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Studies of the Photochemistry of Aromatic Diazo Compounds. II. The Electronic Structures of Some *p*-Substituted Benzenediazonium Cations

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The electronic structures and electronic absorption spectra of *p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-methoxy-, and *p*-dimethylaminobenzenediazonium cations were studied by making molecular orbital calculations and by measuring the visible and near-ultraviolet absorption spectra. From the calculations it is understood that when an electron-donating group is introduced at the *p*-position of the benzenediazonium cation, the $^1A_1$-$^1A_1$ transition shows a very large shift to longer wavelengths, while the $^1A_1$-$^1B_1$ transition is not so much affected; at the same time, the N–N bond order in the ground state decreases. It is shown that there is a linear relationship between the N–N bond order and the wave number of the N–N stretching of the *p*-substituted benzenediazonium salt. It is concluded from the calculations that the electron affinity of the nonsubstituted benzenediazonium cation has a large value, such as 2.40 eV.

The electronic absorption spectra of *p*-substituted benzenediazonium compounds have been studied by several investigators from the experimental point of view;[1-4] there has also been reported a theoretical study,[5] in which the Hückel LCAO MO method was used. In spite of these works, however, it may be said that the origin of the visible and near-ultraviolet absorption spectra of *p*-substituted benzenediazonium cations has not yet been clarified.

The measurements of the infrared absorption spectra of several diazonium salts have been reported, and it has been supposed, from the wave number of the N–N stretching, the N–N bond orders of those compounds are about three.[6-8] However, no theoretical consideration has been made from the standpoint of the molecular orbital method.

The present authors obtained a reasonable set of wave functions for the π electron system of the benzenediazonium cation in their previous paper, which reported on the electronic structure and photodecomposition of the benzenediazonium cation.[9] In the present study the visible and near-ultraviolet absorption spectra of several *p*-substituted benzenediazonium fluoroborates were measured in aqueous solutions, and then the intramolecular charge-transfer interactions[10,11] of the benzenediazonium cation with such electron donors as F, Cl, Br, I, OCH_3 and $N(CH_3)_2$ were studied. The N–N π bond orders were compared at the same time with the vibrational energies of the N–N stretching of the *p*-substituted benzenediazonium fluoroborates.

Experimental

Materials. *p-Substituted Benzenediazonium Fluoroborate.*[12,13] An aqueous solution of sodium nitrite was dropped into a mixture of *p*-substituted aniline and an aqueous hydrochloric acid solution below 5°C; then a 40% fluoroboric acid aqueous solution was dropped in the solution of *p*-substituted benzenediazonium chloride thus formed. The crude product was recrystallized from acetone and methanol. The *p*-substituted benzenediazonium fluoroborate was obtained as a needle or a plate crystal. The substituents were F, Cl, Br, I, OCH_3, and $N(CH_3)_2$.

Measurements. The visible and 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

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[1] I. Fukushima and M. Horio, *Kōgyō Kwagaku Zasshi (J. Soc. Chem. Ind., Japan)*, **34**, 832, 836 (1931).

[2] G. T. Morgan and E. G. Couzens, *J. Chem. Soc.*, **97**, 1691 (1910).

[3] L. A. Kazitsyna, N. B. Kupletskaya, V. A. Ptisyna and O. A. Reutov, *Zh. Obshch. Khim.*, **33**, 3243 (1963).

[4] B. A. Porai-Koshits, *Tetrahedron*, **11**, 30 (1960).

[5] P. Schuster and O. E. Polansky, *Mh. Chem.*, **96**, 396 (1965).

[6] M. Aroney, R. J. W. LeFevre and R. F. Werner, *J. Chem. Soc.*, **1955**, 276.

[7] K. B. Whetsel, G. F. Hawkins and F. E. Johnson, *J. Am. Chem. Soc.*, **78**, 3360 (1956).

[8] B. A. Porai-Koshits and I. L. Bagel, *Latvijas PSR Zinatnu Akad. Vestis. Chem. Ser.*, 569 (1965), *Chem. Abstr.*, **64**, 9570 (1966).

[9] M. Sukigara and S. Kikuchi, This Bulletin, **40**, 461 (1967).

[10] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

[11] H. C. Longuet-Higgins and J. N. Murrel, *Proc. Roy. Soc.*, **A68**, 601 (1955).

[12] E. S. Lewis and W. H. Hinds, *J. Am. Chem. Soc.*, **74**, 304 (1952).

[13] M. D. Johnson, *J. Chem. Soc.*, **1965**, 805.

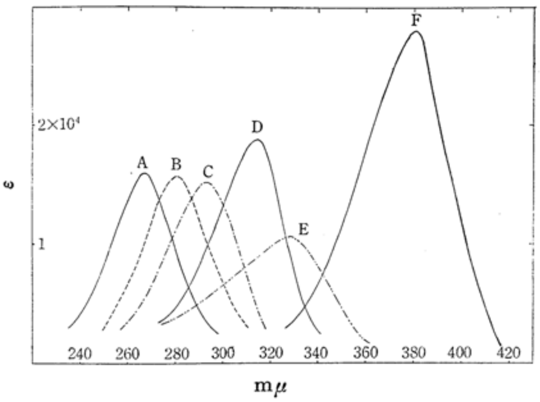

Fig. 1. The visible and near ultraviolet absorption spectra of the *p*-substituted benzenediazonium fluoroborates.

A : *p*-Fluorobenzenediazonium fluoroborate
B : *p*-Chlorobenzenediazonium fluoroborate
C : *p*-Bromobenzenediazonium fluoroborate
D : *p*-Methoxybenzenediazonium fluoroborate
E : *p*-Iodobenzenediazonium fluoroborate
F : *p*-Dimethylaminobenzenediazonium fluoroborate

TABLE 1. THE OBSERVED PEAK WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS FOR *p*-SUBSTITUTED BENZENEDIAZONIUM CATIONS

Substituent	λ_{max}, mμ	$\log \varepsilon_{max}$
F	267	4.229
Cl	281	4.195
Br	293	4.178
I	327.5	4.036
OCH_3	315	4.283
$N(CH_3)_2$	380	4.448

peak wavelengths and molar extinction coefficients are tabulated in Table 1.

The infrared absorption spectra of the samples were measured as Nujol mulls with a Nippon Bunko infrared spectrophotometer, DS-301. The wave numbers of the N–N stretching, $\nu_{\rm NN}$, are tabulated in Table 5.

Theoretical

The geometrical structure of the benzenediazonium cation[14] is known to be as is shown in Fig. 2, but those of the *p*-substituted benzenediazonium cations are still unknown. We assumed that the bond distance between the substituent and the nearest neighbor carbon of a *p*-substituted benzenediazonium cation is, to a first approximation, equal to that of the corresponding monosubstituted benzene (as listed in Table 3). We also assumed that the geometrical structure of the benzenediazonium framework is unchanged by the substitutions considered in the present paper.

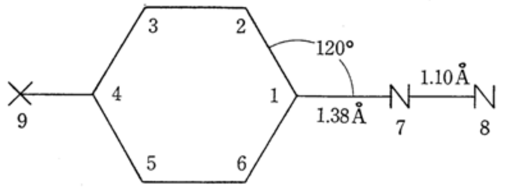

Fig. 2. The geometrical structure of *p*-substituted benzenediazonium cation.

Calculation of the Electronic States. The π electron energy levels and the wave functions of the *p*-fluorobenzenediazonium cation, the *p*-chlorobenzenediazonium cation, the *p*-bromobenzenediazonium cation, the *p*-iodobenzenediazonium cation, the *p*-methoxybenzenediazonium cation, and the *p*-dimethylaminobenzenediazonium cation were calculated by taking the configurational interactions into account. The respective molecules were separated into the two components, the electron donors, F-, Cl-, Br-, I-, H_3CO-, and $(CH_3)_2N$-, and the electron acceptor, -$C_6H_4N_2{}^+$. The interaction between them was considered by means of the configurational interaction among π electron configurations, which were constructed by putting the ten π electrons into the appropriate orbitals of the components.

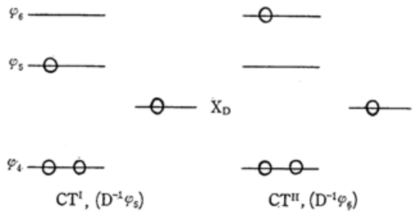

Fig. 3. The intramolecular charge-transfer configurations of the *p*-substituted benzenediazonium cations.

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, $\rm CT^I$ and $\rm CT^{II}$, brought about by the electron-transfers from the electron donor toward the unoccupied molecular orbittals, φ_5 and φ_6, of the electron acceptor and the locally-excited configurations of A_1 and B_1 symmetries, $\rm LE^I$ and $\rm LE^{II}$, were considered. The charge-transfer configurations, $\rm CT^I$ and $\rm CT^{II}$, have the A_1 or B_1 symmetry respectively. The ground configuration and the two locally-excited configurations are linear combinations of several π electron configurations.[9] The energy of the ground configuration, $H_{\rm G}$, was taken as the standard. The energies of the locally-excited configurations, $H_{\rm LE}^{\rm I}$ and $H_{\rm LE}^{\rm II}$, were set as equal to 4.75 eV and 4.13 eV, the ${}^1A_1$-${}^1A_1$ and ${}^1A_1$-${}^1B_1$ transition energies of the benzenediazonium cation as previously evaluated

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[14] Chr. Römming, *Acta Chem. Scand.*, **17**, 1444 (1963).

theoretically by the present authors.[9] The energies of the charge-transfer configurations, H^{I}_{CT} and H^{II}_{CT}, were calculated by the following equations:

$$H^{\mathrm{I}}_{\mathrm{CT}} = I_{\mathrm{D}} - A^{\mathrm{I}} - \sum_{p} C^2{}_{5p}\ (\mathrm{pp/DD})$$

$$H^{\mathrm{II}}_{\mathrm{CT}} = I_{\mathrm{D}} - A^{\mathrm{II}} - \sum_{p} C^2{}_{6p}\ (\mathrm{pp/DD})$$

Here the I_{D}'s are the ionization potentials of the electron-donating groups, *i. e.*, F-, Cl-, Br-, I-, H_3CO-, and $(CH_3)_2N$-. They were taken to be 12.61, 11.28, 10.53. 9.54, 10.25, and 7.89 eV respectively from the ionization potentials of methylfluoride, methylchloride, methylbromide, methyliodide, dimethyl ether, and trimethylamine.[15,16] A^{I} is the electron affinity of the electron-accepting group, $-C_6H_4N_2{}^+$, which was used as a parameter of the present calculations. A^{II} was taken as equal to $A^{\mathrm{I}} - 1.90$, for the value of the energy difference between the configurations, $E(\varphi_4{}^{-1}\varphi_6) - E(\varphi_4{}^{-1}\varphi_5)$, is equal to 1.90 eV. D indicates the pπ atomic orbital for the lone-pair electrons of the donor.

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

$H_{\mathrm{G}}=0$ $H^{\mathrm{I}}_{\mathrm{LE}}=4.75$ $H^{\mathrm{II}}_{\mathrm{LE}}=4.18$
$H^{\mathrm{I}}_{\mathrm{CT}}=5.93(\mathrm{F})$ $4.99(\mathrm{Cl})$ $4.41(\mathrm{Br})$ $3.60(\mathrm{I})$ $3.69(\mathrm{OCH_3})$ $1.53(\mathrm{N(CH_3)_2})$
$H^{\mathrm{II}}_{\mathrm{CT}}=7.44(\mathrm{F})$ $6.42(\mathrm{Cl})$ $5.85(\mathrm{Br})$ $5.07(\mathrm{I})$ $4.05(\mathrm{OCH_3})$ $2.90(\mathrm{N(CH_3)_2})$
$H_{\mathrm{GLE^I}}=0$ $H_{\mathrm{GCT^I}}=-0.711\beta_{\mathrm{CD}}$
$H_{\mathrm{GLE^{II}}}=0$ $H_{\mathrm{GCT^{II}}}=0$
$H_{\mathrm{LE^ICT^I}}=0.504\beta_{\mathrm{CD}}$ $H_{\mathrm{LE^ICT^{II}}}=0$
$H_{\mathrm{LE^{II}CT^I}}=0$ $H_{\mathrm{LE^{II}CT^{II}}}=0.468\beta_{\mathrm{CD}}$

The values of β_{CD} are tabulated in Table 3.

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

Substituent X	Interatomic distance of C_4-X, Å	Overlap integral S	Resonance integral β_{CD}, eV	Electron repulsion integral, eV	
				$\sum_p C^2{}_{5p}(\mathrm{pp/DD})$	$\sum_p C^2{}_{6p}(\mathrm{pp/DD})$
F	1.31	0.139	−1.95	4.28	4.69
Cl	1.70	0.151	−1.50	3.89	4.36
Br	1.86	—	−1.73	3.72	4.18
I	2.08	0.184	−1.55	3.54	3.97
OCH_3	1.36	0.158	−2.00	4.16	4.70
$N(CH_3)_2$	1.41	0.207	−2.27	3.96	4.48

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

Substituent	Energy, eV	Wave function
F	$W_{\mathrm{O}}=-0.32$	$\Psi_{\mathrm{O}}=0.9738\Phi_{\mathrm{G}}-0.0433\Phi^{\mathrm{I}}_{\mathrm{LE}}-0.2231\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{A}}=4.29$	$\Psi_{\mathrm{A}}=0.1364\Phi_{\mathrm{G}}+0.8966\Phi^{\mathrm{I}}_{\mathrm{LE}}+0.4214\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{B}}=4.09$	$\Psi_{\mathrm{B}}=0.9879\Phi^{\mathrm{II}}_{\mathrm{LE}}+0.1549\Phi^{\mathrm{II}}_{\mathrm{CT}}$
Cl	$W_{\mathrm{O}}=-0.22$	$\Psi_{\mathrm{O}}=0.9782\Phi_{\mathrm{G}}-0.0312\Phi^{\mathrm{I}}_{\mathrm{LE}}-0.2052\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{A}}=4.21$	$\Psi_{\mathrm{A}}=0.1466\Phi_{\mathrm{G}}+0.8039\Phi^{\mathrm{I}}_{\mathrm{LE}}+0.5765\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{B}}=4.06$	$\Psi_{\mathrm{B}}=0.9851\Phi^{\mathrm{II}}_{\mathrm{LE}}+0.1722\Phi^{\mathrm{II}}_{\mathrm{CT}}$
Br	$W_{\mathrm{O}}=-0.33$	$\Psi_{\mathrm{O}}=0.9650\Phi_{\mathrm{G}}-0.0443\Phi^{\mathrm{I}}_{\mathrm{LE}}-0.2586\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{A}}=3.90$	$\Psi_{\mathrm{A}}=0.2146\Phi_{\mathrm{G}}+0.7000\Phi^{\mathrm{I}}_{\mathrm{LE}}+0.6811\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{B}}=4.06$	$\Psi_{\mathrm{B}}=0.9818\Phi^{\mathrm{II}}_{\mathrm{LE}}+0.1902\Phi^{\mathrm{II}}_{\mathrm{CT}}$
I	$W_{\mathrm{O}}=-0.32$	$\Psi_{\mathrm{O}}=0.9597\Phi_{\mathrm{G}}-0.0428\Phi^{\mathrm{I}}_{\mathrm{LE}}-0.2799\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{A}}=3.47$	$\Psi_{\mathrm{A}}=0.2610\Phi_{\mathrm{G}}+0.5030\Phi^{\mathrm{I}}_{\mathrm{LE}}+0.8239\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{B}}=4.06$	$\Psi_{\mathrm{B}}=0.9761\Phi^{\mathrm{II}}_{\mathrm{LE}}+0.2174\Phi^{\mathrm{II}}_{\mathrm{CT}}$
OCH_3	$W_{\mathrm{O}}=-0.51$	$\Psi_{\mathrm{O}}=0.9403\Phi_{\mathrm{G}}-0.0641\Phi^{\mathrm{I}}_{\mathrm{LE}}-0.3341\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{A}}=3.47$	$\Psi_{\mathrm{A}}=0.3056\Phi_{\mathrm{G}}+0.5905\Phi^{\mathrm{I}}_{\mathrm{LE}}+0.7469\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{B}}=3.59$	$\Psi_{\mathrm{B}}=0.6633\Phi^{\mathrm{II}}_{\mathrm{LE}}+0.7483\Phi^{\mathrm{II}}_{\mathrm{CT}}$
$N(CH_3)_2$	$W_{\mathrm{O}}=-1.09$	$\Psi_{\mathrm{O}}=0.8242\Phi_{\mathrm{G}}-0.1088\Phi^{\mathrm{I}}_{\mathrm{LE}}-0.5557\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{A}}=2.20$	$\Psi_{\mathrm{A}}=0.5562\Phi_{\mathrm{G}}+0.3401\Phi^{\mathrm{I}}_{\mathrm{LE}}+0.7583\Phi^{\mathrm{I}}_{\mathrm{CT}}$
	$W_{\mathrm{B}}=2.66$	$\Psi_{\mathrm{B}}=0.3725\Phi^{\mathrm{II}}_{\mathrm{LE}}+0.9280\Phi^{\mathrm{II}}_{\mathrm{CT}}$

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15) K. Watanabe, T. Nakayama and J. Mottle, *J. Quart. Spectrosc. Radiat. Transfer*, **2**, 369 (1964).

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

TABLE 5. THE CALCULATED N-N BOND ORDERS (q_{NN}), VALUES OF WAVE NUMBER OF N-N STRETCHING (ν_{NN}), CALCULATED AND OBSERVED TRANSITION ENERGIES AND OSCILLATOR STRENGTHS

Substituent	q_{NN}	ν_{NN}, cm^{-1}	Transition	Transition energy, eV		Oscillator strength
				Obs.	Calcd.	
F	0.857	2290	W_O-W_A	4.64	4.61	0.522
			W_O-W_B		4.41	0.043
Cl	0.858	2295	W_O-W_A	4.39	4.43	0.551
			W_O-W_B		4.28	0.042
Br	0.854	2285	W_O-W_A	4.23	4.23	0.705
			W_O-W_B		4.39	0.041
I	0.852	2280	W_O-W_A	3.79	3.79	0.745
			W_O-W_B		4.38	0.041
OCH_3	0.847	2255	W_O-W_A	3.94	3.98	0.764
			W_O-W_B		4.08	0.017
$N(CH_3)_2$	0.816	2150	W_O-W_A	3.27	3.29	1.095
			W_O-W_B		3.75	0.004

The two-center Coulomb repulsion integrals, (pp/DD), were evaluated by Pariser and Parr's method.[17]

The energies and the off-diagonal elements of the configurations used in the present calculations are tabulated in Table 2. The core resonance integrals, β_{CF}, β_{CCl}, β_{CBr}, β_{CI}, β_{CO} and β_{CN} were used as parameters.

By solving the determinants constructed by the matrix elements given in Table 2, the π electron energy levels and the wave functions for the *p*-fluorobenzenediazonium cation, the *p*-chlorobenzenediazonium cation, the *p*-bromobenzenediazonium cation, the *p*-iodobenzenediazonium cation, the *p*-methoxybenzenediazonium cation, and the *p*-dimethylaminobenzenediazonium cation were evaluated. The most appropriate results were obtained when A^I was taken to be equal to 2.40 eV. The results are shown in Table 4.

The calculated transition energies and oscillator strengths are shown in Table 5, together with the observed results. The calculated N–N π bond orders and the observed wave numbers of the N–N stretching of the *p*-substituted benzenediazonium fluoroborates are also listed in Table 5.

Discussion

From the calculated values of the transition energies and oscillator strengths of the *p*-substituted benzenediazonium cations, together with the observed values, the strong absorption in the visible and near-ultraviolet regions can be safely ascribed to the $^1A_1$-$^1A_1$ transition, as tabulated in Table 5. It may be considered that the weak absorptions of the $^1A_1$-$^1B_1$ transition are hidden in the large absorption bands of the $^1A_1$-$^1A_1$ transition.

The energy change in the three lowest electronic states of the benzenediazonium cation by the several substituents at the *p*-position are shown in Fig. 4, from which it can be seen that an electron-donating group at the *p*-position exerts a very large stabilizing effect on the lowest excited $^1A_1$ electronic state.

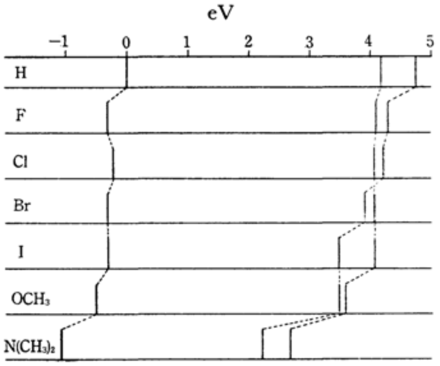

Fig. 4. The relation between the electronic state energy and the electron-donating ability of F, Cl, Br, I, OCH_3 and $N(CH_3)_2$.

The contributions of the charge transfer configurations, CT^I and CT^{II}, in the three electronic states are shown in Table 6. As Table 6 shows, the contributions of the intramolecular charge-transfer configurations, $(D^{-1}\varphi_5)$, in the excited $^1A_1$ states of the *p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-methoxy-, and *p*-dimethylaminobenzenediazonium cations are 17.8, 33.2, 46.4, 67.9, 55.8, and 57.8% respectively. Thus the strong absorption bands of the *p*-iodo-, *p*-methoxy-, and *p*-dimethylaminobenzenediazonium cations have the character of intramolecular charge-transfer bands of $(D^{-1}\varphi_5)$. On the other hand, the strong bands of the *p*-fluoro-, *p*-chloro-, and *p*-bromobenzenediazonium cations have the property of the local

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[17] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

TABLE 6. THE CONTRIBUTIONS OF THE CHARGE-TRANSFER CONFIGURATIONS IN THE GROUND, EXCITED $^1A_1$ AND $^1B_1$ STATES

Substituent	Contribution of CT^I, %		Constribution of CT^{II}, % $^1B_1$ state
	Ground state	Excited $^1A_1$ state	
F	5.0	17.8	2.4
Cl	4.2	33.2	3.0
Br	6.7	46.4	3.6
I	7.7	67.9	4.7
OCH_3	11.2	55.8	56.0
$N(CH_3)_2$	30.9	57.4	86.1

excitation within the benzenediazonium framework.

The contributions of the intramolecular charge-transfer configurations, $(D^{-1}\varphi_6)$, in the excited $^1B_1$ states of the *p*-halogenated benzenediazonium cations amount to only a few percent in all cases, but in the $^1B_1$ states of *p*-methoxy- and *p*-dimethylaminobenzenediazonium cations these contributions amount to 56.0 and 86.1%. From these values it can be said that the weak absorption bands of the *p*-halogenated benzenediazonium cations, though they were not observed, may be interpreted as the local excitation bands in the benzenediazonium cation. On the other hand, the weak transitions of the *p*-methoxy- and *p*-dimethylaminobenzenediazonium cations may be regarded as the intramolecular charge-transfer bands.

The contributions of the charge-transfer configuration, CT^I, in the ground and excited $^1A_1$ states and the contribution of CT^{II} in the $^1B_1$ state decrease in the following order: the *p*-dimethylaminobenzenediazonium cation > the *p*-methoxybenzenediazonium cation ≧ the *p*-iodobenzenediazonium cation > the *p*-bromobenzenediazonium cation > the *p*-chlorobenzenediazonium cation ≧ the *p*-fluorobenzenediazonium cation. The same tendency may be seen, from Fig. 4, in the stabilizing effect of the substituent on the electronic state energies of the *p*-substituted benzenediazonium cation. These facts indicate that the electron-donating power of the substituents decreases in the order of $N(CH_3)_2 > OCH_3 \geqq I > Br > Cl \geqq F$. It is very interesting that the contribution of the charge-transfer structure in the lowest $^1B_1$ state is very large in the cases of the *p*-methoxy- and *p*-dimethylaminobenzenediazonium cations. It is also noteworthy that, in the ground state, the contribution of the charge-transfer configuration in the *p*-fluorobenzenediazonium cation is a little larger than that in the *p*-chlorobenzenediazonium cation; this is consistent with the experimental finding in the infrared absorption spectra which is discussed below.

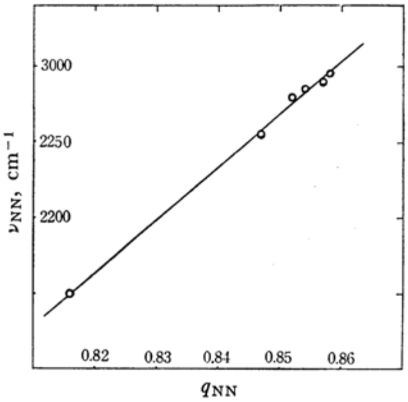

Fig. 5. The relation between the wave number of N-N stretching (ν_{NN}) and the N-N bond order.

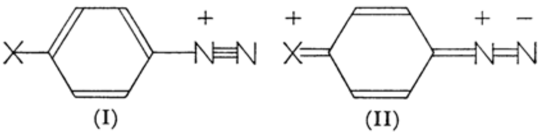

Fig. 6. The resonance structures of *p*-substituted benzenediazonium cation.

The wave numbers of the N–N stretching, ν_{NN}, of the *p*-substituted benzenediazonium salts are plotted against the N–N bond orders of the corresponding cations in Fig. 5, from which it may be seen that there is a linear relationship between ν_{NN} and the N–N bond order. Thus, the values of the N–N bond order in the present calculations may be regarded as reasonable.[18] The fact that the N–N bond order decreases and, at the same time, the contribution of the charge-transfer in the ground state increases with an increase in the electron-donating power of the substituent shows that the contribution of the resonance structure, II in Fig. 6, becomes larger in the ground state upon an increase in the electron-donating power of a substituent at the *p*-position, as has been expected by many investigators.[19]

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[18] H. Siebert, *Z. anorg. u. allgem. Chem.*, **273**, 170 (1953).

[19] See, for example, H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York (1961).