# Magnetic Circular Dichroism Studies on *o*-, *m*-, and *p*-Nitroanilines and *o*-, *m*-, and *p*-Aminobenzoic Acids

Akira KAITO, Akio TAJIRI, and Masahiro HATANO

*Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai 980*

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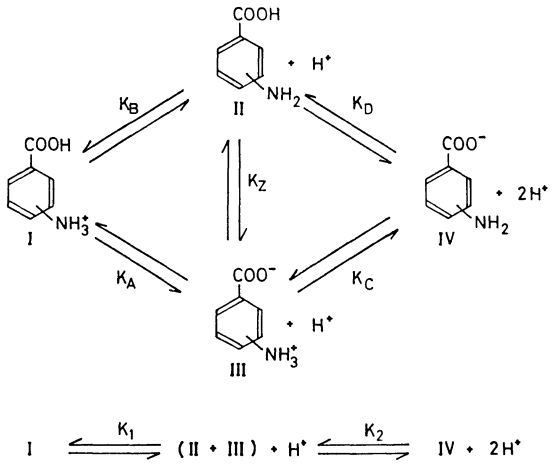
The MCD and UV spectra of *o*-, *m*-, and *p*-nitroanilines and *o*-, *m*-, and *p*-aminobenzoic acids were measured. Some ambiguous absorption bands, which strongly overlap each other, can be separated in the MCD spectra. The Faraday *B* terms were calculated using wave functions obtained from the Pariser-Parr-Pople (PPP) method; the values are in good agreement with the experimental values derived from the MCD spectra. The spectral assignments are discussed not only by comparing the excited states of nitroanilines and aminobenzoic acids with those of benzene itself, but also by taking account of the electron migration between the benzene ring and the substituent groups. On the other hand, it turns out from the measurements of the MCD spectra that the zwitterion, $C_6H_4(NH_3^+)CO_2^-$, exists in aqueous solutions of *o*- and *m*-aminobenzoic acids.

The magnetic circular dichroism (MCD) technique has been shown to be useful for elucidating the magnetic moments in the degenerate electronic states and for analyzing the electronic spectra.[1-4] For highly symmetrical molecules, we can expect the Faraday *A* and *C* terms originating from the Zeeman splitting of the degenerate ground and excited states. On the other hand, only the Faraday *B* term, due to the mixing of the electronic states by the external magnetic field, is present for the molecules of lower symmetry.

The MCD spectra of substituted benzenes have been extensively investigated,[5-11] because the experimental results are sensitive to the substituents' effects. However, only slight attention has been paid to the MCD of the benzenes containing both electron-donating and electron-accepting substituents, whose electronic spectra are characterized by the appearance of an intense absorption band in the lower wave number region (25000—40000 $cm^{-1}$). The dissimilarity of the electronic spectra of these benzene derivatives from that of benzene itself is considered to be based on the fact that some intramolecular charge-transfer transitions have been found in the former along with the $\pi \rightarrow \pi^*$ transitions of the benzene ring. Tanaka[12] has given the spectral assignments of *p*-nitroaniline by measuring the polarized absorption spectrum of single crystals of *p*-nitroaniline. Some bands which are ambiguous and hidden in solution become evident in the crystalline spectrum.

On the other hand, the MCD technique is occasionally used for elucidating the complicated electronic spectra of ions and molecules. The strongly overlapping absorption bands of some aromatic organic compounds[13] have been separated, and the hidden transitions of substituted biphenyls[14] have been detected in the MCD spectra. It is one of the purposes of this work to apply the MCD technique to clarification of the ambiguous and complicated electronic spectra of *o*-, *m*-, and *p*-nitroanilines and *o*-, *m*-, and *p*-aminobenzoic acids.

In aqueous solutions of *o*-, *m*-, and *p*-aminobenzoic acids, there seem to exist four chemical species in equilibria, as shown in the diagram below.




The ionization constants, $K_1$ and $K_2$, have been determined experimentally by the titration method.[15] Some investigators[15,16] have estimated the equilibrium constant, $K_z$, for ionization of neutral aminobenzoic acid (II) to the zwitterion (III). However, it is difficult to recognize the existence of the zwitterion (III) with the aid of the usual spectroscopic methods, such as absorption spectroscopy. This is because the absorption spectra of aminobenzoic acids are so complicated that the bands characteristic of the zwitterion (III) are hidden behind the bands due to other species of aminobenzoic acids. Another purpose of this work is to analyze the complicated electronic spectra of aminobenzoic acids in aqueous solutions in various pH ranges on the basis of the signs of the MCD spectra, and to show the existence of the zwitterion (III) in aqueous solutions.

## Experimental

*o*-, *m*-, and *p*-Nitroanilines and *o*- and *p*-aminobenzoic acids were purified by recrystallization from water-ethanol. *m*-Aminobenzoic acid was sublimed after recrystallization from water. The MCD and UV spectra were measured with a JASCO J-20A recording spectropolarimeter equipped with a 12.5 kG electromagnet and with a Hitachi EPS-3T recording spectrophotometer, respectively. The experimental Faraday *B* terms were obtained by the use of the following equation:

$$B = -(1/33.53\nu_{max}) \int_{band} [\theta]_M d\nu \qquad (1)$$

## Theoretical

The electronic transition energies and the Faraday *B* terms of nitroanilines and aminobenzoic acids were

calculated by the Pariser-Parr-Pople (PPP) approximation,[17] including configuration interactions (CI) among all singly excited configurations. One-center electron repulsion integrals and one-center core integrals were evaluated from valence state ionization potentials and electron affinities. The Nishimoto-Mataga[18] method was used for the estimation of two-center electron repulsion integrals. The resonance integrals were calculated in accordance with the Wolfsberg-Helmholtz equation.[19]

The Faraday $B$ terms of a transition $j \leftarrow a$ is given by[1-4]

$$B_{a\to j} = \mathrm{Im}\{\sum_{k\neq a} (\langle k|\boldsymbol{\mu}|a\rangle/(E_k-E_a))\cdot\langle a|\boldsymbol{m}|j\rangle\times\langle j|\boldsymbol{m}|k\rangle + \sum_{k\neq j} (\langle j|\boldsymbol{\mu}|k\rangle/(E_k-E_j))\cdot\langle a|\boldsymbol{m}|j\rangle\times\langle k|\boldsymbol{m}|a\rangle\}, \quad (2)$$

where $\boldsymbol{m}$ and $\boldsymbol{\mu}$ stand for the magnetic and electric dipole moment operators, respectively, and $E_a$, $E_j$, and $E_k$ are the energies of states, $a$, $j$, and $k$, respectively. The electric transition moments in Eq. 2 were evaluated by the use of the dipole length operator, $\boldsymbol{r}$, and the dipole velocity operator, $\boldsymbol{\nabla}$. The orthogonalized atomic orbital obtained by the Löwdin procedure[20] was used for the calculation of the magnetic and electric moments in Eq. 2.

It is known that the Faraday $B$ terms calculated for a noncentric molecule using a limited basis set are origin dependent.[7,21] Caldwell and Eyring[7] have suggested that the error introduced by employing a limited basis set is minimized at the center of charge density. Accordingly, the origin is chosen at the center of charge of the ground state in this work.

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

## Results and Discussion

The MCD (A) and UV (B) spectra of *o*- and *m*-nitroanilines are shown in Figs. 1 and 2. The single absorption band of *m*-nitroaniline observed in the higher wave number region (38000—48000 cm$^{-1}$) is split into two in the MCD spectrum, whereas the MCD spectrum of *o*-nitroaniline is weak and ambiguous in this spectral region.

The MCD and UV spectra of *p*-nitroaniline are shown in Fig. 3. In the region of 33000—39000 cm$^{-1}$, one can see a positive MCD band originating from the second $\pi\to\pi^*$ transition, which is obscured by the first intense $\pi\to\pi^*$ transition in the absorption spectrum. Two MCD bands appear with opposite signs in the higher wavenumber region (39000—48000 cm$^{-1}$), although these transitions are strongly overlapping in the absorption spectrum.

Figures 4—6 show the MCD and UV spectra of *o*-, *m*-, and *p*-aminobenzoic acids in heptane–dioxane (9 : 1 in volume) solution, in which only the neutral aminobenzoic acid (II) may be stable. *p*-Aminobenzoic acid exhibits negative and positive MCD bands at 33800 and at 36800 cm$^{-1}$, respectively, while a single absorption band appears in this spectral region. Each sign of the MCD spectra of *o*- and *m*-aminobenzoic acids is the same as that of *p*-aminobenzoic acid.

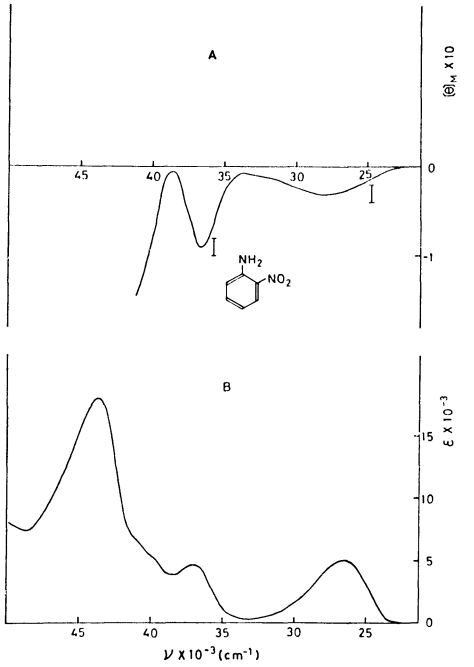



Fig. 1. MCD (A) and UV (B) spectra of *o*-nitroaniline in heptane solution at room temperature.

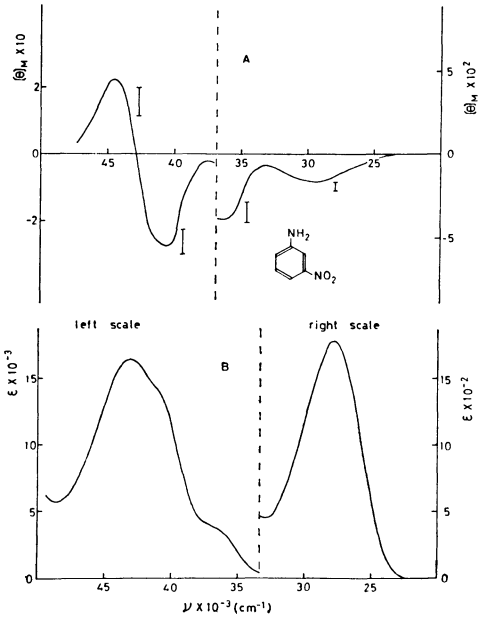



Fig. 2. MCD (A) and UV (B) spectra of *m*-nitroaniline in heptane-dioxane (9 : 1 in volume) solution at room temperature.

Thus, the MCD technique can be said to be a useful tool for elucidating the ambiguous absorption bands which are strongly overlapping in the absorption spectra. Three or four electronic transition scan be identified in the MCD and absorption spectra of nitroanilines and aminobenzoic acids.

The observed and calculated transition energies and Faraday $B$ terms are summarized in Table 1, where

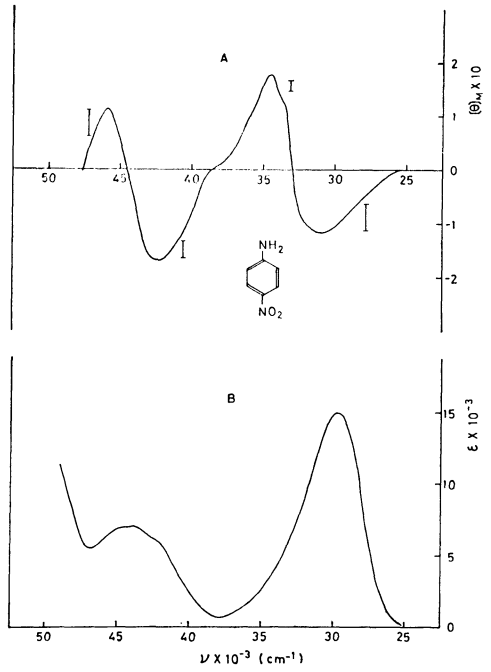



Fig. 3. MCD (A) and UV (B) spectra of *p*-nitroaniline in heptane-dioxane (9 : 1 in volume) solution at room temperature.

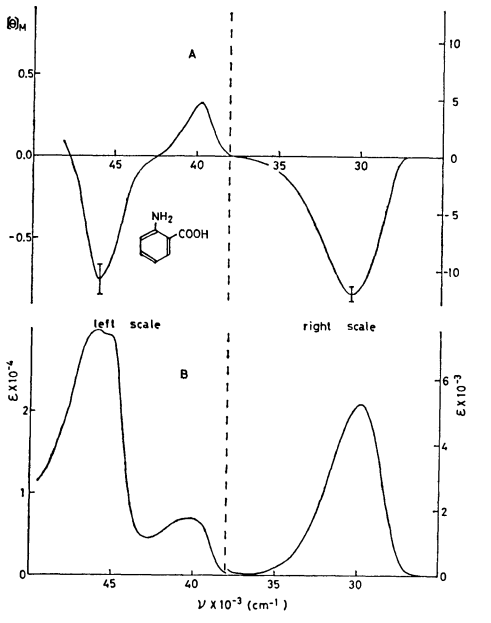



Fig. 4. MCD (A) and UV (B) spectra of *o*-aminobenzoic acid in heptane-dioxane (9 : 1 in volume) solution at room temperature.

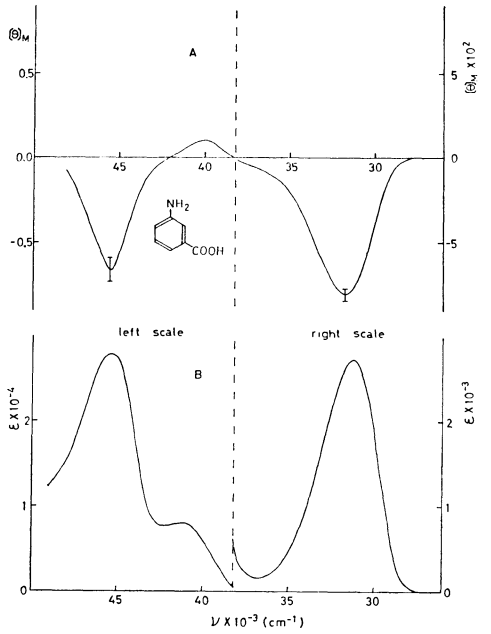



Fig. 5. MCD (A) and UV (B) spectra of *m*-aminobenzoic acid in heptane-dioxane (9 : 1 in volume) solution at room temperature.

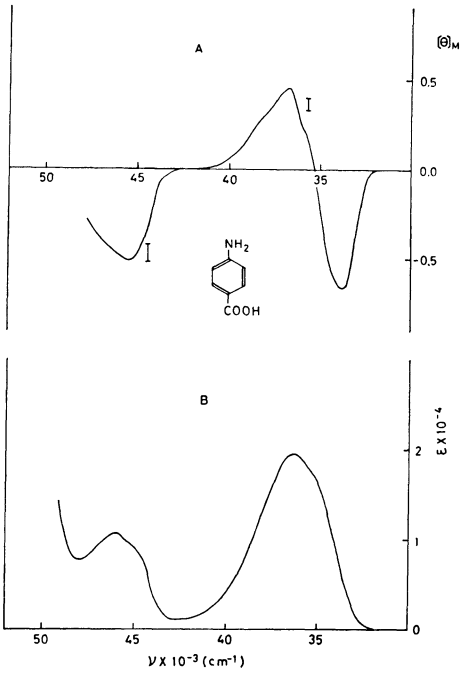



Fig. 6. MCD (A) and UV (B) spectra of *p*-aminobenzoic acid in heptane-dioxane (9 : 1 in volume) solution at room temperature.

$B_{\text{calcd}}(\boldsymbol{r})$ and $B_{\text{calcd}}(\boldsymbol{\nabla})$ denote the calculated Faraday $B$ terms whose electric moment matrices are evaluated by the use of the dipole length and dipole velocity operators, respectively. The calculated transition energies are in good agreement with the observed values. The theoretical Faraday $B$ terms also show fairly good agreement with the experimental values both in sign and in magnitude, except for the second $\pi \rightarrow \pi^*$ transitions of *o*- and *m*-nitroanilines. For these Faraday $B$ terms of *o*- and *m*-nitroanilines, a large negative contribution from the mixing with the fourth excited state and a large positive contribution from the mixing with the first, third, and other higher excited states cancel each other. Therefore, it seems to be difficult to predict accurately the signs of these Faraday $B$ terms of *o*- and *m*-nitroanilines.

It may be interesting to relate the excited states of nitroanilines and aminobenzoic acids to those of benzene

TABLE 1. OBSERVED AND CALCULATED TRANSITION ENERGIES ($cm^{-1}$) AND FARADAY $B$ TERMS ($10^{-5}\beta D^2/cm^{-1}$) OF $o$-, $m$-, AND $p$-NITROANILINES AND $o$-, $m$-, AND $p$-AMINOBENZOIC ACIDS

| Compound | $\nu_{obsd}$ | $\nu_{calcd}$ | $B_{obsd}$ | $B_{calcd}(r)$ | $B_{calcd}(\nabla)$ |
|---|---|---|---|---|---|
| $o$-Nitroaniline | 26500 | 27600 | 20.8 | 18.9 | 13.5 |
| | 35300 | 38500 | 18.0 | 22.1 | −6.3 |
| | 40800 | 42500 | positive | 65.0 | 39.1 |
| | 43200 | 44600 | | 4.3 | −2.0 |
| $m$-Nitroaniline | 27800 | 27700 | 9.7 | 12.1 | 6.4 |
| | 35100 | 38100 | 7.1 | 9.9 | −8.6 |
| | 40300 | 41400 | 66.9 | 211.8 | 93.9 |
| | 44100 | 44800 | −47.8 | −186.9 | −73.0 |
| $p$-Nitroaniline | 29700 | 32600 | 45.8 | 228.9 | 69.6 |
| | 34600 | 34700 | −41.2 | −248.6 | −88.8 |
| | 42600 | 43100 | 44.9 | 93.3 | 37.7 |
| | 45700 | 48700 | −16.2 | −12.1 | −12.7 |
| $o$-Aminobenzoic acid | 30500 | 30200 | 49.6 | 83.3 | 42.1 |
| | 39700 | 40200 | −49.5 | −117.7 | −52.9 |
| | 45700 | 46000 | 126.9 | 97.9 | 52.5 |
| | | 47600 | | 181.8 | 68.2 |
| $m$-Aminobenzoic acid | 31700 | 31900 | 32.6 | 74.7 | 23.6 |
| | 40000 | 40800 | −16.4 | −120.0 | −42.6 |
| | 45700 | 45200 | 118.7 | 210.3 | 91.0 |
| $p$-Aminobenzoic acid | 33800 | 34900 | 109.3 | 440.2 | 171.9 |
| | 36800 | 37100 | −109.4 | −500.6 | −188.6 |
| | 45700 | 47500 | 111.4 | 245.5 | 92.0 |

itself. The lowest four excited states of benzene are expressed as

$$|^1B_{2u}\rangle = (1/\sqrt{2})[\Psi(\phi_x\rightarrow\phi_\xi) - \Psi(\phi_y\rightarrow\phi_\eta)], \quad (3)$$

$$|^1B_{1u}\rangle = (1/\sqrt{2})[\Psi(\phi_x\rightarrow\phi_\eta) + \Psi(\phi_y\rightarrow\phi_\xi)], \quad (4)$$

$$|^1E_{1ux}\rangle = (1/\sqrt{2})[\Psi(\phi_x\rightarrow\phi_\xi) + \Psi(\phi_y\rightarrow\phi_\eta)], \quad (5)$$

$$|^1E_{1uy}\rangle = (1/\sqrt{2})[\Psi(\phi_x\rightarrow\phi_\eta) - \Psi(\phi_y\rightarrow\phi_\xi)], \quad (6)$$

where $\Psi(\phi_x\rightarrow\phi_\xi)$ is a configuration in which one electron is excited from the molecular orbital, $\phi_x$ to $\phi_\xi$, and $\phi_x$, $\phi_y$, $\phi_\xi$, and $\phi_\eta$ stand for the highest occupied and the lowest vacant orbitals and transform like X, Y, $(X^2-Y^2)/2$, and XY, respectively. Nitroanilines and aminobenzoic acids have six occupied orbitals $\phi_1,\cdots,\phi_6$, and four vacant orbita ls$\phi_7,\cdots,\phi_{10}$. As shown in Fig. 7, the highest occupied orbital $\phi_6$ consists of $\phi_y$ and the nonbonding orbital of the amino group. The molecular orbitals $\phi_5$ and $\phi_8$, correspond to $\phi_x$ and $\phi_\eta$ of benzene itself. The molecular orbitals $\phi_7$ and $\phi_9$, are expressed as linear combinations of $\phi_\xi$ and the lowest vacant orbital of the nitro or carboxyl group. Coefficients of the main configurations in each excited state are given in the third column of Table 2.

On the other hand, the displacement of the charge distribution associated with each transition should be taken into account. If the magnitude of the net charge density on a substituent group or on the benzene ring is larger than 0.5, the intramolecular charge-transfer configuration between the benzene ring and the substituent group is considered to be predominant. The calculated net charge densities on the phenyl, amino, and nitro or carboxyl groups in each excited state are listed in the fourth column of Table 2.

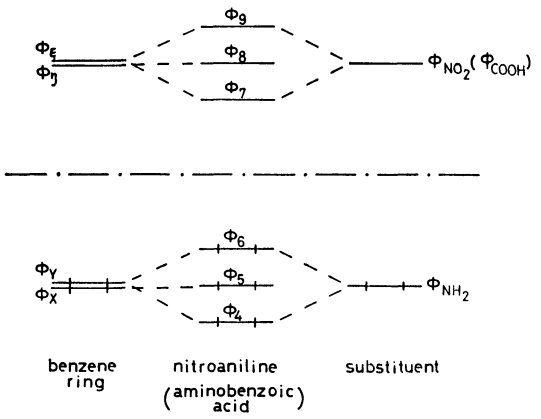



Fig. 7. Interaction of the highest occupied and the lowest vacant molecular orbitals of the benzene ring with the orbitals of the substituent groups.

The first $\pi\rightarrow\pi^*$ transitions of $o$-, $m$-, and $p$-nitroanilines can be assigned to the intramolecular charge-transfer band between the anilino and nitro groups; this can be also verified by the fact that large solvent effects are observed for these transitions. The first excited states of $o$- and $m$-aminobenzoic acids and the second excited state of $p$-aminobenzoic acid consist of the $^1B_{1u}$ state of benzene and the intramolecular charge-transfer state between the amino and carboxyphenyl groups. The first excited state of $p$-aminobenzoic acid and the second excited states of other compounds are said to be the $^1B_{2u}$ state of benzene with an appreciable contribution from the intramolecular charge-transfer configuration. The fourth excited state

TABLE 2. STATE FUNCTIONS AND NET CHARGE DENSITIES ON THE BENZENE RING AND SUBSTITUENT GROUPS

| Compound | $\nu_{calcd}$ ($cm^{-1}$) | State function[a] | Net charge density $-NH_2$ | Net charge density $-Ph$ | Net charge density $-NO_2(-CO_2H)$ | Assignment |
|---|---|---|---|---|---|---|
| *o*-Nitroaniline | 27600 | $0.98\Psi_{6\to7}+0.18\Psi_{5\to8}$ | 0.57 | 0.04 | −0.61 | CT |
| | 38500 | $0.75\Psi_{5\to7}-0.53\Psi_{6\to8}$ | 0.33 | 0.14 | −0.47 | $^1B_{2u}$ |
| | 42500 | $0.58\Psi_{5\to7}-0.64\Psi_{6\to9}$ | 0.45 | 0.13 | −0.58 | CT |
| | 44600 | $0.71\Psi_{6\to8}+0.52\Psi_{6\to9}$ | 0.51 | −0.28 | −0.24 | |
| *m*-Nitroaniline | 27700 | $0.96\Psi_{6\to7}+0.19\Psi_{5\to8}$ | 0.54 | 0.04 | −0.58 | CT |
| | 38100 | $0.77\Psi_{5\to7}-0.54\Psi_{6\to8}$ | 0.31 | 0.16 | −0.46 | $^1B_{2u}$ |
| | 41400 | $0.58\Psi_{5\to7}+0.65\Psi_{6\to8}$ | 0.42 | 0.10 | −0.52 | CT, $^1E_{lux}$ |
| | 44800 | $0.41\Psi_{6\to8}-0.85\Psi_{6\to9}$ | 0.49 | −0.21 | −0.28 | |
| *p*-Nitroaniline | 32600 | $0.98\Psi_{6\to7}+0.12\Psi_{5\to8}$ | 0.47 | 0.16 | −0.62 | CT |
| | 34700 | $0.58\Psi_{5\to7}-0.78\Psi_{6\to8}$ | 0.38 | −0.19 | −0.19 | $^1B_{2u}$ |
| | 43100 | $0.79\Psi_{5\to7}+0.58\Psi_{6\to8}$ | 0.38 | 0.17 | −0.55 | CT, $^1E_{lux}$ |
| | 48700 | $0.33\Psi_{5\to8}+0.90\Psi_{6\to9}$ | 0.47 | −0.11 | −0.36 | $^1B_{1u}$ |
| *o*-Aminobenzoic acid | 30200 | $0.96\Psi_{6\to7}+0.23\Psi_{5\to8}$ | 0.57 | −0.22 | −0.35 | CT, $^1B_{1u}$ |
| | 40200 | $0.50\Psi_{5\to7}-0.78\Psi_{6\to8}$ | 0.43 | −0.22 | −0.21 | $^1B_{2u}$ |
| | 46000 | $0.47\Psi_{5\to8}+0.70\Psi_{6\to9}$ | 0.51 | −0.14 | −0.37 | $^1B_{1u}$, CT |
| | 47600 | $0.82\Psi_{5\to7}+0.41\Psi_{6\to8}$ | 0.36 | 0.06 | −0.41 | $^1E_{lux}$ |
| *m*-Aminobenzoic acid | 31900 | $0.90\Psi_{6\to7}+0.29\Psi_{5\to8}$ | 0.50 | −0.24 | −0.26 | $^1B_{1u}$, CT |
| | 40800 | $0.48\Psi_{5\to7}-0.79\Psi_{6\to8}$ | 0.43 | −0.23 | −0.20 | $^1B_{2u}$ |
| | 45200 | $0.83\Psi_{5\to7}+0.50\Psi_{6\to8}$ | 0.33 | −0.05 | −0.28 | $^1E_{lux}$ |
| *p*-Aminobenzoic acid | 34900 | $0.47\Psi_{5\to7}-0.84\Psi_{6\to8}$ | 0.41 | −0.34 | −0.07 | $^1B_{2u}$ |
| | 37100 | $0.96\Psi_{6\to7}+0.15\Psi_{5\to8}$ | 0.45 | −0.08 | −0.38 | $^1B_{1u}$ |
| | 47500 | $0.83\Psi_{5\to7}+0.48\Psi_{6\to8}$ | 0.35 | −0.04 | −0.31 | $^1E_{lux}$ |

a) The coefficients of the most important configurations. $\Psi_{i\to k}$ is a configuration in which one electron is excited from $\phi_i$ to $\phi_k$.

of *o*-aminobenzoic acid, and the third excited states of *m*- and *p*-aminobenzoic acids and *m*- and *p*-nitroanilines are composed of the $^1E_{lux}$ state of benzene and the intramolecular charge-transfer state. The former is predominant in *o*-, *m*-, and *p*-aminobenzoic acids, the latter in *m*- and *p*-nitroanilines.

The present assignment for *p*-nitroaniline is consistent with the results reported by Tanaka.[12] However, the second transition observed at about 37000 $cm^{-1}$ in the crystalline spectrum is shifted to 34600 $cm^{-1}$ in heptane–dioxane (9 : 1 in volume) solution.

As mentioned before, four ionic and molecular species are expected to be present in aqueous solutions of *o*-, *m*-, and *p*-aminobenzoic acids. The values of the experimental ionization constants,[15] $K_1$ and $K_2$, are listed in Table 3. The MCD and UV spectra of *o*- and *m*- aminobenzoic acids in aqueous solutions are presented in Figs. 8 and 9. As seen from Table 3, the MCD and UV spectra of aminobenzoic acids at pH 13 are due to aminobenzoate ion (IV), while the

TABLE 3. EXPERIMENTAL p$K$ VALUES[a] FOR THE PROTON IONIZATION OF *o*-, *m*-, AND *p*-AMINOBENZOIC ACIDS

| Compound | p$K_1$ | p$K_2$ |
|---|---|---|
| *o*-Aminobenzoic acid | 2.09 | 4.97 |
| *m*-Aminobenzoic acid | 3.07 | 4.79 |
| *p*-Aminobenzoic acid | 2.43 | 4.85 |

a) p$K$ = −log $K$.

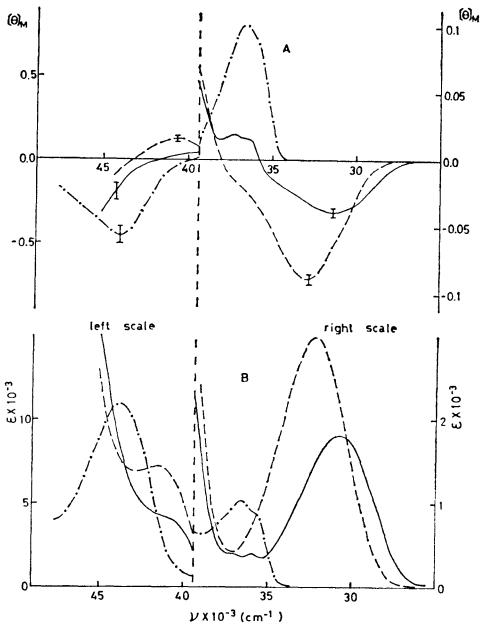



Fig. 8. MCD (A) and UV (B) spectra of *o*-aminobenzoic acid in aqueous solutions at pH 0 (—·—), pH 4.1 (——), and pH 13 (----).

spectra at pH 0 or 1 correspond to those of protonated aminobenzoic acid (I). The solid lines in Figs. 8 and 9 express the MCD and UV spectra of *o*- and *m*-aminobenzoic acids, respectively, in acetic acid–sodium

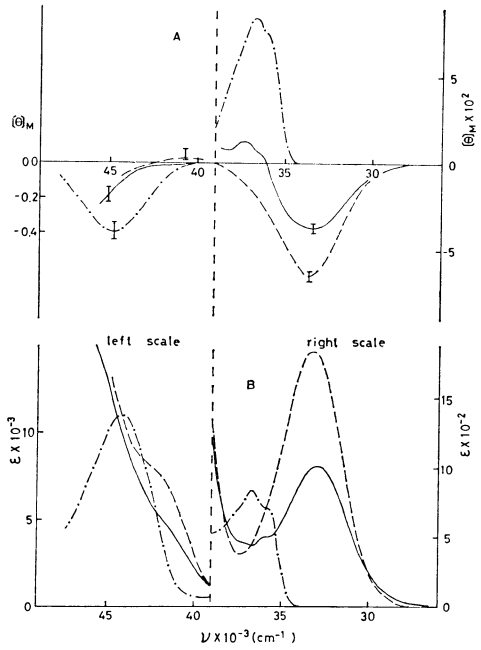



Fig. 9. MCD (A) and UV (B) spectra of *m*-aminobenzoic acid in aqueous solutions at pH 1 (—·—), pH 4.7 (——), and pH 13 (----).

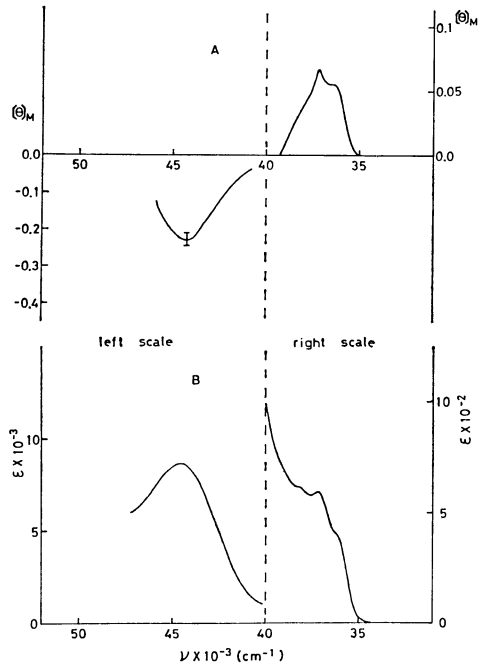



Fig. 10. MCD (A) and UV (B) spectra of benzoate ion in 0.1 M NaOH solution at room temperature.

acetate buffer solutions (pH's 4.1, 4.7), where neutral aminobenzoic acid (II), the zwitterion (III), and aminobenzoate ion (IV) are expected to coexist. Since the MCD and UV spectra of neutral aminobenzoic acid (II) and aminobenzoate ion (IV) are known and the MCD and UV spectra of the zwitterion (III) are expected to be analogous to those of benzoate ion (Fig. 10), it is possible to analyze the complicated MCD and UV spectra of *o*- and *m*-aminobenzoic acids in acetic acid–sodium acetate buffer solutions. The first positive MCD band observed in the region of 27000 —36000 cm$^{-1}$ is induced by the first $\pi \rightarrow \pi^*$ transitions of neutral aminobenzoic acid (II) and aminobenzoate ion (IV). The positive MCD band observed at about 37300 cm$^{-1}$ is considered to be due to the first $\pi \rightarrow \pi^*$ transitions of the zwitterion (III), because of the resemblance to the MCD band of benzoate ion (Fig. 10). Thus, the electronic transitions of the zwitterion (III) of *o*- and *m*-aminobenzoic acids were detected in the MCD spectra. However, it is difficult to see from the MCD spectra whether the zwitterion (III) exists in an aqueous solution of *p*-aminobenzoic acid or not, because the MCD of neutral aminobenzoic acid (II) and aminobenzoate ion (IV) may be much stronger than that of the zwitterion (III) in *p*-aminobenzoic acid.

We conclude that the magnetic circular dichroism technique can be a useful tool for separating the overlapping absorption bands and for detecting the hidden transitions. An analysis of the MCD spectrum assisted by the PPP method allows us to elucidate the spectroscopic assignments. It is also concluded, from a detailed analysis of the MCD spectra of aminobenzoic acids in aqueous solutions, that the second positive MCD bands of *o*- and *m*-aminobenzoic acids in acetic acid–sodium acetate buffer solutions provide spectroscopic evidence for the existence of the zwitterion (III).

## References

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