Ultraviolet Absorption Spectra of o-, m- and p-Dinitrobenzene

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Introduction of a substituent group for hydrogen in a benzene nucleus has been considered to shift in general the spectrum of the original benzene derivative to longer wavelengths. In the previous papers[1,2], however, the author found that absorption maximum bands of *m*-dinitrobenzene, 1, 3, 5-trinitrobenzene and 2, 4, 6-trinitrotoluene shifted to the blue as compared with the intense 260 mμ band of nitrobenzene.

In the present paper, an attempt has been made to investigate the influence of the introduction of one more nitro group in the ortho-, meta-, or para-position upon the spectrum of nitrobenzene.

Experimental

Materials.—*o*-Dinitrobenzene, Tokyo Kasei Co. guaranteed reagent, was used directly; m.p. 118.1°C (lit. 118°C). Commercial pure *m*-dinitrobenzene was recrystallized three times from ethanol; m.p. 90.4°C (lit. 90°C). *p*-Dinitrobenzene, Tokyo Kasei Co. guaranteed reagent, was recrystallized once from methanol; m.p. 174.7°C (lit. 174°C). Commercial guaranteed ethanol was fractionally distilled after the usual treatment.

Spectra.—The spectra of the dinitrobenzenes in ethanol were measured with a Hitachi quartz spectrophotometer, Model EPU-2 at room temperature. Path length of absorption cells was 1 cm.

Results and Discussion

As indicated in Fig. 1 and Table I, the maximum absorption band of *m*-dinitrobenzene is at a shorter wavelength and has a greater molar extinction coefficient than that of nitrobenzene, while the

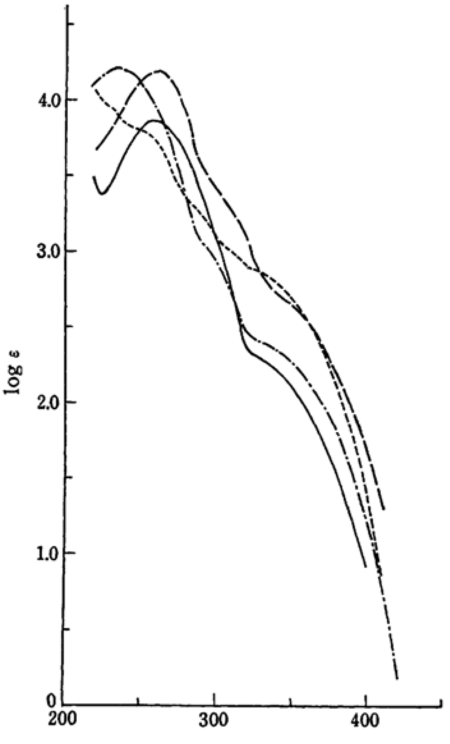

Fig. 1. Absorption spectra of nitrobenzene (——), *o*-dinitrobenzene (------), *m*-dinitrobenzene (—·—), and *p*-dinitrobenzene (— —), all in ethanol.

TABLE I. VALUES OF THE ABSORPTION MAXIMA OF DINITROBENZENES IN ETHANOL

	λ_{max}, mμ	ε
Nitrobenzene	260	8140
o-Dinitrobenzene	—	—
m-Dinitrobenzene	233	17200
p-Dinitrobenzene	261	15600

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[1] T. Abe, This Bulletin, 31, 904 (1958).

[2] T. Abe, ibid., 32, 339 (1959).

absorption maximum of *p*-dinitrobenzene gives a more intense absorption band at the same region as the 260 mμ band of nitrobenzene. The 260 mμ band of nitrobenzene has been interpreted by Doub and Vandenbelt[3] and later by Wenzel[4] to correspond to the 200 mμ band of benzene which has the same intensity, but has been interpreted by Nagakura and Tanaka[5] in terms of the intramolecular charge transfer involving an excitation of a bonding electron of the highest occupied energy-level of benzene to the vacant energy-level of the nitro group.

From the concept of the intramolecular charge transfer, the maximum absorption bands of *m*- and *p*-dinitrobenzene will be discussed by considering interactions between the highest occupied energy-levels of nitrobenzene and the vacant level of the nitro group on substituting the second nitro group in the meta- or para-carbon atom of nitrobenzene. According to the energy level diagrams given by Nagakura and Tanaka[6,7], the vacant energy-level ($V_{NO_2}=-6.85$ eV.) of the nitro group is lower than the lowest vacant energy-level ($V_N=-4.65$ eV.) of nitrobenzene, to which the V_{NO_2} mainly contributes. On introducing one more nitro group in nitrobenzene, the energy-levels of nitrobenzene, indicated in Fig. 2, may be approximately affected by only the vacant level (V_{NO_2}) of the nitro group with such interaction as was given by Nagakura and Tanaka[5], because interactions with other occupied levels of the nitro group, which are remote or of different symmetry, are negligibly small. According to Nagakura and Tanaka's theory, as a result of the interaction with the V_{NO_2}, an energy-level ($E=H_{N1}$ or H_{N2}) of nitrobenzene shifts below by the following magnitude:

$$\varDelta E=1/2\left[(E-V_{NO_2})+\{(E-V_{NO_2})^2+4C_N^2C_{NO_2}^2\beta^2\}^{1/2}\right] \tag{1}$$

Here C_N and C_{NO_2} are a coefficient of an atomic orbital of a carbon atom in the molecular orbital of E and a coefficient of an atomic orbital of the nitrogen atom in the molecular orbital of V_{NO_2}, respectively, where the carbon atom and the nitrogen one are joined together. The β is the resonance integral between the atomic orbital of the carbon atom and the orbital of the nitrogen atom. It is obvious that the $\varDelta E$ increases as C_N increases or as $(E-V_{NO_2})$ decreases. On the other hand, the V_{NO_2} of the nitro group similarly interacts with the levels of nitrobenzene, especially with the H_{N1}, H_{N2} and the V_N that is nearest to the V_{NO_2}. When the nitro group is substituted in the meta-position of nitrobenzene, two intense absorption bands of intramolecular charge transfer can be expected to appear at longer wavelengths for *m*-dinitrobenzene owing to transitions involving excitations of bonding electrons of the occupied levels (H_{m1} and H_{m2}) to the lowest vacant level (V_m), because the V_{NO_2} interacts with both the levels of H_{N1} and H_{N2}, as in the case of some disubstituted benzenes[6]. On substituting the nitro group in the para-position of nitrobenzene, a transition of a bonding electron in H_{p2} to the lowest vacant level (V_p) can be predicted to show only an intense band of intramolecular charge transfer at a longer wavelength, the B_1-level (H_{N1}) in nitrobenzene being intact. The blue shift of 260 mμ band of nitrobenzene for

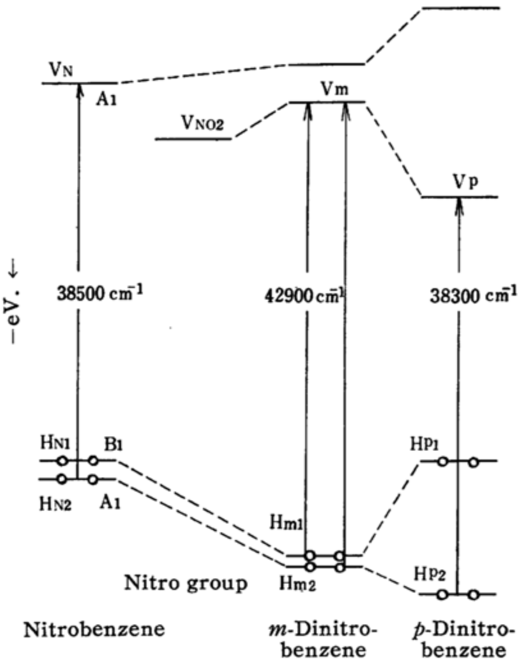

Fig. 2. Spectra of intramolecular charge transfer in dinitrobenzenes.

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[3] L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

[4] A. Wenzel, *J. Chem. Phys.*, **22**, 1623 (1954).

[5] S. Nagakura and J. Tanaka, ibid., **22**, 236 (1954); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 331 (1954).

[6] J. Tanaka and S. Nagakura, *J. Chem. Phys.*, **24**, 1274 (1956); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1200 (1957).

[7] S. Nagakura and J. Tanaka, This Bulletin, **32**, 734 (1959).

m-dinitrobenzene means the great interaction of V_{NO2} with H_{m1} and H_{m2}. Consequently, these levels will shift in nitrobenzene as indicated Fig. 2. In this case, the occupied B_1-level (H_{N1}) as well as the A_1-level (H_{N2}) in nitrobenzene may be predicted to become low in *m*-dinitrobenzene, because the coefficient of the atomic orbital belonging to the meta-carbon atom in the molecular orbital of the occupied B_1-level (H_{N1}) of nitrobenzene is greater than the corresponding coefficient in the A_1-level, although the H_{N1} is slightly higher than the H_{N2}. In the molecular orbital of the occupied A_1-level (H_{N2}) of nitrobenzene, the coefficient of the atomic orbital for the para-carbon atom is apparently greater than that for the meta-carbon atom. Accordingly, the A_1-level (H_{N2}) of nitrobenzene can be considered to become lower in *p*-dinitrobenzene than in *m*-dinitrobenzene, as given from Eq. 1. The maximum absorption band of *p*-dinitrobenzene lies at the wavelength close to that of nitrobenzene. From these it may be expected that the V_{NO2}-level shifts below to the same extent, as compared with the H_{N2}, in *p*-dinitrobenzene, owing to the great interaction between the V_{NO2} and the V_N. In comparison with the case of *m*-dinitrobenzene, it is known that the coefficient of the atomic orbital of the para-carbon atom is probably much greater than that of the meta-carbon atom in the molecular orbital of the vacant A_1-level (V_N) of nitrobenzene. From the above discussion, the maximum absorption bands of dinitrobenzenes may be interpreted to be owing to the electronic transitions illustrated in Fig. 2.

An ortho-substituted benzene usually shows a spectrum resembling that of a meta-substituted benzene⁶⁾, while the absorption curve of *o*-dinitrobenzene is different from that of *m*-dinitrobenzene, giving only shoulders at 250, 290, 310 and 360 mμ. This may be understood in terms of steric hindrance by the adjacent large nitro groups of *o*-dinitrobenzene. This steric hindrance may interfere with a coplanar arrangement of the nitro groups with benzene nucleus.

The weak shoulder of nitrobenzene at 290 mμ, which has been interpreted by Nagakura and Tanaka[6,8)] to be related to the 260 mμ band of benzene, becomes more distinct in *m*- and *p*-dinitrobenzene.

The molar extinction coefficients of the 360 mμ bands for *o*- and *p*-dinitrobenzene are greater than those of *m*-dinitrobenzene, which are slightly larger than the corresponding molar extinction coefficient for nitrobenzene. The 360 mμ band of nitrobenzene has been interpreted by Wenzel[4)] to be due to the nitro group.

Summary

In ethanol, *m*-dinitrobenzene shows the maximum absorption band at shorter wavelengths than nitrobenzene, while *p*-dinitrobenzene gives the absorption maximum at the wavelength near to that of nitrobenzene. These bands have briefly been discussed from the concept of the intramolecular charge transfer. The absorption curve of *o*-dinitrobenzene, indicating no absorption maximum but shoulders, are different from those of the other dinitrobenzenes, probably owing to steric hindrance by the adjacent large nitro groups.

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[8)] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1114 (1958).