BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1082—1086 (1967)

# Studies of the Photochemistry of Aromatic Diazo Compounds. III. The Electronic Structures of Some *m*-Substituted Benzenediazonium Cations

Mitsunori SUKIGARA and Shin-ichi KIKUCHI

*The Institute of Industrial Science, The University of Tokyo, Azabu, Minato-ku, Tokyo*

(Rceived November 7, 1966)

The electronic structures and electronic absorption spectra of *m*-fluoro-, *m*-chloro-, *m*-bromo-, and *m*-methoxybenzenediazonium cations were studied by making molecular orbital calculations and by measuring the near-ultraviolet absorption spectra. From the calculations it is understood that when an electron-donating group is introduced at the *m*-position of the benzenediazonium cation, a mixing of the lowest locally-excited $^1B_1$ state within the benzenediazonium cation and the intramolecular charge-transfer state arising from the electron transfer from the electron-donating group at the *m*-position to the lowest unoccupied molecular orbital of the benzenediazonium framework comes to show a large contribution of the substituted cation in the lowest excited state while at the same time the energy of the corresponding state is lowered. The ground and the excited $^1A_1$ states of the nonsubstituted cation are not so greatly affected by the *m*-substitution as is the $^1B_1$ state. The degree of the mixing of the $^1A_1$ and $^1B_1$ state of the benzenediazonium cation by the *m*-substitution is not so impotant in the ground and lower excited states of the *m*-substituted benzenediazonium cation.

The electronic absorption spectra of *m*-substituted benzenediazonium salts have been studied by several investigators from the experimental point of view,[1,2] but no theoretical study has been reported. Most of the electronic absorption spectra of *m*-substituted benzenediazonium salts have two bands in the near-ultraviolet and/or visible regions, but the characters of the absorption bands have not yet been understood.

A reasonable set of wave functions for the $\pi$ electron system of the benzenediazonium cation has previously been obtained by the present authors,[3] and the $\pi$ electron structures of several *p*-substituted benzenediazonium cations have been studied in terms of an intramolecular electron transfer.[4]

In the present study the near-ultraviolet absorption spectra of several *m*-substituted benzenediazonium fluoroborates were measured in aqueous solutions and then the charge-transfer interaction of the benzenediazonium cation with such electron donors as F, Cl, Br and $OCH_3$ was studied. The calculation was carried out by taking configurational interactions[5,6] among the ground configuration, two locally-excited configurations, and two intramolecular charge-transfer configurations which arise from the electron transfers from the $2p\pi$ orbital of the substituent at the *m*-position to the unoccupied molecular orbitals of the benzenediazonium framework.

## Experimental

**Materials.** *m-Substituted Benzenediazonium Fluoroborate.*[7,8] An aqueous solution of sodium nitrite was dropped into a mixture of *m*-substituted aniline, where the substituents were F, Cl, Br and $OCH_3$, and aqueous hydrochloric acid solution below 5°C; then a 40% fluoroboric acid aqueous solution was dropped into the solution of *m*-substituted benzenediazonium chloride thereby formed. The crude product thus obtained was recrystallized from acetone and methanol. The *m*-substituted benzenediazonium fluoroborate was obtained as a needle or a plate crystal.

**Measurements.** The near-ultraviolet absorption spectra of the above-mentioned samples were measured in the aqueous solutions with a Shimadzu spectrophotometer, MPS-50, a quartz cell 1 cm long being used. The results are shown in Fig. 1, while the peak wavelengths and the molar extinction coefficients are tabulated in Table 1.

## Theoretical

The geometrical structure of the benzenediazonium cation was reported by Römming[9] to be

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[1] I. Fukushima and M. Horio, *Kōgyō Kwagaku Zasshi (J. Soc. Chem. Ind., Japan)*, **34**, 825, 836 (1931).

[2] R. Landau, P. Piot de Moira and A. S. Tanenbaum, *J. Phot. Sci.*, **13**, 144 (1965).

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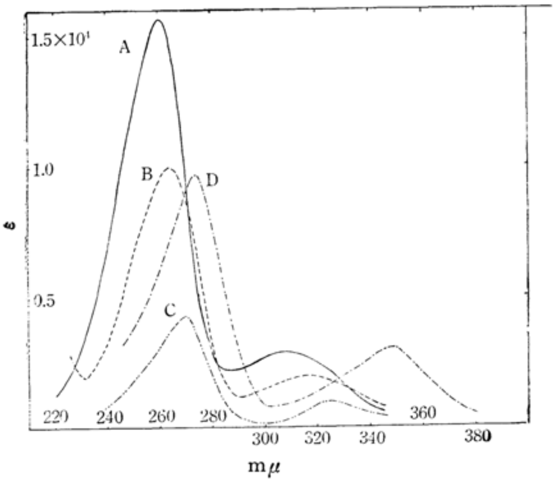

Fig. 1. The near-ultraviolet absorption spectra of the *m*-substituted benzenediazonium fluoroborates.
A: *m*-fluorobenzenediazonium fluoroborate.
B: *m*-chlorobenzenediazonium fluoroborate.
C: *m*-bromobenzenediazonium fluoroborate.
D: *m*-methoxybenzenediazonium fluoroborate.

TABLE 1. THE OBSERVED PEAK WAVE LENGTHS AND MOLAR EXTINCTION COEFFICIENTS FOR *m*-SUBSTITUTED BENZENEDIAZONIUM CATIONS

| Substituent | $\lambda_{max}$, mμ | log $\varepsilon_{max}$ |
|---|---|---|
| F | 262 | 4.160 |
| | 308 | 3.457 |
| Cl | 266 | 4.000 |
| | 317 | 3.299 |
| Br | 268.5 | 3.625 |
| | 323 | 2.972 |
| $OCH_3$ | 273.5 | 3.982 |
| | 348 | 3.475 |

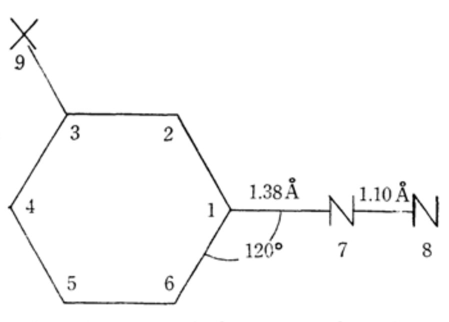

Fig. 2. The geometrical structure of *m*-substituted benzenediazonium cation.

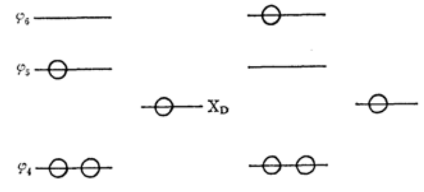

Fig. 3. The intramolecular charge-transfer configurations of the *m*-substituted benzenediazonium cations.

as is shown in Fig. 2, but those of *m*-substituted benzenediazonium cations are still unknown. As the basis of the present study, it was assumed that the bond distance between the substituent and its nearest neighboring carbon atom of a *m*-substituted benzenediazonium cation is, for the first approximation, equal to that of the corresponding monosubstituted benzene listed in Table 3. It was also assumed that the geometrical structure of the benzenediazonium framework is unchanged by the substitutions considered in the present paper.

**Calculation of the Electronic States.** The $\pi$ electron energy levels and the wave functions of the *m*-fluorobenzenediazonium cation, the *m*-chlorobenzenediazonium cation, the *m*-bromobenzenediazonium cation, and the *m*-methoxybenzenediazonium cation were calculated by taking the configurational interactions into account.

Each molecule was separated into the two components, the electron donors, F-, Cl-, Br-, and $H_3CO$-, and the electron acceptor, $-C_6H_4N_2^+$. The interaction between them was considered by means of the configurational interaction among $\pi$ electron configurations, which were constructed by putting the ten $\pi$ electrons into the appropriate orbitals of the components.

Among the electron configurations actually taken up in the present calculation, the charge-transfer configurations are shown in Fig. 3. In addition to the ground configuration, G, the charge-transfer configurations, $CT^I$ and $CT^{II}$, brought about by the electron-transfers from the electron donor toward the unoccupied molecular orbitals, $\varphi_5$ and $\varphi_6$, of the electron acceptor and the locally-excited configurations within the benzenediazonium framework, $LE^I$ and $LE^{II}$, were considered. The ground configuration, G, and the locally-excited configurations, $LE^I$ and $LE^{II}$, are linear combinations of several $\pi$ electron configurations.³⁾ The energy of the ground configuration, $H_G$, was taken as the standard. The energies of the locally-excited configurations, $H^{I}_{LE}$ and $H^{II}_{LE}$, were set as

TABLE 2. THE ENERGIES AND THE OFF DIAGONAL ELEMENTS OF THE ELECTRONIC CONFIGURATIONS

$H_G=0$ $H^{I}_{LE}=4.75$ $H^{II}_{LE}=4.18$
$H_{CT}=6.08(F)$ $5.07(Cl)$ $4.47(Br)$ $3.76(OCH_3)$
$H^{II}_{CT}=6.93\,(F)$ $6.08\,(Cl)$ $5.55\,(Br)$ $4.70\,(OCH_3)$
$H^{I}_{GLE}=0$ $H^{II}_{GLE}=0$ $H^{I}_{GCT}=0.253\ \beta_{CD}$
$H^{II}_{GCT}=0.671\ \beta_{CD}$ $H^{I\ \ I}_{LE\,CT}=0.120\ \beta_{CD}$
$H^{I\ \ II}_{LE\,CT}=0.162\beta_{CD}$ $H^{II\ II}_{LE\,CT}=-0.442\beta_{CD}$
$H^{II\ II}_{LE\,CT}=0.133\beta_{CD}$

The values of $\beta_{CD}$ are tabulated in Table 3.

TABLE 3. THE OVERLAP INTEGRALS, RESONANCE INTEGRALS AND ELECTRON REPULSION INTEGRALS OF THE *m*-SUBSTITUTED BENZENEDIAZONIUM CATIONS

| Substituent | Interatomic distance of C-X, Å | Overlap integral $S$ | Resonance integral $\beta_{CD}$, eV | Electron repulsion integral, eV | |
|---|---|---|---|---|---|
| | | | | $\sum_p C^2{}_{5p}$(pp/DD) | $\sum_p C^2{}_{6p}$(pp/DD) |
| F | 1.31 | 0.139 | $-1.95$ | 4.13 | 5.18 |
| Cl | 1.70 | 0.151 | $-1.50$ | 3.81 | 4.70 |
| Br | 1.86 | – | $-1.73$ | 3.66 | 4.48 |
| $OCH_3$ | 1.36 | 0.158 | $-2.00$ | 4.09 | 5.50 |

TABLE 4. THE ENERGY LEVELS AND WAVE FUNCTIONS FINALLY OBTAINED WITH THE *m*-SUBSTITUTED BENZENEDIAZONIUM CATIONS

| Substituent | Energy, eV | Wave function |
|---|---|---|
| F | $W_0=-0.28$ | $\Psi_0=\ 0.9807\Phi_G+0.0148\Phi^{I}_{LE}-0.0045\Phi^{II}_{LE}+0.0772\Phi^{I}_{CT}+0.1787\Phi^{II}_{CT}$ |
| | $W_1=\ 3.83$ | $\Psi_1=\ 0.0190\Phi_G-0.0635\Phi^{I}_{LE}+0.9282\Phi^{II}_{LE}-0.3576\Phi^{I}_{CT}+0.0791\Phi^{II}_{CT}$ |
| | $W_2=\ 4.69$ | $\Psi_2=-0.0442\Phi_G+0.9827\Phi^{I}_{LE}+0.0930\Phi^{II}_{LE}+0.0919\Phi^{I}_{CT}+0.1235\Phi^{II}_{CT}$ |
| Cl | $W_0=-0.19$ | $\Psi_0=\ 0.9847\Phi_G+0.0104\Phi^{I}_{LE}-0.0036\Phi^{II}_{LE}+0.0719\Phi^{I}_{CT}+0.1586\Phi^{II}_{CT}$ |
| | $W_1=\ 3.81$ | $\Psi_1=\ 0.0248\Phi_G-0.0681\Phi^{I}_{LE}+0.8788\Phi^{II}_{LE}-0.4646\Phi^{I}_{CT}+0.0811\Phi^{II}_{CT}$ |
| | $W_2=\ 4.68$ | $\Psi_2=-0.0460\Phi_G+0.9638\Phi^{I}_{LE}+0.1441\Phi^{II}_{LE}+0.1560\Phi^{I}_{CT}+0.1551\Phi^{II}_{CT}$ |
| Br | $W_0=-0.27$ | $\Psi_0=\ 0.9764\Phi_G+0.0147\Phi^{I}_{LE}-0.0083\Phi^{II}_{LE}+0.0916\Phi^{I}_{CT}+0.1951\Phi^{II}_{CT}$ |
| | $W_1=\ 3.53$ | $\Psi_1=\ 0.0440\Phi_G-0.0983\Phi^{I}_{LE}+0.7694\Phi^{II}_{LE}-0.6237\Phi^{I}_{CT}+0.1014\Phi^{II}_{CT}$ |
| | $W_2=\ 4.63$ | $\Psi_2=-0.0799\Phi_G+0.9112\Phi^{I}_{LE}+0.2462\Phi^{II}_{LE}+0.2155\Phi^{I}_{CT}+0.2374\Phi^{II}_{CT}$ |
| $OCH_3$ | $W_0=-0.42$ | $\Psi_0=\ 0.9599\Phi_G+0.0214\Phi^{I}_{LE}-0.0083\Phi^{II}_{LE}+0.1193\Phi^{I}_{CT}+0.2527\Phi^{II}_{CT}$ |
| | $W_1=\ 3.05$ | $\Psi_1=-0.0653\Phi_G+0.0081\Phi^{I}_{LE}-0.6265\Phi^{II}_{LE}+0.7600\Phi^{I}_{CT}-0.1382\Phi^{II}_{CT}$ |
| | $W_2=\ 4.48$ | $\Psi_2=-0.1689\Phi_G+0.7700\Phi^{I}_{LE}+0.3112\Phi^{II}_{LE}+0.2456\Phi^{I}_{CT}+0.4705\Phi^{II}_{CT}$ |

equal to 4.75 and 4.18 eV, the ${}^1A_1$-${}^1A_1$ and ${}^1A_1$-${}^1B_1$ transition energies of the benzenediazonium cation as evaluated theoretically by the present authors.3) The energies of the charge-transfer configurations, $H^{I}_{CT}$ and $H^{II}_{CT}$, were calculated by the following equations:

$$H^{I}_{CT} = I_D - A^{I} - \sum_p C^2{}_{5p}\ (pp/DD)$$

$$H^{II}_{CT} = I_D - A^{II} - \sum_p C^2{}_{6p}\ (pp/DD)$$

Here the $I_D$'s are the ionization potentials of the electron-donating groups, *i. e.*, F-, Cl-, Br-, and $H_3CO$-. They were taken to be 12.62, 11.28, 10.53, and 10.25 eV for the fluoro, chloro, bromo, and methoxy groups respectively from the ionization potentials of methylfluoride, methylcloride, methylbromide, and dimethyl ether.10,11) $A^{I}$ is the electron affinity of the electron-accepting group, $-C_6H_4N_2{}^+$; it was previously estimated to be 2.40 eV by the present authors.4) $A^{II}$ was taken to be equal to $A^{I}-1.90$ eV from a theoretical consideration.4) D indicates the p$\pi$ atomic orbital for the lone-pair electrons of the donor. The two-center Coulomb repulsion integrals, (pp/DD), were evaluated by Pariser and Parr's method.12)

The energies and the off-diagonal elements of the configurations used in the present calculations are tabulated in Table 2. The values of the core resonance integrals, $\beta_{CF}$, $\beta_{CCl}$, $\beta_{CBr}$, and $\beta_{CO}$, were taken to be $-1.95$, $-1.50$, $-1.73$, and $-2.00$ eV respectively; these are the same values as those reported in a previous paper.4)

TABLE 5. THE CALCULATED AND OBSERVED TRANSITION ENERGIES AND OSCILLATOR STRENGTHS

| Substituent | Transition | Transition energy, eV | | Oscillator strength |
|---|---|---|---|---|
| | | obs. | calcd. | |
| F | $W_0-W_1$ | 4.03 | 4.10 | 0.065 |
| | $W_0-W_2$ | 4.73 | 4.97 | 0.267 |
| Cl | $W_0-W_1$ | 3.91 | 4.00 | 0.065 |
| | $W_0-W_2$ | 4.66 | 4.87 | 0.261 |
| Br | $W_0-W_1$ | 3.84 | 3.80 | 0.057 |
| | $W_0-W_2$ | 4.61 | 4.90 | 0.183 |
| $OCH_3$ | $W_0-W_1$ | 3.56 | 3.47 | 0.040 |
| | $W_0-W_2$ | 4.54 | 4.89 | 0.055 |

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10) K. Watanabe, T. Nakayama and J. Mottle, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1964).

11) K. Higasi, I. Omura and T. Tsuchiya, *Monograph Ser. Res. Inst. Appl. Elect. Hokkaido Univ.*, No. 4, 141 (1954—1957).

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By solving the determinants constructed by the matrix elements given in Table 2 with an electronic computer (OKITAK 5090), the $\pi$ electron energy levels and the wave functions for the *m*-fluorobenzenediazonium cation, the *m*-chlorobenzenediazonium cation, the *m*-bromobenzenediazonium cation, and the *m*-methoxybenzenediazonium cation were evaluated. The results are shown in Table 4. From these results the transition energies and the oscillator strengths were calculated for these diazonium cations. The results are shown in Table 5, together with the observed results.

## Discussion

***m*-Fluorobenzenediazonium Cation.** As is shown in Fig. 1 and Table 1, the *m*-fluorobenzenediazonium cation shows two absorption bands in the near-ultraviolet region. The 308 m$\mu$ band can be assigned to the $W_0$-$W_1$ transition. From Table 6 it may be seen that the band has the character of the local excitation, LE$^{\mathrm{II}}$. The contribution of the intramolecular charge-transfer configuration, CT$^{\mathrm{I}}$, is only 12.8%. The band at 262 m$\mu$ is due to the $W_0$-$W_2$ transition, which has the property of the local excitation of LE$^{\mathrm{I}}$. In this cation the mixing of the the two locally-excited configurations, LE$^{\mathrm{I}}$ and LE$^{\mathrm{II}}$, is very small in the ground and two excited states. The contributions of the two intramolecular charge-transfer configurations, CT$^{\mathrm{I}}$ and CT$^{\mathrm{II}}$, are also very small in the ground and the second-lowest excited states.

TABLE 6. THE CONTRIBUTIONS OF THE CHARGE-TRANSFER CONFIGURATIONS AND THE LOCAL EXCITATION CONFIGURATIONS IN THE ELECTRONIC STATES

| Substituent | Configuration | Ground state, % | First excited state, % | Second excited state, % |
|---|---|---|---|---|
| F | CT$^{\mathrm{I}}$ | 0.6 | 12.8 | 0.8 |
| | CT$^{\mathrm{II}}$ | 3.2 | 0.6 | 1.5 |
| | LE$^{\mathrm{I}}$ | 0.0 | 0.4 | 96.5 |
| | LE$^{\mathrm{II}}$ | 0.0 | 86.1 | 0.8 |
| Cl | CT$^{\mathrm{I}}$ | 0.5 | 21.6 | 2.4 |
| | CT$^{\mathrm{II}}$ | 2.5 | 0.7 | 2.4 |
| | LE$^{\mathrm{I}}$ | 0.0 | 0.5 | 92.9 |
| | LE$^{\mathrm{II}}$ | 0.0 | 77.2 | 2.1 |
| Br | CT$^{\mathrm{I}}$ | 0.8 | 38.2 | 4.6 |
| | CT$^{\mathrm{II}}$ | 3.8 | 1.0 | 5.6 |
| | LE$^{\mathrm{I}}$ | 0.0 | 0.7 | 83.0 |
| | LE$^{\mathrm{II}}$ | 0.0 | 59.2 | 6.1 |
| $OCH_3$ | CT$^{\mathrm{I}}$ | 1.4 | 57.8 | 6.0 |
| | CT$^{\mathrm{II}}$ | 6.4 | 1.9 | 22.1 |
| | LE$^{\mathrm{I}}$ | 0.0 | 0.7 | 59.3 |
| | LE$^{\mathrm{II}}$ | 0.0 | 39.2 | 9.7 |

***m*-Chlorobenzenediazonium Cation.** The *m*-chlorobenzenediazonium cation shows two absorption peaks, at 317 m$\mu$ and 266 m$\mu$. The 317 m$\mu$ band can be assigned to the $W_0$-$W_1$ transition; this band is regarded as the locally-excited, LE$^{\mathrm{II}}$, band in the benzenediazonium framework. The contribution of CT$^{\mathrm{I}}$ in the lowest excited state is 21.6%, which is larger than that in the *m*-fluorobenzenediazonium cation. The 266 m$\mu$ band is ascribed to the $W_0$-$W_2$ transition, which has the property of the local excitation, LE$^{\mathrm{I}}$. In this cation the mixing of LE$^{\mathrm{I}}$ and LE$^{\mathrm{II}}$ in the ground and two excited states is very small, but a little larger than that in the *m*-fluorobenzenediazonium cation. In the ground state the contribution of the charget-ransfer configurations are a little smaller than those in the *m*-fluorobenzenediazonium cation, and, correspondingly, the stabilizing energy in the ground state of the *m*-fluorobenzenediazonium cation is a little larger than that of the *m*-chlorobenzenediazonium cation.

***m*-Bromobenzenediazonium Cation.** The absorption spectrum of the *m*-bromobenzenediazonium cation has two peaks in the near-ultraviolet region. The weak band at 323 m$\mu$, which corresponds to the $W_0$-$W_1$ transition, has the character of both the intramolecular charge-transfer of CT$^{\mathrm{I}}$ and the local excitation of LE$^{\mathrm{II}}$. The contribution of CT$^{\mathrm{I}}$ in the lowest excited state is 38.9%, which is much larger than those in the *m*-fluoro- and *m*-chlorobenzenediazonium cations. The absorption band at 268.5 m$\mu$ is due to the $W_0$-$W_2$ transition, which has the property of the local excitation within the benzenediazonium framework, LE$^{\mathrm{I}}$. The contributions of the two intramolecular charge-transfer configurations, CT$^{\mathrm{I}}$ and CT$^{\mathrm{II}}$, in the ground state are only 0.8 and 3.8% respectively.

***m*-Methoxybenzenediazonium Cation.** The *m*-methoxybenzenediazonium cation shows two absorption peaks, at 348 m$\mu$ and 273.5 m$\mu$. The 348 m$\mu$ band can be assigned to the $W_0$-$W_1$ transition, in which the contribution of the intramolecular charge-transfer configuration of CT$^{\mathrm{I}}$ amounts to 57.8% and that of the local excitation configuration of LE$^{\mathrm{II}}$ decreases to 39.2%. Therefore, it may be seen that the band has the character of the intramolecular charge-transfer band. The band at

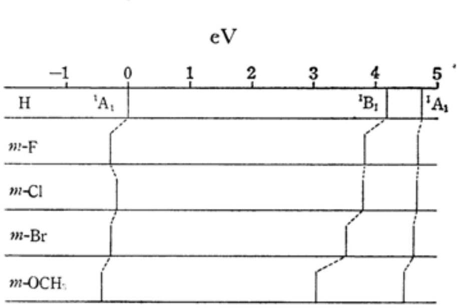

Fig. 4. The relation between the electronic state energy and the electron-donating ability of F, Cl, Br and $OCH_3$.

273.5 m$\mu$, which is due to the $W_0$-$W_2$ transition, may be regarded as the local excitation band, but in this transition the contribution of the intramolecular charge-transfer configuration comes to have a large value, such as 22.1%, at the same time. In the second excited state, the contributions of the local excitation configurations, $LE^{I}$ and $LE^{II}$, are about 59 and 10% respectively, so the mixing of the locally-excited states becomes larger than in the above-mentioned *m*-halogenated benzenediazonium cations.

As may be seen from Table 6, the contributions of the charge-transfer configurations in the ground state decrease in the following order: the *m*-methoxybenzenediazonium cation > the *m*-bromobenzenediazonium cation > the *m*-fluorobenzenediazonium cation > the *m*-chlorobenzenediazonium cation. In the two excited states, the *m*-fluorobenzenediazonium cation and the *m*-chlorobenzenediazonium cation are reversed. The same tendency can be seen in the order of the stabilizing energies of the three states, as is illustrated in Fig. 4; that is to say, the larger the contribution of the charge-transfer configuration in one state, the lower the energy of the state. The above-mentioned tendency of the *m*-substituted benzenediazonium cations is the same as in the *p*-substituted benzenediazonium cations, which were reported in the preceding paper.[4)]