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Experimental and Theoretical Study of Substituent Effects of Iodonitrobenzenes

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The electronic structures and substituent effects of *o*-, *m*-, and *p*-iodonitrobenzene have been studied by ultraviolet photoelectron spectroscopy (UPS). The observed bands were interpreted on the basis of empirical arguments and theoretical calculations. The analysis of electronic effects of the donor/acceptor substituent groups is essential for the reliable assignment of the observed photoelectron spectra. The investigation of π- and *n*-orbital ionization potentials enabled us to describe the correlation between substituent effects and the relative reactivities of the iodonitrobenzenes. It was found that the energy order of the π_2 and $n_{\|}$ orbitals is reversed as a result of the combined influence of the electron-withdrawing nitro group and the electron-donating iodine atom. Distinct changes of the π and *n* bands occur in *o*-iodonitrobenzene. This characteristic depends on the conjugation between the π orbitals of the benzene ring and the nitro group and the interaction of in-plane lone pairs of iodine and one of the oxygen atoms of the nitro group in the adjacent position. This might contribute to the high reactivity of *o*-iodonitrobenzene in a number of reactions.

Introduction

The reactivity of substituted benzene derivatives has been extensively studied and has led to the notion of substituent effects (SEs). Overall SEs can be conceptually partitioned into electronic, steric, and solvent contributions. A molecular descriptor that is closely related to the electronic substituent effect is the ionization energy. This energy can be accurately measured by ultraviolet photoelectron spectroscopy (UPS).[1] It is a useful tool to investigate the effects of substituent groups on the electronic structure of parent hydrocarbons.[2] The study of electronic structure and electronic substituent effects can also be performed by theoretical methods. For example, DiLabio et al.[3] used DFT calculations to obtain the first ionization energies of 55 para- and meta-disubstituted benzenes. The substituent groups in their study were both electron-withdrawing (EW) and electron-donating (ED) types.

There has been a considerable amount of work on the electronic structures of organic nitro and halogen compounds.[4] However, the molecular orbital structures of iodonitrobenzenes, which have wide applications in organic chemistry,[5] biochemistry,[6] and electrochemistry,[7] is not well understood. Only one report on the adiabatic ionization potential of *p*-iodonitrobenzene has been published.[8]

o-Iodonitrobenzene, an interesting molecule with strong electron-withdrawing and electron-donating substituents in the neighboring 1 and 2 positions of benzene, has abnormally high reactivity in a number of reactions, such as Ullmann coupling.[9] Ullmann (1875–1939) was one of the pioneers in the use of copper to promote reactions of aryl halides.[10] The ease of Ullmann coupling follows the sequence ArI > ArBr > ArCl. The reactivity is affected to different degrees by different substituents in different positions on the aryl halide.

The purpose of this work was to study the electronic structures of *o*-, *m*-, and *p*-iodonitrobenzene by means of photoelectron spectroscopy and use these results to improve the understanding of the SE for benzene derivatives containing both EW and ED groups. Because the ionizations of π and *n* orbitals are sensitive internal probes for electronic effects of substituents, we investigated the correlation between substituent effects and the relative reactivity of the iodonitrobenzenes.

Experimental and Theoretical Methods

Samples of *o*-, *m*-, and *p*-iodonitrobenzene were purchased from Acros Company and were identified by mass spectrometry. The photoelectron spectra of the iodonitrobenzenes were recorded on a double-chamber UPS-II machine[11] that was built specifically to detect transient species at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band. A sample inlet temperature in the range of 100–200 °C was employed to obtain sufficient vapor pressure in the ionization region. Experimental vertical ionization energies were calibrated by simultaneous addition of small amounts of argon and methyl iodide to the sample.

To assign the bands of the UPS spectra, the vertical ionization energies were calculated using Cederbaum's outer-valence Green's function (OVGF) method,[12] based on the geometry optimization at the B3LYP/6-311++G** level. For iodine, a relativistic basis set that has been found to be reliable[13] was used. Natural bond orbital (NBO) analysis at the B3LYP/6-311++G** level was used for a better understanding of the nature of the intermolecular interactions.[14] The quantum chemical calculations were performed using the Gaussian 03 program package.[15]

Results

The HeI ultraviolet photoelectron spectra of *o*-, *m*-, and *p*-iodonitrobenzene are shown in Figures 1–3, respectively. As

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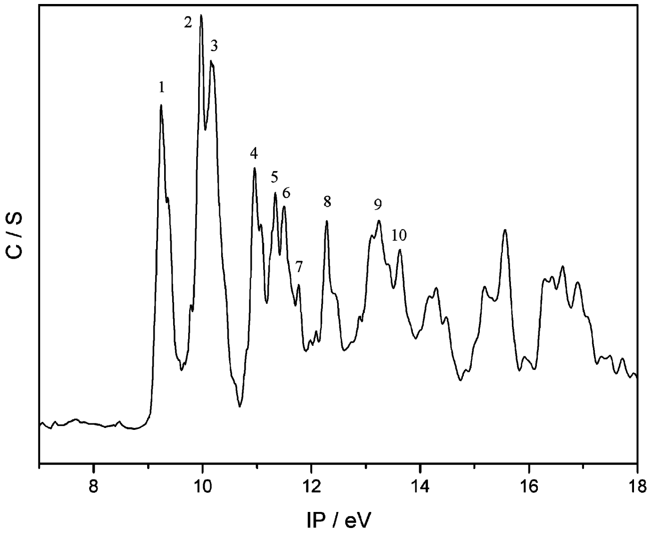

Figure 1. HeI photoelectron spectrum of *o*-iodonitrobenzene.

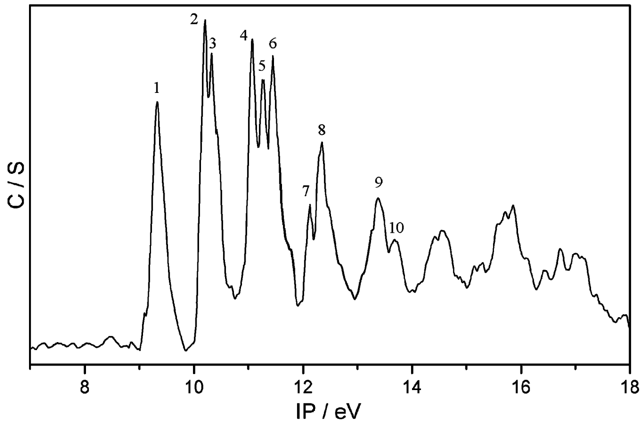

Figure 2. HeI photoelectron spectrum of *m*-iodonitrobenzene.

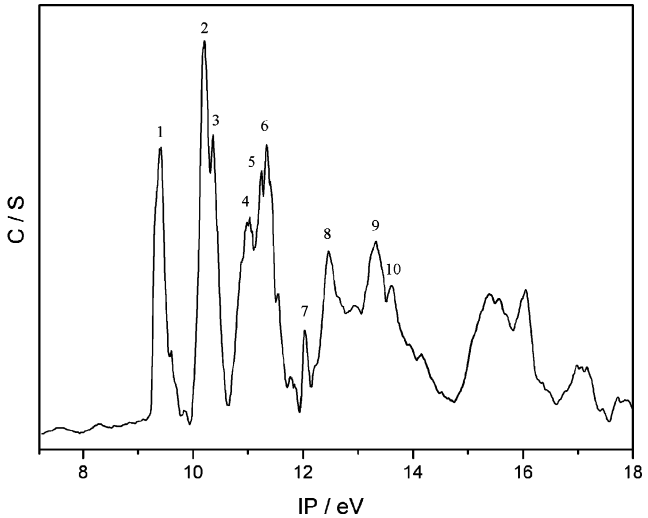

Figure 3. HeI photoelectron spectrum of *p*- iodonitrobenzene.

TABLE 1: Experimental and Calculated Vertical Ionization Potentials and MO Characters for *o*-Iodonitrobenzene

	IP (eV)			
band	experimental	calculated[a]	MO	character[b]
1	9.26	9.34	58	π_3
2	10.03	9.79	57	$n_{\parallel}$
3	10.16	10.25	56	π_2
4	11.01	11.01	55	$n_{\perp}$
5	11.35	11.40	54	σ
6	11.49	11.46	53	$n_{O(\pi)}$[c]
7	11.81	11.88	52	n_O
8	12.31	12.32	51	σ
9	13.28	13.55	50	σ
10	13.63	13.69	49	π_1
11	14.27	14.59	48	σ
12	15.57	15.78	47	σ

[a] OVGF calculations at the 6-311++G** basis set level. [b] Symbols $n_{\parallel}$ and $n_{\perp}$ indicate an orbital predominantly due to the iodine 5p orbitals distributed parallel and perpendicular, respectively, to the benzene ring. [c] This orbital is just like a π orbital.

TABLE 2: Experimental and Calculated Vertical Ionization Potentials and MO Characters for *m*-Iodonitrobenzene

	IP (eV)			
band	experimental	calculated[a]	MO	character[b]
1	9.35	9.43	13a″	π_3
2	10.18	10.17	45a′	$n_{\parallel}$
3	10.31	10.41	12a″	π_2
4	11.06	11.21	11a″	$n_{\perp}$
5	11.24	11.23	44a′	σ
6	11.41	11.40	10a″	$n_{O(\pi)}$
7	12.01	11.99	43a′	n_O
8	12.35	12.25	42a′	σ
9	13.38	13.58	41a′	σ
10	13.70	13.88	9a″	π_1
11	14.57	14.68	40a′	σ
12	15.82	15.80	39a′	σ

[a] OVGF calculations at the 6-311++G** basis set level. [b] Symbols $n_{\parallel}$ and $n_{\perp}$ indicate an orbital predominantly due to the iodine 5p orbitals distributed parallel and perpendicular, respectively, to the benzene ring.

TABLE 3: Experimental and Calculated Vertical Ionization Potentials and MO Characters for *p*-Iodonitrobenzene

	IP (eV)			
band	experimental	calculated[a]	MO	character[b]
1	9.40	9.50	$9b_1$	π_3
2	10.19	10.23	$17b_2$	n
3	10.36	10.34	$4a_2$	π_2
4	11.03	11.20	$8b_1$	$n_{\perp}$
5	11.23	11.29	$28a_1$	σ
6	11.36	11.36	$3a_2$	$n_{O(\pi)}$
7	12.00	11.91	$16b_2$	n_O
8	12.44	12.44	$27a_1$	σ
9	13.34	13.43	$15b_2$	σ
10	13.56	13.58	$7b_1$	π_1
11	15.51	15.56	$14b_2$	σ
12	16.01	15.95	$26a_1$	σ

[a] OVGF calculations at the 6-311++G** basis set level. [b] Symbols $n_{\parallel}$ and $n_{\perp}$ indicate an orbital predominantly due to the iodine 5p orbitals distributed parallel and perpendicular, respectively, to the benzene ring.

can be seen, the UPS spectra commonly show 10 lower-energy bands in the region from 7 to 14 eV, with the strongest band being the one that is second lowest energy.

The experimental vertical ionization potentials of iodonitrobenzenes were obtained from the observed UPS data. To assign the UPS bands, the vertical ionization energies were calculated using the OVGF method, based on the geometry optimized at the DFT level of theory. Tables 1−3 list the experimental and theoretical vertical ionization potentials and molecular orbital (MO) characters for *o*-, *m*-, and *p*-iodonitrobenzene. In these tables, the theoretical ionization potentials are in good agreement with the experimental ionization potentials.

As determined from the calculated geometries, the *m*- and *p*-iodonitrobenzene have a planar structure, but for *o*-iodoni-

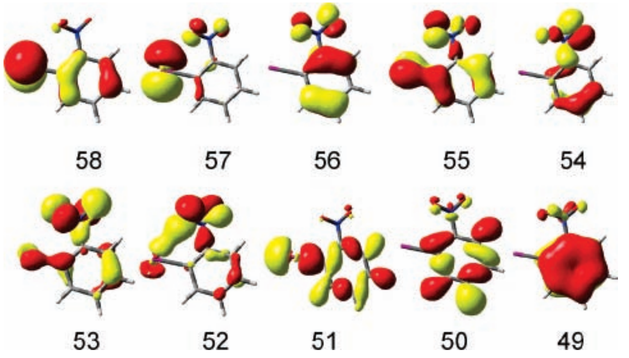

Figure 4. Characters of the occupied molecular orbitals for *o*-iodonitrobenzene.

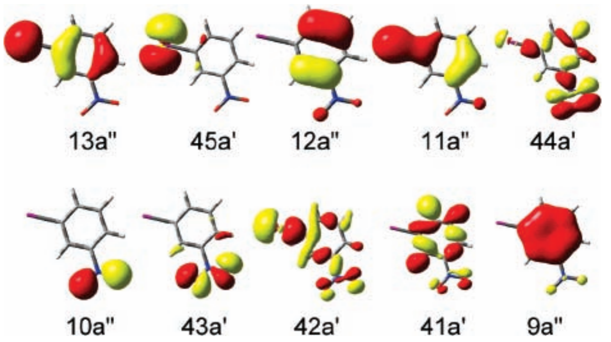

Figure 5. Characters of the occupied molecular orbitals for *m*-iodonitrobenzene.

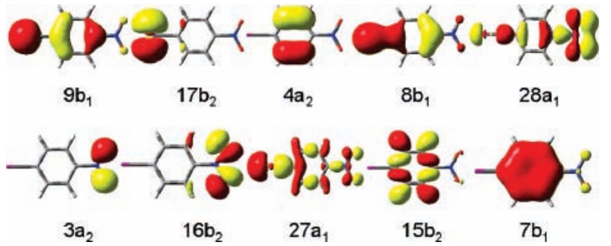

Figure 6. Characters of the occupied molecular orbitals for *p*-iodonitrobenzene.

trobenzene, the NO_2 group is twisted by about 40° from the benzene ring plane because of steric hindrance. This twisting commonly takes place in ortho-disubstituted benzene (e.g., NO_2, NMe_2, OMe, CHO, COMe, and CO_2Me).[16]

Discussion

Assignments of UPS Bands. By combining empirical arguments (relative band intensities, band profiles, comparisons with the assigned spectra of corresponding compounds) and theoretical methods (OVGF calculations), we developed reliable assignments of the bands in the UPS spectra. Figures 4−6 show the shapes of the occupied molecular orbitals of *o*-, *m*-, and *p*-iodonitrobenzene listed in Tables 1−3.

Certain common features can be traced throughout the photoelectron spectra of benzene derivatives. In its UPS spectrum, benzene itself has a lowest-energy band centered at 9.25 eV corresponding to the removal of an electron from the $1e_{1g}(\pi)$ orbital.[17] Then, there is a gap of about 1 eV, followed by a second band having its midpoint at 11.53 eV. In substituted benzenes, the first band, i.e., the one at 9.25 eV in benzene, is still apparent, but frequently, it is broadened (as in C_6H_5F[18] and $C_6H_5CH_3$[19]) or split into two components (as in C_6H_5I,[20] $C_6H_5NH_2$,[21] and C_6H_5OH[17]). The gap of 1 eV between the first two bands in the spectrum of benzene is frequently occupied by one or more sharper peaks in the spectra of substituted benzenes (as in C_6H_5I[20] and $C_6H_5NH_2$,[21] for example). These peaks are derived from the ionization of electrons largely localized on lone-pair-type orbitals. Before we discuss the peaks appearing in the spectra of iodonitrobenzenes in terms of substituent effects, we must first assign the spectra reliably.

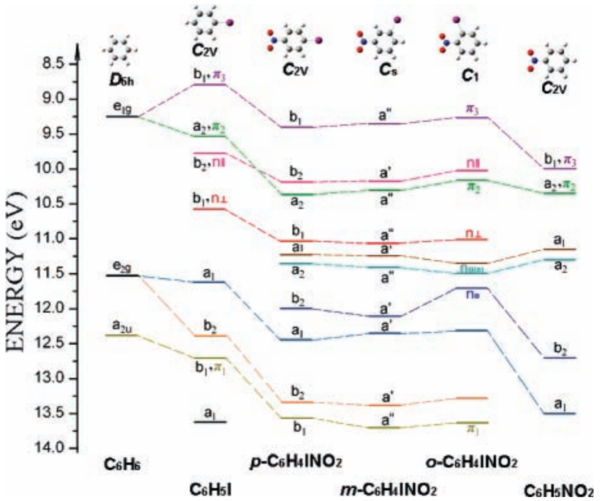

Figure 7. Correlation diagram of the experimentally determined vertical ionization potentials for benzene, iodobenzene, nitrobenzene and iodonitrobenzenes.

o-Iodonitrobenzene. The assignment of the spectrum of *o*-iodonitrobenzene is given in Table 1. We compared it with the spectra of C_6H_5I[20] and $C_6H_5NO_2$[22] to support the reported assignments. The correlation diagram for the orbital energies of these compounds is shown in Figure 7.

The combined use of empirical and theoretical methods suggests that low-energy bands 1−4 correspond to the ionizations of the π_3 (like a″), $n_{\|}$ (like a′), π_2 (like a″), and $n_{\perp}$ (like a″) orbitals, which are caused by the interaction among the highest occupied doubly degenerate π orbitals, e_{1g}(S) and e_{1g}(A), of the benzene ring and the iodine lone-pair (n) orbitals. As is clearly seen in Figure 4, the first and fourth HOMOs are antibonding and bonding combinations between π_3 and $n_{\perp}$ and are delocalized over both the benzene ring and the iodine atom, whereas the second and third highest occupied nonbonding $n_{\|}$ and π_2 orbitals remain localized on the iodine atom and benzene ring, respectively. In the spectra of monohalogenbenzenes, there are two bands due to halogen lone pairs. The reason is that the in-plane ($n_{\|}$) and out-of-plane ($n_{\perp}$) halogen orbitals interact to different extents with the benzene σ- and π-electron systems. Furthermore, a narrow and sharp PE band suggests ionization of an electron from an essentially nonbonding molecular orbital, and hence, there is little change in geometry upon ionization. From the band positions and profiles, we can assign the second and fourth bands to the $n_{\|}$ and $n_{\perp}$ orbitals, respectively.

After the assignment of the π_3/π_2 and $n_{\|}/n_{\perp}$ bands, we can easily relate band 5 to the σ orbital localized along the C−NO_2 bond and bands 6 and 7 to the oxygen lone pairs of the −NO_2 group from the comparison of the orbital energies of nitrobenzene and calculated IPs. Orbital 53 or 52, corresponding to band 6 or 7, is analogous to the out-of-plane $n_{O(\pi)}$ orbital or in-plane n_O orbital of nitrobenzene. This is clearer for the 10a″ or 43a′ orbital of *m*-iodonitrobenzene and the $3a_2$ or $16b_2$ orbital of *p*-iodonitrobenzene in Figures 5 and 6. For the meta and para isomers, these orbitals are more localized on the nitro group than for the ortho isomer.

An interesting feature of the character of orbital 52 is that it reveals an interaction between the in-plane lone pairs of iodine

TABLE 4: Selected Energy Level Separations[a] (eV) in Benzene, Nitrobenzene, Iodobenzene, and Iodonitrobenzenes

	$\langle\pi\rangle$	$\Delta\pi$	$\langle n_I\rangle$	Δn_I	$\langle n_O\rangle$	Δn_O
benzene	9.25	0				
nitrobenzene	10.17	0.36			12.00	1.40
iodobenzene	9.16	0.74	10.18	0.81		
o-iodonitrobenzene	9.71	0.90	10.52	0.98	11.65	0.32
m-iodonitrobenzene	9.83	0.96	10.62	0.88	11.71	0.60
p-iodonitrobenzene	9.88	0.96	10.61	0.84	11.68	0.64

[a] $\langle\pi\rangle = (\pi_3 + \pi_2)/2$, $\Delta\pi = \pi_3 - \pi_2$, $\langle n_I\rangle = (n_{||} + n_\perp)/2$, $\Delta n_I = n_{||} - n_\perp$, $\langle n_O\rangle = [n_{O(\pi)} + n_O]/2$, $\Delta n_O = n_{O(\pi)} - n_O$.

and one of the oxygen atoms of the nitro group with the involvement of a bonding I−O σ orbital. *o*-Iodonitrobenzene has C_1 symmetry, and all MOs can mix. A single-crystal X-ray investigation of certain derivatives of *o*-iodonitrobenzene indicates the existence of an intramolecular I−O bond.[23] This finding supports the hypothesis that the enhanced reactivity of *o*-nitrohaloarenes in Ullmann coupling reactions could be a result of formation of a strong hypervalent donor−acceptor bond between oxygen and halogen atoms in a transition state or an intermediate.

In the spectrum of *o*-iodonitrobenzene, bands 8 and 9 are the results of removal of electrons from the highest doubly degenerate σ orbitals (51 and 50) of the benzene ring, whereas band 10 is attributed to the lower π_1 orbital of the benzene ring. They are correlated to the $3e_{2g}$ and $1a_{2u}$ orbitals of benzene. The sharp and narrow shape of band 8 is clear in comparison to that of band 9, because orbital 51 involves the sp-hybridized character of the iodine atom extending far outside the surface of the benzene ring along the C−I bond.

The broad and featureless bands above 14.0 eV arise because of the removal of some of the remaining σ electrons. Little useful information can be obtained from them. Consequently, we will not discuss the spectral region above 14.0 eV.

m- and p-Iodonitrobenzene. The assignments of the spectra of *m*- and *p*-iodonitrobenzene were carried out as in the case of *o*-iodonitrobenzene and are indicated in Figure 7. Changes of relative substituent positions on the ring produce shifts of ionization potentials but no change in their relative order. As before, bands 1−4 are assigned to the π_3, $n_{||}$, π_2, and $n_\perp$ orbitals. Both the π_3 and $n_\perp$ orbitals can be identified as the combination of a π orbital of the benzene ring and an out-of-plane iodine lone pair. The π_3 orbital is mainly localized on the benzene ring, whereas the $n_\perp$ orbital is localized on the iodine lone pair.

Substituent Effects and Relative Reactivity. In this work, we are interested in electronic substituent effects, especially in regard to the relative reactivity of iodonitrobenzenes as monitored by measured ionization potentials pertaining to well-resolved π and n bands. Table 4 lists the following descriptors of SEs from pertinent ionization potentials: $\langle\pi\rangle = (\pi_3 + \pi_2)/2$, $\Delta\pi = \pi_3 - \pi_2$, $\langle n_I\rangle = (n_{||} + n_\perp)/2$, $\Delta n_I = n_{||} - n_\perp$, $\langle n_O\rangle = [n_{O(\pi)} + n_O]/2$, and $\Delta n_O = n_{O(\pi)} - n_O$.

Harada et al.[20] studied the relative reactivity of the π and n orbitals of monohalogenbenzenes upon electrophilic attack by metastable helium atoms on the basis of the relative intensities of the π and n bands in the Penning ionization electron spectra. They found that the relative reactivities of the π and n orbitals of monohalogenbenzenes depend on the electronic factor due to the size of the halogen p orbitals and the conjugation between the benzene ring and the halogen atoms, as well as on the steric factor due to the benzene ring shielding some orbitals from the impact of metastable atoms. In the following discussion, we attempt to analyze the changes in the π and n orbitals resulting from electronic and steric factors. This is essential for the identification of the assignments of the observed UPS bands.

Substituent Effects. Electronic SEs arise from the complex interplay of inductive (I) and resonance (R) effects. With the I and R effects, the nitro group is considered to be a strong electron-withdrawing substituent. As a result, the ionization potentials of corresponding orbitals in iodonitrobenzenes all increase relative to those in iodobenzene. This makes the $\langle\pi\rangle$ and $\langle n_I\rangle$ values in *o*-, *m*-, and *p*-iodonitrobenzene larger than those in iodobenzene. However, the energy separation (Δn_I) of the $n_{||}$ and $n_\perp$ orbitals does not greatly change. This is in agreement with the conclusions of Baker et al.[24] that substituents removing charge from the benzene ring by either the I or R effect do not alter the energy separation of the halogen peaks.

On the other hand, from the perspective of substituent effects, the halogen can be classified as both a π donor and a σ acceptor.[25] However, iodine is a stronger π donor than σ acceptor. Consequently, the $\langle\pi\rangle$ and $\langle n_O\rangle$ values in iodonitrobenzenes become smaller than those in nitrobenzene. The highest occupied π_3 orbital also shifts from nitrobenzene to lower ionization energy as a result of the electron-donating effect of iodine.

It can be noticed that the energy order of the first four highest occupied molecular orbitals (HOMOs) for monohalogenbenzenes is $\pi_3 > \pi_2 > n_{||} > n_\perp$.[20] However, the order of the π_2 and $n_{||}$ orbitals is reversed in the case of iodonitrobenzenes. This is supported by the fact that the observed second band in the UPS spectra of *o*-, *m*-, and *p*-iodonitrobenzene is always sharp and intense. The reversal is due to the fact that the π_2 orbital of iodonitrobenzenes, which does not interact with the iodine lone pair, is greatly stabilized by the electron-withdrawing effect of nitro group. This characteristic is the result of the combined influence of both the electron-donor and electron-acceptor substituents.

A study on some 1,4-disubstituted benzene derivatives found that the introduction of two substituents, A and B, causes the separation of the π_3 and π_2 orbitals to be equal, within experimental error, to the sum of the separations in the monosubstituted compounds, C_6H_5A and C_6H_5B.[24] A similar result was found in our work. The $\Delta\pi$ values in iodonitrobenzenes (0.90−0.96 eV) are approximately equal to the sum of the $\Delta\pi$ values in nitrobenzene and iodobenzene (1.10 eV).

Relative Reactivity. Substituents in the 2 position of iodobenze have a remarkable activating effect in a number of reactions, such as Ullmann coupling.[9] Han et al.[26] studied the photodissociation dynamics of halotoluenes and found that the ortho isomer has a special photodissociation channel. This correlates with the electronic effects of the substituents on aromatic hydrocarbons.

NBO analysis provides some information on the nature and magnitude of the behavior of iodonitrobenzenes substituted in the 1 and 2 positions. The results obtained from NBO analysis are summarized in Table 5. For *o*-iodonitrobenzes, the net charge transfer to the NO_2 group is decreased, whereas the orbital occupancy values of π_{C-C} are increased. This clearly indicates that the electron-withdrawing effect of the nitro group is reduced in *o*-iodonitrobenzene. The second-order perturbation analysis further substantiates the information. The stabilization energy of $\pi_{C-C} \rightarrow \pi^*_{N-O}$ in *o*-iodonitrobenzene is the smallest.

On the basis of the relative changes in the π and n orbitals of *o*-, *m*-, and *p*-iodonitrobenzes, one can also analyze the contributions of the effects of substituent in different positions. The observed photoelectron spectra clearly indicate the changes in the orbital levels. From Table 4, one can see that the $\langle\pi\rangle$ and

TABLE 5: Natural Bond Orbital Analysis for *o, m, p*-Iodonitrobenzene with the B3LYP Method at the 6-311++G Basis Set Level**

	charge (NO_2) (au)	occupancy (au)		$E^{(2)}$ (kcal/mol)	
o-iodonitrobenzene	−0.1060	$\pi_{C(2)-C(3)}$	1.6544	$\pi_{C(2)-C(3)} \rightarrow \pi^*_{N(12)-O(13)}$	19.57
m-iodonitrobenzene	−0.1526	$\pi_{C(2)-C(3)}$	1.6469	$\pi_{C(2)-C(3)} \rightarrow \pi^*_{N(12)-O(13)}$	23.34
p-iodonitrobenzene	−0.1669	$\pi_{C(3)-C(4)}$	1.6423	$\pi_{C(3)-C(4)} \rightarrow \pi^*_{N(12)-O(13)}$	27.34

$\langle n_I \rangle$ values in *o*-iodonitrobenzene are smaller than those in the meta- and para-substituted isomers. This can be interpreted in terms of the decreasing conjugation between the benzene e_{1g}-(S)-like π orbital and the nitro group π orbital as a result of the twisting of the nitro group from the plane of the benzene ring by the steric hindrance of the iodine atom. Compared to the *m*- and *p*-iodonitrobenzene, the decreasing conjugation reduces the electron-withdrawing effect of the nitro group in *o*-iodonitrobenzene and increases the electron density of the benzene ring π orbital. Therefore, the ionization energies of π_3, π_2, and $n_\perp$ involving the benzene ring π orbital become lower, which makes the $\langle \pi \rangle$ and $\langle n_I \rangle$ values in *o*-iodonitrobenzene smaller. The quite small splitting between the first two vertical ionization potentials of *o*-nitrotoluene is also explained by decreased conjugation due to twisting of the nitro group.[27] When the decreased conjugation increases the electron density of the benzene ring π orbital, it also decreases that of the nitro group $n_{O(\pi)}$ orbital in *o*-iodonitrobenzene compared to those in *m*- and *p*-iodonitrobenzene, making its ionization energy increase. However, the $\langle n_O \rangle$ value ($[n_{O(\pi)} + n_O]/2$) in *o*-iodonitrobenzene does not increase obviously. This indicates that the electron density of the n_O orbital changes in the opposite direction from $n_{O(\pi)}$, causing the ionization energy of the n_O orbital to decrease. This can be rationalized by an additional through-space interaction between in-plane lone pairs of iodine and oxygen in the neighboring 1 and 2 positions, which pushes the n_O orbital up greatly in *o*-iodonitrobenzene. It is also the reason why the Δn_O value ($n_{O(\pi)} - n_O$) in *o*-iodonitrobenzene decreases remarkably (Table 4). Studies of some iodobenzene molecules have revealed the existence of intramolecular through-space interactions between vicinal iodine atoms.[28]

In short, the electron-withdrawing nature of the nitro group, the electron-donating nature of the iodine atom, the inhibition of conjugation caused by steric factors, and the additional through-space interaction between in-plane lone pairs of the iodine and oxygen atoms produce readily demonstrable effects in the photoelectron spectra of iodonitrobenzenes and might contribute to the high reactivity of *o*-iodonitrobenzene.

Conclusion

HeI ultraviolet photoelectron spectra were used to study the electronic structures of iodonitrobenzenes. On the basis of empirical arguments (relative band intensities, band profiles, and comparisons with the assigned spectra of corresponding compounds) and theoretical methods (OVGF calculations), the observed bands in the UPS spectra were assigned. The substituent effects of iodonitrobenzenes are discussed in terms of the careful analysis of ionization potentials corresponding to π and n orbitals. This is essential for the reliable assignment of the observed photoelectron spectra. Owing to the effects of the electron-withdrawing nature of the nitro group and the electron-donating nature of the iodine atom, the first ionization potentials of iodonitrobenzenes are greater than that of iodobenzene but smaller than that of nitrobenzene, and the energy order of the first four HOMOs is $\pi_3 > n_\parallel > \pi_2 > n_\perp$. Sterically induced twisting of the nitro group from the benzene ring plane decreases the conjugation between the benzene π orbital and the nitro group π orbital and causes a distinct change in $\langle \pi \rangle$ and $\langle n_I \rangle$ in *o*-iodonitrobenzene. The interaction of in-plane lone pairs on adjacent iodine and oxygen atoms leads to a marked decrease of Δn_O in *o*-iodonitrobenzene. These characteristics, depending on the electronic effects of the substituents, might contribute to the high reactivity of *o*-iodonitrobenzene in a number of reactions.

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