

fects of substituents, and we are presently pursuing this line of investigation.

References and Notes

- (1) Part 2: J. Michl, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (2) J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 1).
- (3) J. W. Kenney, III, D. A. Herold, J. Michl, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 16).
- (4) W. Moffitt, *J. Chem. Phys.*, **22**, 320-333, 1820-1829 (1954).
- (5) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, N.Y., 1975.
- (6) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).
- (7) J. G. Foss and M. E. McCarville, *J. Am. Chem. Soc.*, **89**, 30-32 (1967).
- (8) S. L. Wallace, A. Castellan, D. Muller, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 5).
- (9) M. Vašák, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 7).
- (10) M. Vašák, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 12).
- (11) R. P. Steiner and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 11).
- (12) E. W. Thulstrup, J. W. Downing, and J. Michl, *Chem. Phys.*, **23**, 307-319 (1977).
- (13) M. R. Whipple, M. Vašák, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 8).
- (14) M. Vašák, M. R. Whipple, A. Berg, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 13).
- (15) W. Gerhartz and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 14).
- (16) J. C. Sutherland and H. Low, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 276-280 (1976).

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 4.¹ Aza Analogues of Benzene

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Abstract: Magnetic circular dichroism of pyridine and the three diazines is analyzed. The B terms of the $n\pi^*$ transition are very small and negative. Those of the $L_b \pi\pi^*$ transition are small and positive and thus opposite to those one might expect from a simple extension of the empirical rule for substituted benzenes to the aza "substituent", but they are in excellent agreement with the general qualitative theory of parts 1-3 for even-soft MCD chromophores. The results indicate that MCD will be generally useful for the separation of inductive and mesomeric effects of substituents.

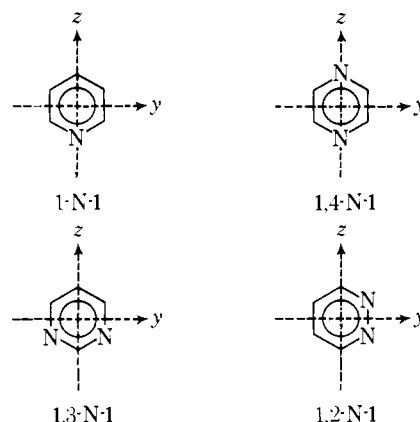
Introduction

The first three papers of this series^{1,3,4} presented an analysis of the consequences of a simple π -perimeter model for MCD signs of transitions in cyclic conjugated π systems which can be related to the two L and two B states of the $(4N+2)$ -electron perimeter. In this and the following papers, we attempt to determine the scope of validity of the results by comparison with experimental data. Presently, we report results for four aza analogues of benzene (1): pyridine (1-N-1), pyrazine (1,4-N-1), pyrimidine (1,3-N-1), and pyridazine (1,2-N-1). These can be viewed as benzene with one or two +I substituents and, according to the simple theory,^{3,4} should represent even-soft MCD chromophores. A study of the effect of E substitution on azines, confirming this conclusion, appears as part 5.⁵

Singlet excited states of the azines have been analyzed in considerable detail. Electronic spectroscopy,⁶ photoelectron spectroscopy,⁷ and calculations⁸ show that the weak first singlet-singlet absorption band near 30-35 000 cm^{-1} is due to an $n\pi^*$ transition (1-N-1, $n \rightarrow -s$; 1,4-N-1, $n_+ \rightarrow -s$; 1,3-N-1, $n_- \rightarrow -a$; 1,2-N-1, $n_- \rightarrow -a$, using the nomenclature of ref 1 for labeling π orbitals of a perturbed annulene with respect to mirroring in the xz plane implied in the formulas). The next band near 40 000 cm^{-1} is of $\pi\pi^*$ nature and corresponds to the L_b transition (B_{2u} state) of benzene. A stronger $\pi\pi^*$ band near 50 000 cm^{-1} corresponds to the L_a transition (B_{1u} state of benzene). Higher energy states lie outside the experimental region accessible to us presently.

Magnetic circular dichroism of the azines was briefly mentioned in our preliminary communication.^{9a} Professors Hezemans (Utrecht) and Hatano (Sendai) have informed us recently of their respective independent studies of the MCD of these compounds; the latter has just appeared in print.^{9b}

Their interest centers on the $n\pi^*$ transitions in the free-base azines and on numerical calculations of the B terms in the spectra, both of which are of secondary importance in the present paper, so that a very small degree of overlap results.



Experimental Section and Calculations

Absorption and MCD spectra were recorded at room temperature in spectral-grade cyclohexane (Eastman). Protonated 1-N-1 was run in 0.5 N aqueous HCl. Standard volumetric techniques were used for sample preparation. The measurements were done on Cary 17 and modified Cary 60 instruments. The latter was equipped with a 45-kG superconducting magnet and was calibrated using *d*-camphorsulfonic acid. The accuracy of the measured MCD intensities is estimated at about 10% and was double-checked by comparison with published data for several organic and inorganic compounds. The spectra were digitized and plotted using a PDP-11/10 minicomputer, which also calculated B terms ($\beta_e D^2/\text{cm}^{-1}$) from the formula¹⁰ $B = (1/33.53) \cdot \int [\theta]_M \bar{\nu}^{-1} d\bar{\nu}$, where $[\theta]_M$ is molar ellipticity in $\text{deg L m}^{-1} \text{mol}^{-1} \text{G}^{-1}$ and $\bar{\nu}$ is wavenumber, and oscillator strengths f from the formula f

= $4.319 \times 10^{-9} \int \epsilon d\bar{\nu}$, where ϵ is the decadic molar extinction coefficient. Integration limits were over one electronic band. Corrections for overlap were guessed. This was relatively easy in the spectra of the azines, but in many instances throughout this series of papers, the values of B and f are only a little better than order-of-magnitude estimates.

Pyridine, triply distilled from KOH, was purified by GLC. Pyrimidine and pyridazine were purified by preparative GLC; pyrazine was gradient sublimed.

Although in our interpretations the emphasis is on comparison with the simple qualitative model of parts 1-3,^{1,3,4} we are also interested in evaluating the performance of the standard simple version of the Pariser-Parr-Pople (PPP) method with all singly excited configurations without any refinements for MCD purposes and with unoptimized parameter values. The parameters were obtained from various sources in the literature in a fairly consistent fashion but undoubtedly could be much improved. They are listed below for all atoms which appear throughout this series of papers. In units of eV and in standard notation, $\beta = -2.318$ (neighbors only) for all combinations, except for the nitrile $C\equiv N$ bond, $\beta = -3.0$, the $C-S$ bond, $\beta = -1.62$, and the $C-Se$ bond, $\beta = -1.39$; $I_C = 11.42$; $I_N = 14.1$ (aza, nitrile); I_O (carbonyl) = 17.7; $I_{F+} = 40.0$; I_{O+} (hydroxy) = 27.17; I_{N+} (amino) = 23.13; $I_{NCH_3+} = 22.18$; I_{S+} (sulfide) = 20.27; I_{Se+} (selenide) = 19.17; $A_C = 0.58$; $A_N = 1.80$; $A_{N+} = 1.95$; (azonia) $A_O = 2.47$; $A_{F+} = 16.0$; $A_{O+} = 11.54$; $A_{N+} = 9.1$; $A_{NCH_3+} = 8.15$; $A_{S+} = 9.42$; $A_{Se+} = 8.83$. Where noted, the somewhat higher values $A_{O+} = 12.59$, $A_{N+} = 10.15$, $A_{NCH_3+} = 9.2$, $A_{S+} = 10.47$, and $A_{Se+} = 9.88$ were used as well, without much effect on the MCD results. The Mataga-Nishimoto formula¹¹ was used for two-center electron repulsion integrals, all bond lengths were equal to 1.4 Å, except for $C\equiv N = 1.2$ Å, $C-S = 1.76$ Å, and $C-Se = 1.92$ Å, and regular polygonal geometries were assumed unless stated otherwise. The Linderberg relation¹² was used for matrix elements of linear momentum, and B terms were obtained by summing contributions $B_{i,F}^F$, $B_{i,G}^F$, and $(B_{G,F}^F + B_{F,G}^F)$ over all states obtained in the calculation as in our earlier MCD work:^{3,13}

$$B(G \rightarrow F) = \sum_{l,l \neq G,F} B_{l,G}^F + \sum_{l,l \neq G,F} B_{l,F}^F + (B_{F,G}^F + B_{G,F}^F)$$

$$B_{l,G}^F = \text{Im} \{ \langle l | \hat{M} | G \rangle \cdot \langle G | \hat{M} | F \rangle \times \langle F | \hat{M} | l \rangle / [W(l) - W(G)] \}$$

$$B_{l,F}^F = \text{Im} \{ \langle F | \hat{M} | l \rangle \cdot \langle F | \hat{M} | G \rangle \times \langle G | \hat{M} | l \rangle / [W(l) - W(F)] \}$$

$$B_{F,G}^F + B_{G,F}^F = \text{Im} \{ \langle F | \hat{M} | G \rangle \cdot \langle G | \hat{M} | F \rangle \times ((\langle F | \hat{M} | F \rangle - \langle G | \hat{M} | G \rangle) / [W(F) - W(G)] \}$$

Im stands for "imaginary part of", the sums run over all molecular electronic states l except as indicated, $\hat{M} = \sum_i \hat{m}_i$ is the electric dipole moment operator, $\hat{M} = \sum_i \hat{\mu}_i$ is the magnetic dipole moment operator (i runs over all electrons), and $W(A)$ is the energy of the A th state. The state vectors $|G\rangle$, $|F\rangle$, and $|l\rangle$ are those of an unperturbed molecule (no magnetic field). Origin dependence was found to be negligible for choice of origin anywhere inside the molecular framework.

Results

The results are given in Figures 1-4. For all four azines, the MCD intensity is very weak, but correspondence to absorption peaks is clear. For 1-N-1, 1,4-N-1, and 1,3-N-1, the MCD effect is much weaker for the $n\pi^*$ band than for the $L_b \pi\pi^*$ band; in 1,2-N-1, their intensities are about equal. No new transitions are revealed by the spectra. In all four azines, the $n\pi^*$ transition has a negative B term (positive MCD peak) and the $\pi\pi^*$ transition, a positive B term. In 1,2-N-1, the onset of the L_a band appears and indicates that its B term is also positive.

The MCD curves follow the absorption shapes quite faithfully but generally show less well resolved vibrational structure, probably due to instrumental limitations. The $n\pi^*$ transition of 1-N-1 is severely overlapped by the much stronger $\pi\pi^* L_b$ band in the absorption spectrum; it is more distinct in the MCD curve, although the overlap is still strong. Within the limits imposed by the low resolution available, the vibrational frequencies observed in the absorption⁶ and MCD spectra are

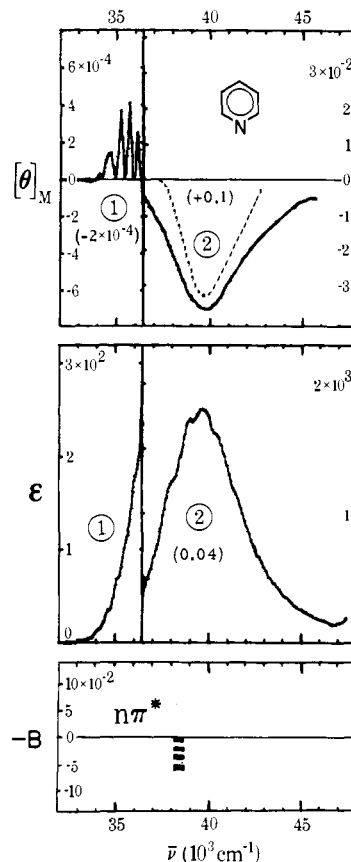


Figure 1. Pyridine (dashed line, pyridinium cation): top, MCD (B terms given in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$); center, absorption (oscillator strengths given); bottom, calculation ($n\pi^*$ only; broken line indicates horizontal polarization with respect to the formula given).

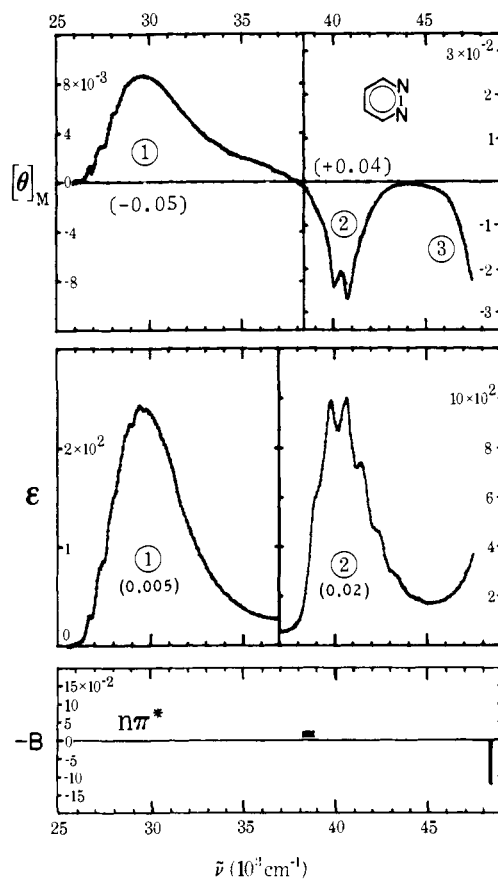


Figure 2. Pyridazine. See caption to Figure 1.

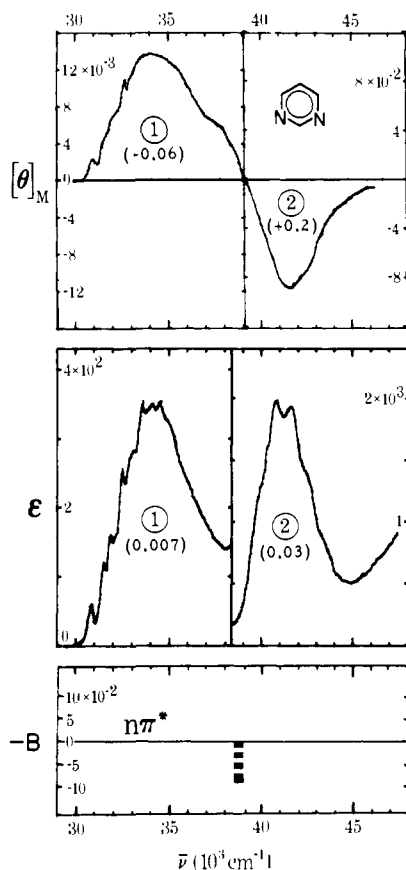


Figure 3. Pyrimidine. See caption to Figure 1.

identical, and vibronic interactions are not manifested in the MCD of $n\pi^*$ and L_b bands.

Discussion

Perturbed Benzenes. The $\pi\pi^*$ states of the azines can be viewed as states of perturbed **1** and it is natural to attempt a comparison of their MCD spectra with those of substituted benzenes. Derivatives of **1** have been studied in considerable detail ever since it was found¹⁴ that the B term of the L_b band correlates with the substituent σ_p Hammett constant and is positive if an ortho-para-directing substituent is present and negative if a meta-directing substituent is present. This result has been related^{15,16} to the signs of the empirical "spectroscopic moments"¹⁷ of the substituents. The correct absolute sign for several benzene derivatives resulted from PPP calculations using either London orbitals and finite perturbation theory¹⁸ or ordinary AO's and first-order perturbation theory for the magnetic field.¹⁹⁻²¹ In the PPP model, the approximate mirror-image relation of MCD spectra of +E (electron-withdrawing) and -E (electron-donating) substituted benzenes, and of +I and -I substituted benzenes, can be viewed²⁰ as a consequence of the mirror-image pairing theorem²² which states that two π -electron systems paired, or approximately paired, in the sense of alternant symmetry will have a mirror-image relation in the signs of their MCD spectra. Since +E and -E substituted benzenes are isoelectronic with the mutually paired benzyl cation and anion, respectively, the mirror-image property follows. The aza "substituent" clearly does not fit the general picture in that it is meta-directing and yet induces a positive B term for the L_b band. The results of part 3¹ permit us to show that this anomaly results from the circumstance that the aza "substituent", unlike all others studied previously, has no E effect and operates only by its I effect.

E-Substituted Benzenes as Hard Chromophores. A simple consideration of orbital interactions shows that for a -E sub-

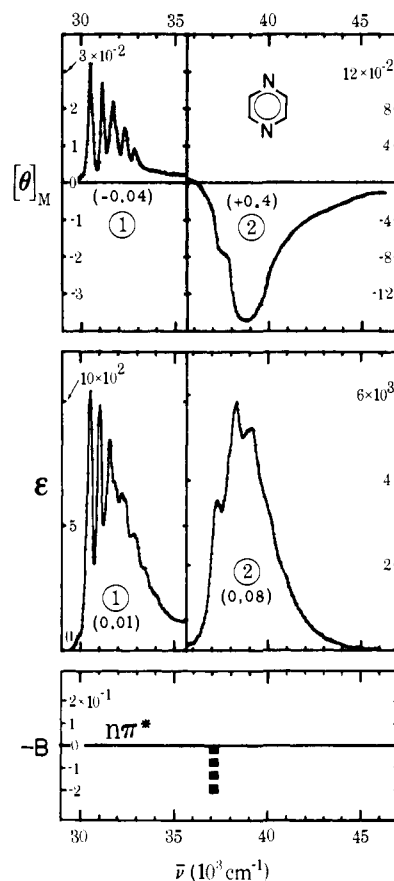


Figure 4. Pyrazine. See caption to Figure 1.

stituted $(4N + 2)$ -electron $[4N + 2]$ annulene, $\Delta\text{HOMO} > \Delta\text{LUMO}$ ($\Delta\text{HOMO} = |E(\mathbf{a}) - E(\mathbf{s})|$, $\Delta\text{LUMO} = |E(-\mathbf{a}) - E(-\mathbf{s})|$), so that the μ^+ contribution to $B(L_b)$ is positive, whereas in a +E substituted annulene, $\Delta\text{HOMO} < \Delta\text{LUMO}$, and the expected μ^+ contribution to $B(L_b)$ is negative. The μ^- contribution to both should be small and positive. These results are in excellent qualitative agreement with semiempirical calculations and with the available experimental evidence quoted above, particularly with the finding²³ that the B terms of substituted benzenes are better correlated with the σ_R substituent constant which reflects the conjugative effect of the substituent than with the ordinary σ_p Hammett constant and with the recent report of the experimental ΔHOMO and ΔLUMO values obtained from photoelectron and electron transmission spectroscopy.²⁴

The Azines as Even-Soft Chromophores. Previous numerical calculations for 1-substituted benzenes²⁰ predicted almost vanishing B terms for the L bands, but at that time no simple explanation was offered. It is now clear that this result is due to the approximate equality of ΔHOMO and ΔLUMO and that it holds generally for +I or -I substituted $(4N + 2)$ -electron $[4N + 2]$ annulenes. It is of interest to note on a specific example the origin of the relation $\Delta\text{HOMO} \approx \Delta\text{LUMO}$ and of the orbital ordering $\mathbf{s}, \mathbf{a}, -\mathbf{s}, -\mathbf{a}$ (or $\mathbf{a}, \mathbf{s}, -\mathbf{a}, -\mathbf{s}$), characteristic of even-soft chromophores. The squares of the coefficients in the four frontier orbitals of benzene are shown in Figure 5. The MO's \mathbf{s} and $-\mathbf{s}$ and the MO's \mathbf{a} and $-\mathbf{a}$ are paired in the sense of alternant symmetry, so that $c_{\kappa,\mathbf{s}}^2 = c_{\kappa,-\mathbf{s}}^2$ and $c_{\kappa,\mathbf{a}}^2 = c_{\kappa,-\mathbf{a}}^2$ for any position κ . To the first order in perturbation theory, the effect of aza replacement on the energy of i th orbital is given by $\Delta E_i = \sum_{\kappa} c_{\kappa,i}^2 \Delta\alpha_{\kappa}$, where the negative quantity $\Delta\alpha_{\kappa}$ is a measure of the increased electronegativity of position κ due to the introduction of nitrogen. From photoelectron spectra and Koopmans' theorem, it has been estimated²⁵ that $\Delta\alpha = -3.3$ eV in the position of replacement, $\Delta\alpha$

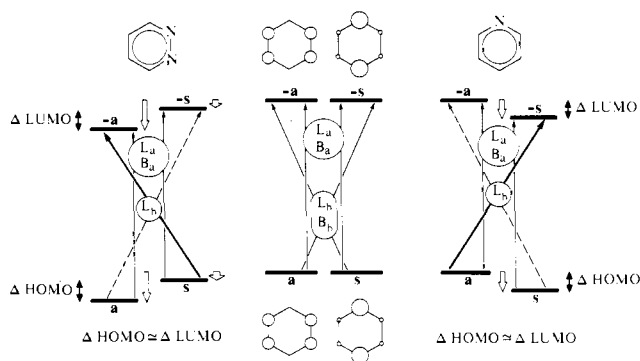


Figure 5. An example of the effect of inductive (I) substitution on the Δ HOMO and Δ LUMO values of a $(4N + 2)$ -electron $[4N + 2]$ annulene.

$= -1.0$ eV in the neighboring positions, and $\Delta\alpha$ is close to 0 elsewhere. In this approximation, two mutually paired orbitals shift to lower energies by equal amounts, as shown in Figure 5 for 1-N-1 and 1,3-N-1, producing both the orbital ordering and the relation Δ HOMO = Δ LUMO characteristic of an even-soft chromophore (i.e., a vanishing μ^+ contribution).

Use of second-order perturbation theory or a full numerical PPP calculation with standard parameters (e.g., ref 11) reveals that the relation Δ HOMO = Δ LUMO, while fulfilled quite well, does not hold exactly, so that the μ^+ contribution does not vanish exactly. This is clearly seen in the bottom parts of Figures 1-4, which show the calculated μ^+ contribution alone (in an annulene of this type, the μ^- contribution originates in next-nearest-neighbor matrix elements^{1,3,4} neglected in the simple PPP method). In 1-N-1, 1,3-N-1, and 1,4-N-1, Δ HOMO > Δ LUMO, and a small positive μ^+ contribution to $B(L_b)$ results, particularly in the latter two cases; in 1,2-N-1, Δ HOMO < Δ LUMO, and a very small negative contribution to $B(L_b)$ results. The signs of the contributions to $B(L_a)$ are just the opposite.

The magnitude of the small positive μ^- contribution to $B(L_b)$ depends on the magnitude of Δ HOMO; simple consideration of the form of benzene orbitals (Figure 5) as well as numerical calculations shows that this should be the same in 1-N-1, 1,2-N-1, and 1,3-N-1 and twice larger in 1,4-N-1.

The simple theory thus predicts unequivocally small positive $B(L_b)$ terms for 1-N-1, 1,3-N-1, and 1,4-N-1, increasing in this order, in excellent agreement with experiment. In 1,2-N-1, the very small μ^+ and μ^- contributions oppose each other, and it is difficult to predict the outcome with confidence. In reality, the resulting $B(L_b)$ term, which is the smallest of all as expected, has the positive sign demanded by the μ^- contribution. The theory also predicts very weakly negative $B(L_a)$ for 1-N-1 and a little more pronounced negative $B(L_a)$ for 1,3-N-1 and 1,4-N-1, as well as a very weakly positive $B(L_a)$ for 1,2-N-1. It is quite likely that the MCD effect of the L_a transition will be dominated by vibronic effects. Since this transition lies beyond our present instrumental limit, we shall not be further concerned with it [the positive $B(L_a)$ in 1,2-N-1 agrees with expectations].

In summary, the predictions based on the general simple theory of parts 1-3^{1,3,4} for the L_b band, limiting magnetic mixing to the L_b , L_a , B_b , and B_a states, have been fulfilled, and one can now have reasonable confidence in its predictions for other azabenzene and aza $[4N + 2]$ annulenes in general. A more demanding test of the soft nature of these chromophores is an investigation of the response to E substitution, and this

is reported in part 5. Both sets of results are very encouraging for a general study of the separation of mesomeric and inductive effects of substituents by MCD.

Neither the simple model of parts 1-3^{1,3,4} nor the PPP calculations performed in this study permits a rationalization of the MCD signs of the $n\pi^*$ transitions, and these are at the moment not at the forefront of our interest. Their existence still poses an important problem for the interpretation of the MCD signs of $\pi\pi^*$ transitions, as does the existence of other types of states, such as $\sigma\pi^*$ and $\pi\sigma^*$, which can also be mixed magnetically with the ground state and with $\pi\pi^*$ excited states. In part 2,⁴ we have stated arguments for our belief that the contributions of such mixing to the B terms of $\pi\pi^*$ transitions are of secondary importance. In accord with such a belief, the present results show that consideration of $\pi\pi^*$ states alone permits a satisfactory rationalization of their B terms. In order to account for their magnitudes quantitatively, it may, of course, well be necessary to consider the $n\pi^*-\pi\pi^*$ mixing as well, and this has been discussed very recently in ref 9b. Note, however, that protonation of 1, which removes its $n\pi^*$ transition, has hardly any effect on the MCD spectrum in the $\pi\pi^*$ region.

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References and Notes

- (1) Part 3: J. Michl, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (2) NATO Fellow 1975-1976.
- (3) J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 1).
- (4) J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 2).
- (5) S. L. Wallace, A. Castellan, D. Muller, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 5).
- (6) K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectrosc.*, **22**, 125-147 (1967).
- (7) R. Gleiter, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **55**, 255-274 (1972); E. Haselbach, Z. Lanyiova, and M. Rossi, *ibid.*, **56**, 2889-2899 (1973); C. Fridh, L. Åsbrink, B. O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **8**, 101-118 (1972).
- (8) For leading references to calculated and additional experimental data, see R. W. Wagner, P. Hochmann, and M. Ashraf El-Bayoumi, *J. Mol. Spectrosc.*, **54**, 167-181 (1975); H. Shinoda, H. Tatematsu, and T. Miyazaki, *Bull. Chem. Soc. Jpn.*, **46**, 2950-2955 (1973); M. Zerner and J. Ridley, *Theor. Chim. Acta*, **32**, 111-134 (1973); J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807-1813 (1968).
- (9) (a) J. Michl, *Chem. Phys. Lett.*, **43**, 457-460 (1976); (b) A. Kaito, M. Hatano, and A. Tajiri, *J. Am. Chem. Soc.*, **99**, 5241-5246 (1977).
- (10) P. N. Schatz and A. J. McCaffery, *Q. Rev., Chem. Soc.*, **23**, 552-584 (1969).
- (11) N. Mataga and K. Nishimoto, *Z. Phys. Chem. (Frankfurt am Main)*, **13**, 140-157 (1957).
- (12) J. Linderberg, *Chem. Phys. Lett.*, **1**, 39-41 (1967).
- (13) S. M. Warnick and J. Michl, *J. Am. Chem. Soc.*, **96**, 6280-6289 (1974).
- (14) J. G. Foss and M. E. McCarville, *J. Am. Chem. Soc.*, **89**, 30-32 (1967).
- (15) L. Seamans, Ph.D. Dissertation, University of Minnesota, 1971.
- (16) D. J. Shieh, S. H. Lin, and H. Eyring, *J. Phys. Chem.*, **77**, 1031-1038 (1973).
- (17) J. Petruska, *J. Chem. Phys.*, **34**, 1111-1120; 1120-1136 (1961).
- (18) L. Seamans and J. Linderberg, *Mol. Phys.*, **24**, 1393-1405 (1972).
- (19) D. W. Miles and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3754-3758 (1973).
- (20) J. Michl and J. Michl, *J. Am. Chem. Soc.*, **96**, 7887-7892 (1974).
- (21) A. Kaito, A. Tajiri, and M. Hatano, *J. Am. Chem. Soc.*, **98**, 384-388 (1976).
- (22) J. Michl, *J. Chem. Phys.*, **61**, 4270-4273 (1974).
- (23) D. J. Shieh, S.-T. Lee, Y.-C. Yim, S. H. Lin, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 452-453 (1975).
- (24) K. D. Jordan, J. A. Michejda, and P. D. Burrow, *J. Am. Chem. Soc.*, **98**, 7189-7191 (1976).
- (25) F. Brogli, E. Heilbronner, and T. Kobayashi, *Helv. Chim. Acta*, **55**, 274-288 (1972).