The Electronic Spectra and Electronic Structures of the Nitrobenzene and Nitrotoluene Anions

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Recently the study of the electronic and ESR spectra of anion radicals of organic compounds has made remarkable progress. The ESR spectra of the nitrobenzene and nitrotoluene anions have been observed by several research workers, and the hyperfine structures of these spectra have been analyzed.[1-7] The electronic spectra of these anions, however,

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[1] T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissmann, *J. Phys. Chem.*, **57**, 504 (1953).

[2] G. E. Pake, S. I. Weissmann and J. Townsend, *Trans. Faraday Soc.*, **19**, 147 (1955).

[3] R. L. Ward and M. P. Klein, *J. Chem. Phys.*, **28**, 518 (1958).

[4] R. L. Ward, ibid., **30**, 852 (1959).

[5] D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

[6] R. L. Ward, ibid., **83**, 1296 (1961).

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have never been observed. In view of this, we undertook to measure their electronic absorption spectra in parallel with their ESR spectra for the purpose of deepening our knowledge about the electronic structures of substituted benzene ion radicals. Furthermore, in order to clarify the nature of the observed electronic absorption bands, a theoretical study of the π-electron system of the nitrobenzene anion has been carried out by considering the configurational interaction among several electron configurations, such as ground, locally excited and charge-transfer configurations.

Experimental

Commercial nitrobenzene of E. P. grade was purified by vacuum distillation. Commercial *p*-nitrotoluene of E. P. grade was purified by repeating recrystallization from ethanol. Tetrahydrofuran (abbreviated hereafter to THF) and dimethoxyethane (abbreviated hereafter to DME) used as solvents were dried over calcium chloride, refluxed with sodium metal for two days, and fractionally distilled. Since the anion radicals are very sensitive to oxygen and moisture, their preparations and the measurements of their ESR and electronic spectra must be done in vacuo (10^{-4}~10^{-5} mmHg). Therefore, a vacuum line system with a tube attached for the ESR measurement and a quartz cell of 1 cm. path length for the electronic absorption measurement was used for the preparation of the anion radicals (see Fig. 1). They were prepared by keeping the 10^{-2}~10^{-3} M solutions of nitrobenzene or nitrotoluene in contact with a pure alkali metal film made by distillation in vacuo.

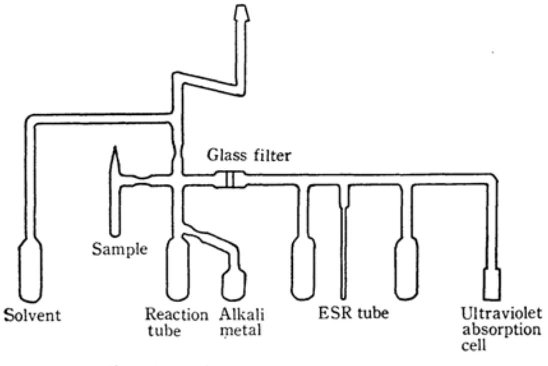

Fig. 1. The vacuum line system.

A Cary recording spectrophotometer model 14 M was used for the measurements of the near infrared, visible and ultraviolet absorption spectra. The ESR spectra were measured with a Hitachi ESR spectrometer model MPU-2B (X band, 100 kc. modulation).

Experimental Results

The Electronic Absorption of the Nitrobenzene Anion. — The DME solution of nitrobenzene turned a shallow brown when in contact with a potassium metal film and showed the ESR spectrum. With the progress of the reaction, the ESR absorption became stronger, the 260 mμ band of neutral nitrobenzene gradually decreased its intensity, and at the same time new absorption bands appeared. The color of the solution changed from brown to reddish orange and then to deep reddish purple. The electronic absorption spectrum and ESR spectrum of this solution were measured in parallel. The observed electronic absorption spectrum is shown in Fig. 2. The observed hyperfine structure of the ESR spectrum was explained well on the basis of the coupling constants determined by Ward et al.⁶⁾ The spin concentration of the solution was determined, with the result that 5~10% of nitrobenzene was converted into the radical in the solution.

The observed electronic spectrum of the solution consists of five absorption bands. However, great caution must be used in the identification of the electronic spectrum, since the solution might contain not only the nitrobenzene anion radical but also other byproducts. When the solution was exposed to air, it immediately changed color from reddish purple to yellow and no longer showed the ESR signal. The electronic spectrum of the solution of the decomposed products was measured and compared with that of the anion radical solution. From this comparison, it was concluded that, among the five bands shown in Fig. 2, the two bands at 292 and 560 mμ which disappeared when the anion radical solution was in contact with air may safely be ascribed to the nitrobenzene anion.

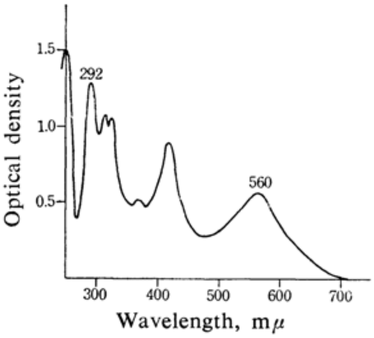

Fig. 2. The electronic spectrum of the DME solution of the nitrobenzene anion.

The Electronic Spectrum of the *p*-Nitrotoluene Anion.—A similar experimental study was also carried out with *p*-nitrotoluene. When in contact with a potassium metal film, the THF solution of *p*-nitrotoluene turned blue and gave the electronic spectrum shown in Fig. 3. This spectrum is composed of three bands at 302, 607 and 875 mμ. The ESR spectrum was also measured; the result was completely coincident with that obtained by Maki et al.[7] The three electronic absorption bands shown in Fig. 3 and the ESR spectrum disappeared in parallel when the solution was exposed to air. Therefore, the 302, 607 and 875 mμ bands may safely be assigned to the *p*-nitrotoluene anion.

Theoretical

Molecular orbital calculations of the π-electron system of the nitrobenzene anion were carried out in order to clarify the nature of the observed transition bands and obtain some knowledge about the electronic structure of the anion radical. In the actual calculations, the nitrobenzene anion was separated into two components; the benzene anion and the nitro group. The interaction between the components was calculated by taking into account the interaction among such π-electron configurations as ground, locally excited and charge-transfer configurations. In order to perform this kind of calculation, we need knowledge about the energy values and wave functions for the respective components. Therefore, first of all, the calculation of the benzene anion was carried out.

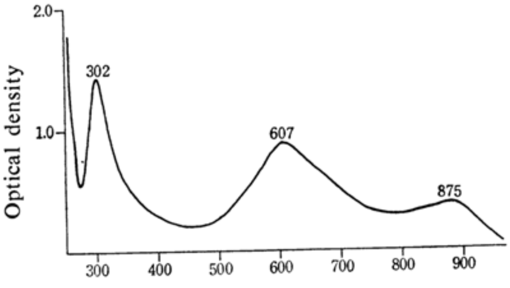

Fig. 3. The electronic spectrum of the THF solution of the *p*-nitrotoluene anion.

The calculation of the energy levels of the benzene anion was carried out by considering the configurational interaction among the two ground and nine excited π-electron configurations which are obtained by putting seven π-electrons into the molecular orbitals of the neutral benzene. The detailed description of our calculations may be omitted, since similar calculations have been made by Hoijtink.[8] In the actual calculation, the approximation of zero differential overlap was adopted.[9] The repulsion integrals of the (AA/AA) and (AA/BB) types necessary for the evaluation of the configuration energies and the interaction energies between the configurations were obtained by the method of Pariser and Parr.[9] The finally-evaluated energy levels and wave functions are given in Table I. These results are in good agreement with those obtained by Hoijtink.[8]

Using the above results about the π-electron structure of the benzene anion, the energy levels and wave functions of the nitrobenzene anion were calculated by a method similar to that used for the theoretical consideration of the π-electron structures of the nitromethyl anion,[10] nitrobenzene,[11] nitroamide, and ethyl nitrate.[12] That is to say, the effect of the nitro group on the energy levels of the benzene anion was considered in terms of the configuration interaction among the ground, locally excited and charge-transfer configurations. The geometrical configuration of the nitrobenzene anion necessary for the actual calculation was assumed to be equal to that of nitrobenzene itself as determined by Trotter.[13]

In the evaluation of the ground configuration energy, electrostatic interaction energy was taken into account. This is because there is a large heterogeneity in the π-electron distribution of the nitro group and the nitrogen atom is positively charged to a great extent. The thirteen locally excited configurations were considered. The energy values of the twelve configurations caused by the local excitation within the benzene anion were calculated by adding electrostatic interaction energy to the calculated excitation energy of the benzene anion given in Table I. The energy of the configuration locally excited within the nitro group was determined from the experimental value of the $\pi \rightarrow \pi^*$ transition energy of the nitromethane[9] and the electrostatic energy.

In addition to these, a charge-transfer configuration which is caused by moving an electron in the highest occupied orbital of the benzene anion to the lowest vacant orbital of the nitro group was taken into consideration. The energy of this configuration was obtained as follows: (Ionization potential of the benzene anion) − (electron affinity of the nitro group) = (electron affinity of benzene) − (electron affinity of the nitro group) = $-0.54 -0.4 = -0.94$ (eV.) The electron affinity of benzene was taken from the paper by Hush

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[10] S. Nagakura, *Mol. Phys.*, **3**, 152 (1960).

[11] *J. Mol. Spectroscopy*, to be published.

[12] This Bulletin, to be submitted.

[13] J. Trotter, *Acta Cryst.*, **12**, 884 (1959).

TABLE I. ENERGY LEVELS AND WAVE FUNCTIONS OF THE BENZENE ANION

Energy, eV.	Wave function*
0	$\Psi_1=\phi_1$
0	$\Psi_2=\phi_2$
2.390	$\Psi_3=-0.2318\phi_4+0.2318\phi_6-0.1640\phi_{7a}-0.2839\phi_{7b}+0.8860\phi_9$
4.895	$\Psi_4=-0.2667\phi_4+0.6842\phi_6+0.2559\phi_{7a}+0.6287\phi_{7b}+0.0001\phi_9$
4.895	$\Psi_5=-0.2666\phi_3+0.6842\phi_5+0.2559\phi_{8a}+0.6288\phi_{8b}$
5.534	$\Psi_6=\ \ 0.6454\phi_4+0.4606\phi_6+0.4501\phi_{7a}-0.4107\phi_{7b}+0.0001\phi_9$
5.534	$\Psi_7=\ \ 0.6455\phi_3+0.4605\phi_5+0.4502\phi_{8a}-0.4106\phi_{8b}$
7.081	$\Psi_8=\ \ 0.4427\phi_4-0.4432\phi_6+0.3136\phi_{7a}+0.5425\phi_{7b}+0.4636\phi_9$
6.072	$\Psi_9=\ \ 0.4998\phi_3-0.5003\phi_5+0.3535\phi_{8a}+0.6124\phi_{8b}$
7.536	$\Psi_{10}=-0.5124\phi_4-0.2637\phi_6+0.7789\phi_{7a}-0.2473\phi_{7b}-0.0002\phi_9$
7.536	$\Psi_{11}=-0.5123\phi_3-0.2638\phi_5+0.7790_{8a}-0.2472\phi_{8b}$

* ϕ_i's are the wave functions of the π-electron configurations used for the calculation of the benzene anion. They are represented by the following equations:

$\phi_1=|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5|$
$\phi_2=|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4|$
$\phi_3=|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\varphi_5\bar{\varphi}_5|$
$\phi_4=|\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\varphi_4\bar{\varphi}_4|$
$\phi_5=|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\varphi_4\bar{\varphi}_4|$
$\phi_6=|\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\varphi_5\bar{\varphi}_5|$
$\phi_{7a}=1/\sqrt{2}\,(|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_4\varphi_5|-|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\bar{\varphi}_3\varphi_4\varphi_5|)$
$\phi_{7b}=1/\sqrt{6}\,(|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_4\varphi_5|+|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\bar{\varphi}_3\varphi_4\varphi_5|-2|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\varphi_4\bar{\varphi}_5|)$
$\phi_{8a}=1/\sqrt{2}\,(|\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\varphi_4\bar{\varphi}_5|-|\varphi_1\bar{\varphi}_1\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_5|)$
$\phi_{8b}=1/\sqrt{6}\,(|\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\varphi_4\bar{\varphi}_5|+|\varphi_1\bar{\varphi}_1\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_5|-2|\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\bar{\varphi}_4\varphi_5|)$
$\phi_9=|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_6|$
where φ_i's are the molecular orbitals of benzene.

TABLE II. ENERGIES AND WAVE FUNCTIONS OF THE π-ELECTRON CONFIGURATIONS USED FOR THE CALCULATIONS OF THE NITROBENZENE ANION

Wave function*	Energy, eV.	Symmetry**	Character
$\phi'_1=\Psi_1\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	−0.857	S	Ground configurations
$\phi'_2=\Psi_2\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	−0.733	A	
$\phi'_3=\Psi_3\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	1.599	S	Locally (in the benzene ring) excited configurations
$\phi'_4=\Psi_4\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	4.057	S	
$\phi'_5=\Psi_5\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	4.150	A	
$\phi'_6=\Psi_6\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	4.785	S	
$\phi'_7=\Psi_7\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	4.699	A	
$\phi'_8=\Psi_8\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	6.290	S	
$\phi'_9=\Psi_9\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	5.281	A	
$\phi'_{10}=\Psi_{10}\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	6.747	S	
$\phi'_{11}=\Psi_{11}\,|\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b|$	6.741	A	
$\phi'_{12a}=1/\sqrt{2}\,(|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c|$ $-|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c|)$	5.894	S	Locally (in the nitro group) excited configurations
$\phi'_{12b}=1/\sqrt{6}\,(|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c|$ $+|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c|$ $-2|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\bar{\varphi}_4\varphi_a\bar{\varphi}_a\varphi_b\varphi_c|)$	5.894	S	
$\phi'_{13a}=1/\sqrt{2}\,(|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c|$ $-|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c|)$	5.832	A	
$\phi'_{13b}=1/\sqrt{6}\,(|\varphi_1\varphi_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c|$ $+|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c|$ $-2|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\bar{\varphi}_5\varphi_a\bar{\varphi}_a\varphi_b\varphi_c|)$	5.832	A	
$\phi'_{14}=|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\varphi_c|$	−0.94	S	Charge-transfer configuration

* φ_a, φ_b, φ_c, are the molecular orbitals of the nitro group evaluated by Tanaka (J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Soc. (Nippon Kagaku Zasshi)*, **78**, 1636 (1957)).

** S and A mean symmetric and antisymmetric, respectively, with respect to the symmetry plane perpendicular to the plane of the nitrobenzene anion.

and Pople.[14] The electron affinity of the nitro group was taken to be 0.4 eV., the value used for the calculation of a series of nitro compounds.[10-12] The energies and wave functions of the configurations taken up in the present calculations are shown in Table II.

The off-diagonal matrix elements ($\boldsymbol{H}_{ij}$'s) of the total electronic Hamiltonian which represent the interaction between two appropriate configurations were evaluated by the aid of the method presented by Pople[15] and by Murrell and Longuet-Higgins.[16] The results are shown in Table III. The repulsion integrals necessary for the evaluation of the interaction energies between configurations locally excited in different parts of the molecule were obtained in the same way as in the case of the benzene anion. The interaction energies between the charge-transfer configuration and the others are expressed using the core resonance integral, β_{CN}, between the adjacent nitrogen and carbon atoms. The best value of β_{CN} was estimated to be -2.30 eV. for neutral nitrobenzene.[10] It may be expected that the $|\beta_{CN}|$ of the nitrobenzene anion is larger than that of neutral nitrobenzene. In the present calculations, β_{CN} was estimated to be -3.0 eV. By solving the secular equation composed of the elements given in Tables II and III by the aid of an electronic computer (IBM 7090), the energy levels and wave functions of the nitrobenzene anion were evaluated. (see Fig. 4). Of these, the lowest four energy levels and their wave functions are shown in Table IV.

TABLE III. OFF-DIAGONAL MATRIX ELEMENTS USED FOR THE CALCULATIONS OF THE NITROBENZENE ANION

$\boldsymbol{H}_{1.14} = -1.214$ eV. $(0.408\ \beta_{CN})$
$\boldsymbol{H}_{3.12a} = 0.162$
$\boldsymbol{H}_{3.14} = -0.761$ $(0.254\ \beta_{CN})$
$\boldsymbol{H}_{4.12a} = 0.066$
$\boldsymbol{H}_{5.13a} = 0.176$
$\boldsymbol{H}_{6.12a} = -0.036$
$\boldsymbol{H}_{7.13a} = -0.302$
$\boldsymbol{H}_{8.12a} = 0.317$
$\boldsymbol{H}_{8.14} = -0.398$ $(0.133\ \beta_{CN})$
$\boldsymbol{H}_{10.12a} = -0.281$
$\boldsymbol{H}_{11.13a} = -0.070$

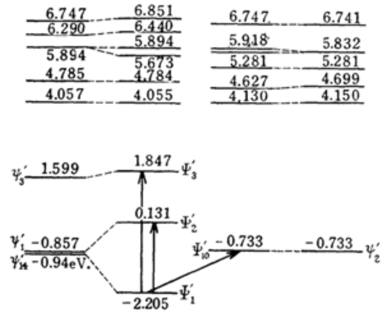

Fig. 4. The energy diagram of the nitrobenzene anion.

Furthermore, the oscillator strength (f) values of the three longer wavelength transitions were calculated by means of the usual equation, $f=1.085\times10^{-5}\nu Q^2$, where Q and ν are the transition moment (in units of Å) and the evaluated transition energies (in units of cm^{-1}) respectively. The evaluated oscillator strength values are shown in Table V, together with observed and calculated transition energies.

TABLE V. OBSERVED AND CALCULATED DATA FOR THE ABSORPTION SPECTRUM OF THE NITROBENZENE ANION

Transition	Transition energy, eV.		Calculated oscillator strength
	Obs.	Calcd.	
$\Psi'_1 \rightarrow \Psi'_{10}$	—	1.471	1.64×10^{-3}
$\Psi'_1 \rightarrow \Psi'_2$	2.214	2.336	4.13×10^{-1}
$\Psi'_1 \rightarrow \Psi'_3$	4.245	4.052	5.51×10^{-2}

TABLE IV. THE LOWEST FOUR ENERGY LEVELS OF THE NITROBENZENE ANION AND THEIR WAVE FUNCTIONS

Energy, eV.	Wave function	Symmetry
$W_1 = -2.205$	$\Psi'_1=0.6616\phi'_1+0.1470\phi'_3+0.0000\phi'_4-0.0000\phi'_6$ $+0.0346\phi'_8-0.0001\phi'_{10}-0.0043\phi'_{12a}+0.7345\phi'_{14}$	S
$W_2 = 0.131$	$\Psi'_2=0.7365\phi'_1-0.3115\phi'_3-0.0002\phi'_4+0.0001\phi'_6$ $-0.0393\phi'_8+0.0005\phi'_{10}+0.0110\phi'_{12a}-0.5991\phi'_{14}$	S
$W_3 = 1.847$	$\Psi'_3=0.1408\phi'_1+0.9380\phi'_3+0.0011\phi'_4-0.0004\phi'_6$ $-0.0255\phi'_8-0.0021\phi'_{10}-0.0358\phi'_{12a}-0.3136\phi'_{14}$	S
$W_{10} = -0.733$	$\Psi'_{10}=\Psi'_2$	A

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[14] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[15] J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

[16] H. C. Longuet-Higgins and J. N. Murrel, ibid., **A68**, 601 (1955).

Discussion

On the basis of the comparison of the calculated transition energies and oscillator strengths with the observed results, the 560 mμ and 292 mμ bands can safely be ascribed to the $W_1 \rightarrow W_2$ and $W_1 \rightarrow W_3$ transitions respectively. As may easily be seen from the wave functions given in Table IV, the W_1 and W_2 states may be said to be mainly caused by the resonance interaction between the ground and charge-transfer configurations, although there are also small contributions from locally excited configurations. Therefore, the strongest 560 mμ band may be regarded as the intramolecular charge-transfer band. In the upper state of the 292 mμ band, the contribution of the local excitation within the benzene anion is large, amounting to 88%. Therefore, this band can be interpreted as the shifted band of the 600 mμ band of the benzene anion. It is noteworthy that the band of the benzene anion shows a large blue shift when the nitro group is introduced. This blue shift phenomenon exhibits a striking contrast to the red shift phenomena usually observed with the 260 mμ band of the neutral benzene molecule.[17] In the case of the nitrobenzene anion, the resonance between the ground and charge-transfer configurations is strong; consequently, the stabilization energy of the ground configuration due to the resonance is larger than that of the locally excited configuration. This is the reason why the 600 mμ band of the benzene anion shows the blue shift when the nitro group is introduced.

In addition to the above-mentioned two bands, the theoretical results show that another weak band, one corresponding to the $W_1 \rightarrow W_{10}$ transition, may appear in the near infrared region, say, the 800 mμ region. Although a weak and broad absorption was found in that region, no clear absorption peak could be observed in the case of the nitrobenzene anion.

This may be due to the fact that the band should be very weak, as is revealed by the small value of the calculated oscillator strength; moreover, the solvent absorption in the expected wavelength region prevents any accurate absorption measurement. In the case of the *p*-nitrotoluene anion, we observed the absorption peak at 875 mμ. This may correspond to the same transition.

TABLE VI. ODD ELECTRON DENSITIES AND COUPLING CONSTANTS OF THE NITROBENZENE ANION

Atom	Odd electron density		Coupling constant,
	Calcd.	Obs.	gauss obs.
N	0.2651	0.212	10.33
C^o	0.0401	0.124	3.46
C^m	0.0401	0.040	1.13
C^p	0.1495	0.138	3.86

The observed coupling constants[6] and the odd electron densities derived from them are shown in Table VI, together with the theoretical values of odd electron densities evaluated by the use of the wave function Ψ_1' in Table IV. The odd electron densities on the ring carbon atoms, ρ_i^c's, were obtained using the usual equation, $\rho_i^c = a_i^H/Q_H$.[18] Here a_i^H is the observed coupling constant of the ring proton adjacent to the carbon atom under consideration and Q_H was taken to be 28 gauss.[19] The odd electron density on the nitrogen atom, ρ^N, was obtained by using a similar equation, $\rho^N = a^N/Q_N$, where a^N the observed coupling constant and Q_N was assumed to be 49 gauss, the mean value of the coupling constants of nitrogen in the anion radicals of several aliphatic nitro compounds.[20] The odd electron densities estimated from the coupling constants are in good agreement with the theoretical ones except in the case of the ortho carbon atom.

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