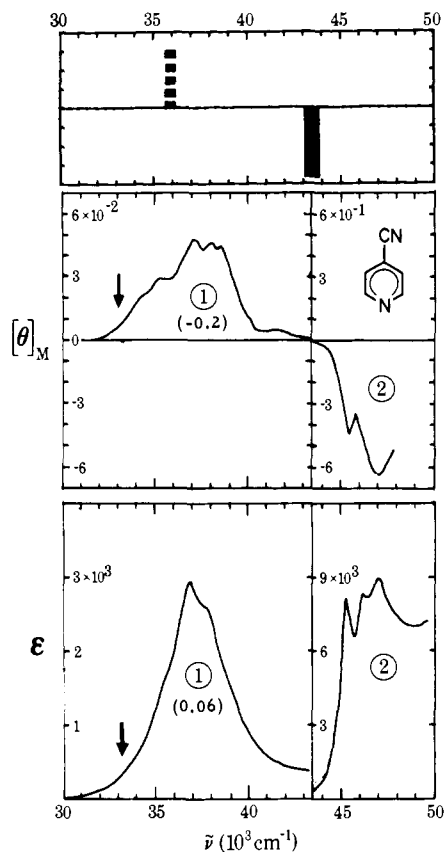


Figure 9. 4-Cyanopyridine. See caption to Figure 1. A full bar indicates vertical polarization and a broken bar horizontal polarization with respect to the formula shown.

The mechanism of this change is analogous to that discussed below for a position of type DS. The effect of the CN group appears to be strong enough to bring 1 close to but not beyond a zero-soft condition, with a small positive μ^+ contribution to $B(L_1)$ and a small negative one to $B(L_2)$ superimposed on the small positive μ^- contributions to both. This interpretation

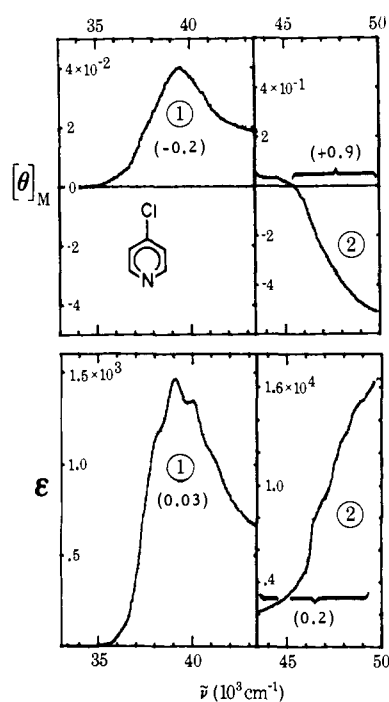


Figure 10. 4-Chloropyridine. See caption to Figure 1.

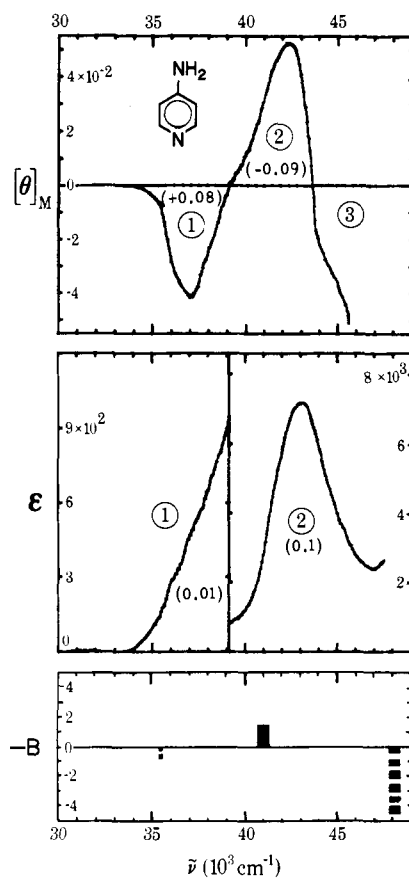


Figure 11. 4-Aminopyridine. See caption to Figures 1 and 9.

agrees with the numerical PPP calculations which show the μ^+ contributions only.

The fact that both +E and -E substitution induces the same MCD signs is striking, considering that these same substituents induce mutually opposite signs on the structurally closely related chromophore, benzene, but it follows in a straightforward manner from the simple theory of parts 1-3.⁴⁻⁶

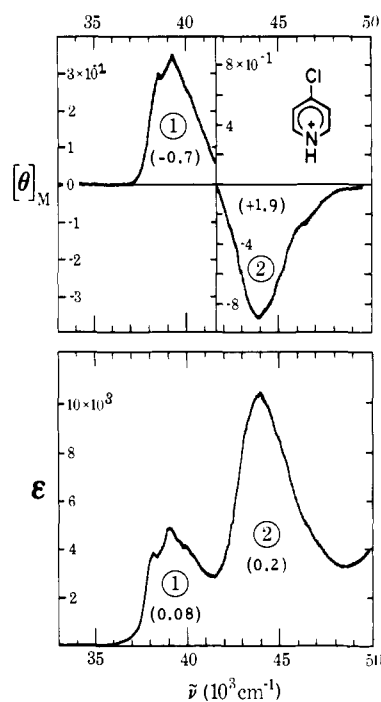


Figure 12. 4-Chloropyridinium cation. See caption to Figure 1.

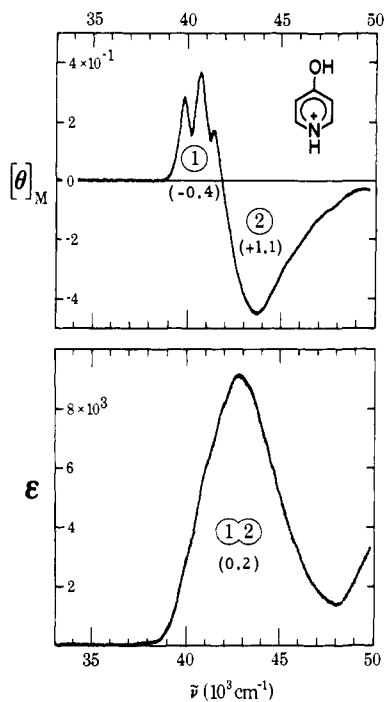


Figure 13. 4-Hydroxypyridinium cation. See caption to Figure 1.

E Substitution in 1. Position 4. Position 4 is +E dominant and -E subdominant (DS);⁵ thus, the predicted effects are quite different from those expected and found in positions 2 and 3. For +E substitution, one expects $\Delta HOMO < \Delta LUMO$ and thus a negative μ^+ contribution to $B(L_1)$ and a positive one to $B(L_2)$ from the mixing of the two L states. This is observed for 4-CN-1 (Figure 9). For weak -E substitution, one again expects $\Delta HOMO < \Delta LUMO$ and μ^+ contributions of the same signs as above. This is observed for 4-Cl-1 (Figure 10). Sufficiently strong -E substitution is expected to produce $\Delta HOMO > \Delta LUMO$, a positive μ^+ contribution to $B(L_1)$, and a negative μ^+ contribution to $B(L_2)$. This is observed for 4-NH₂-1 (Figure 11). A similar theoretically predicted switch-over is observed in another even-soft chromophore, the pyri-

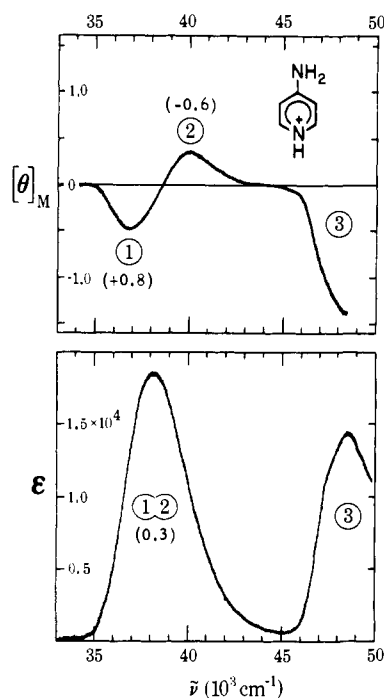


Figure 14. 4-Aminopyridinium cation. See caption to Figure 1.

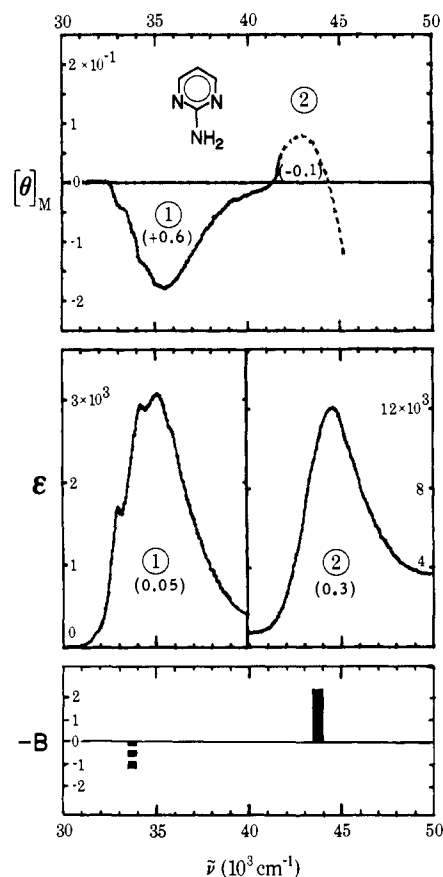


Figure 15. 2-Aminopyrimidine. See captions to Figures 1 and 9.

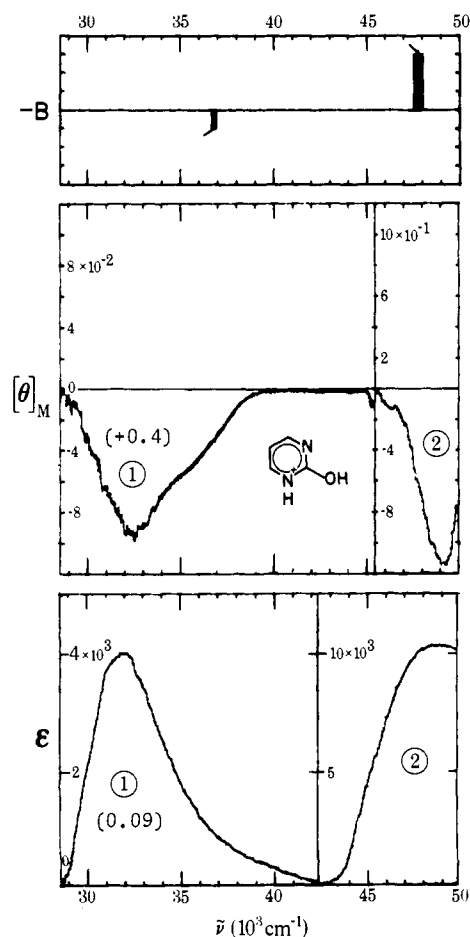


Figure 16. 2-Hydroxypyridinium cation. See caption to Figure 1.

dinium cation. Once again, weak $-E$ substitution in position 4 (Cl and OH) produces $B(L_b) < 0$, $B(L_a) > 0$, but strong $-E$ substitution (NH_2) produces the opposite signs (Figures 12–14).

The gradual change in the sign of the substituent-induced B term with the change of substituent strength may appear sufficiently peculiar that it warrants a closer description. This is given in Figure 17, based on model PPP calculations for a series of 4-substituted derivatives of **1**. Unlike the qualitative theory of part 2,⁵ they incorporate the two-electron part of the perturbing operator, but this has no significant effect on the results. The strength of the $-E$ substituent increases from left to right in Figure 17. The substituent–ring bond length and resonance integral, as well as the one-center electron repulsion integral (16.3 eV) were kept constant. The variation of $-E$ strength was achieved by changing the first ionization potential of the electron pair on the substituent (A_{X^+}). The bottom of Figure 17 reflects the much larger substituent effect on the s orbital compared with any of the others. Initial decrease of ΔHOMO to zero followed by an increase results and is in accord with the schematic figures of part 3.⁶ It leads to $\Delta\text{HOMO} < \Delta\text{LUMO}$ initially but then clearly to $\Delta\text{HOMO} > \Delta\text{LUMO}$, once the substituent E effect dominates over the preferences imposed by the ring nitrogen. Configuration energies are shown above and follow the behavior of orbital energy differences quite faithfully. The crossing of the $a \rightarrow -s$ and $s \rightarrow -a$ configuration energies is a consequence of the behavior of the orbital energies. The configuration mixing now predictably occurs in the way dictated by the configuration energies. For the purposes of Figure 17, we write it in a way which is simply related to that used in part 2⁵ (α is about 35° for **1**):

$$|L_b\rangle = |s \rightarrow -a\rangle \sin \alpha - |a \rightarrow -s\rangle \cos \alpha$$

$$|L_a\rangle = |s \rightarrow -s\rangle \sin \beta + |a \rightarrow -a\rangle \cos \beta$$

In this formulation, the signs of the μ^+ contributions are ruled by the sign of the product $\cos 2\alpha \cos 2\beta$. The $s \rightarrow -s$ configuration dominates the L_a state, and $\beta > 45^\circ$. The wave function of the L_b state is dominated by the $a \rightarrow -s$ configuration if the substituent is weak, but its weight gradually decreases, that of $s \rightarrow -a$ increases, as expected from the behavior of configuration energies, and somewhere near the value for the OH substituent the two configurations contribute equally. Thereafter, $s \rightarrow -a$ predominates over $a \rightarrow -a$. Thus, $\alpha < 45^\circ$ for weak substituents, but $\alpha > 45^\circ$ for strong ones. This illustrates graphically the effect of the sign of $\Delta\text{HOMO} - \Delta\text{LUMO}$ on the sign of $\cos 2\alpha \cos 2\beta$, which will be positive if α and β lie on the same side of 45° and negative if they lie on opposite sides.

The calculated transition moment directions $\langle G|\hat{M}|L_b\rangle$ and $\langle G|\hat{M}|L_a\rangle$ are displayed on top of Figure 17 with a choice of phase such that the magnetic moment $\langle L_b|\hat{M}/i|L_a\rangle$ points to the reader. The transition moment of the L_a transition is seen to point downward and to gradually acquire intensity as the substituent becomes stronger and $s \rightarrow -s$ begins to prevail strongly over $a \rightarrow -a$. This is qualitatively reasonable since the contributions from $s \rightarrow -s$ and $a \rightarrow -a$ to the transition moment oppose each other and cancel almost exactly in **1** in this model; in an exactly even-soft chromophore they would cancel exactly. The transition moment of the L_b transition is also composed of two opposed contributions, due to the $a \rightarrow -s$ and $s \rightarrow -a$ configurations. At first, $a \rightarrow -s$ prevails and imposes its direction for the moment which thus points to the right. However, its magnitude decreases with the growing substituent strength due to increasing importance of the $s \rightarrow -a$ configuration in the L_b wave function. Eventually, it drops to zero, and thereafter, it points to the left as the $s \rightarrow -a$ configuration takes over. The sign of the triple vector product $\langle F|\hat{M}/i|I\rangle \cdot \langle F|\hat{M}|G\rangle \times \langle G|\hat{M}|I\rangle$ changes at that point also,

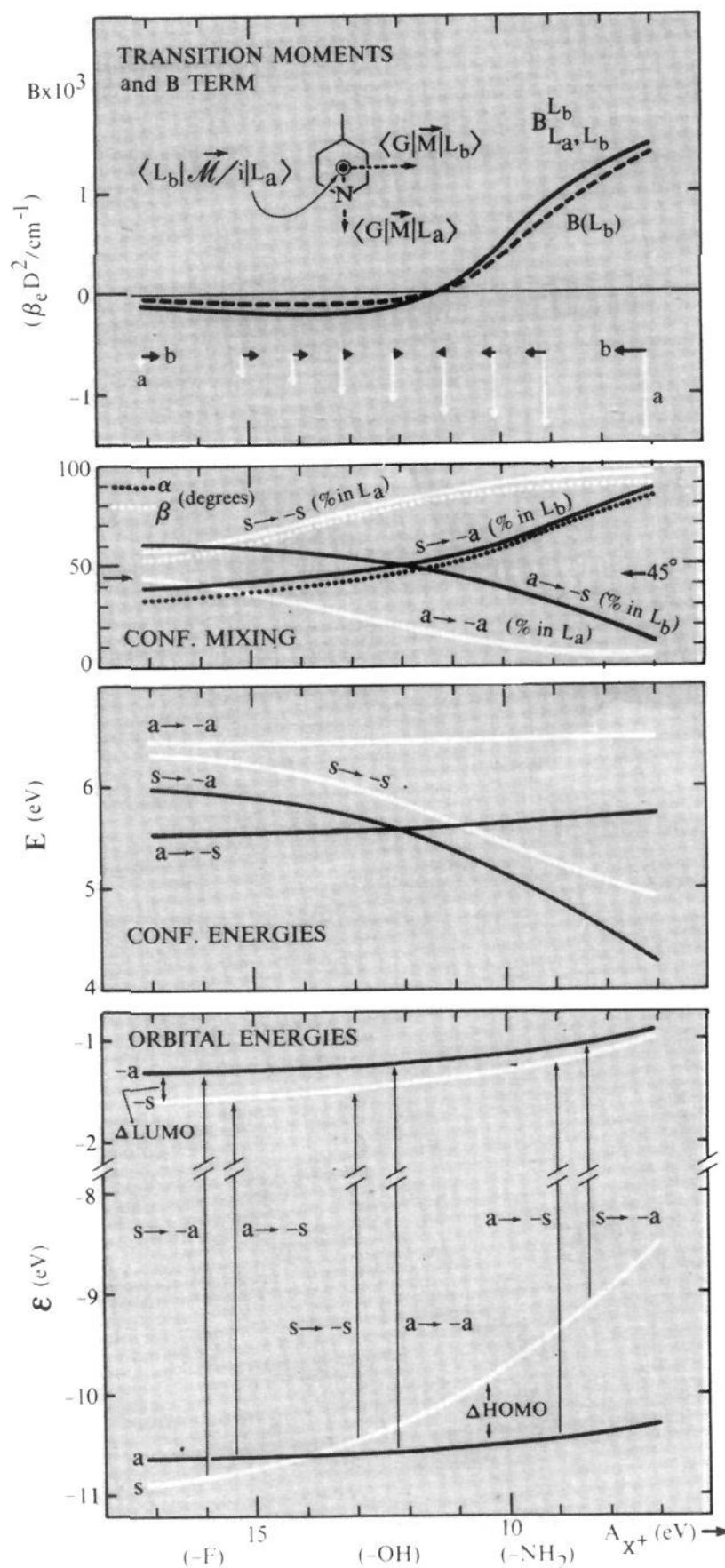


Figure 17. Reversal of the sign of $B(L_b)$ with increasing substituent E effect. See text.

and a simultaneous reversal of the sign of the $B_{L_a, L_b}^{L_b}$ contribution to $B(L_b)$ is expected. This is indeed observed; moreover, the total value of $B(L_b)$ shows the same trend. The reversal occurs at a point where the dipole strength of the L_b band vanishes; at this point, the system represents an odd-soft MCD chromophore. The observed weak intensity of L_b in 4- NH_2 -**1** indicates that it lies relatively close to the point at which the MCD sign inversion occurs. It would be difficult to find a real substituent with exactly the desired strength to make the intensity of L_b zero, but overall, Figure 17 clearly shows the trends and the mechanism by which E substitution in a subdominant position propagates its effect so that it is eventually expressed in the sign of $B(L_b)$.

Position 2 in **2** is of SD type and the signs observed in Figures 15 and 16 are in good agreement with the simple theory. It will be also noted that the full PPP calculations agree both with the simple analysis and with the experimental signs for all positions of substitution considered here. Further, the complete neglect

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-