CHEMISTRY LETTERS, pp. 903-907, 1972. Published by the Chemical Society of Japan

PHOTOELECTRON SPECTRA OF NITRO-COMPOUNDS

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Molecular photoelectron spectra of nitromethane and nitrobenzenes were measured. The assignment of the observed spectra was made, the results of the CNDO/2 and extended Hückel calculations being referred. The steric hindrance effect was found to be significant in the interpretation of the observed photoelectron spectra.

The steric hindrance effect of o-substituted methyl groups upon physico-chemical properties of nitrobenzene has been studied on the dipole moments,1) electronic spectra,2-7) infrared spectra,7,8) and NMR spectra.9) Owing to this effect, the nitro group of 2,4,6-trimethylnitrobenzene is twisted by 66°10) from the benzene ring plane. For o-nitrotoluene, though no experimental data has been obtained, the twisting angle may be considered to be equal to the value (40°) obtained for 1-bromo-2,4-dinitrobenzene.11) This is because the van der Waals radius of a bromine atom is similar to that of a methyl group.

The photoelectron spectroscopy gives some direct information about molecular orbital energies, and therefore may be expected to be a useful method to investigate the orbital energy change due to the steric inhibition of the π-electron migration between the benzene ring and the nitro group. Thus, we have undertaken to measure the photoelectron spectra (PES) of nitrobenzene, o-, m-, and p-nitrotoluenes, 2,4- and 2,6-dimethylnitrobenzenes, and nitromethane, and to interpret the observed spectra with the aid of calculated MO energies paying special attention upon the steric effect of o-methyl groups.

Experimental and Theoretical

PES of nitromethane, nitrobenzene, o-, m-, and p-nitrotoluenes, 2,4- and 2,6-dimethylnitrobenzenes, benzene, toluene, and m-xylene were recorded on a JASCO model PE-1 photoelectron spectrometer. Ionization was effected by irradiation of the 584 Å He(I) resonance line. The observed spectra were calibrated based on the Xe spectrum.

The CNDO/212) and extended Hückel molecular orbital (EHMO)13) calculations of the compounds under consideration were carried out by a FACOM 270-30 computer at the Institute of Physical and Chemical Research. The geometrical structures of these compounds were properly assumed on the basis of the data given in Ref. (14).

Results and Discussion

The vertical ionization potentials (I_V's) of nitrobenzene and its related compounds obtained from their PES are summarized in Table 1. The correlation diagram for the orbital energies of these compounds obtained on the assumption $\varepsilon = -I_V$ (Koopmans' theorem15)) is shown in Fig. 1. As is seen in Table 1, nitrobenzene and its methyl derivatives commonly have four bands in the range between 9 and 11 eV.

TABLE 1. VERTICAL IONIZATION POTENTIALS (I_V) OBTAINED FROM THE BAND MAXIMA OF THE OBSERVED PESa) IN eV

Benzene	9.23	11.67	12.32	13.97	
Toluene	8.85	9.34	11.43		
m-Xylene	8.71	9.03	11.24		
Nitromethane	11.31	11.81	14.50	15.65	17.35
Nitrobenzene	9.88	10.29	10.97	11.15	12.56*
o-Nitrotoluene	9.69	9.89*	10.92*	11.08*	12.49*
m-Nitrotoluene	9.49	10.04	10.84*	11.12	12.32*
p-Nitrotoluene	9.54	10.05	10.85	11.07	12.37*
2,4-Dimethylnitrobenzene	9.38	9.67	10.87*		12.10*
2,6-Dimethylnitrobenzene	9.17	9.53*	10.90*	11.29	12.03*

a) The experimental errors for the I_V values are within ±0.01∼±0.02 eV except for those marked with an asterisk for which larger experimental errors (ca. ±0.04 eV) are expected.

First, let us consider the PES of nitromethane. The CNDO/2 calculation predicts that the first, second, and third bands of nitromethane, which appear at 11.31, 11.81, and 14.50 eV, respectively, may be assigned to the ionization from orbitals b, a, and c shown in Fig. 2, respectively. In view of the insufficient reliability of the CNDO/2 calculation, however, it seems to be necessary to check this assignment from the experimental point of view. In actuality, we have re-examined the assignment of the bands of nitromethane with the aid of the experimental results of the methyl substituent effect on the PES of nitrobenzene. Consequently, the 11.31 and 11.81 eV bands of nitromethane were found to be due to the ionization from orbitals a and b in Fig. 2, respectively.

Nitrobenzene and its methyl derivatives have two bands in the range between 10.8 and 11.4 eV; one of them, the third band, appears at ∼10.9 eV and the other, the fourth band, at ∼11.1 eV. From their positions, shapes, and relative intensities, the third and fourth bands are correlated with the 11.31 and 11.81 eV bands of nitromethane, respectively, as shown in Fig. 1. In view of the π-electron attracting ability of the nitro group in aromatic compounds, we can understand a general tendency that the bands of nitromethane shift toward the lower energy side in nitrobenzene and its derivatives.

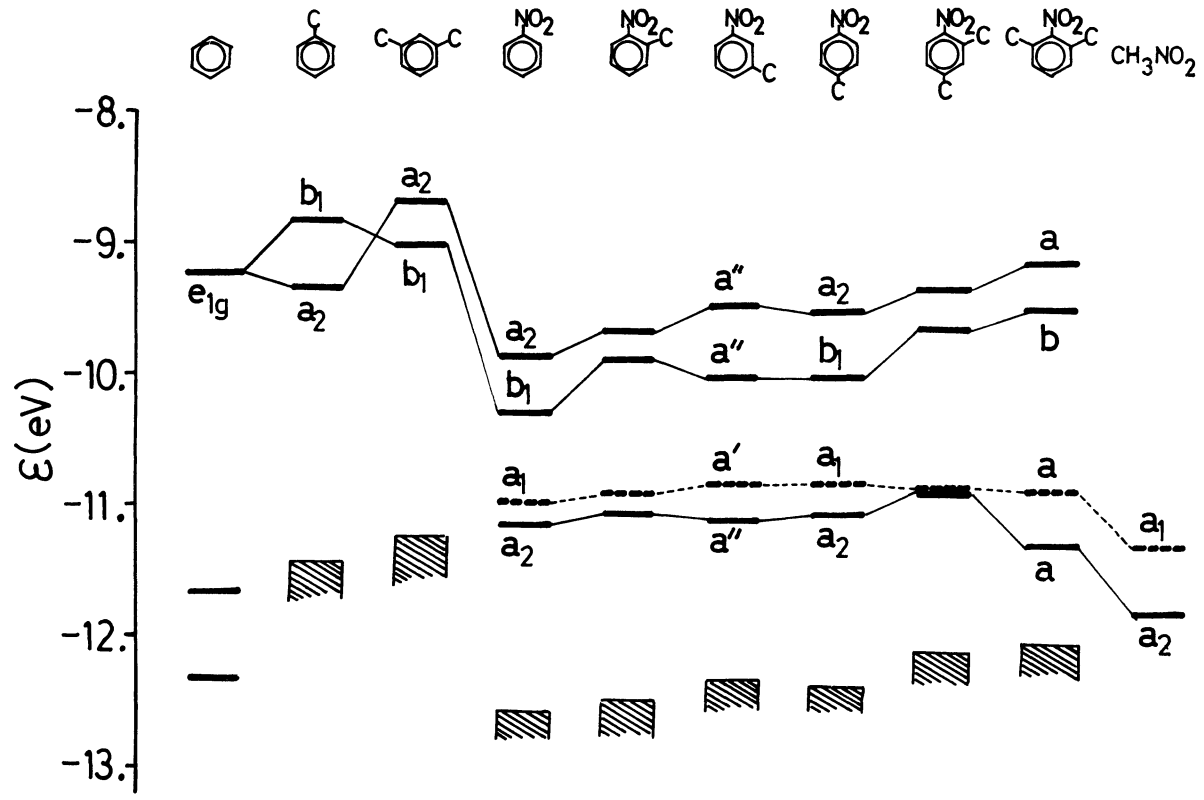

Fig. 1. Correlation diagram for the higher occupied orbitals of benzene, toluene, m-xylene, nitrobenzene, methyl-substituted nitrobenzenes, and nitromethane. The orbital energies, ε's, are those obtained on the assumption, $\varepsilon = -I_V$ (Koopmans' theorem).

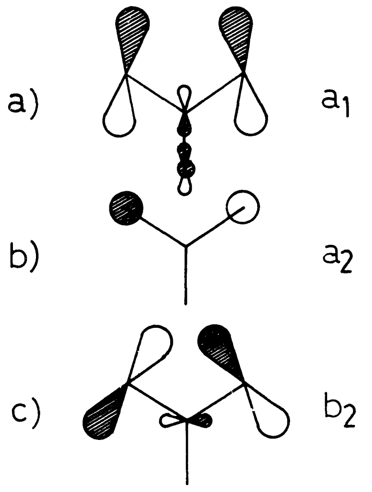

Fig. 2. Schematic representation of nitromethane MO's

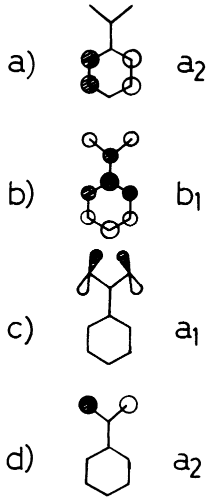

Fig. 3. Schematic representation of the higher occupied MO's of nitrobenzene

The third bands around 10.9 eV of nitrobenzene and its methyl derivatives are rather insensitive to the methyl substitution in the benzene ring. Therefore, the 11.31 eV band of nitromethane and the third bands of the aromatic nitro compounds may safely be attributed to the n-orbital (a in Fig. 2 and c in Fig. 3) mainly localized on the two oxygen atoms of the nitro group. The fourth bands of the nitrobenzenes correlated with the 11.81 eV band of nitromethane are more sensitive to the methyl substitution in the benzene ring compared with the third bands. In particular, it may be noticed that the fourth band of 2,6-dimethylnitrobenzene shifts greatly toward the higher energy side than that of 2,4-dimethylnitrobenzene. This fact can be explained on the basis of the assignment of the band to the nitro group π-orbital (d in Fig. 3), because, according to the EHMO calculation, the orbital mixes to a greater extent with the e_{1g} (A)[16] type π-orbital of the benzene ring and therefore is more stabilized for 2,6-dimethylnitrobenzene than for 2,4-dimethylnitrobenzene. Thus, the 11.81 eV band of nitromethane and the fourth bands of aromatic nitro compounds may be ascribed to the π-orbital mainly localized on the oxygen atoms of the nitro group (b in Fig. 2 and d in Fig. 3).

From the molecular orbital consideration, the first and second bands of nitrobenzene may be assigned, respectively, to the π-orbirals a and b in Fig. 3, which correspond to the doubly degenerated orbitals of benzene, e_{1g} (A) and e_{1g} (S). Both orbitals are lowered for nitrobenzene because of the decreasing electron population on the benzene ring caused by the electron attracting property of the nitro group. In addition to this, the e_{1g} (S) orbital is stabilized to some extent in nitrobenzene by the interaction with the lowest vacant π-orbital of the nitro group and becomes lower than the e_{1g} (A) orbital.

As stated before, the nitro group is twisted by ~40° for o-nitrotoluene because of the steric hindrance due to the o-methyl group. It may be expected that the steric inhibition of conjugation decreases the stabilization of the e_{1g} (S) orbital due to the interaction with the lowest vacant orbital of the nitro group and reduces the second I_V of o-nitrotoluene relative to that of m- or p-nitrotoluene. This expectation is satisfied by the result shown in Fig. 1 and Table 1. From the same reason, we can explain the finding that the second I_V of 2,6-dimethylnitrobenzene is smaller than that of 2,4-dimethylnitrobenzene.

The first I_V's observed with the aromatic nitro compounds under consideration decrease in the following order; nitrobenzene > o-nitrotoluene > p-nitrotoluene > m-nitrotoluene > 2,4-dimethylnitrobenzene > 2,6-dimethylnitrobenzene. This decreasing order of I_V may be reasonable, with an exception of o-nitrotoluene, judging from the fact that the electron population on the benzene ring increases in the same order. o-Nitrotoluene may be expected to be greater in the electron population on the benzene ring and therefore to be smaller in the first I_V than p-nitrotoluene. The observed values, however, show that the reverse is the case. According to EHMO calculation, e_{1g} (A) orbital of the benzene ring is stabilized through the interaction with the lowest vacant π orbital of the nitro group for the system with a methyl group on one of the o-positions.[17] This is one of the possible reasons for the discrepancy observed with o-nitrotoluene. Another possible reason is that the destabilization of the e_{1g} (A) orbital caused by the interaction with the b orbital in Fig. 2 is reduced for o-nitrotoluene with the nitro group twisted by ~40° from the benzene ring plane compared with p-nitrotoluene. The EHMO calculation shows that the former effect is more predominant than the latter one.[18)]

In view of the large twisting angle (66°) of the nitro group it may be expected that the first and second I_V values of 2,6-dimethylnitrobenzene are close to those of m-xylene compared with those of the other aromatic nitro compounds. This is the case: in particular the separations between the first and second I_V values are almost equal for both compounds.

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16) The e_{1g} (S) and e_{1g} (A) orbitals are taken as follows:

$$e_{1g}\,(S) = 1/\sqrt{12}\,(2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6)$$

$$e_{1g}\,(A) = 1/2\,(\chi_2 + \chi_3 - \chi_5 - \chi_6)$$

where χ_i is the $2p_z$ AO of the i-th carbon atom.
17) This interaction may be expected to occur for m-nitrotoluene in which one of the m-positions is replaced by the methyl group. According to the EHMO calculation, however, this effect is much smaller for m-nitrotoluene than for o-nitrotoluene.
18) Both effects may be expected to occur for 2,4-dimethylnitrobenzene as well as o-nitrotoluene. A rather narrow separation between the first and second I_V's observed for 2,4-dimethylnitrobenzene may be attributed to these effects.

(Received August 2, 1972)