Observed and Calculated Faraday *B* Terms in Monosubstituted Benzenes

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Abstract: MCD spectra of monosubstituted benzenes were measured. From these spectra, Faraday *B* terms were determined and compared with *B* terms calculated using wavefunctions obtained from the Pariser–Parr–Pople (P–P–P) approximation. The calculated *B* terms are in good agreement with the experimental values derived from MCD spectra both in signs and in magnitudes. A dipole velocity operator was found to be superior in explaining experimental results to a dipole length operator. It was shown that the observed Faraday *B* terms were well explained by taking into account four or five lower lying excited states of monosubstituted benzenes.

The technique of magnetic circular dichroism (MCD) has been extremely useful in analyzing ambiguous and complicated electronic absorption spectra and in elucidating the magnetic properties of electronic states of ions and molecules.[1-3] Recently, the MCD spectra of the $^1E_{1u} \leftarrow {}^1A_{1g}$ transitions of benzene derivatives studied[4-6] and the magnetic moments of the $^1E_{1u}$ states have been extracted. These values are in good agreement with those[7] calculated using wavefunctions obtained from the Pariser–Parr–Pople (P–P–P) approximation.[8-10] SCF-MO theory has also succeeded in explaining the experimental magnetic moments of various nonbenzenoid aromatic hydrocarbons.[11-14]

In the absence of an *n*-fold axis ($n \geq 3$), one can expect only the Faraday *B* term, which arises from the mixing of electronic states by an external magnetic field. Several authors have calculated the Faraday *B* terms of substituted benzenes,[15,16] indole derivatives,[16] and alternant[17] and nonalternant[18] aromatic hydrocarbons and found good agreement between the calculated and experimental values. Of particular interest has been the magnetic circular dichroism of monosubstituted benzenes[19-21] because of the intriguing spectral changes induced by substitutions. Foss and McCarville[19] have correlated the signs and magnitudes of the magnetic circular dichroism of mono- and disubstituted benzenes with the Hammett σ_{para} values of substituents. Shieh et al.[20] have reported that the Faraday *B* term of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of monosubstituted benzene is proportional to the empirical transition moment parameter, *q*, advanced by Petruska,[22] but they have neither discussed the Faraday *B* terms of the second $\pi \rightarrow \pi^*$ transition nor performed the quantum mechanical calculation of the Faraday *B* terms. Therefore, we have calculated the Faraday *B* terms of monosubstituted benzenes by the P–P–P approximation and compared them with the observed values.

Monosubstituted benzenes have C_{2v} or C_s symmetry, in which all $\pi \rightarrow \pi^*$ transitions become electronically allowed. For phenol and anisole, the first and second excited states correspond to the $^1B_{2u}$ and $^1B_{1u}$ states of benzene, respectively. However, the second transitions of aniline, styrene, benzaldehyde, and nitrobenzene are assigned to intramolecular charge-transfer bands between benzene ring and substituent groups.[23-25] We report and discuss the first two transitions of monosubstituted benzenes because the magnetic circular dichroism in vacuum ultraviolet region can not be measured with a conventional circular dicrometer with quartz optics.

Experimental Section

Aniline, anisole, phenol, styrene, benzonitrile, benzaldehyde, and nitrobenzene were distilled under reduced pressure, and benzoic acid was purified by recrystallization from water. The MCD and uv spectra were measured on a JASCO J-20A recording circular dichrometer equipped with a 12.5-kG electromagnet and on a Hitachi EPS-3T recording spectrophotometer, respectively. The maximum absorbance range used for measurements was 0.9–1.3. All the measurements were carried out at room temperature using *n*-heptane as a solvent.

Theoretical Section

We have calculated the electronic transition energies, the oscillator strengths, and the Faraday *B* values of monosubstituted benzenes by use of the P–P–P approximation, including configuration interactions (CI) among all singly excited configurations. One-center-core and repulsion atomic integrals were evaluated from the valence state ionization potentials and electron affinities. Two-center-core and repulsion integrals were calculated by use of Wolfsberg–Helmholtz[26] and Nishimoto–Mataga[27] equations, respectively.

The Faraday *B* terms of a transition $a \rightarrow j$ are given by[1]

$$B_{a \rightarrow j} = Im \left\{ \sum_{k \neq a} \frac{\langle k|\mu|a\rangle}{E_k - E_a} \cdot \langle a|\mathbf{m}|j\rangle \times \langle j|\mathbf{m}|k\rangle + \sum_{k \neq j} \frac{\langle j|\mu|k\rangle}{E_k - E_j} \cdot \langle a|\mathbf{m}|j\rangle \times \langle k|\mathbf{m}|a\rangle \right\} \quad (1)$$

where μ and $\mathbf{m}$ denote the magnetic and electric moment operators, respectively, and E_a, E_j and E_k are energies of states *a*, *j*, and *k*, respectively. The magnetic moments were computed according to the procedure described in our earlier paper.[7] The electric moments were evaluated by use of a dipole length operator, $\mathbf{r}$ and a dipole velocity operator, ∇.[28] The orthogonalized set of atomic oribitals obtained from the Löwdin procedure[29] was used for the computation of these quantities.

It has been pointed out by Seamans and Moscowitz[30] and Caldwell and Eyring[31] that the Faraday *B* terms calculated for a noncentric molecule using an incomplete set of state functions are origin dependent. Caldwell and Eyring[31] have proposed that origin-dependent quantities should be evaluated at the midpoint between the centers of charge for the ground and excited states. In this work, the origin is set at the center of charge of the ground state, because of the small displacement of the center of charge of the ground state from that of the excited states.

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

Results and Discussion

The MCD and uv spectra of the monosubstituted benzenes are shown in Figures 1–6, where ϵ and $[\theta]_M$ denote

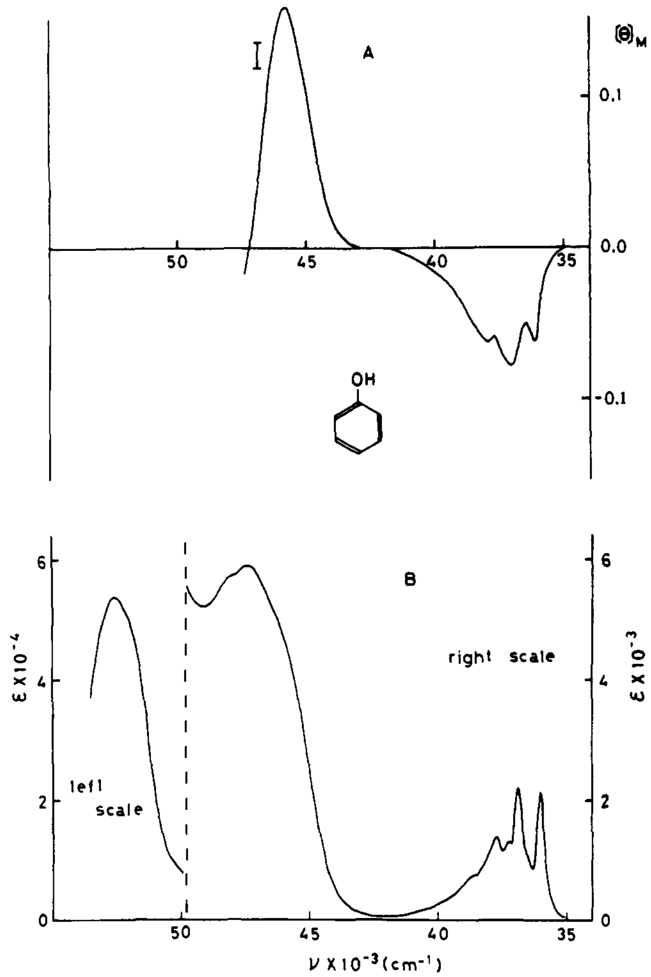

Figure 1. MCD (A) and uv (B) spectra of phenol in *n*-heptane solution at room temperature.

the molar extinction coefficient in liter mole^{-1} centimeter^{-1} and molar ellipticity in degree deciliter decimeter^{-1} mole^{-1} gauss^{-1}, respectively. The MCD spectra of aniline and nitrobenzene coincide with those of Shieh et al.[20] and are not included in the figures in this paper. The first and second $\pi \to \pi^*$ transitions of monosubstituted benzenes are observed in the spectral regions of 34-40 × 10^3 cm^{-1} and 38-50 × 10^3 cm^{-1}, respectively. In the case of aniline, phenol, and anisole, which are benzene derivatives with electron-donating groups, the negative and positive magnetic circular dichroism is observed for the first and second $\pi \to \pi^*$ transitions, respectively. Benzonitrile, benzoic acid, benzaldehyde, and nitrobenzene show positive and negative magnetic circular dichroism for the first and second $\pi \to \pi^*$ transitions, respectively, which is typical of the benzene derivatives with electron-accepting groups. These results are in good agreement with the data reported by Foss and McCarville[19] and Shieh et al.[20] The MCD spectrum of styrene is similar to that of benzene derivatives with electron-accepting substituents, but smaller in magnitude than that of the other monosubstituted benzenes. The vibronic effect is not considered to be negligible for the MCD spectrum of styrene. The $n \to \pi^*$ transition of benzaldehyde was clearly observed with its vibronic structures in the lowest wavenumber region (25-34 × 10^3 cm^{-1}) of MCD and uv spectra, while nitrobenzene indicated weak and ambiguous magnetic circular dichroism in the region of the $n \to \pi^*$ transition. We have resolved the overlapping MCD and absorption bands by a curve fitting procedure using gaussian functions and then obtained the Faraday B values by use of the method of moments.[2] These values are listed in Tables I and II.

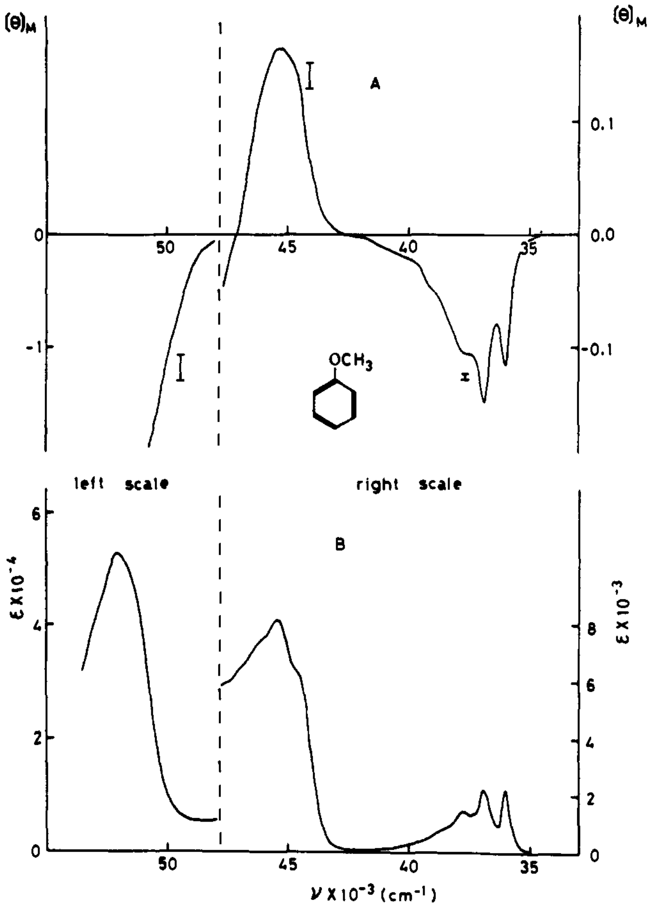

Figure 2. MCD (A) and uv (B) spectra of anisole in *n*-heptane solution at room temperature.

The experimental and theoretical transition energies and oscillator strengths are presented in Table III, where $f_{\text{calcd}}(\mathbf{r})$ and $f_{\text{calcd}}(\nabla)$ stand for the oscillator strengths calculated by use of dipole length and dipole velocity operators, respectively. The $f_{\text{calcd}}(\nabla)$ values agree with the f_{obsd} values, while the $f_{\text{calcd}}(\mathbf{r})$ values are larger than their experimental data. The calculated transition energies are in good agreement with the observed values. Tables I and II show that the calculated B values also agree fairly well with the experimental values both in signs and in magnitudes. Although the $B_{\text{calcd}}(\mathbf{r})$ values tend to be larger than B_{obsd} values, the $B_{\text{calcd}}(\nabla)$ values are in good agreement with the experimental data except for the second $\pi \to \pi^*$ transitions of styrene, benzonitrile, benzoic acid, and anisole. For these transitions, the vibronic effects seem to be significant because the magnetic circular dichroism of these transitions are comparable in order of magnitude with that of the $^1B_{1u} \leftarrow {}^1A_{1g}$ symmetry-forbidden transition of benzene itself.

The major part of the Faraday B terms of the first two $\pi \to \pi^*$ transitions may come from the mixing with the lowest four or five excited electronic states, because the terms with larger denominators in eq 1 are considered to be negligibly small. Therefore, eq 1 leads to

$$B_{a\to j} = \sum_{k\neq a,j}^{4\text{ or }5} B_{a\to j}{}^{k},$$

$$B_{a\to j}{}^{k} = Im\left\{\frac{\langle j|\mu|k\rangle}{E_k - E_j}\cdot\langle a|\mathbf{m}|j\rangle \times \langle k|\mathbf{m}|a\rangle\right\} \qquad (2)$$

where summation is over the lowest four or five excited states. Equation 2 accounts for 80-105% of the total calcu-

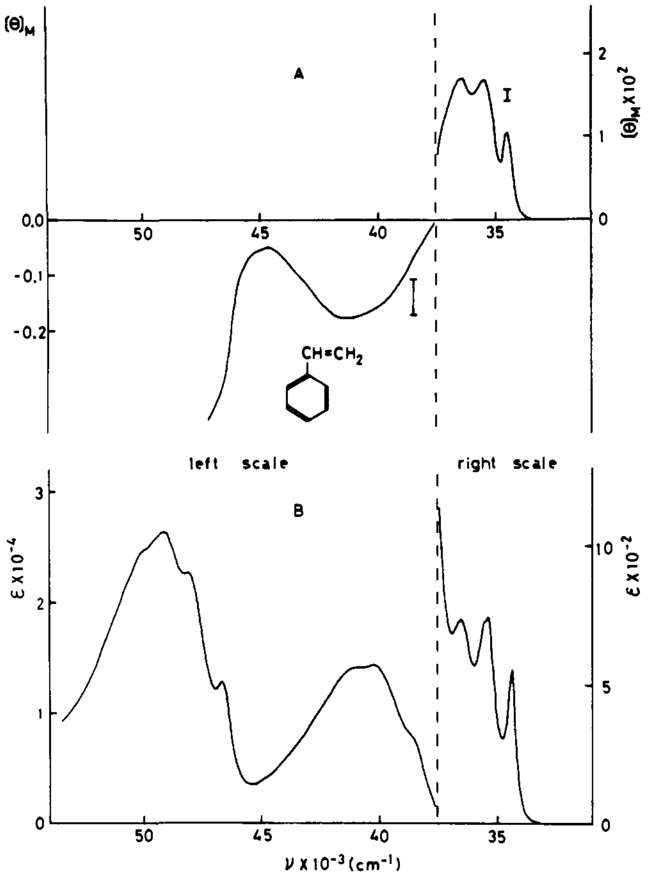

Figure 3. MCD (A) and uv (B) spectra of styrene in *n*-heptane solution at room temperature.

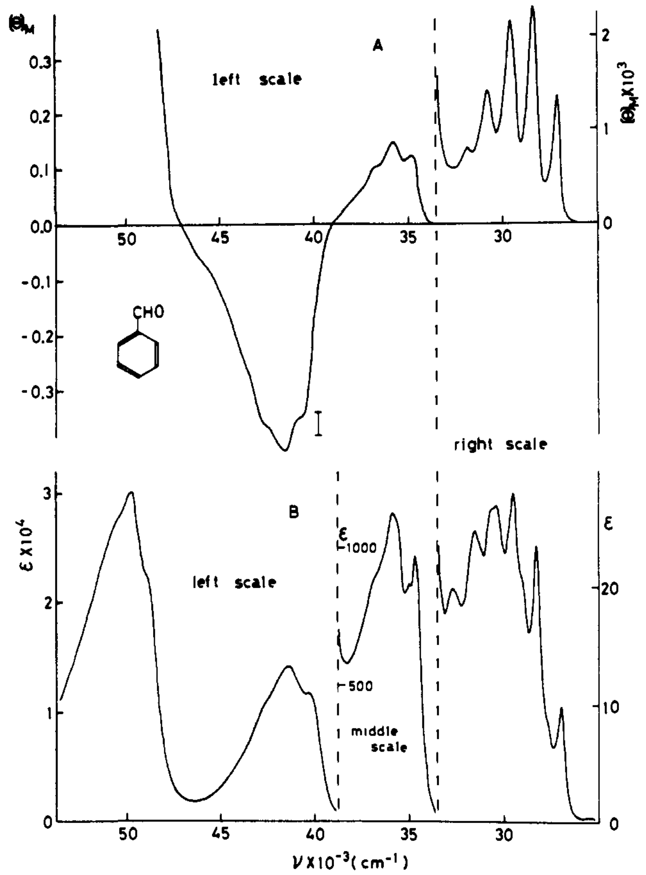

Figure 5. MCD (A) and uv (B) spectra of benzaldehyde in *n*-heptane solution at room temperature.

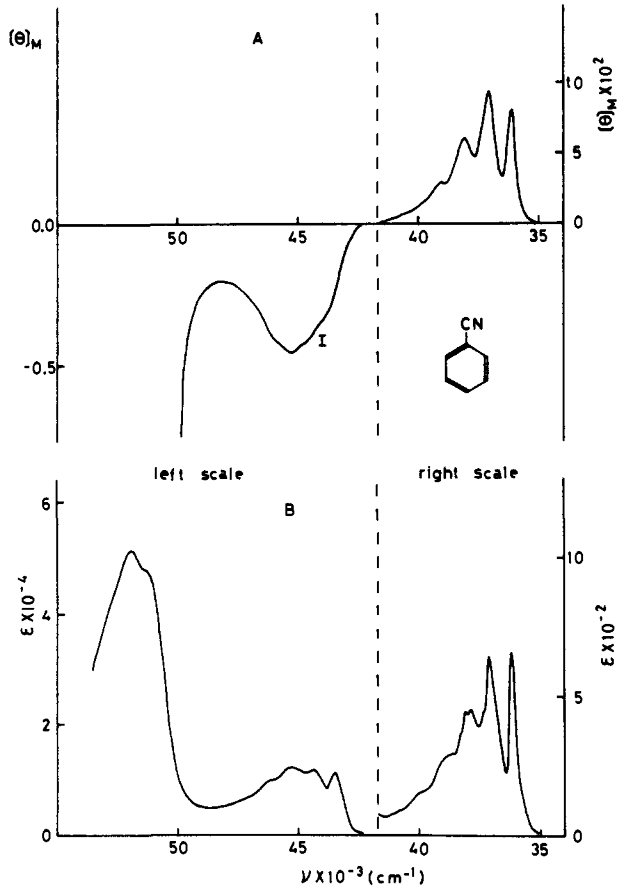

Figure 4. MCD (A) and uv (B) spectra of benzonitrile in *n*-heptane solution at room temperature.

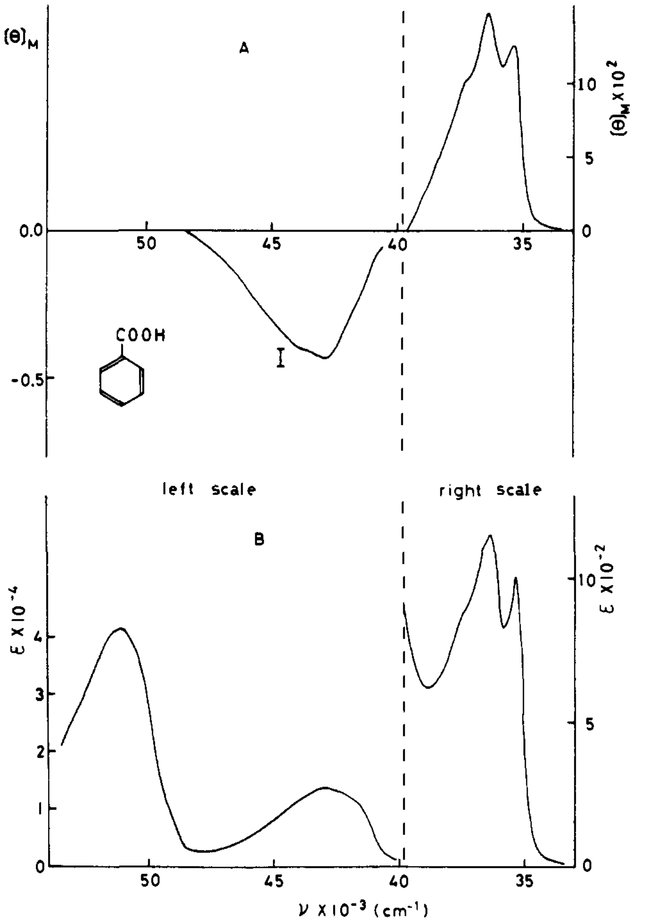

Figure 6. MCD (A) and uv (B) spectra of benzoic acid in *n*-heptane solution at room temperature.

Table I. Observed and Calculated Faraday B Values of the First $\pi \rightarrow \pi^*$ Transitions of Monosubstituted Benzenes (10^{-5} $\beta D^2/cm^{-1}$)

	B_{obsd}	$B_{calcd}(r)^a$	$B_{calcd}(\nabla)^a$
Aniline	49.0	136.6	49.2
Phenol	18.3	66.3	24.2
Anisole	29.9	73.0	27.1
Styrene		−0.5	1.0
Benzonitrile	−18.9	−33.5	−13.7
Benzaldehyde	−37.5	−86.1	−32.3
Benzoic acid	−37.5	−47.8	−18.0
Nitrobenzene	−46.0	−166.6	−49.4

[a] Calculated at the center of charge.

Table II. Observed and Calculated Faraday B Values of the Second $\pi \rightarrow \pi^*$ Transitions of Monosubstituted Benzenes (10^{-5} βD^2 cm^{-1})

	B_{obsd}	$B_{calcd}(r)^a$	$B_{calcd}(\nabla)^a$
Aniline	−94.5	−233.3	−84.6
Phenol		−157.4	−60.8
Anisole	−27.5	−162.8	−64.6
Styrene	53.8	45.9	19.6
Benzonitrile	102.9	113.0	51.3
Benzaldehyde	118.1	173.0	69.1
Benzoic acid	130.2	141.4	56.3
Nitrobenzene	93.3	257.0	78.4

[a] Calculated at the center of charge.

Table III. Observed and Calculated Transition Energies and Oscillator Strengths of Monosubstituted Benzenes

	ν_{obsd},^{a} cm^{-1}	ν_{calcd}, cm^{-1}	f_{obsd}	f_{calcd} (r)	f_{calcd} (∇)
Aniline	35200	35100	0.024	0.078	0.022
	42900	43200	0.178	0.446	0.195
	50800	52000	0.638	0.502	0.199
		53800		0.960	0.397
Phenol	37100	37000	0.021	0.056	0.017
	47300	46300		0.230	0.099
	52700	54200		0.877	0.360
		54800		1.185	0.489
Anisole	37100	37000	0.021	0.053	0.016
	46100	45900	0.131	0.283	0.129
	52100	54000	0.730	0.848	0.344
		54500		1.150	0.486
Styrene	35400	37500		0.0	0.0
	40800	42100	0.292	0.674	0.336
	49600	50700	0.619	0.493	0.186
		52500		0.743	0.332
		53500		0.0	0.0
Benzonitrile	37400	38000	0.003	0.006	0.0015
	45300	44900	0.210	0.556	0.326
	52000	53100	0.737	0.799	0.316
		53100		0.943	0.476
Benzaldehyde	35800	37100	0.010	0.020	0.006
	41700	42200	0.235	0.501	0.274
	50500	50300	0.551	0.354	0.127
		52600		0.567	0.270
Benzoic acid	36600	37700	0.010	0.013	0.004
	43300	44100	0.259	0.445	0.244
	51400	50800	0.657	0.055	0.027
		52900		0.728	0.258
		53400		0.709	0.337
Nitrobenzene	35400	35800	0.008	0.034	0.008
	39900	39700	0.203	0.541	0.201
	49700	47900	0.075	0.045	0.027
		50200		0.310	0.044
	51600	52200	0.439	0.450	0.175

[a] Obtained from a curve fitting procedure.

Table IV. Theoretical $B_{a \rightarrow j}{}^k$ Values[a] of the First and Second $\pi \rightarrow \pi^*$ Transitions of Monosubstituted Benzenes ($\sim 10^{-5}$ $\beta D^2/cm^{-1}$)

	j/k	1	2	3	4	5
Aniline	1	0.0	60.8	0.0	−18.5	
	2	−60.8	0.0	−24.6	0.0	
Phenol	1	0.0	35.8	0.0	−14.1	
	2	−35.8	0.0	−27.3	0.0	
Anisole	1	0.0	40.5	−0.1	−16.2	
	2	−40.5	0.0	−27.2	0.0	
Styrene	1	0.0	1.3	−0.2	−0.3	0.0
	2	−1.3	0.0	15.6	2.1	0.0
Benzonitrile	1	0.0	−22.5	0.0	9.5	
	2	22.5	0.0	22.7	0.0	
Benzaldehyde	1	0.0	−43.9	−0.9	14.0	
	2	43.9	0.0	12.0	−0.3	
Benzoic acid	1	0.0	−28.3	0.6	1.4	9.4
	2	28.3	0.0	3.8	20.4	0.8
Nitrobenzene	1	0.0	−58.6	0.0	0.0	13.6
	2	58.6	0.0	5.5	1.8	0.0

[a] Calculated at the center of charge by use of ∇ operator.

Table V. The Faraday B Values Calculated at the Point, Being 10 Å Away from the Center of Charge of the Ground State in the Direction of the Long Axis of the Molecules (10^{-5} $\beta D^2/cm^{-1}$)

	1st $\pi \rightarrow \pi^*$ transition		2nd $\pi \rightarrow \pi^*$ transition	
	B_{calcd} (r)	B_{calcd} (∇)	B_{calcd} (r)	B_{calcd} (∇)
Aniline	126.0	41.7	−209.1	−84.6
Phenol	66.1	20.3	−111.8	−60.8
Anisole	70.4	21.8	−119.5	−64.7
Styrene	−0.5	0.7	34.8	14.9
Benzonitrile	−30.5	−9.7	92.2	51.3
Benzaldehyde	−74.7	−23.6	151.1	67.5
Benzoic acid	−42.8	−12.9	74.7	53.0
Nitrobenzene	−126.8	−34.3	143.4	78.4

lated Faraday *B* terms. The values of $B_{a \rightarrow j}{}^k$ are presented in Table IV. The most dominant contribution to the Faraday *B* terms comes from the mixing between the first two excited states, resulting in the opposite sign of the Faraday *B* terms of these transitions. The magnitude of the Faraday *B* term of the first transition decreases through the mixing with the third, fourth, and fifth excited electronic states, while that of the second transition increases through the mixing with these higher excited states.

As mentioned before, the theoretical Faraday *B* terms depend on the choice of origin in the present calculations. In order to find out how strongly the calculated Faraday *B* terms depend on the origin, we have also calculated the Faraday *B* terms at the point, *P*, being 10 Å away from the center of charge in direction of the long axis of the molecule. These values are shown in Table V. The origin dependence of the calculated Faraday *B* values is at most 40-50% per 10 Å.

Conclusion

The calculated Faraday *B* terms of monosubstituted benzenes within the framework of the P-P-P approximation are in good agreement with experimental data both in sign and in magnitude. However, it is concluded that the dipole velocity method is preferable to the dipole length method in such a sense that the former reproduces the experimental values well.

It is also concluded that the Faraday *B* terms of the lowest two $\pi \rightarrow \pi^*$ transitions in monosubstituted benzenes are mainly induced by the mixing among the lowest four or five excited states, although the first term in eq 1 and the higher excited states should not be neglected for the larger molecules having more closely spaced electronic states.

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Ab Initio SCF Computations on Benzene and the Benzenium Ion Using a Large Contracted Gaussian Basis Set

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Abstract: Improved SCF computations on the benzene molecule and especially the benzenium ion (protonated benzene), using a large contracted gaussian basis set including polarization functions, are presented. The results for the benzenium ion are consistent with the conventional model of a $C_5H_5^+$ structure with an attached CH_2 group, the whole somewhat modified and stabilized by hyperconjugation. The calculations predict the equilibrium HCH angle at the protonated carbon atom to be 103.5° and that the distance to the adjacent carbon atom is lengthened by 0.055 Å. The proton affinity is found to be 189 kcal/mol as compared with an experimental value of 183.1. One-electron properties are compared with corresponding benzene values, and changes at the ring positions are discussed. A population analysis for both σ and π (and quasi-π) overlap populations and charges is reported and discussed. From the overlap populations in the ring bonds, it is estimated that the lateral C-C bonds are shortened by 0.015 Å, and the C-C bonds para to the CH_2 group are lengthened by 0.020 Å, as compared with benzene.

In 1954 Muller, Pickett, and Mulliken[3] published some semiempirical π-electron-only SCF calculations bearing on the question of hyperconjugation (HCJ) in $C_6H_7^+$, that is, protonated benzene. Allowance for charge reorganization in the σ-electron framework was made by use of the so-called ω technique. When the authors made these relatively crude calculations, they looked forward to the day when a good all-electron SCF calculation could be made.

From the results of these calculations, estimates of the contribution of HCJ to the stabilization energy of $C_6H_7^+$ (in the free state, of course, whereas experimental observations[4] are mostly in solution) yielded values which depended on the assumed values of the semiempirical parameters used. However, with a fairly reasonable choice of parameters ($\omega = 1.4$ for charge redistribution and $\delta = -0.2$ for electronegativity of hydrogen vs. carbon), a vertical HCJ energy of 21 kcal/mol was obtained, or a net HCJ energy of 14 kcal/mol after allowing for changes in bond length as a result of HCJ.

Empirical evidence[5] has led organic chemists to assume a localized model (see Figure 1) for $C_6H_7^+$ in which five carbon atoms (2-6 in Figure 2) form a semi-aromatic $C_5H_5^+$ structure, while the sixth ring carbon (1 in Figure 2) is bound in an essentially aliphatic CH_2 group with its plane perpendicular to the ring (symmetry C_{2v} if the ring remains planar). However, an examination of HCJ resonance structures (Figure 1) shows two groups of structures which are hyperisovalent; that is, the number of π plus quasi-π bonds is the same in both. The one group of structures has full benzene aromaticity: two Kekule (plus three Dewar) structures each having three π bonds, with the plus charge on the H_2. The other group of three structures has the plus charge on the C_5H_5 with the CH_2 neutral; here there are two π and one quasi-π bonds. One expects stronger HCJ in such an isovalent case than occurs in the case of sacrificial HCJ (see Figure 1 for an example of the latter)[6] and, in ref 3, it was argued that, as a result, the aromatic character of the benzene ring would be present to a considerable extent in $C_6H_7^+$. However, the empirical evidence, and, it may be said here, the results of the present computation, indicate that this partial preservation of the aromatic character of the ring, through HCJ, while certainly present, is less important than suggested in ref. 3.

Rather recently,[7] Hehre and Pople have carried through an all-electron SCF computation on the benzenium ion. In most of their computations, they used a minimal basis set