The reverse may be the case in B and C since here the product (boroxine or trihydroxylboroxine) is potentially aromatic. However, the available evidence suggests that the aromatic stabilization energy is much less than that in benzene (20 kcal/mol).[25]

In D-F, the inductive effects of the alkyl groups should stabilize the esters and so tend to make ΔH (and hence h) more negative. This is supported by the fact that the heat of reaction of ethanol with boric acid (F) is more negative than that of methanol (E).

In the conversion of boronic acid to **1**, neither resonance nor inductive effects should significantly affect the heat of reaction. From the examples above, it would seem that the value of h in such circumstances should be greater than zero but less than 7 kcal/mol. Since eq 1 involves loss of water from three separate pairs of OH groups, the corresponding heat of reaction should then lie between 0 and 21 kcal/mol; using this value and the heats of formation cited above, we find:

$$-165.3 \leqslant \Delta H_f(\mathbf{1}) \leqslant -144.3 \text{ kcal/mol} \qquad (2)$$

This agrees reasonably well with our MNDO estimate (−142.9 kcal/mol) but is very much less than the claimed experimental value (−200.4 kcal/mol; Table IV). It seems clear that the latter must be grossly in error and that the best available estimate of the heat of formation of **1** is −155 ± 10 kcal/mol.

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CNDO Treatment for Faraday *B* Terms of Some Azaheterocycles

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Abstract: The magnetic circular dichroism (MCD) spectra of pyridine, pyridazine, pyrimidine, pyrazine, and 1,3,5-triazine were measured in the wavenumber region of 25000-50000 cm^{-1}. The transition energies, the oscillator strengths, and the Faraday B terms were calculated within the framework of the CNDO/S-CI approximation. The agreement between theoretical and experimental results is satisfactory. The perturbing mechanism for the Faraday B terms of the lowest $\pi^* \leftarrow$ n and the lowest $\pi^* \leftarrow \pi$ transitions were clarified on the basis of the calculated results.

The value of the magnetic circular dichroism (MCD) technique as a useful tool of spectral and molecular structural analysis has been confirmed extensively by an introduction of the quantum mechanical treatments of the Faraday parameters. It has been shown that the Pariser-Parr-Pople (PPP) method[1] has explained well the experimental Faraday A terms of aromatic organic compounds,[2-5] which originate from the Zeeman splitting of the ground or excited electronic state. The Faraday B terms arising from the magnetic mixing among electronic states have also been successfully interpreted[6-8] by the PPP method. Although the PPP method can easily treat $\pi^* \leftarrow \pi$ transitions of large aromatic systems within relatively short computer time and small computer capacity, several authors have pointed out the importance of an inclusion of all valence electrons in the molecular orbital treatment of the Faraday parameters.[9-12] The CNDO method,[13,14] a semiempirical LCAOMO-SCF procedure for all valence electrons, has advantage not only in taking account of the effects of the polarization of σ core, but also in dealing with the $\pi^* \leftarrow \sigma$ and $\sigma^* \leftarrow \pi$ transitions. Recently Sprinkel et al.[11] have indicated the necessity of including the π^*-σ states and interpreted that the main contribution to the Faraday B terms of the lowest $\pi^* \leftarrow \pi$ transition of indole comes from the magnetic coupling of the π^*-σ states around 50000 cm^{-1} with the lowest π^*-π state. The Faraday B terms of the vibronically induced $\pi^* \leftarrow$ n transition in formaldehyde[10a] and the allowed $^1A_{2u} \leftarrow {}^1A_{1g}$ ($\pi^* \leftarrow \sigma$) transition in benzene[12] have also been calculated using wave functions obtained from the CNDO approximation.

On the other hand, the electronic structures of pyridine, diazines, and 1,3,5-triazine have been investigated with the aid

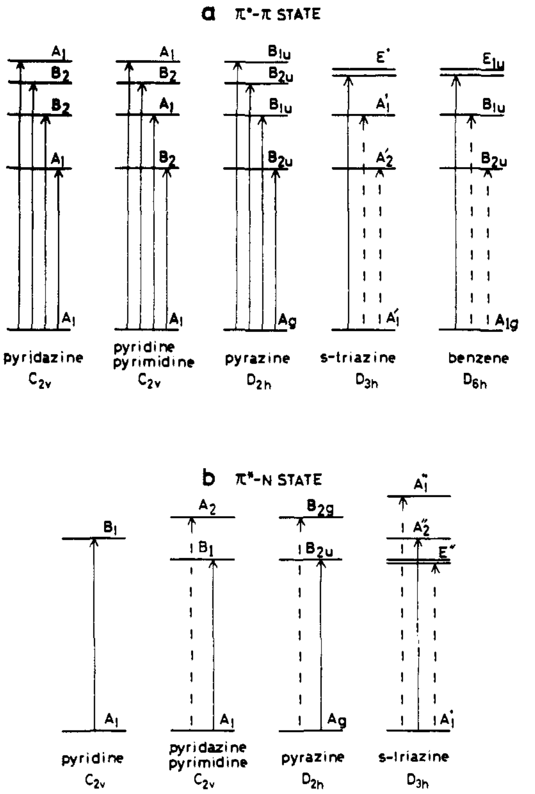

Figure 1. (a) Four lowest π^*-π states of benzene, pyridine, and azines. (b) π^*-n states of pyridine and azines arising from electron promotion from the lone pair orbital of nitrogen atoms to the lowest vacant π orbital. Solid and dashed vertical lines denote the allowed and forbidden transitions, respectively.

Table I. Atomic Parameters (eV) Used in the Present Calculations

	U_{ss}	U_{pp}	γ_{AA}	$\gamma_{\pi\pi}$	$\gamma_{\pi\sigma}$	β
C	−50.686	−41.530	10.207	10.93	9.88	−17.5
N	−70.093	−57.848	11.052	11.88	10.47	−24.4
H	−13.593		12.848			−5.9
$\kappa = 0.6$						

of the all valence-electron molecular orbital theory.[14,15] The electronic states expected in the lower energy region are presented in Figure 1. Four lowest π^*-π states are related to the $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ states of benzene. However, in pyridine and diazines, the degeneracy of the $^1E_{1u}$ state is removed and two lowest $\pi^* \leftarrow \pi$ transitions become electrically allowed because of the symmetry reduction. The presence of the lone pair on nitrogen atom causes the possibility of $\pi^* \leftarrow$ n transitions, one of which is electrically allowed (see Figure 1b), and is observed at lower wavenumber than the first $\pi^* \leftarrow \pi$ transition. Because of these closely spaced $\pi^* \leftarrow$ n and $\pi^* \leftarrow \pi$ transitions, these azaheterocycles are considered to be suitable materials for the theoretical MCD work including the $\pi^* \leftarrow \sigma$ type transitions which are polarized along the axis perpendicular to the molecular plane. In the present article, we apply the CNDO/S-CI method to the calculation of the B terms of pyridine, diazines, and 1,3,5-triazine, aiming at elucidating the perturbing mechanism for the Faraday B terms of the $\pi^* \leftarrow$ n and $\pi^* \leftarrow \pi$ transitions of these compounds.

Experimental Section

Spectrograde pyridine (Tokyo Chemical Industry Co., Ltd.) was used without further purification. Pyridazine and pyrimidine (Tokyo Chemical Industry Co., Ltd.) were purified by distillation under reduced pressure. Pyrazine (Wako Pure Chemical Industries, Ltd.) was recrystallized from petroleum ether and finally dried in vacuo. Under reduced pressure 1,3,5-triazine (Tokyo Chemical Industry Co., Ltd.) was twice sublimed. All measurements were performed at room temperature using spectrograde n-heptane as a solvent.

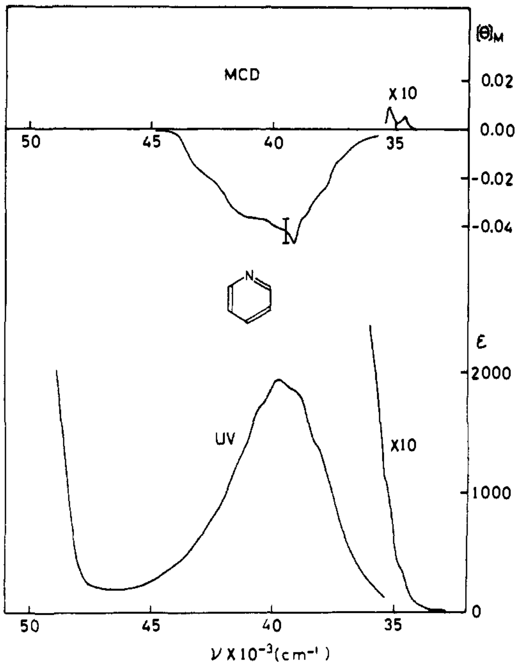

Figure 2. MCD and UV spectra of pyridine in n-heptane solution at room temperature.

The MCD spectra were recorded with a JASCO J-20A recording circular dichrometer equipped with a 11.4 kG electromagnet. The MCD spectra were calibrated with freshly prepared potassium ferricyanide, $[\theta]_M$ at 4220 Å = 1.0° cm^2 mol^{-1} G^{-1}. The UV spectra were measured on a Hitachi EPS-3T recording spectrophotometer.

Theoretical Section

The quantum mechanical model used in this work is principally based on the CNDO/S-CI method proposed by Pople, Santry, and Segal.[13] However, some modifications were made along the lines of the CNDO/S-CI method proposed by Del Bene and Jaffé.[14] One-center electron repulsion integrals, γ_{AA}, and one-center core parameters, U_{ss} and U_{pp}, in the Hartree-Fock matrix elements were taken from the values determined by Sichel and Whitehead.[16] Two-center electron-repulsion integrals were calculated using the Nishimoto-Mataga equation.[17] The values of the bonding parameter, β, and the empirical parameter, κ, were adjusted so that the ionization potentials and the transition energies of benzene, pyridine, and hydrogen molecule are well reproduced.

Configuration interaction (CI) among singly excited configurations below 10 eV was taken into account. The electron repulsion integrals in the π^*-π CI matrix elements, $\gamma_{\pi\pi}$, were set to be equal to γ_{pp}, and those in the π^*-σ and σ^*-π CI matrix elements, $\gamma_{\pi\sigma}$, were assumed to be $(\gamma_{ps} + 2\gamma_{pp'})/3$. The values of the electron repulsion integrals, γ_{pp}, γ_{ps}, and $\gamma_{pp'}$, were evaluated from the valence state energy data of Hinze and Jaffé,[18] as common with the parametrization of Sichel and Whitehead.[16] The parameters used in the present calculations are summarized in Table I.

According to the theoretical consideration of Buckingham and Stephens,[19] the Faraday B term of a transition $j \leftarrow a$ is expressed as

$$B(j \leftarrow a) = \sum_{k \neq a,j} B_{j,k} + \sum_{k \neq a,j} B_{k,a} + B_{j,a} \qquad (1)$$

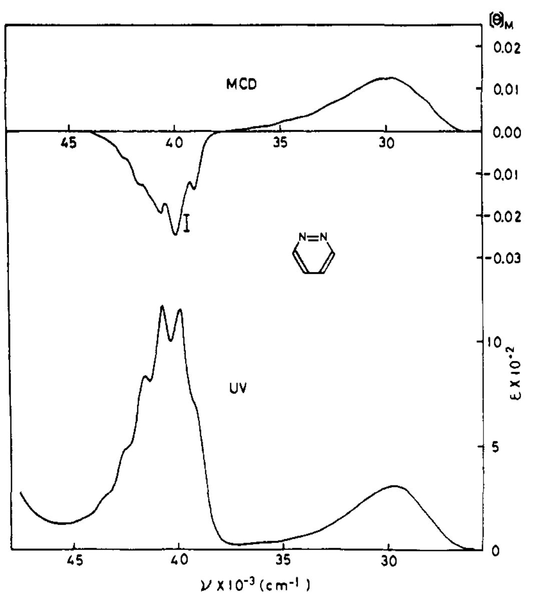

Figure 3. MCD and UV spectra of pyridazine in *n*-heptane solution at room temperature.

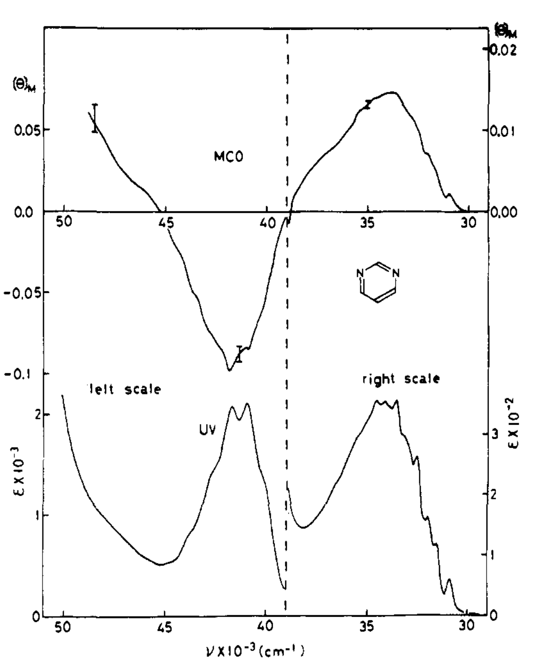

Figure 4. MCD and UV spectra of pyrimidine in *n*-heptane solution at room temperature.

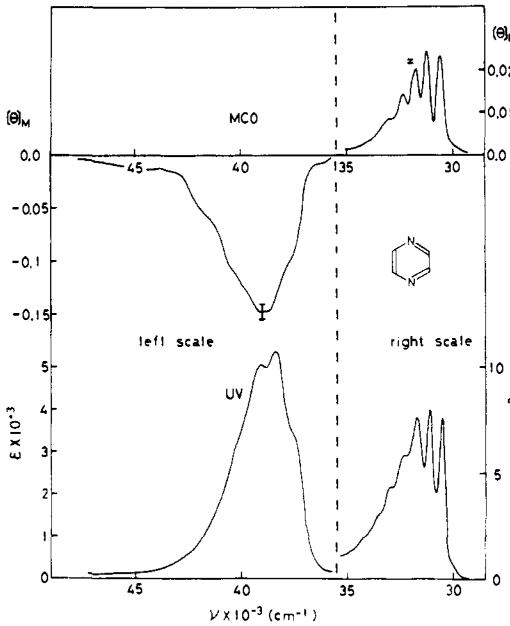

Figure 5. MCD and UV spectra of pyrazine in *n*-heptane solution at room temperature.

where

$$B_{j,k} = \mathrm{Im}\,\langle j|\mu|k\rangle \cdot \langle a|\mathbf{m}|j\rangle \times \langle k|\mathbf{m}|a\rangle/(E_k - E_j) \quad (2)$$

$$B_{k,a} = \mathrm{Im}\,\langle k|\mu|a\rangle \cdot \langle a|\mathbf{m}|j\rangle \times \langle j|\mathbf{m}|k\rangle/(E_k - E_a) \quad (3)$$

$$B_{j,a} = \mathrm{Im}\,\langle j|\mu|a\rangle \cdot \langle a|\mathbf{m}|j\rangle \times (\langle j|\mathbf{m}|j\rangle - \langle a|\mathbf{m}|a\rangle)/(E_j - E_a) \quad (4)$$

In eq 2-4, $\mathbf{m}$ and μ are the electric and magnetic moment operators, respectively, and E_a, E_j, and E_k are the energies of states a, j, and k, respectively. $B_{j,k}$ stands for the magnetic mixing of the electronic state k with the excited state j, and $B_{k,a}$ represents the coupling of the state k with the ground state a. $B_{j,a}$ arises from the magnetic coupling between the ground state a and the excited state j. The electric transition moments were calculated with the dipole length operator method. The LCAO-MO coefficients with respect to the orthogonalized CNDO atomic orbital basis were deorthogonalized by the inverse Löwdin transformation[20] and the atomic integrals were calculated using Slater atomic orbitals[21] according to the description in ref 22 and 23.

It should be noted that the Faraday B terms calculated for noncentric molecules using a limited basis set are origin dependent.[24,25] Caldwell and Eyring[25] have shown that the error introduced by using a limited basis set is minimized at the center of charge density. Several authors have reported that the location of the origin within the framework of the molecule gives qualitatively correct results.[6,7,11] Therefore, in this work, the origin is set at the center of the electron cloud in the ground state.

Computations were carried out using an NEAC 2200 computer in the computer center of Tohoku University.

Results and Discussion

The MCD and UV spectra of pyridine are shown in Figure 2. The lowest $\pi^* \leftarrow \pi$ transition shows a negative MCD band at 40000 cm^{-1}. At the lower wavenumber edge of the lowest $\pi^* \leftarrow \pi$ transition, we can see a positive weak MCD, which can be assigned to the lowest $\pi^* \leftarrow$ n transition.

The MCD and UV spectra of diazines are displayed in Figures 3-5. The lowest allowed $\pi^* \leftarrow$ n transition exhibits a positive MCD band in the lowest wavenumber region (26000-38000 cm^{-1}), while the lowest $\pi^* \leftarrow \pi$ transition shows a negative MCD band in the middle wavenumber region (36000-45000 cm^{-1}). As shown in Figure 1, another $\pi^* \leftarrow$ n transition is expected in these wavenumber regions. This is, however, electrically forbidden and may be obscured by the stronger allowed transitions. In the higher wavenumber region (45000-50000 cm^{-1}) of the MCD spectrum of pyrimidine, the positive MCD due to the second $\pi^* \leftarrow \pi$ transition is observed. However, the MCD of the second $\pi^* \leftarrow \pi$ transition in the remaining compounds was not clearly detected because of the limitation of the instrument.[26]

The MCD and UV spectra of 1,3,5-triazine are shown in Figure 6. Three π^*-n states arise from electron promotion from the highest occupied n orbital (e′) to the lowest vacant π orbital (e″) and belong to the ^{1}E″, ^{1}A$_2$″, and ^{1}A$_1$″ symmetries (Figure 1b). The lowest positive MCD band observed at 37000 cm^{-1} is considered to be mainly induced by the electric dipole al-

Table II. Observed and Calculated Transition Energies (cm^{-1}), Oscillator Strengths, and Faraday *B* Terms ($\beta D^2/\mathrm{cm}^{-1}$)

Compd	ν_{obsd}	ν_{calcd}	f_{obsd}	f_{calcd}	$B_{obsd} \times 10^5$	$B_{calcd} \times 10^5$	Assignment
Pyridine	34 800	35 700		0.0040	Negative	−6.7	$\pi^* \leftarrow n\ ^1B_1$
	40 000	39 300	0.041	0.061	15	18.9	$\pi^* \leftarrow \pi\ ^1B_2$
	49 800[a]	49 900	0.1[a]	0.043		−83.1	$\pi^* \leftarrow \pi\ ^1A_1$
	55 000[a]	57 000	1.3[a]	1.037		1306	$\pi^* \leftarrow \pi\ ^1B_2$
	56 400[a]	58 000		1.252		−1245	$\pi^* \leftarrow \pi\ ^1A_1$
Pyridazine	30 500	32 000	0.0062	0.0077	−6.0	−14.0	$\pi^* \leftarrow n\ ^1B_1$
		38 800		Forbidden		Forbidden	$\pi^* \leftarrow n\ ^1A_2$
	40 900	39 700	0.017	0.059	4.4	6.7	$\pi^* \leftarrow \pi\ ^1A_1$
	50 000[a]	50 000	0.10[a]	0.0014		−14.1	$\pi^* \leftarrow \pi\ ^1B_2$
	57 300[a]	56 200		1.092		322	$\pi^* \leftarrow \pi\ ^1B_2$
		59 100		1.230		−274	$\pi^* \leftarrow \pi\ ^1A_1$
Pyrimidine	34 600	35 700	0.0073	0.0066	−7.6	−14.9	$\pi^* \leftarrow n\ ^1B_1$
		39 400		Forbidden		Forbidden	$\pi^* \leftarrow n\ ^1A_2$
	41 700	40 600	0.033	0.059	24	17.2	$\pi^* \leftarrow \pi\ ^1B_2$
	52 300[a]	51 300	0.16[a]	0.038	Negative	−65.8	$\pi^* \leftarrow \pi\ ^1A_1$
	58 500[a]	56 900	1.0[a]	0.953		338	$\pi^* \leftarrow \pi\ ^1A_1$
		59 700		1.172		−365	$\pi^* \leftarrow \pi\ ^1B_2$
Pyrazine	32 100	27 900	0.0092	0.0063	−4.7	−11.8	$\pi^* \leftarrow n\ ^1B_{3u}$
	39 300	37 800	0.081	0.168	46	36.2	$\pi^* \leftarrow \pi\ ^1B_{2u}$
		40 900		Forbidden		Forbidden	$\pi^* \leftarrow n\ ^1B_{2g}$
	50 900[a]	50 600	0.15[a]	0.095		−146	$\pi^* \leftarrow \pi\ ^1B_{1u}$
	60 700[a]	60 500	1.0[a]	0.906			$\pi^* \leftarrow \pi\ ^1B_{2u}$
		60 500		1.225			$\pi^* \leftarrow \pi\ ^1B_{1u}$
s-Triazine		39 600		Forbidden		Forbidden	$\pi^* \leftarrow n\ ^1E''$
	37 000	40 200	0.020	0.016	−12	−31.2	$\pi^* \leftarrow n\ ^1A_2''$
		42 200		Forbidden		Forbidden	$\pi^* \leftarrow n\ ^1A_1''$
	44 000	43 500	0.002	Forbidden		Forbidden	$\pi^* \leftarrow \pi\ ^1A_2'$
		54 100		Forbidden		Forbidden	$\pi^* \leftarrow \pi\ ^1A_1'$
		59 500		2.014			$\pi^* \leftarrow \pi\ ^1E'$

[a] K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectrosc.*, **22**, 125 (1967).

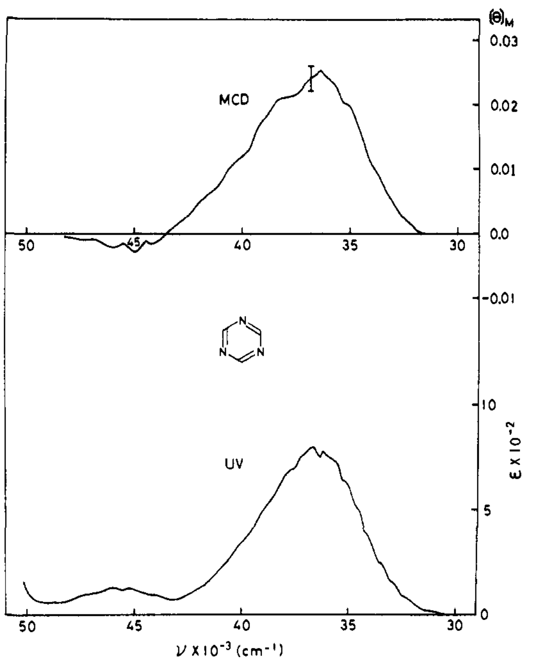

Figure 6. MCD and UV spectra of 1,3,5-triazine in *n*-heptane solution at room temperature.

lowed $^1A_2'' \leftarrow {}^1A_1'$ ($\pi^* \leftarrow n$) transition. The negative weak MCD band in the region of 43000–49000 cm^{-1} is assigned to the vibronically induced $^1A_2' \leftarrow {}^1A_1'$ ($\pi^* \leftarrow \pi$) transition.

Table III. Contribution to the Faraday *B* Term ($\beta D^2/\mathrm{cm}^{-1}$) of the Lowest $\pi^* \leftarrow \pi$ Transition from Each Excited State

	$B_{j,k} \times 10^5$ for state k =				$B \times 10^5$
Compd	2nd π^*-π	3rd π^*-π	4th π^*-π	1st π^*-n	(total *B* term)
Pyridine	39.6	0.0	−19.2	−0.5	18.9
Pyridazine	7.2	−3.9	0.0	3.3	6.7
Pyrimidine	33.1	−21.4	0.0	3.7	17.2
Pyrazine	75.2	0.0	−35.1	−0.6	36.2

The overlapping MCD and absorption bands were resolved by a curve-fitting procedure using Gaussian functions and then the experimental *B* terms were obtained by the use of the method of moments.[27] Table II presents the observed and calculated transition energies, oscillator strengths, and Faraday *B* terms. Several $\pi^* \leftarrow \sigma$ and $\sigma^* \leftarrow \pi$ transitions are predicted in the region higher than 42000 cm^{-1}. However, these transitions are omitted from Table II, because they are too weak to play an important role in the MCD and UV spectra. The agreement between the theoretical and experimental results is satisfactory. The calculated transition energies are in good agreement with the experimental data, and the ordering of the electronic states is consistent with the results of the INDO calculations reported by Ridley and Zerner.[15] Although the values of the calculated oscillator strengths and Faraday *B* terms tend to be somewhat larger than the observed values, the predicted signs of the *B* terms are completely correct.

Table IV. Contribution to the Faraday *B* Term ($\beta D^2/cm^{-1}$) of the Lowest Allowed $\pi^* \leftarrow n$ Transition from Three Terms in Equation 1

Compd	$\sum_{k \neq a,j}^{\pi^*\pi} B_{j,k} \times 10^5$	$\sum_{k \neq a,j}^{\pi^*\sigma} B_{k,a} \times 10^5$	$B_{j,a} \times 10^5$	$B \times 10^5$ (total *B* term)
Pyridine	−2.7	−0.5	−3.5	−6.7
Pyridazine	−8.4	−1.8	−3.8	−14.0
Pyrimidine	−9.2	−2.5	−3.3	−14.9
Pyrazine	−3.7	−8.1	0.0	−11.8
s-Triazine	−14.0	−17.2	0.0	−31.3

Table V. Calculated Faraday *B* Terms at the Point Being 1 Å Away from the Center of Electron Cloud along the C_2 Axis of the Molecules

Compd	ν_{calcd}, cm^{-1}	$B_{calcd} \times 10^5$, $\beta D^2/cm^{-1}$	Assignment
Pyridine	35 700	−5.4	$\pi^* \leftarrow n\ {}^1B_1$
	39 300	21.4	$\pi^* \leftarrow \pi\ {}^1B_2$
	49 900	−80.6	$\Pi^* \leftarrow \pi\ {}^1A_1$
	57 000	1267	$\pi^* \leftarrow \pi\ {}^1B_2$
	58 000	−1191	$\pi^* \leftarrow \pi\ {}^1A_1$
Pyridazine	32 000	−11.8	$\pi^* \leftarrow n\ {}^1B_1$
	38 000	Forbidden	$\pi^* \leftarrow n\ {}^1A_2$
	39 700	6.2	$\pi^* \leftarrow \pi\ {}^1A_1$
	50 000	−13.7	$\pi^* \leftarrow \pi\ {}^1B_2$
	56 200	332	$\pi^* \leftarrow \pi\ {}^1B_2$
	59 100	−270	$\pi^* \leftarrow \pi\ {}^1A_1$
Pyrimidine	35 700	−11.2	$\pi^* \leftarrow n\ {}^1B_1$
	39 400	Forbidden	$\pi^* \leftarrow n\ {}^1A_2$
	40 600	17.7	$\pi^* \leftarrow \pi\ {}^1B_2$
	51 300	−63.0	$\pi^* \leftarrow \pi\ {}^1A_1$
	56 900	334	$\pi^* \leftarrow \pi\ {}^1A_1$
	59 700	−356	$\pi^* \leftarrow \pi\ {}^1B_2$

The major part of the Faraday *B* term of the lowest $\pi^* \leftarrow \pi$ transition arises from the magnetic mixing among excited electronic states (the first term in eq 1). The contribution to the Faraday *B* terms of the lowest $\pi^* \leftarrow \pi$ transition from each excited state, $B_{j,k}$, is given in Table III. The dominant contribution comes from the mixing of the first and second π^*-π states. In pyridazine and pyrimidine, there is an appreciable contribution from the magnetic coupling of the lowest π^*-n state with the lowest π^*-π state, although the contribution from the mixing of the π^*-n state is negligibly small in pyridine and pyrazine. This is because the lowest π^*-π state in the former has nonzero transition density at nitrogen atoms resulting in $\mathrm{Im}\ \langle 1\mathrm{st}\ \pi^*\text{-}\pi | \mu | 1\mathrm{st}\ \pi^*\text{-n} \rangle \neq 0$, whereas that in the latter has a node at nitrogen atoms leading to $\mathrm{Im}\ \langle 1\mathrm{st}\ \pi^*\text{-}\pi | \mu | 1\mathrm{st}\ \pi^*\text{-n} \rangle \approx 0$.

Although the π-electron approximation has explained well the Faraday *B* term of many organic compounds, our results show the significant contribution to the *B* term of the lowest $\pi^* \leftarrow \pi$ transition in pyridazine and pyrimidine is derived from the magnetic mixing of the lowest π^*-n state with the lowest π^*-π state, as found in the lowest $\pi^* \leftarrow \pi$ transition of indole.[11] The PPP method is considered to be valid for the $\pi^* \leftarrow \pi$ transitions which are far from the $\pi^* \leftarrow \sigma$ type transitions. On the other hand, inclusion of the π^*-σ states is necessary when the relatively stronger $\pi^* \leftarrow \sigma$ type transitions lie near by the $\pi^* \leftarrow \pi$ transition of interest.

Table IV shows the contribution to the *B* terms of the lowest $\pi^* \leftarrow n$ transition of pyridine and azines from three terms in eq 1. The magnetic mixing among π^*-σ type states and the coupling of the π^*-π state with the ground state do not contribute to the *B* terms of the $\pi^* \leftarrow \sigma$ type transitions because of parallel orientation of the transition moments in eq 2 and 3. In each case, large contribution arises from the mixing of four lower lying π^*-π states with the lowest π^*-n state (the first term in eq 1). The magnetic coupling of the magnetically allowed π^*-σ and π^*-n states with the ground state contributes to the second term in eq 1. In particular, this term is dominant in pyrazine and 1,3,5-triazine. In pyridine, pyridazine, and pyrimidine, since the lowest $\pi^* \leftarrow n$ transition is both electrically and magnetically allowed, there comes some contribution from the magnetic mixing of the ground and the lowest π^*-n states (the third term in eq 1). This term, however, vanishes in pyrazine and 1,3,5-triazine from the requirement of symmetry.

As mentioned before, the calculated *B* terms of pyridine, pyridazine, and pyrimidine linearly depend on the choice of the origin. Table V shows the *B* terms calculated at the point, being 1 Å away from the center of the electron cloud along the C_2 axis of the molecule. The sign and the order of magnitude of the theoretical *B* terms do not significantly change, as long as the origin is transformed within the molecule.

Conclusion

The Faraday *B* terms of pyridine and azines were calculated using wave functions determined on the basis of the CNDO/S-CI method. The results are in good agreement with the experimental data both for $\pi^* \leftarrow \pi$ transition for $\pi^* \leftarrow n$ transition. Although the *B* term of the lowest $\pi^* \leftarrow \pi$ transition is dominantly caused by the magnetic mixing of the π^*-π states, there comes the significant contribution from the magnetic mixing of the π^*-n states with the lowest π^*-π state in pyridazine and pyrimidine. The *B* term of the lowest $\pi^* \leftarrow n$ transition is originated from the magnetic mixing of the π^*-π states with the lowest π^*-n state and the coupling of the π^*-σ and π^*-n states with the ground state. The origin dependence of the calculated *B* term is too small to be of practical importance.

It is concluded that the CNDO/S-CI method can serve as a quite powerful model for predicting the signs and the order of magnitude of the Faraday *B* terms of aromatic organic compounds.

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Conformational Analysis of Some *trans*-2-Decalone Systems by Combined Molecular Mechanics and ab Initio Calculations

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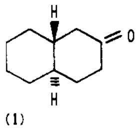
Abstract: The usefulness of combined molecular mechanics and ab initio calculations is demonstrated for the conformational analysis of medium-sized molecules. For *trans*-2-decalone, 10-methyl-*trans*-2-decalone, 1α-methyl-*trans*-2-decalone, 3α-methyl-*trans*-2-decalone, and 1,1,10-trimethyl-*trans*-2-decalone, ab initio energies were calculated for several minimum energy conformations using standard single determinant molecular orbital theory with an STO-3G minimal basis set. The minimum energy conformations were obtained by molecular mechanics. The calculations predict that a significant population of flexible states can be expected for 3α-methyl-*trans*-2-decalone and for 1,1,10-trimethyl-*trans*-2-decalone at moderate temperatures.

Determining the unperturbed conformational behavior of medium-sized molecules is still a challenging task of structural chemistry. The most powerful structural experimental tools presently available operate in the solid state, in which unperturbed molecular systems cannot, by definition, be investigated. Essentially free molecular structures can be observed only in the vapor phase, in which the determination of structure is complicated by randomness and disorder.

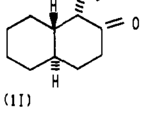
The computational approach to the conformational properties of medium-sized systems is equally imperfect. The most successful theoretical technique usually applied in the conformational analysis of molecules of the order of magnitude of 30 atoms or so is presently based on molecular mechanics and empirical force fields. The method has received much praise[1] and has without any doubt been very valuable in practice. Its empirical nature is a source of dissatisfaction however and it can lead to deficiencies when the conformational situation of a particular test case represents an extrapolation rather than an interpolation with respect to the model systems which were used to define the empirical force field. Unfortunately, it is often not clear which situation is extrapolative rather than interpolative. Additional supporting evidence is therefore desirable and often a necessity.

The present paper is a demonstration of the usefulness of combining ab initio calculations with molecular mechanics conformational analyses. Ab initio studies of medium-sized molecules, e.g., of hydrocarbons with a total number of approximately 30 atoms or more, are by necessity approximate themselves, and it is not presently possible to achieve a complete quantum-mechanical energy optimization, relaxing all geometrical parameters, for molecules of this size. However, a single ab initio calculation at the optimum geometry of a molecular mechanics study is possible for molecules this big. It is hoped that energy differences based on such ab initio calculations will be more reliable than the corresponding empirical estimates. This hope has to be expressed with caution, however, always keeping in mind the approximate nature of present ab initio techniques.

To test the usefulness of this approach, we have calculated ab initio energies for empirically optimized minimum energy conformations of a number of *trans*-2-decalone systems. The investigated systems were *trans*-2-decalone (I), 1α-methyl-*trans*-2-decalone (II), 3α-methyl-*trans*-2-decalone (III),[2] 10-methyl-*trans*-2-decalone (IV), and 1,1,10-trimethyl-*trans*-2-decalone (V). Several of these molecules were recently studied at the University of Arkansas using molecular mechanics combined with gas electron diffraction and vibrational analysis.[3-5]



(I)



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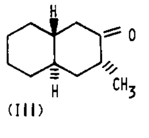

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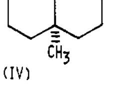

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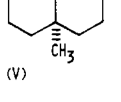

(V)