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Studies of the Photochemistry of Aromatic Diazo Compounds. I. Electronic Structure and Photodecomposition of Benzenediazonium Salt*[1]

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The electronic states of benzene diazonium cation were calculated by a method similar to that of Pariser and Parr. On the basis of the calculations, the 259 mμ and 295 mμ absorption bands were attributed to $^1A_1$-$^1A_1$ and $^1A_1$-$^1B_1$ transitions respectively. When the sample was irradiated in an alcoholic solution by a 295 mμ light, no ESR signal was detected, but fluorescence and phosphorescence were observed; the fluorescence and the absorption spectrum of $^1A_1$-$^1B_1$ transition have the correlation of a mirror image to each other. On the other hand, upon irradiation by a 259 mμ light, this sample showed an ESR spectrum which was attributed to the phenyl σ-radical, but no fluorescence or phosphorescence was observed. From the above experimental results and theoretical considerations, it was concluded that the electronically-excited benzenediazonium salt releases its excess energy by the following processes: (1) From the excited $^1B_1$ state, there occur radiative transition to the ground state and intersystem crossing to the phosphorescent state, though it is as yet uncertain whether $^3B_1$ or any other triplet states are involved. The photodecomposition does not proceed from the excited $^1B_1$ state. (2) From the excited $^1A_1$ state, neither the radiative transition to the ground state nor a nonradiative transition to any fluorescent or phosphorescent states occurs. The molecule decomposes rapidly to give phenyl σ-radical after excitation to this electronic state.

Many experimental studies of the electronic absorption spectra of aromatic diazonium compounds have been carried out,[1-5] and recently Schuster and Plansky[6] reported a theoretical study, in which the Hückel LCAO MO method was used, of the electronic states of aromatic diazonium cations. In spite of these experimental and theoretical studies, however, the origin of the near-ultraviolet absorption spectra of aromatic diazonium compounds has not been yet established.

Several works and reveiws on the mechanism of the photodecomposition of aromatic diazonium salts have appeared.[7-13] Boudreaux and Boulet[7] reported, on the basis of their magnetic susceptibility measurements, that the intermediate of the photodecomposition of aromatic diazonium salt in an aqueous solution is a sort of free radical. Zandstra and Eveleth[8] observed a phenoxy radical in the photodecomposition of aromatic diazonium salt in an aqueous solution. They concluded that this radical is not the primary but the secondary product; nothing is known about the primary processes of the reaction from their experiments. Lee *et al.*[9] asserted, judging from the photodecomposition products in alcohol, that the main intermediate of the reaction is the free radical. They also measured the visible and near-ultraviolet absorption spectrum of irradiated *p*-dimethylaminobenzenediazonium chloride in EPA at −196°C, they concluded that the decomposition occurs through the triplet state, though they did not confirm the origin of the absorption spectrum. Thus one may say that, at present, the electronic state and the primary process through which the photodecomposition occurs are still unknown.

In the present study, we calculated the π-electronic states of benzenediazonium cation, taking its plus charge and N-N triple bond into consideration. We also carried out experimental

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8) P. J. Zandstra and E. M. Eveleth, *ibid.*, **86**, 2664 (1964).
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12) K. H. Saunders, "The Aromatic Diazonium Compounds," 2nd ed., E. Arnold Co., London (1949).
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studies of the fluorescence and phosphorescence spectra and the ESR spectrum of an irradiated benzenediazonium fluoroborate solution.

Experimental

Materials. *Benzenediazonium Fluoroborate.*[14] A sodium nitrite aqueous solution was dropped into a mixture of aniline and a hydrochloric acid aqueous solution. Then an excess 40% fluoroboric acid aqueous solution was dropped into a solution containing benzenediazonium chloride. A crude product was thus recrystallized from acetone and methanol, and white needle crystals of benzenediazonium fluoroborate was obtained. The sample used was recrystallized several times. The solvents used are all of the spectral grade.

Measurements. *Electronic Absorption and Emission Spectra.* The near-ultraviolet absorption spectrum of the above-mentioned sample was measured in an aqueous solution and in an ethanol solution with a Shimadzu spectrophotometer, IV-50A, and a quartz cell 1 cm long. The fluorescence spectrum of the diazonium salt was measured in an ethanol-methanol solution at room temperature with an Aminco Bowman spectrophotofluorometer. The phosphorescence spectrum of the diazonium salt was measured in the same solution and with the same apparatus as in the fluorescence experiment at 77°K.

ESR Spectrum of Ultraviolet-irradiated Benzenediazonium Fluoroborate. The ESR spectrum of near-ultraviolet-irradiated benzenediazonium fluoroborate was measured in methanol at 77°K and at a concentration of about 10^{-2} M with a Japan Electron Optics Laboratory ESR spectrometer. The light source was a 500W high-pressure mercury lamp; a filter, Toshiba IRQ-80, was used when the sample was irradiated with a 295 mμ light.

Experimental Results

The near-ultraviolet absorption spectrum of benzenediazonium fluoroborate in an ethanol solution is shown in Fig. 1. The peak wavelengths and molar extinction coefficients, together with those in an aqueous solution, are tabulated in Table 1. The observed fluorescence emission and excitation spectra are shown in Fig. 2, in which the two spectra have the correlation of mirror images to each other.

From Fig. 2, it can be understood that, when the system was excited to the lowest excited singlet state, the radiative transition occurs from the same excited state. When the diazonium salt was excited by a 259 mμ light, no emission was observed. The observed phosphorescence emission spectrum is shown in Fig. 3; this emission spectrum was observed only when the diazonium salt solution was excited by a 295 mμ light. The ESR spectrum obtained is shown in Fig. 4; this spectrum was observed only when the diazonium salt was irradiated by a 259 mμ light. Upon the 295 mμ excitation no signal appeared, even after long irradiation. The shape of the spectrum, that is, $\Delta H_{msl} \simeq 25$ gauss with no hyperfine structure,

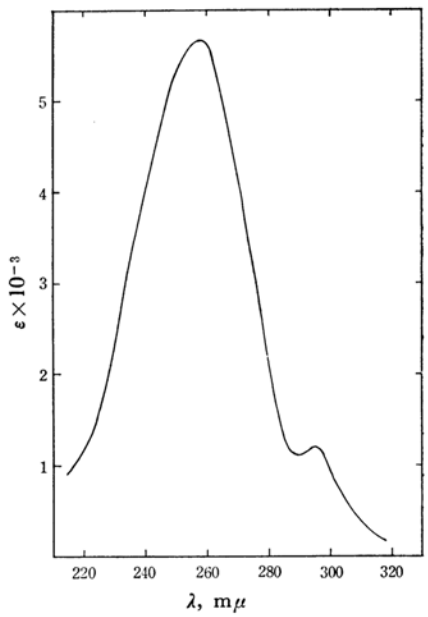

Fig. 1. The near ultraviolet absorption spectrum of benzenediazonium fluoroborate. (in ethanol)

TABLE 1. THE OBSERVED PEAK WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS OF BENZENEDIAZONIUM FLUOROBORATE IN ETHANOL SOLUTION

λ_{max}, mμ	ε_{max}
295 (298)*	1160
259 (263)*	5640

* These values are the peak wavelengths in aqueous solution.

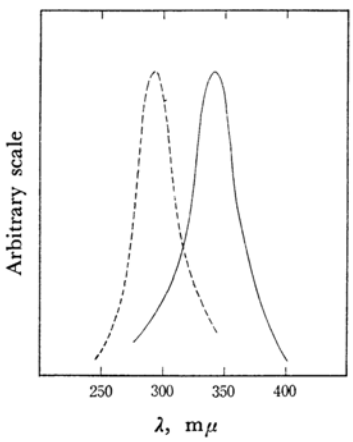

Fig. 2. The fluorescence emission and excitation spectra of benzenediazonium fluoroborate.
—— Emission spectrum
- - - Excitation spectrum

14) M. D. Johnson, *J. Chem. Soc.*, **1965**, 805.

Table 2. The starting MO (Hüeckel MO) in the calculation

	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8
φ_1	0.2965	0.0917	0.0305	0.0171	0.0305	0.0917	0.7038	0.6307
φ_2	0.3562	0.3895	0.4099	0.4168	0.4099	0.3895	0.0492	−0.2258
φ_3	0.5548	0.2605	−0.2863	−0.5556	−0.2863	0.2605	0.0039	−0.2895
φ_4	0	0.5000	0.5000	0	−0.5000	−0.5000	0	0
φ_5	−0.4031	0.3569	0.1592	−0.4657	0.1592	0.3569	−0.3316	0.4531
φ_6	0	−0.5000	0.5000	0	−0.5000	0.5000	0	0
φ_7	0.2088	0.1144	−0.3826	0.4869	−0.3826	0.1144	−0.4731	0.4232
φ_8	−0.5232	0.3627	0.2782	0.2518	−0.2782	0.3627	0.4023	−0.2883

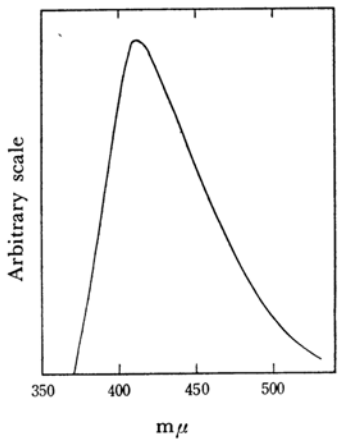

Fig. 3. The phosphorescence spectrum of benzenediazonium fluoroborate at 77°K.

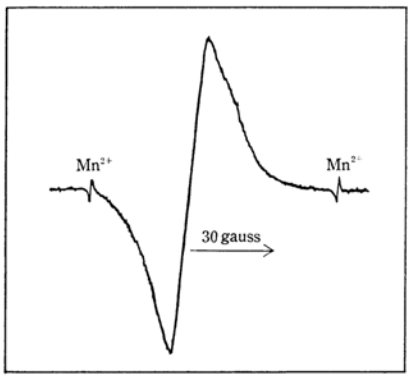

Fig. 4. The ESR spectrum of irradiated benzenediazonium fluoroborate (at 77°K, in methanol).

coincides with that of phenyl σ-radical reported by other laboratories.[15-16]

Theoretical

Method of Calculation. The method used is similar to that of Pariser and Parr.[17] It is based on the framework of the method for antisymmetrized products, in LCAO approximation, including configuration interaction, with only π-electrons considered explicitly. The molecular orbitals (MO), φ_i, are expressed in the form:

$$\varphi_i = \sum_p C_{ip}\chi_p \tag{1}$$

where χ_p is the $2p_y$ atomic orbital (AO) of the p atom. In our calculation the energy integrals should be somewhat different from those of conventional π electronic systems because of the positive charge and the N-N triple bond of the diazonium cation. For the first approximation we neglect the possible effects of the anion. With the parameter, ω, which is the π_x electron density on Atom 7 (see Fig. 5), core integrals and electron repulsion integrals are expressed in the following way. The core integrals of benzenediazonium cation can be written:

$$\begin{aligned}\alpha_7 = {} & (\omega-1)W_7^{\mathrm{I}} + (2-\omega)W_7^{\mathrm{II}} - \sum_{q=1}^{6}[(77/qq) \\ & + (q:77)] - \sum_r (r:77) - [(77/88) \\ & + (2-\omega)(8:77) + (\omega-1)(8:77)^{\mathrm{I}}]\end{aligned} \tag{2a}$$

$$\begin{aligned}\alpha_8 = {} & (2-\omega)W_8^{\mathrm{I}} + (\omega-1)W_8^{\mathrm{II}} - \sum_{q=1}^{6}[(88/qq) \\ & + (q:88)] - \sum_r (r:88) - [(88/77) \\ & + (\omega-1)(7:88) + (2-\omega)(7:88)^{\mathrm{I}}]\end{aligned} \tag{2b}$$

$$\begin{aligned}\alpha_p(p \neq 7,8) = {} & W_p^{\mathrm{I}} - \sum_{q\neq p,\,7,\,8}[(pp/qq) + (q:pp)] \\ & - \sum_r (r:pp) - [(pp/77) + (\omega-1)(7:pp) \\ & + (2-\omega)(7:pp)^{\mathrm{I}}] - [(pp/88) \\ & + (2-\omega)(8:pp) + (\omega-1)(8:qq)^{\mathrm{I}}]\end{aligned} \tag{2c}$$

where $-W_p^{\mathrm{I}}$ and $-W_p^{\mathrm{II}}$ are the valence-state first and second ionization potentials of the p atom, and where $(q:pp)^{\mathrm{I}}$ is a sort of penetration integral which comes to the valence-state first ionization potential of the q atom when the distance between the p and q atoms becomes equal to zero.

The electronic repulsion integral on the p atom, which has the charge of plus x, is written:

15) S. Ohnishi, T. Tanei and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962).
16) K. Morokuma, S. Ohnishi, T. Masuda and K. Fukui, This Bulletin, **36**, 1228 (1963).
17) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

$$(pp/pp) = (-W_p^{I} - A_p) + x(2W_p^{I} - W_p^{II} + A_p) \quad (3a)$$

where A_p is the electron affinity of the p atom, p representing Atoms 7 and 8. Assuming that $-W_p^{I}=14.63$ eV, $-W_p^{II}=29.6$ eV, and $A_p=2.36$ eV,[17] the following equation is obtained:

$$(pp/pp) = (-W_p^{I} - A_p) + 2.7x \quad (3b)$$

The integral (3b) comes into the total π-electronic energy in the form of $(\sum_i C_{ip}^2)^2(pp/pp)$. If we assume that the π_y-electron density on Atom 7 is unity, then the above correction term in the total energy will have the value of $0.7x$. It should be noted that when $p=7$, $x=2-\omega$, and that when $p=8$, $x=-1+\omega$.

Next let us consider the integral (pp/qq). When one or two of the atoms, p and q, have a plus charge, and when the distance (r) between the p and q atoms is not larger than 2.8 Å, we can derive the following formulas using the same approximation as Pariser and Parr:

$$ar + br^2 = (1/2)[(77/77)^0 + (88/88)^0 + 2.7] - (77/88) \quad (4a)$$

$$a'r + b'r^2 = (1/2)[(pp/pp)^0 + (77/77)^0 + 2.7(2-\omega)] - (pp/77) \quad (4b)$$

$$a''r + b''r^2 = (1/2)[(pp/pp)^0 + (88/88)^0 + 2.7(\omega-1)] - (pp/88) \quad (4c)$$

where

$$(pp/pp)^0 = \int \chi_p^*(1)\chi_p^*(2)e^2/r_{12}\chi_p^{(1)}\chi_p^{(2)}dv = -W_p^{I} - A_p$$

The correction terms in Eqs. (4a)—(4c) take the form of approximately (p-q bond order)$^2/4\ f(\omega, r)$ in the total π electronic energy; they are usually very small. When r comes to be larger than 2.8 Å, the correction term in (pp/qq) is negligible.

Calculation of the Electronic States. As the starting MO, we used the Hückel MO in Table 2. In our calculation the following electronic configurations were taken into consideration:

A_1: ψ_0 $\psi_1 = (\varphi_4^{-1}\varphi_6)$ $\psi_2 = (\varphi_3^{-1}\varphi_5)$
$\psi_3 = (\varphi_4^{-1}\varphi_5)^2$ $\psi_4 = (\varphi_3^{-1}\varphi_5)^2$

B_1: $\psi_5 = (\varphi_4^{-1}\varphi_5)$ $\psi_6 = (\varphi_3^{-1}\varphi_6)$

where $(\varphi_i^{-1}\varphi_j)$ represents a singly-excited electronic configuration, while $(\varphi_i^{-1}\varphi_j)^2$ indicates a doubly-excited electronic configuration from the ith molecular orbital to the jth molecular orbital. ψ_0 indicates the electronic ground state,

$$|\varphi_1\overline{\varphi}_1\varphi_2\overline{\varphi}_2\varphi_3\overline{\varphi}_3\varphi_4\overline{\varphi}_4|.$$

From the X-ray analysis of the benzenediazonium chloride crystal,[18] its bond lengths and bond angles were found to be as are shown in Fig. 5. From these data we can evaluate all the matrix elements, which are shown in Table 3. In the present calculations, penetration integrals were neglected for the first approximation. We take values of β_{CC} and β_{CN} similar to those of Pariser and Parr:

$$\beta_{CC} = \int \chi_{C_1}^*(1)H_{core}(1)\chi_{C_2}(1)dv = -2.39 \text{ eV}$$

and

$$\beta_{CN} = \int \chi_{C_1}^*(1)H_{core}(1)\chi_{N_7}(1)dv = -2.42 \text{ eV}$$

β_{NN} and ω are used as parameters. By solving the secular equation composed of the elements in Table 3 by the aid of an electronic computer (OKITAK 5090), the energy levels and wave functions of the benzenediazonium cation were evaluated (see Fig. 6). From among these, the lowest energy levels and wave functions of three singlet states and two triplet states are shown in Table 4. The evaluated oscillator strength values are shown in Table 5, together with the observed and calculated transition energies. Reasonable

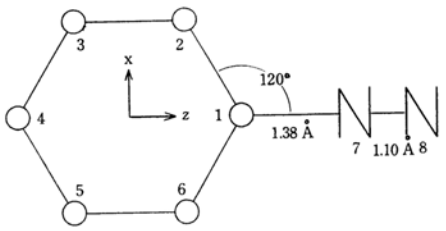

Fig. 5. The geometrical structure of benzenediazonium cation.

TABLE 3. THE MATRIX ELEMENTS OF THE ELECTRON CONFIGURATIONS CONSIDERED IN THE CALCULATION

	Diagonal elements, eV
A_1	$H_0=0$
	$H_1=6.149$ (4.243)*
	$H_2=5.573$ (3.932)*
	$H_3=8.645$
	$H_4=8.993$
B_1	$H_5=4.228$ (3.012)*
	$H_6=7.885$ (6.758)*

	Off diagonal elements, eV
A_1	$H_{01}=-0.450$
	$H_{02}=-0.651$ $H_{12}=0.683$ (-0.177)*
	$H_{03}=0.578$ $H_{13}=-0.270$ $H_{23}=0.062$
	$H_{04}=0.825$ $H_{14}=0.000$ $H_{24}=-1.692$ $H_{34}=0.199$
B_1	$H_{56}=-0.867$ (-0.177)*

* These values are the matrix elements for the triplet states.

18) Chr. Romming, *Acta Chem. Scand.*, **17**, 1444 (1963).

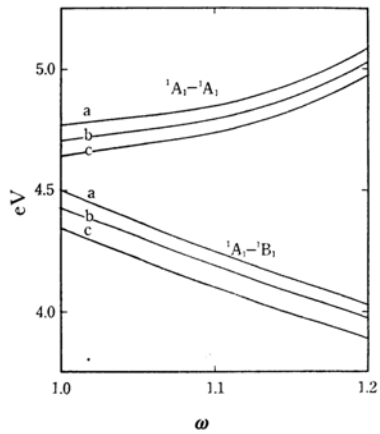

Fig. 6. Changes of the transition energy with β_{NN} and ω.

a : $\beta_{NN} = -3.50$ eV
b : $\beta_{NN} = -3.30$ eV
c : $\beta_{NN} = -3.10$ eV

Table 4. The energy levels and wave functions of lowest three singlet and two triplet states

Energy, eV	Wave function
$^1A_1$ $W_0 = -0.202$	$\Phi_0 = 0.988\phi_0 + 0.056\phi_1 + 0.108\phi_2 - 0.061\phi_3 - 0.066\phi_4$
$^1B_1$ $W_1 = 3.976$	$\Phi_1 = 0.885\phi_5 + 0.465\phi_6$
$^1A_1$ $W_2 = 4.543$	$\Phi_2 = -0.050\phi_0 - 0.383\phi_1 + 0.848\phi_2 - 0.047\phi_3 + 0.359\phi_4$
$^3B_1$ $W_3 = 3.000$	$\Phi_3 = 0.962\phi_5 + 0.275\phi_6$
$^3A_1$ $W_4 = 3.852$	$\Phi_4 = 0.407\phi_1 + 0.913\phi_2$

Table 5. The transition energies and oscillator strengths

Transition	Transition energy, eV		Oscillator strength
	obs.	calcd.	calcd.
$W_0 \rightarrow W_1$	4.20	4.18	0.085
$W_0 \rightarrow W_2$	4.79	4.75	0.316
$W_0 \rightarrow W_3$	3.35*	3.20	
$W_0 \rightarrow W_4$		4.07	

* The value was evaluated from the phosphorescence spectrum supposing that the phosphorescent state was $^3B_1$.

results were obtained when the β_{NN} and ω were taken as -3.10 eV and 1.05 respectively.

Discussion

On the basis of a comparison of the calculated transition energies and oscillator strengths with the observed results, the 295 mμ and 259 mμ absorption bands can safely be ascribed to the $^1A_1$–$^1B_1$ and $^1A_1$–$^1A_1$ transitions respectively. In the calculations, that the value of the ω parameter is 1.05 means that the N_7 atom bears almost all the positive charge of benzenediazonium cation; it also means that the bond order between N_7 and N_8 is nearly three.

From the infrared absorption spectra of aromatic diazonium salts, it has been claimed that diazonium salts have N-N triple bonds;[19-21] this experimental finding is one proof of our calculations.

From the results of the fluorescence, phosphorescence and ESR measurements, and from the theoretical considerations, the processes by which electronically-excited benzenediazonium salt releases its excess energies may be explained. From the excited $^1B_1$ state two processes occur; one is the radiative transition to the ground state, while the other is the intersystem crossing to a phosphorescent state. No detectable photochemical decomposition occurs after the $^1A_1$–$^1B_1$ transition. It is known that the n–π^* absorption band of the aromatic azo compound appears in the visible region,[13] but that of the diazonium compound has not yet been observed and the position of the n–π^* triplet of the benzenediazonium cation remains obscure at the present time. Therefore, it is still uncertain whether the phosphorescent state is $^3B_1$, $^3(n$–$\pi^*)$, or any other electronic state.

The fact that neither fluorescence nor phosphorescence was detected after the $^1A_1$–$^1A_1$ transition shows that no radiative process occurs from the excited $^1A_1$ state and that no internal conversion or intersystem crossing to a radiative state occurs. From this excited state the molecule decomposes rapidly to give phenyl σ-radical. It is not certain, however, that this radical is produced at the first stage of the photodecomposition; it was reported that the shortest Cl^--to-N distance is 3.225 Å[18] in a crystal of benzenediazonium chloride and the distance should be much larger in solution, so it is not improbable that phenyl cation,  , is produced at the first stage of the photodecomposition and then this cation accepts one electron rapidly from an electron donor such as fluoroborate anion. Another signal than that of phenyl σ-radical was observed in the ESR measurements of several *p*-substituted benzenediazonium fluoroborates at the temperature of liquid nitrogen, as will be discussed in a following report of this series; it yet remains unknown whether phenyl σ-radical is produced directly or not in the first stage of the photodecomposition. As may be seen in Tables 2 and 4, the bond order of C_1–N_7 in the excited $^1A_1$ state is larger than that in the ground state at the equilibrium interatomic distances, so it does not seem to be natural to think that this electronic state is repulsive. It is

19) K. B. Whetsel, G. F. Hawkins and F. E. Johnson, *J. Am. Chem. Soc.*, **78**, 3360 (1956).
20) L. A. Kazitsyna, *Ah. Fiz. Khim.*, **34**, 850 (1960).
21) B. A. Porai-Koshits and I. L. Bagel, *Latvijas PSR Zinatnu Akad. Vestis, Kim. Ser.*, **1965**, 569; *Chem. Abstr.*, **64**, 9570 (1966).

very probable that the C-N stretching is excited to its high vibrational level with the electronic excitation,[22] because this vibration keeps the symmetry of C_{2v}. Our calculations of the electronic states of the benzenediazonium cation were carried out with only the equilibrium nuclear position, and the n-π^* band has not yet been observed in the electronic absorption spectra; therefore, it is still uncertain whether the decomposition occurs from the electronically-excited $^1A_1$ state directly, from a repulsive electronic state lying near the $^1A_1$ state, or from the high vibrational level of the ground electronic state arising from the internal conversion from the excited $^1A_1$ state.

It can be said that *p*-substituted benzenediazonium salt decomposes photochemically by the same process as the photodecomposition of benzenediazonium salt so long as the magnitude of the transition energy does not become less than the magnitude of the C-N bond energy. The present authors have observed that diazonium salts from *p*-anisidine, (*N*, *N*-dimethyl)*p*-phenylenediamine and 4-amino-4'-methoxystilbene decompose photochemically under irradiation by 315 mμ, 380 mμ, and 432 mμ lights respectively; these correspond to the transitions with transition moments along the long axis of the molecule, and no fluorescence was observed after these excitations. These observations will be discussed further later in a paper in this series.

The authors gratefully acknowledge helpful discussions with Dr. Akira Kuboyama, Government Chemical Industrial Research Institute, Tokyo. We also indebted to him for the fluorescence and phosphorescence measurements.

22) B. Stevens, *Can. J. Chem.*, **36**, 96 (1958).