

References and Notes

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Theoretical Elucidation of Faraday *B* Terms in the Magnetic Circular Dichroism of Monosubstituted Benzenes. Use of the CNDO/S-CI Approximation

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Abstract: The transition energies, the oscillator strengths, and the Faraday *B* terms of phenol, aniline, benzaldehyde, nitrosobenzene, and nitrobenzene were calculated within the framework of the CNDO/S-CI approximation. The results were in good agreement with the experimental data obtained from the magnetic circular dichroism (MCD) and absorption spectra. The excited electronic states of these monosubstituted benzenes were characterized not only by comparing the excited states of the monosubstituted benzenes with those of benzene itself but also by considering the electron migration between the benzene ring and the substituent groups. The perturbing mechanism for the Faraday *B* terms of $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transition in monosubstituted benzenes was clarified. The signs of the magnetic mixing among four lowest $\pi^* \leftarrow \pi$ states in phenol, aniline, and benzaldehyde were explained by the simplified model consisting of four frontier molecular orbitals.

The magnetic circular dichroism (MCD) spectra of substituted benzenes have provided considerable interest for many investigators, because of the sensitivity to the nature of the substituent groups.¹⁻⁶ The first and the second $\pi^* \leftarrow \pi$ transition of substituted benzenes containing an electron-donating substituent exhibit the negative and positive MCD bands, respectively, whereas the situation is reversed for the benzenes with electron-accepting groups. The signs and magnitudes of the MCD of various substituted benzenes have been correlated with the Hammett σ_{para} values of substituents¹ and with the empirical transition moment parameter.² The sign and the order of magnitude of the MCD of various substituted benzenes have been clearly reproduced by the numerical calculations^{3-5,6a} on the basis of the Pariser-Parr-Pople (PPP) method.⁷ Recently Michl^{6,8} has explained the approximate mirror image relation of the MCD spectra of the benzenes having substituent groups of opposite nature, as a result of the removal of alternant pairing symmetry in the parent benzene chromophore.

On the other hand, several authors⁹⁻¹⁶ have calculated the Faraday *B* terms of the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow \sigma$ transitions of aromatic organic compounds within the framework of the complete neglect of differential overlap (CNDO),^{17,18} all valence electrons LCAOMO-SCF procedure. The CNDO method has much advantage not only in evaluating the effects of the magnetic mixing between $\pi^* \leftarrow \sigma$ and $\pi^* \leftarrow \pi$ states, but also in calculating the Faraday *B* terms of the $\pi^* \leftarrow n$ transitions. Sprinkel et al.¹³ have calculated the *B* terms of indole and interpreted that the main contribution to the Faraday *B* terms of the lowest $\pi^* \leftarrow \pi$ transition of indole comes from the mag-

netic coupling of the $\pi^* \leftarrow \sigma$ states around 50 000 cm^{-1} with the lowest $\pi^* \leftarrow \pi$ state. The Faraday *B* terms of the vibronically induced $\pi^* \leftarrow n$ transition in formaldehyde¹¹ and those for the allowed ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ($\pi^* \leftarrow \sigma$) transition in benzene¹⁴ have also been calculated using wave functions obtained from the CNDO method. More recently, Faraday *B* terms of two lowest $\pi^* \leftarrow \pi$ transitions of aniline, phenol, fluorobenzene, benzonitrile, and benzaldehyde have been calculated using the CNDO/S-CI method.¹⁵ In the previous paper,¹⁶ we have reported the CNDO treatment for the Faraday *B* terms of the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions of pyridine and azines. Although the *B* term of the $\pi^* \leftarrow \pi$ transition in these azaheterocycles is mainly induced by the magnetic mixing among $\pi^* \leftarrow \pi$ states, the effect of the mixing of the $\pi^* \leftarrow \sigma$ states with the $\pi^* \leftarrow \pi$ state cannot be neglected in the lowest $\pi^* \leftarrow \pi$ transition of pyridazine and pyrimidine. The Faraday *B* term of the lowest $\pi^* \leftarrow n$ transition in the azaheterocycles is shown to originate from the magnetic mixing of the $\pi^* \leftarrow \pi$ states with the lowest $\pi^* \leftarrow n$ state and from the coupling of the $\pi^* \leftarrow n$ states to the ground state.

In the present article, we apply the CNDO/S-CI method to the calculation of the Faraday *B* terms of the $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions of phenol, aniline, benzaldehyde, nitrosobenzene, and nitrobenzene, and discuss the perturbing mechanism for the Faraday *B* terms of the low-lying electronic transitions of these monosubstituted benzenes.

Experimental Section

Nitrosobenzene (Tokyo Chemical Industry Co., Ltd.) was purified by vacuum sublimation. The MCD spectra were recorded with a

JASCO J-20A recording circular dichrometer equipped with a 11.4-kG electromagnet. The absorption spectra were measured on a Hitachi EPS-3T recording spectrophotometer. The measurements were carried out at room temperature using spectrograde *n*-heptane as a solvent.

Theoretical Section

The transition energies, the oscillator strengths, and the Faraday *B* terms were calculated within the framework of the CNDO/S-CI approximation.¹⁸ The configuration interactions (CI) among singly excited configurations below 10 eV were taken into account. The effects of the configurations higher than 10 eV on the calculated results were also investigated. One-center core integrals and one-center electron repulsion integrals were taken from the values determined by Sichel and Whitehead.¹⁹ Two-center electron repulsion integrals were calculated using the Nishimoto-Mataga equation.²⁰ The bonding parameter, β , and the empirical parameter κ , were determined so that the experimental transition energies and ionization potentials are well reproduced ($\beta_C = -17.5$ eV, $\beta_N = -24.4$ eV, $\beta_O = -35.4$ eV, $\kappa = 0.6$). The details in the parametrization were shown in our previous report.^{16,21}

The Faraday *B* term of a transition from the ground state, *a*, to the excited state, *j*, is expressed as²²

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

where

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

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

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

In eq 2-4, E_a , E_j , and E_k are the energies of the states *a*, *j*, and *k*, respectively, and \mathbf{M} and μ are the electric and magnetic moment operators, 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* to the ground state *a*. $B_{j,a}$ originates from the magnetic mixing between the ground state, *a*, and the excited state, *j*. The electric moments were calculated by the dipole length method. The LCAO-MO coefficients regarding the orthogonalized CNDO atomic orbitals were deorthogonalized by the inverse Löwdin transformation,²³ and then the atomic integrals of the electric and magnetic moments were calculated using Slater atomic orbitals,²⁴ according to the procedure described in ref 25 and 26.

Since the sums in eq 1 are practically over limited electronic states, the Faraday *B* term calculated for noncentric molecules changes by the origin displacement.^{27,28} Here the origin was set at the center of the electron cloud in the ground state according to the theoretical arguments of Caldwell and Eyring.²⁸ The degree of the origin dependence of the calculated *B* terms was also studied.

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

Results and Discussion

Experimental Results. The MCD and absorption spectra of nitrosobenzene in the ultraviolet region are shown in Figure 1, where $[\theta]_M$ is the molar ellipticity in $\text{deg dm}^{-1} \text{ dL mol}^{-1} \text{ G}^{-1}$, and ϵ is the extinction coefficient in $\text{L mol}^{-1} \text{ cm}^{-1}$. The MCD and absorption spectra of nitrosobenzene are characterized by the appearance of the strong MCD and absorption bands in the lower wavenumber region ($30\,000\text{--}40\,000 \text{ cm}^{-1}$),

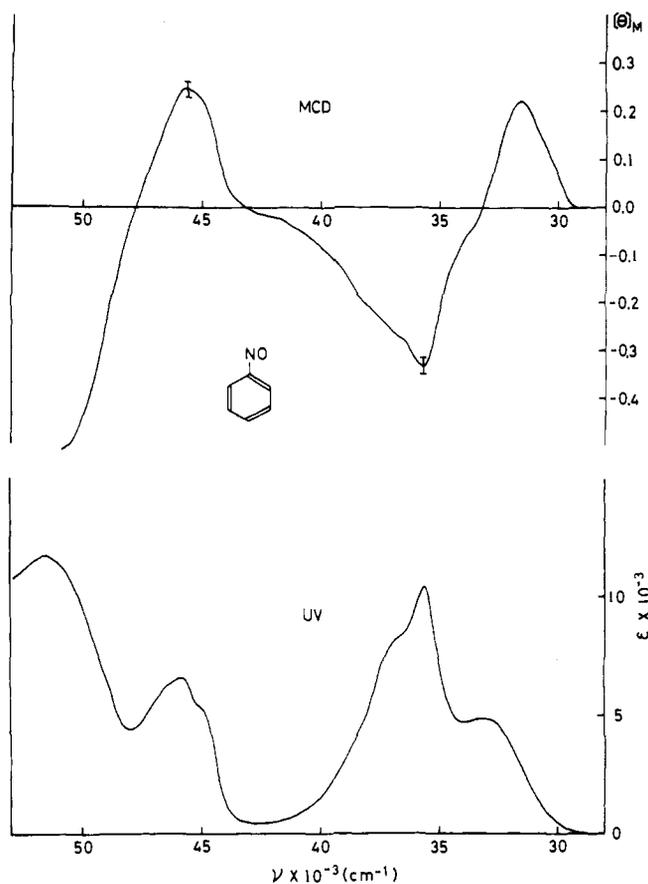


Figure 1. MCD and absorption spectra of nitrosobenzene in the wavenumber region of $28\,000\text{--}53\,000 \text{ cm}^{-1}$.

in which other monosubstituted benzenes show only a weak band with ${}^1B_{2u} \leftarrow {}^1A_{1g}$ character. This can be understood as a result of the strong electron-withdrawing nature of the nitroso group. In the wavenumber region of $30\,000\text{--}40\,000 \text{ cm}^{-1}$, two bands which are fairly overlapping with each other in the absorption spectrum are observed with opposite signs in the MCD spectrum, showing the presence of two independent electronic transitions in this spectral region. Four electronic transitions are identified in the MCD and absorption spectra of the ultraviolet region ($28\,000\text{--}53\,000 \text{ cm}^{-1}$). The signs of the MCD of nitrosobenzene are the same as those of the benzenes having electron-accepting substituents: positive for the first $\pi^* \leftarrow \pi$ transition and negative for the second $\pi^* \leftarrow \pi$ transition.

The MCD and absorption spectra of nitrosobenzene in the wavenumber region of $10\,000\text{--}20\,000 \text{ cm}^{-1}$ are displayed in Figure 2. The positive MCD band at $13\,000 \text{ cm}^{-1}$ is assigned to the lowest $\pi^* \leftarrow n$ transition of the nitroso group.

The MCD and absorption spectra of aniline, phenol, benzaldehyde, and nitrobenzene have been recently reported.^{2,5} In each case, the sign of the MCD of the monosubstituted benzenes with electron-donating groups is negative for the first $\pi^* \leftarrow \pi$ transition and positive for the second $\pi^* \leftarrow \pi$ transition, and the results for the benzenes with electron-accepting groups are opposite to this.

Comparison between the Experimental and Theoretical Results. The experimental and theoretical transition energies, oscillator strengths, and Faraday *B* terms are shown in Table I. The overlapping MCD and absorption bands were resolved by a curve-fitting procedure using Gaussian functions, and then the experimental oscillator strengths and Faraday *B* terms were obtained by the method of moments.²⁹ Several weak $\pi^* \leftarrow \sigma$ and $\sigma^* \leftarrow \pi$ transitions predicted in the region higher than $45\,000 \text{ cm}^{-1}$ are omitted from Table I. The agreement between the theoretical and experimental results is satisfactory.

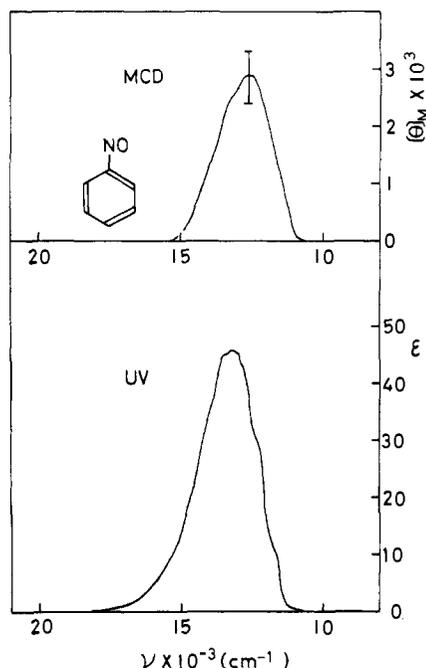


Figure 2. MCD and absorption spectra of nitrosobenzene in the wave-number region of 10 000–20 000 cm^{-1} .

As usual in the dipole length method, the calculated oscillator strengths and Faraday B terms tend to be larger than the experimental values. However, the signs of the calculated B terms perfectly agree with the experimental data.

Origin Dependence of the Calculated B Terms. The Faraday B terms calculated using a limited basis set linearly depend on the origin. We have also calculated the Faraday B terms with the origin moved by 1 Å along the long and short axes of the molecules. In most cases, the amounts of the origin dependence of the Faraday B terms are found to be the order of several percent per 1 Å, and the sign and the order of magnitude of the Faraday B terms are not affected by the origin displacement within the molecular framework.

Dependence on the extent of CI. In order to investigate the effect of the higher electronic configurations on the calculated results, we have performed two calculations for nitrosobenzene, including lowest 42 (below 10 eV) singly excited configurations and lowest 100 (below 13.5 eV) singly excited configurations. The transition energies of low-lying electronic transitions are relatively insensitive to the electronic configurations which lie at 10–13.5 eV. The magnitude of the Faraday B term of the lowest $\pi^* \leftarrow n$ transition of nitrosobenzene increases by 32% by the inclusion of these higher configurations. The oscillator strengths and the Faraday B terms of the low-lying $\pi^* \leftarrow \pi$ transitions are changed to the amount of 0–18% by these higher configurations. Thus, neither the CI with higher configurations nor the magnetic mixing of the higher electronic states is of much importance in the calculation of the transition energies, the oscillator strengths, and the Faraday B terms of the lower lying electronic transitions.

Characterization of the Electronic States. The excited states of substituted benzenes have been interpreted in terms of the locally excited states in the benzene ring and the intramolecular charge-transfer states between the benzene ring and the substituent groups. Nagakura and his co-workers³⁰ have shown that the second $\pi^* \leftarrow \pi$ transition of the benzene with strong substituent³¹ is regarded as the intramolecular charge-transfer transition. On the other hand, the results of the CNDO calculations made by Del Bene and Jaffé³² have suggested that the $\pi^* \leftarrow \pi$ transitions of the substituted benzenes are accompanied by only a small amount of charge transfer.

In this subsection, we characterize the electronic states of

monosubstituted benzenes not only by comparing the excited states of substituted benzenes with those of benzene itself, but also by taking account of the electron migration between the benzene ring and the substituent groups.

Figure 3 shows the interaction of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the benzene ring with the π orbitals of the substituent groups. The HOMOs, ϕ_x and ϕ_y , and the LUMOs, ϕ_ξ and ϕ_η , transform like x , y , $(x^2 - y^2)/2$, and xy , respectively. The MO, ϕ_y , in phenol and aniline is lifted by the mixing of the nonbonding π orbital of the substituent group, while the MO, ϕ_ξ , in benzaldehyde is lowered by the interaction with the unoccupied π^* orbital of the formyl group. However, four frontier MOs of these compounds approximately correspond to the MOs ϕ_x , ϕ_y , ϕ_ξ , and ϕ_η of benzene itself. On the other hand, in nitrobenzene and nitrosobenzene, the unoccupied π^* orbital of the substituent group is inserted below the LUMOs of the benzene ring and considerably mixed with the MO, ϕ_ξ , of the benzene ring. In addition, the occupied π orbital of the nitro group, which hardly interacts with the MOs of the benzene ring, lies near the HOMOs, ϕ_x and ϕ_y , of the benzene ring.

Coefficients of the main configurations in the $\pi^* \leftarrow \pi$ excited states are given in Table II, along with the change in the electron density on the benzene ring (ΔQ_{b2}) associated with the $\pi^* \leftarrow \pi$ transitions. As seen from Figure 3 and Table II, four lowest excited states of phenol, aniline, and benzaldehyde approximately correspond to the ${}^1B_{2u}$, ${}^1B_{1u}$, and ${}^1E_{1u}$ states of benzene, respectively. The present calculation shows the smaller amount of charge-transfer character in the second $\pi^* \leftarrow \pi$ states of aniline and benzaldehyde than the results of the molecules in molecules method.³⁰

For nitrosobenzene and nitrobenzene, the transitions with charge-transfer character are predicted in the lower wave-number region. The first and the second $\pi^* \leftarrow \pi$ transitions of nitrosobenzene and the second and the third $\pi^* \leftarrow \pi$ transitions of nitrobenzene can be regarded as the intramolecular charge-transfer transitions from the benzene ring to the substituent groups. The third $\pi^* \leftarrow \pi$ state of nitrosobenzene and the first $\pi^* \leftarrow \pi$ state of nitrobenzene correspond to the ${}^1B_{2u}$ state of benzene, although the transitions to these excited states are accompanied by significant amount of electron transfer from the benzene ring to the substituent groups. The fourth $\pi^* \leftarrow \pi$ state of nitrosobenzene and the fifth $\pi^* \leftarrow \pi$ state of nitrobenzene are closely related to the ${}^1B_{1u}$ state of benzene. The fifth and the sixth $\pi^* \leftarrow \pi$ states of nitrosobenzene and the eighth and the ninth $\pi^* \leftarrow \pi$ states of nitrobenzene are analogous to the ${}^1E_{1u}$ state of benzene.

Table III shows the coefficients of the prevailing configurations in the lowest $\pi^* \leftarrow n$ states of benzaldehyde, nitrosobenzene, and nitrobenzene, together with the changes in the electron density on the oxygen atoms (ΔQ_O) associated with the lowest $\pi^* \leftarrow n$ transition. $\psi_{n \rightarrow 5}$ stands for the configuration in which one electron is promoted from the highest occupied nonbonding orbital to the fifth π orbital. In each case, the lowest $\pi^* \leftarrow n$ transition is well interpreted as a one-electron jump from the highest occupied nonbonding orbital to the lowest unoccupied π^* orbital, accompanied by the electron transfer along the C–O and N–O bonds.

Contributions to the Faraday B Terms of the $\pi^* \leftarrow \pi$ Transitions from Each Excited State. The Faraday B terms of the $\pi^* \leftarrow \pi$ transitions are mainly caused by the magnetic mixing among $\pi^* \leftarrow \pi$ states, the first term in eq 1, $B_{j,k}$. The contributions from the magnetic mixing of the $\pi^* \leftarrow \sigma$ states with the $\pi^* \leftarrow \pi$ state are found to be negligibly small (less than 3%) in substituted benzenes, in contrast to the cases of pyrimidine, pyridazine,¹⁶ and indole.¹³ This results from the fact that the electric transition moment of the $\pi^* \leftarrow n$ transition in the former is much smaller than in the latter.

Table I. Observed and Calculated Transition Energies (ν), Oscillator Strengths (f), and Faraday B Terms (B)

Compd	$\nu_{\text{obsd}} \times 10^{-3}$, cm $^{-1}$	$\nu_{\text{calcd}} \times 10^{-3}$, cm $^{-1}$	f_{obsd}	f_{calcd}	$B_{\text{obsd}} \times 10^5$, $\beta D^2/\text{cm}^{-1}$	$B_{\text{calcd}} \times 10^5$, $\beta D^2/\text{cm}^{-1}$	Assignment
Phenol	37.1	37.7	0.021	0.014	18.3	20.3	$\pi^* \leftarrow \pi$ $^1A'$
	47.3	46.9	0.117	0.110	Negative	-58.7	$\pi^* \leftarrow \pi$ $^1A'$
		54.3		1.222			$\pi^* \leftarrow \pi$ $^1A'$
	52.7		0.649				$\pi^* \leftarrow \pi$ $^1A'$
Aniline		54.3		1.164			$\pi^* \leftarrow \pi$ $^1A'$
	35.2	37.1	0.024	0.025	49.0	48.4	$\pi^* \leftarrow \pi$ 1B_2
	42.9	45.0	0.178	0.235	-94.5	-107.0	$\pi^* \leftarrow \pi$ 1A_1
		53.5		0.936	Positive	5969	$\pi^* \leftarrow \pi$ 1B_2
Benzaldehyde		53.6		0.963		-5983	$\pi^* \leftarrow \pi$ 1A_1
	30.3	25.1	0.0006	7×10^{-6}	-0.71	-0.037	$\pi^* \leftarrow \pi$ $^1A''$
	35.8	37.7	0.010	0.0086	-38	-33.2	$\pi^* \leftarrow \pi$ $^1A'$
	41.7	45.0	0.234	0.396	118	114.9	$\pi^* \leftarrow \pi$ $^1A'$
Nitrosobenzene		52.0		0.637		-900	$\pi^* \leftarrow \pi$ $^1A'$
		52.9		1.018		1143	$\pi^* \leftarrow \pi$ $^1A'$
	13.5	12.6	0.0005	0.0004	-1.5	-2.3	$\pi^* \leftarrow \pi$ $^1A''$
	32.2	33.2	0.035	0.043	-53	-257	$\pi^* \leftarrow \pi$ $^1A'$
Nitrobenzene		36.3		0.677	117	337	$\pi^* \leftarrow \pi$ $^1A'$
		39.4		0.0002		-2.6	$\pi^* \leftarrow \pi$ $^1A''$
	45.8	44.1	0.073	0.077	-53	-100	$\pi^* \leftarrow \pi$ $^1A'$
	51.5 ^a	50.4	0.256 ^a	0.143	Positive	152	$\pi^* \leftarrow \pi$ $^1A'$
	54.6		0.602		810	$\pi^* \leftarrow \pi$ $^1A'$	
	57.5 ^a		0.831 ^a			-957	$\pi^* \leftarrow \pi$ $^1A'$
	55.6		0.889				$\pi^* \leftarrow \pi$ $^1A'$
Nitrobenzene	29.4	24.0		0.00015	Negative	-2.0	$\pi^* \leftarrow \pi$ 1B_1
		25.1					$\pi^* \leftarrow \pi$ 1A_2
	35.4	37.6	0.008	0.016	-46.0	-24.9	$\pi^* \leftarrow \pi$ 1B_2
	39.9	43.6	0.203	0.240	93.3	91.1	$\pi^* \leftarrow \pi$ 1A_1
		45.5		0.0014		-15.3	$\pi^* \leftarrow \pi$ 1B_2
	49.7		0.075		Negative		
		48.0		0.141		-154.1	$\pi^* \leftarrow \pi$ 1B_2
	51.6	49.6	0.44	0.445		257.9	$\pi^* \leftarrow \pi$ 1A_1
		52.3		0.001		-13.7	$\pi^* \leftarrow \pi$ 1A_1
		54.0		0.020		-6.9	$\pi^* \leftarrow \pi$ 1B_2
	57.9		1.825		5040	$\pi^* \leftarrow \pi$ 1B_2	
	61.0 ^b		0.87 ^b				$\pi^* \leftarrow \pi$ 1B_2
	58.0		0.610			-5164	$\pi^* \leftarrow \pi$ 1A_1

^a K. Tabei and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **38**, 965 (1965). ^b S. Nagakura, M. Kojima, and Y. Maruyama, *J. Mol. Spectrosc.*, **13**, 174 (1964).

The contributions to the B terms of the $\pi^* \leftarrow \pi$ transitions from $\pi^* \leftarrow \pi$ states are given in Table IV. In each case, the B terms of the two lowest $\pi^* \leftarrow \pi$ transitions are mainly induced by the mutual mixing of the two lowest $\pi^* \leftarrow \pi$ states, leading to the opposite sign of the B terms of these transitions. Their magnitudes are, however, influenced to some extent by the mixing of the higher $\pi^* \leftarrow \pi$ states.

In the case of phenol, aniline, and benzaldehyde, more than 85% of the Faraday B term of the two lowest $\pi^* \leftarrow \pi$ transitions originates from the magnetic mixing among the four lowest $\pi^* \leftarrow \pi$ states corresponding to the $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ states of benzene itself. Then, we try to explain the signs of the magnetic mixing among these excited states using a simplified model consisting of four frontier MOs.

The excited states of substituted benzenes corresponding to the $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ states are approximated as

$$\psi_{1B_{2u}} = C_1\psi(\phi_x \rightarrow \phi_\xi) - C_2\psi(\phi_y \rightarrow \phi_\eta) \quad (5)$$

$$\psi_{1B_{1u}} = C_3\psi(\phi_x \rightarrow \phi_\eta) + C_4\psi(\phi_y \rightarrow \phi_\xi) \quad (6)$$

$$\psi_{1E_{1ux}} = C_2\psi(\phi_x \rightarrow \phi_\xi) + C_1\psi(\phi_y \rightarrow \phi_\eta) \quad (7)$$

$$\psi_{1E_{1uy}} = C_4\psi(\phi_x \rightarrow \phi_\eta) - C_3\psi(\phi_y \rightarrow \phi_\xi) \quad (8)$$

where the coefficients C_1 – C_4 are taken to be positive. If four frontier MOs can be assumed to be insensitive to the substitutions, the following relations between molecular integrals of the electric moment and the angular momentum are obtained using alternate pairing properties^{6b,c}

$$\langle \phi_y | m_x | \phi_\eta \rangle \approx \langle \phi_x | m_x | \phi_\xi \rangle \approx \langle \phi_x | m_y | \phi_\eta \rangle \approx -\langle \phi_y | m_y | \phi_\xi \rangle \equiv m \quad (9)$$

$$\text{Im} \langle \phi_\xi | l_z | \phi_\eta \rangle \approx \text{Im} \langle \phi_x | l_z | \phi_y \rangle \equiv l \quad (10)$$

where m_x and m_y are the x and y components of the one-electron operator of the electric moment, and l_z is the z component of the one-electron operator of the orbital angular momentum. From eq 5–10, the electric and magnetic transition moments among electronic states are found to be

$$\langle \psi_{1A_{1g}} | M_x | \psi_{1B_{2u}} \rangle = \sqrt{2}(C_1 - C_2)m \quad (11)$$

$$\langle \psi_{1A_{1g}} | M_y | \psi_{1B_{1u}} \rangle = \sqrt{2}(C_3 - C_4)m \quad (12)$$

$$\langle \psi_{1A_{1g}} | M_x | \psi_{1E_{1ux}} \rangle = \sqrt{2}(C_1 + C_2)m \quad (13)$$

$$\langle \psi_{1A_{1g}} | M_y | \psi_{1E_{1uy}} \rangle = \sqrt{2}(C_3 + C_4)m \quad (14)$$

$$\text{Im} \langle \psi_{1B_{2u}} | \mu_z | \psi_{1B_{1u}} \rangle = -(\beta/\hbar)(C_1 + C_2)(C_3 + C_4)l \quad (15)$$

Table II. Wave Function of the $\pi^*-\pi$ State and the Change in the Electron Density of the Benzene Ring Associated with the $\pi^* \leftarrow \pi$ Transition (ΔQ_{bz})

Compd	State	Wave function	ΔQ_{bz}
Benzene	${}^1B_{2u}$	$\{\psi(\phi_x \rightarrow \phi_\xi) - \psi(\phi_y \rightarrow \phi_\eta)\}/\sqrt{2}$	0.0
	${}^1B_{1u}$	$\{\psi(\phi_x \rightarrow \phi_\eta) + \psi(\phi_y \rightarrow \phi_\xi)\}/\sqrt{2}$	0.0
	${}^1E_{1ux}$	$\{\psi(\phi_x \rightarrow \phi_\xi) + \psi(\phi_y \rightarrow \phi_\eta)\}/\sqrt{2}$	0.0
	${}^1E_{1uy}$	$\{\psi(\phi_x \rightarrow \phi_\eta) - \psi(\phi_y \rightarrow \phi_\xi)\}/\sqrt{2}$	0.0
Phenol	1st $\pi^*-\pi$	$0.61\psi_{3\rightarrow 6} - 0.78\psi_{4\rightarrow 5}$	0.05
	2nd $\pi^*-\pi$	$0.48\psi_{3\rightarrow 5} + 0.87\psi_{4\rightarrow 6}$	0.08
	3rd $\pi^*-\pi$	$0.79\psi_{3\rightarrow 6} + 0.61\psi_{4\rightarrow 5}$	0.04
	4th $\pi^*-\pi$	$0.87\psi_{3\rightarrow 5} - 0.48\psi_{4\rightarrow 6}$	0.03
Aniline	1st $\pi^*-\pi$	$0.57\psi_{3\rightarrow 6} - 0.82\psi_{4\rightarrow 5}$	0.10
	2nd $\pi^*-\pi$	$0.34\psi_{3\rightarrow 5} + 0.93\psi_{4\rightarrow 6}$	0.22
	3rd $\pi^*-\pi$	$0.81\psi_{3\rightarrow 6} + 0.57\psi_{4\rightarrow 5}$	0.13
	4th $\pi^*-\pi$	$0.93\psi_{3\rightarrow 5} - 0.32\psi_{4\rightarrow 6}$	0.07
Benzaldehyde	1st $\pi^*-\pi$	$0.74\psi_{3\rightarrow 5} - 0.63\psi_{4\rightarrow 6}$	-0.05
	2nd $\pi^*-\pi$	$0.30\psi_{3\rightarrow 6} + 0.94\psi_{4\rightarrow 5}$	-0.19
	3rd $\pi^*-\pi$	$0.58\psi_{3\rightarrow 5} + 0.57\psi_{4\rightarrow 6} - 0.47\psi_{3\rightarrow 6}$	-0.23
	4th $\pi^*-\pi$	$0.77\psi_{3\rightarrow 6} - 0.25\psi_{4\rightarrow 5} + 0.41\psi_{4\rightarrow 6}$	-0.15
Nitrosobenzene	1st $\pi^*-\pi$	$0.89\psi_{3\rightarrow 5} - 0.36\psi_{4\rightarrow 6}$	-0.46
	2nd $\pi^*-\pi$	$0.96\psi_{4\rightarrow 5}$	-0.53
	3rd $\pi^*-\pi$	$0.59\psi_{3\rightarrow 7} - 0.70\psi_{4\rightarrow 6}$	-0.27
	4th $\pi^*-\pi$	$0.74\psi_{3\rightarrow 6} + 0.66\psi_{4\rightarrow 7}$	-0.01
	5th $\pi^*-\pi$	$0.58\psi_{3\rightarrow 6} - 0.64\psi_{4\rightarrow 7}$	0.12
	6th $\pi^*-\pi$	$0.76\psi_{3\rightarrow 7} + 0.58\psi_{4\rightarrow 6}$	0.05
Nitrobenzene	1st $\pi^*-\pi$	$0.79\psi_{5\rightarrow 6} - 0.51\psi_{3\rightarrow 7}$	-0.23
	2nd $\pi^*-\pi$	$0.97\psi_{3\rightarrow 6}$	-0.65
	3rd $\pi^*-\pi$	$0.60\psi_{5\rightarrow 8} - 0.50\psi_{3\rightarrow 7} - 0.58\psi_{5\rightarrow 6}$	-0.56
	4th $\pi^*-\pi$	$0.91\psi_{4\rightarrow 6}$	0.42
	5th $\pi^*-\pi$	$0.91\psi_{5\rightarrow 7} + 0.37\psi_{3\rightarrow 8}$	-0.08
	6th $\pi^*-\pi$	$1.00\psi_{4\rightarrow 7}$	0.98
	7th $\pi^*-\pi$	$0.92\psi_{4\rightarrow 8}$	0.45
	8th $\pi^*-\pi$	$0.63\psi_{5\rightarrow 8} + 0.66\psi_{3\rightarrow 7}$	0.01
	9th $\pi^*-\pi$	$0.92\psi_{3\rightarrow 8} - 0.35\psi_{5\rightarrow 7}$	-0.10

Table III. Wave Function of the Lowest $\pi^*-\pi$ State and Change in the Electron Density on the Oxygen Atom Associated with the Lowest $\pi^* \leftarrow \pi$ Transition (ΔQ_O)

Compd	Wave function	ΔQ_O
Benzaldehyde	$0.77\psi_{n\rightarrow 5} + 0.57\psi_{n\rightarrow 7}$	-0.30
Nitrosobenzene	$0.81\psi_{n\rightarrow 5}$	-0.26
Nitrobenzene	$0.90\psi_{n\rightarrow 6}$	-0.29

$$\text{Im}\langle \psi_{1B_{2u}} | \mu_z | \psi_{1E_{1uy}} \rangle = (\beta/\hbar)(C_1 + C_2)(C_3 - C_4)l \quad (16)$$

$$\text{Im}\langle \psi_{1B_{1u}} | \mu_z | \psi_{1E_{1ux}} \rangle = -(\beta/\hbar)(C_1 - C_2)(C_3 + C_4)l \quad (17)$$

where β is the Bohr magneton. If one substitutes eq 11-17 into eq 2, the magnetic mixings among ${}^1B_{2u}$, ${}^1B_{1u}$, and ${}^1E_{1u}$ states are expressed as

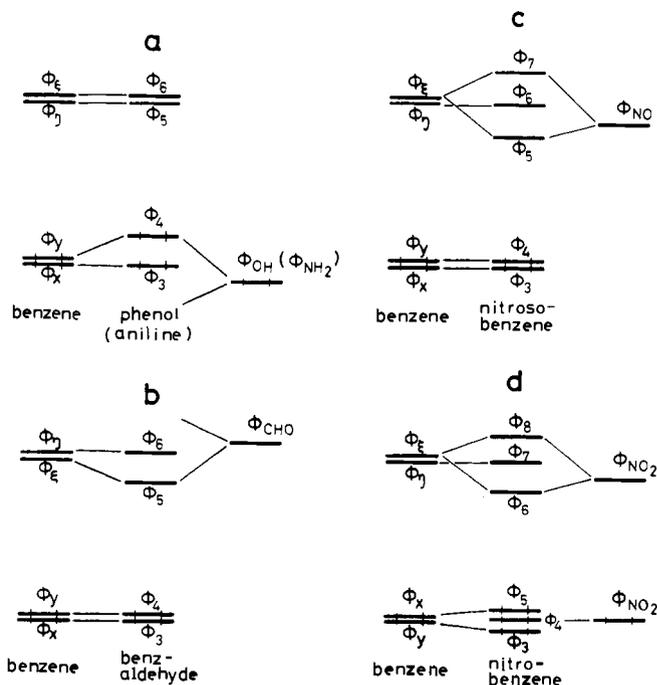
$$B_{1B_{2u}, 1B_{1u}} = -2(\beta/\hbar)(C_1^2 - C_2^2)(C_3^2 - C_4^2)m^2l / (E_{1B_{1u}} - E_{1B_{2u}}) \quad (18)$$

$$B_{1B_{2u}, 1E_{1uy}} = 2(\beta/\hbar)(C_1^2 - C_2^2)(C_3^2 - C_4^2)m^2l / (E_{1E_{1uy}} - E_{1B_{2u}}) \quad (19)$$

$$B_{1B_{1u}, 1E_{1ux}} = 2(\beta/\hbar)(C_1^2 - C_2^2)(C_3^2 - C_4^2)m^2l / (E_{1E_{1ux}} - E_{1B_{1u}}) \quad (20)$$

where $B_{1B_{2u}, 1B_{1u}}$ stands for the partial B term of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition induced by the magnetic coupling of the ${}^1B_{1u}$ state, and $E_{1B_{2u}}$ is the energy of the ${}^1B_{2u}$ state.

The value of l is not significantly affected by the substituent groups, and calculated to be negatively signed. Therefore, the

**Figure 3.** Interaction of the HOMOs and LUMOs of the benzene ring with the orbitals of the substituent group.

magnitudes and the signs of the partial B terms in eq 18-20 are determined by the coefficients, C_1-C_4 . For benzene itself, eq 18-20 lead to zero, since $C_1 = C_2 = C_3 = C_4 = 1/\sqrt{2}$.

Table IV. Contributions to the Faraday B Terms ($\beta D^2/\text{cm}^{-1}$) of Two Lowest $\pi^* \leftarrow \pi$ Transitions from Each $\pi^* \leftarrow \pi$ State

Compd	State, j	$B_{j,k} \times 10^5$ for state $k =$				$B \times 10^5$ (total B term)
		1st $\pi^* \leftarrow \pi$	2nd $\pi^* \leftarrow \pi$	3rd $\pi^* \leftarrow \pi$	4th $\pi^* \leftarrow \pi$	
Phenol	1st $\pi^* \leftarrow \pi$	0.0	37.0	-0.2	-17.0	20.3
	2nd $\pi^* \leftarrow \pi$	-37.0	0.0	-24.1	0.0	-58.7
Aniline	1st $\pi^* \leftarrow \pi$	0.0	77.7	0.0	-34.6	48.4
	2nd $\pi^* \leftarrow \pi$	-77.7	0.0	-26.7	0.0	-107.00
Benzaldehyde	1st $\pi^* \leftarrow \pi$	0.0	-57.4	2.6	24.3	-33.2
	2nd $\pi^* \leftarrow \pi$	57.4	0.0	35.9	4.8	114.9
Nitrosobenzene	1st $\pi^* \leftarrow \pi$	0.0	-275.5	-3.3	20.2	-257
	2nd $\pi^* \leftarrow \pi$	275.5	0.0	23.2	1.2	337
Nitrobenzene	1st $\pi^* \leftarrow \pi$	0.0	-54.0	0.0	0.0	-24.9
	2nd $\pi^* \leftarrow \pi$	54.0	0.0	-4.1	0.2	91.1

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

Compd	$\sum_{k \neq a, j}^{\pi^* \leftarrow \pi} B_{j,k} \times 10^5$	$\sum_{k \neq a, j}^{\pi^* \leftarrow \sigma} B_{k,a} \times 10^5$	$B_{j,a} \times 10^5$	$B \times 10^5$ (total B term)
Benzaldehyde	-0.034	0.121	-0.124	-0.037
Nitrosobenzene	-0.284	-1.809	0.049	-2.044
Nitrobenzene	-0.292	0.436	-2.458	-2.314

Figure 3a shows that the HOMO, ϕ_y , in phenol and aniline lies above the MO, ϕ_x , although the orbital energies of the MOs, ϕ_ξ and ϕ_η , are nearly identical. As the energies of the configurations of $\psi(\phi_y \rightarrow \phi_\xi)$ and $\psi(\phi_y \rightarrow \phi_\eta)$ are smaller than those of $\psi(\phi_x \rightarrow \phi_\xi)$ and $\psi(\phi_x \rightarrow \phi_\eta)$, the coefficients C_4 and C_2 are larger than C_1 and C_3 . The signs of the partial B terms of phenol and aniline are predicted as follows.

$$B_{1B_{2u}, 1B_{1u}} > 0, B_{1B_{2u}, 1E_{1u}} < 0, \text{ and } B_{1B_{1u}, 1E_{1u}} < 0 \quad (21)$$

The situation is completely inverted for the benzenes with electron-accepting groups. As shown in Figure 3b, the LUMO, ϕ_ξ , lies lower than the MO, ϕ_η , resulting in $C_1, C_4 > C_2, C_3$. The signs of the partial B terms of benzaldehyde are opposite to eq 21:

$$B_{1B_{2u}, 1B_{1u}} < 0, B_{1B_{2u}, 1E_{1u}} > 0, \text{ and } B_{1B_{1u}, 1E_{1u}} > 0 \quad (22)$$

As shown above, the signs of the partial B terms due to the magnetic mixing among the four lowest $\pi^* \leftarrow \pi$ states in phenol, aniline, and benzaldehyde are dependent only on the relative magnitude of the coefficients, $C_1 \text{--} C_4$, in which the nature of the substituent group is reflected. On the basis of this view, the signs of the partial B terms induced by the magnetic mixing among the four lowest $\pi^* \leftarrow \pi$ states were clearly explained.

On the other hand, the mixing of the higher $\pi^* \leftarrow \pi$ states is of importance in the B terms of nitrosobenzene and nitrobenzene, because of the presence of the intramolecular charge-transfer states in the lower energy region. The unoccupied orbitals in the nitroso and nitro group strongly interact with the LUMO, ϕ_ξ , of the benzene ring, and eq 9 and 10 no longer hold. Because of these complicated situations, the simplified treatment cannot be applied to nitrosobenzene and nitrobenzene.

Separate Contributions to the Faraday B Term of the Lowest $\pi^* \leftarrow n$ Transition. Table V shows the contributions to the Faraday B term of the lowest $\pi^* \leftarrow n$ transition of substituted benzene from three terms in eq 1. The magnetic mixing among $\pi^* \leftarrow \sigma$ type states and the coupling of the $\pi^* \leftarrow \pi$ state to the ground state do not contribute to the B terms of $\pi^* \leftarrow \sigma$ type transitions because of the parallel orientation of the transition moments in eq 2 and 3. The contributions from the mixing of the $\pi^* \leftarrow \pi$ states with the lowest $\pi^* \leftarrow n$ state are found to be small in these substituted benzenes, different from the cases of azaheterocycles.¹⁶ The B term of the lowest $\pi^* \leftarrow n$ transition in nitrobenzene predominantly arises from the mixing of the magnetically allowed $\pi^* \leftarrow n$ states with the ground state, $B_{k,a}$.

The magnetic mixing of the ground and the lowest $\pi^* \leftarrow n$ state, $B_{j,a}$, is most important in nitrosobenzene.

Conclusions

The Faraday B terms of some monosubstituted benzenes were calculated using the CNDO/S-CI method. The calculated values are in good agreement with the experimental data. The Faraday B terms of the two lowest $\pi^* \leftarrow \pi$ transitions are interpreted as predominantly arising from the magnetic coupling of several low-lying $\pi^* \leftarrow \pi$ states. The Faraday B terms of the lowest $\pi^* \leftarrow n$ transitions of nitrosobenzene and nitrobenzene mainly originate from the magnetic mixing of the $\pi^* \leftarrow n$ states with the ground state.

Although the four lowest $\pi^* \leftarrow \pi$ states of phenol, aniline, and benzaldehyde approximately correspond to the $1B_{2u}$, $1B_{1u}$, and $1E_{1u}$ states of benzene, intramolecular charge-transfer transitions are found in the ultraviolet region in the cases of nitrosobenzene and nitrobenzene.

In conclusion, the CNDO/S-CI method is suited for calculating the Faraday B terms of $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions of organic aromatic compounds. Furthermore, it can be conclusively stated that the measurements of the MCD spectrum, in combination with the quantum mechanical calculation of the Faraday parameter, are of great use for the investigation of the electronic structure.

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Excitation Functions of Slow Proton Transfer Reactions Involving Negative Ions

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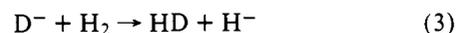
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Abstract: Excitation functions were determined for a series of slow proton and deuteron transfer reactions involving negative ions using a tandem mass spectrometer. Some of the reactions observed, for example, $\text{ND}_2^- + \text{D}_2 \rightarrow \text{D}^- + \text{ND}_3$, exhibit translational energy thresholds, even though they are exothermic. Other reactions, such as $\text{CH}_3\text{COCH}_2^- + \text{CD}_3\text{COCD}_3 \rightarrow \text{CH}_3\text{COCH}_2\text{D} + \text{CD}_3\text{COCD}_2^-$, exhibit a complex functional dependence of the cross section upon relative translational energy, which in turn is quite sensitive to the internal energy of the neutral reactant. Rate coefficients determined for these negative ion reactions in the present investigation are compared with analogous data previously reported for thermal energy reactants. The translational energy thresholds observed for several of the reactions are consistent with the existence of a potential energy barrier in the reaction coordinate between the reactants and products. It is demonstrated that the deconvoluted excitation function for the ND_2^-/D_2 reaction is of the form $\sigma \propto (E_{\text{rel}} - E_0)^{1/2}/E_{\text{rel}}$, as required by theory, and that the translational energy threshold corresponds to the Arrhenius activation energy for this process.

Among the many gas-phase ion-neutral reactions which have been studied, proton transfer processes have perhaps been the subject of greatest interest recently, owing largely to their important role in solution chemistry.^{1,2} Much of the recent research has been concerned with proton transfer to negative ions, and has focused on the determination of rate coefficients for thermal energy reactions, and the application of such data in constructing gas-phase acidity and basicity scales.³ While the rates for many of these reactions are typical of those usually observed for exothermic or thermoneutral reactions, several interesting exceptions have been observed. In particular, certain exothermic proton transfer reactions of amide ions^{4,5} and of larger delocalized negative ions⁶ have been found to be remarkably slow. These observations prompted some tentative conclusions with respect to the dynamics of slow proton transfer reactions of negative ions.^{5,6} Such conclusions, based solely on the magnitude of rate coefficients measured at a single temperature, cannot of course provide a detailed picture of the reaction dynamics, since a low rate coefficient for a particular proton transfer reaction of this type could be explained by either an activation energy barrier (as has been suggested for the amide ion reactions⁵) or by a low entropy factor (as suggested for the delocalized negative ion reac-

tions⁶). Obviously, in some cases, both factors might be operative.

Owing to the limitations of rate data which were just discussed, increasing interest has developed in the determination of translational energy dependences of reactive scattering cross sections (so-called "excitation functions") as a probe of reaction dynamics.^{7,8} Such data can provide considerable information with respect to energy barriers for reactions of interest. This is well illustrated by investigations of the three closely related processes,



which have been discussed by Henschman et al.^{9,10} All three of these are nominally thermoneutral reactions. However, the excitation functions for reactions 2 and 3, which are quite similar, both exhibit translational energy thresholds, whereas reaction 1 exhibits no threshold, and its cross section decreases monotonically with increasing energy.⁹⁻¹¹ These results are consistent with the calculated potential surfaces on which these reactions proceed, since the surfaces relevant to reactions 2 and 3 show energy barriers between the reactants and products,^{12,13} while the surface relevant to reaction 1 contains a deep basin

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