Electronic Structure and Substituent Effect of *o*-, *m*- and *p*-C$_6$H$_4$INCS

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Abstract: Aromatic isothiocyanates are interesting pseudohalides molecules which are widely existed in healthy intact plants. However, few attempts were made to analyze their structures and correlate their electronic structure with other properties (e.g., chemical reactivity). In this paper, the electronic structures and substituent effects of *o*-, *m*-, and *p*-iodophenyl isothiocyanates were studied by the ultraviolet photoelectron spectroscopy and discussed through the careful analysis of ionization potentials corresponding to π and n orbitals. Owing to the effects of the iodine atom and the NCS group, the first ionization potentials of iodophenyl isothiocyanates are lower than that of iodobenzene and phenyl isothiocyanate. And the energetic order of the first six MOs is $\pi_3 > \pi_2 > n_S > n_\parallel > \pi_{NCS} > n\perp$. The energy and electron density of the topmost occupied molecular orbitals of iodophenyl isothiocyanates were analyzed. It has been found that the ionization energy of π_{NCS} orbital electrons in *p*-iodophenyl isothiocyanate is the lowest of the three iodophenyl isothiocyanates, which indicates the chemical reactivity of *p*-iodophenyl isothiocyanate is the highest.

INTRODUCTION

In the past century, many sulphur compounds of plant origin attracted attention by their pungency or irritant properties and by their ability to prevent the spoilage of food and fermentation of fruit juices. Two of these substances were revealed to be alkyl isothiocyanate and benzyl isothiocyanate. These discoveries mark the beginning of the chemistry of isothiocyanates. Isothiocyanates are present in an undetectable amount in healthy intact plants. They are present as progenitors and form together with a molecule of glucose and sulphate heteroglycosides called glucosinolates. Isothiocyanates, along with the by-products glucose and sulphate ion are released from glucosinolates after damage to plants by the action of the enzyme myrosinase [1]. And there are lots of investigations on isothiocyanate compounds. Furthermore, isothiocyanates are pseudohalides molecules. Aromatic isothiocyanates are interesting pseudohalides molecules for two reasons. First, they are important precursors in the synthesis of polymer material. The synthetic procedure gives high yields and exhibits no side reactions. Second, aromatic and alkyl isothiocyanates are examples of distorted linear triatomic systems [2]. The distortions from linearity of the NCS moiety have been investigated in some detail [3].

The reactivity of substituted benzene derivatives has been extensively studied and has led to the notion of the substituent effect (SE) [4]. The overall SE can be conceptually partitioned into electronic, steric, and solvent contributions. A molecular descriptor which is closely related to the electronic substituent effect is the ionization energy. This energy can be accurately measured by ultraviolet photoelectron spectroscopy (UPS) [5-10], which is a useful tool to investigate the effect of substituent groups upon the electronic structure of parent hydrocarbons [11-15]. The study of electronic structure and substituent effect can also be performed by theoretical methods. DiLabio *et al*. [16] 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 structure and substituent effect of substituted benzenes or halogen compounds [17-22]. However, the molecular orbital structures of iodophenyl isothiocyanates, which have wide application in organic chemistry [23-26] and medicinal chemistry [27], are not well understood. For isothiocyanates compounds, the electronic structure is relevant for understanding their chemical behavior, so the compounds were investigated previously by UPS and molecular orbital (MO) calculations [28]. Some aromatic isothiocyanates have been included in the UPS/semiempirical MO study [29] and the vertical ionization potentials of phenyl isothiocyanate were measured by using photoelectron spectroscopy [30], but few attempts were made to correlate their electronic structure with other properties (e.g., chemical reactivity). Here we report the analysis of such relationships, including the discussion of intermolecular interactions between the aromatic ring and the NCS group.

The purpose of this work was to study the electronic structure of *o*-, *m*-, and *p*-iodophenyl isothiocyanate by means of UPS and to improve the understanding of substituent effects for benzene derivatives. The ionizations of electrons on π and n orbitals are sensitive internal probes for electronic effects of substituents. We attempt to investigate the correlation between the substituent effects and relative reactivity.

EXPERIMENTAL AND THEORETICAL METHODS

Samples of *o*-, *m*-, and *p*-iodophenyl isothiocyanates were purchased from the Alfa Aesar Company and identified

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by measuring mass spectra. The photoelectron spectra were recorded on the double-chamber UPS-II machine [31-33] which 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 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. Mass analysis of ions is achieved with the time-of-flight mass analyzer mounted directly to the photoionization point. The relatively soft ionization is provided by single-wavelength HeI radiation.

Electronic structure calculations were carried out by using the Gaussian series of programs [34]. The geometries of the iodophenyl isothiocyanates molecules were optimized with ab initio and DFT methods. For iodine a relativistic basis set was used, which has been proved to be reliable in the literature [35-39]. To assign the photoelectron spectra of iodophenyl isothiocyanate molecules, we applied the outer-valence Green's function (OVGF) calculations, which includes sophisticated correlation effects of the self-energy, to the molecules to give accurate results of the vertical ionization energies [40, 41]. Three-dimensional MO plots were obtained with the GaussView program. Each orbital displayed with the 0.05 isodensity value was oriented in a way that allowed for the best view.

RESULTS AND DISCUSSION

Structures and Conformations

As previously reported, both aromatic isothiocyanates and isocyanates are aromatic pseudohalides. They have the similar structures which have close relationship to their properties. Therefore, the structure of NCS group of title molecules will be compared with that of NCO group. The structures of isothiocyanate (NCS) and isocyanate (NCO) and the spatial arrangement of the NCS and NCO groups attached with the phenyl ring or any other group offer an interesting subject of many investigations. It has been established from numerous investigations that the isothiocyanate (NCS) and isocyanate (NCO) groups are primarily linear except in HNCS [42], where the NCS group was found to be bent [43]. However, these groups are not always collinear with the bond through which they are attached to another group. In the organic isothiocyanates (RNCS) and isocyanates (RNCO), the NCS and NCO groups have been found to be inclined at an angle with respect to the R-N bond and the angle of inclination varies from one group to the other. Due to an internal rotation, this inclined structure could give rise to different conformers in a molecule. If the NCS/NCO group is attached to a simple phenyl ring, the existence of the two conformers could not be distinguished because of the symmetry of the ring. In many papers, *o*-fluorophenyl isothiocyanate in the gas phase has two planar conformers viz., *cis* and *trans* [43-46]. The microwave transitions of the *trans* conformer of *o*-fluorophenyl isothiocyanate were found to be much weaker than that of the *cis* conformer [47]. So in the present investigation, we will discuss the conformations of

o-, *m*- and *p*-iodophenyl isothiocyanate which had never been studied.
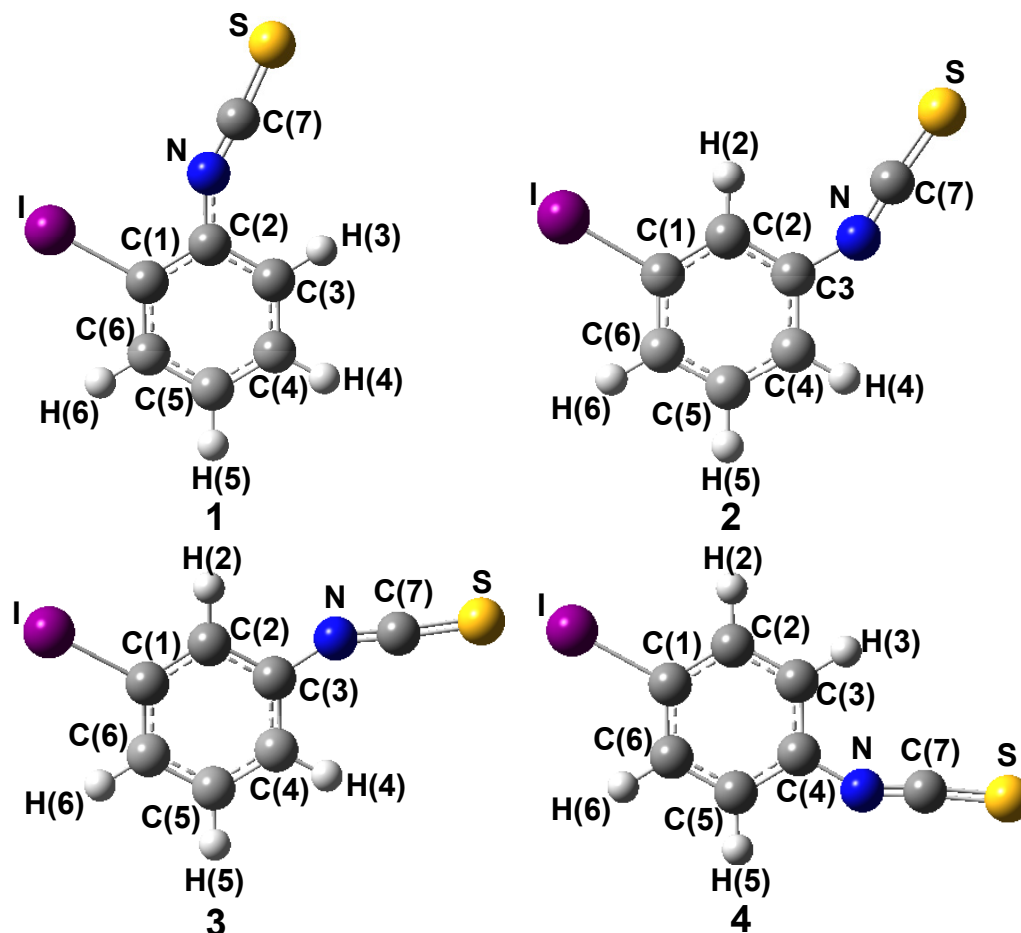
o-Iodophenyl isothiocyanate prefers the *trans* conformation as the most stable form (Fig. **1**), which is different from *o*-fluorophenyl isothiocyanate. In order to search for other possible conformers with different values of $\delta_{C3C2NC7}$, a relax scan of the potential energy surface for *o*-iodophenyl isothiocyanate is performed by rotating the torsional dihedral angle $\delta_{C3C2NC7}$ in steps of 10° using B3LYP/6-31G* and MP2/6-31G* approximation. The resulting potential curves for dihedral angles from 0° to 360° are shown in Fig. (**2**).

As seen from Fig. (**2**), at both levels, there are 2 minima of the calculated potential curves, which implies that with $\delta_{C3C2NC7}$ around 0°-360°, a *trans* structure with $\delta_{C3C2NC7} = 0°$ exists as a stable conformer, while the *cis* structure with $\delta_{C3C2NC7} = 180°$ seems more destabilization than *trans* conformer. According to the results of B3LYP/6-31G* level, the energy of the *cis* conformer is higher (1.15 kcal/mol) than the *trans* conformer. And when the level of MP2/6-31G* is used, the energy of the *cis* conformer is 0.56 kcal/mol higher than that of the *trans* conformer. Therefore, our discussion of the geometry and electronic structure mainly focus on the *trans* conformer of the *o*-iodophenyl isothiocyanate.

According to the theoretical calculations [48], the strong interaction between the positive charge of the C atom of the NCO group and the negative charge of the F atom at the *ortho* position is responsible for the predominant existence of the *cis* form in *o*-fluorophenylisocyanate [47]. However, in the case of *o*-fluorophenyl isothiocyanate, the present of the S atom, which is less electronegative than the O atom of *o*-fluorophenylisocyanate, reduces the net positive charge on the C atom in the NCS group. This, in turn, reduces the strength of interaction between the F atom and the NCS group at the *ortho* position. As a result, the probability of coexistence of both *cis* and *trans* forms increases in this case while the *cis* form is more than the *trans* form in gas phase [43]. For *o*-iodophenyl isothiocyanate, the size of I atom is larger than F atom and the negative charge of I atom is weaker than that of F atom. And the net positive charge of the N atom is large which can be obtained from the analysis of atomic charges (Table **1**). The interaction between the positive charge of the N atom of the NCS group and the weak negative charge of the I atom at the *ortho* position is instead of the interaction between the C atom of NCS group and I atom. And these are responsible for the predominant existence of the *trans* form in *o*-iodophenylisocyanate which is consistent with the results from the calculation (Fig. **2**).

m-Iodophenyl isothiocyanate can, in principle, exist in two different conformeric forms, *cis* and *trans* (Fig. **1**). In order to search for other possible conformers with different values of $\delta_{C2C3NC7}$, we use the same methods as that of *o*-iodophenyl isothiocyanate. The resulting potential curves for dihedral angles from 0° to 360° are shown in Fig. (**3**).

As seen from Fig. (**3**), at both levels, there are 2 minima of the calculated potential curves, which implies that with $\delta_{C2C3NC7}$ around 0°-360°, a *cis* structure with $\delta_{C2C3NC7} = 0°$ and a *trans* structure with $\delta_{C2C3NC7} = 180°$ exist as stable conformers. According to the results of B3LYP/6-31G* level,

Fig. (1). Schematic representation of stable conformers of *o*-, *m*-, and *p*-iodophenyl isothiocyanate (**1** for *o*-iodophenyl isothiocyanate, **2** for *cis m*-iodophenyl isothiocyanate, **3** for *trans m*-iodophenyl isothiocyanate, **4** for *p*-iodophenyl isothiocyanate).

the energy of the *trans* conformer is slight higher (0.039 kcal/mol) than the *cis* conformer. And when the level of MP2/6-31G* is used, energy of the *trans* conformer is 0.068 kcal/mol higher than the *cis* conformer. The energy differences are very small. So both the *cis* and *trans* conformers of *m*-iodophenyl isothiocyanate may exist in the gas phase.
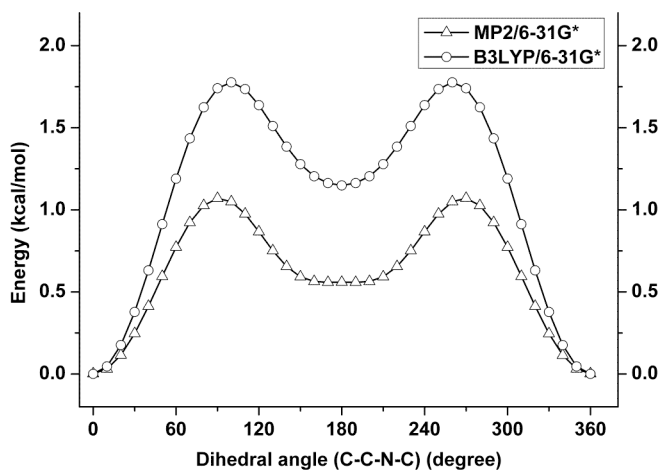
Fig. (2). Conformational energy profile for *o*-iodophenyl isothiocyanate obtained using the relax scan of potential energy surface (rotating the C3C2NC7 dihedral angle in steps of 10°) at the B3LYP/6-31G* and MP2/6-31G* levels.

Table 1.   Atomic Charges (e) for the *o*-, *m*- and *p*-IC$_6$H$_4$NCS, Calculated with the B3LYP/6-311++G Approximation**

Atoms[a]	*o*-IC$_6$H$_4$NCS	*m*-IC$_6$H$_4$NCS	*p*-IC$_6$H$_4$NCS
C1	0.971	-0.584	0.038
C2	-1.240	0.897	-0.373
C3	0.269	-0.912	0.415
C4	-0.469	0.238	-0.782
C5	-0.245	-0.561	0.067
C6	0.028	0.092	-0.169
C7	0.196	0.213	0.196
I	-0.07	-0.123	-0.131
N	0.379	0.264	0.258
S	-0.400	-0.392	-0.394
TAC[b]	0	0	0

[a]For atom numbering, see Fig. (**1**).
[b]Total atomic charge.

For *m*-iodophenyl isothiocyanate, the distance between I atom and NCS group is longer than that of *o*-iodophenyl isothiocyanate. As a result, the interaction between the posi-

tive charge of C atom and N atom and the negative charge of I atom at the *meta* position is much lower than that of *o*-iodophenyl isothiocyanate. It is interesting that the positive charge of C atom of NCS group in *m*-iodophenyl isothiocyanate is stronger than that of *o*-iodophenyl isothiocyanate. It indicates that there exists the interaction between the C atom of NCS group and I atom in *m*-iodophenyl isothiocyanate, so the *cis* structure may be slightly more stable than *trans* conformer. From the analysis, the *m*-iodophenyl isothiocyanate may have two different conformers, *cis* and *trans*, in accordance with the results from the calculation. In this paper, the more stable *cis* conformer is used for discussion.
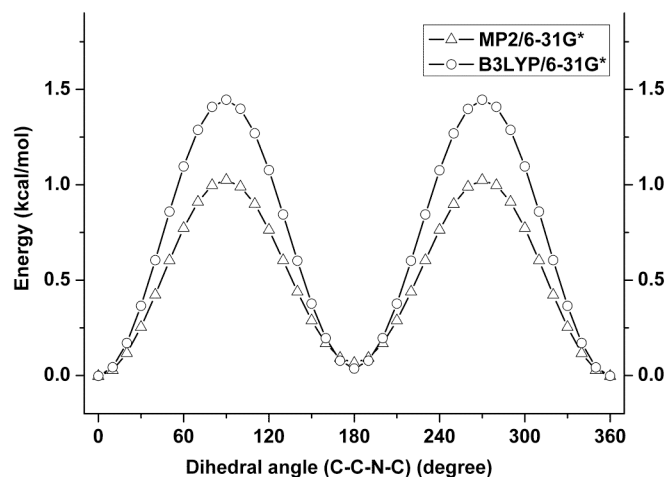
Fig. (3). Conformational energy profile for *m*-iodophenyl isothiocyanate obtained using the relax scan of potential energy surface (rotating the C2C3NC7 dihedral angle in steps of 10°) at the B3LYP/6-31G* and MP2/6-31G* levels.

Due to the symmetry of *p*-iodophenyl isothiocyanate, it has only one conformer which has not been discussed any more.

The structures of *o*-, m- and *p*-iodophenyl isothiocyanates are shown in Table **2**. Table **2** shows that the lengths

of ring–N, N=C and C=S are similar to that of phenyl isothiocyanate and *o*-fluorophenyl isothiocyanate, while the $\alpha_{ring-N=C}$ of iodophenyl isothiocyanates is smaller than that of phenyl isothiocyanate and *o*-fluorophenyl isothiocyanate. This indicates that the substitute effect of iodine slightly affected NCS group.

Photoionization Mass Spectroscopy

The photoionization mass spectroscopy (PIMS) of the three iodophenyl isothiocyanates are shown in Figs. (**4-6**). The PIMS of the *o*-iodophenyl isothiocyanate shows typical fragmentations distribution of *o*-iodophenyl isothiocyanate cation [49]. Normally, HeI photoionization produces a fragmentation distribution that is very similar to the distribution observed using electron-impact ionization. This may be rationalized by a similar energy deposition mechanism for the two methods, because the interaction energies (approximately tens of electronvolts) are comparable. As for the strong peak in the HeI PIMS of *o*-iodophenyl isothiocyanate, the fragment C_6H_4-NCS$^+$ mostly results from the direct dissociation of the I-C bond in the *o*-iodophenyl isothiocyanate parent ions.

The PIMS of *m*-iodophenyl isothiocyanate, which reveals features for $C_6H_4N^+$, C_6H_4-NCS$^+$ and parent ion, respectively. And so does the *p*-iodophenyl isothiocyanate.

In a word, by analyzing the results of PIMS, the fragments $C_6H_4N^+$ and C_6H_4-NCS$^+$ and parent ion found in the mass spectra indicate that after ionization, the iodophenyl isothiocyanates prefer the dissociation of C-I and N=C bonds.

Ultraviolet Photoelectron Spectroscopy

The band profile from UPS provides an insight into the nature of the orbital from which ionization takes place; sharp, narrow band often corresponds to the ionization from strongly localized, non-bonding orbital as suggested by the

Table 2. Selected Bond Distances (Å) and Angles (Degree) of *o*-, *m*- and *p*-Iodophenyl Isothiocyanates Calculated at B3LYP/6-311++G** and MP2/6-311++G** and the Related Molecules

Parameters	*o*-IC₆H₄NCS		*m*-IC₆H₄NCS		*p*-IC₆H₄NCS		C₆H₅NCS[d]	*o*-FC₆H₄NCS[e]
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP		
r_{ring-N}	1.385	1.378	1.392	1.384	1.391	1.383	1.370(5)	1.370
r_{CI}	2.088	2.112	2.097	2.120	2.094	2.118		1.353
$r_{N=C}$	1.216	1.194	1.217	1.194	1.217	1.194	1.21	1.210
$r_{C=S}$	1.569	1.580	1.568	1.581	1.569	1.581	1.55	1.550
α_{CCN}[a]	120.7	120.3	120.0	120.3	120.7	120.9		
$\alpha_{N=C=S}$	174.5	175.9	174.5	175.9	174.6	176.0		
$\alpha_{ring-N=C}$	141.5	150.8	139.9	150.7	140.6	151.4	148.0(5)	146.8
α_{CCI}[b]	119.8	120.2	119.1	119.2	119.6	119.8		
δ_{CCNC}[c]	0	0	0	0	0	0		

[a]For *o*-IC₆H₄NCS, α_{CCN} is the angle of C3C2N, C2C3N for *cis m*-IC₆H₄NCS, and C3C4N for *p*-IC₆H₄NCS.
[b]For *o*-IC₆H₄NCS, α_{CCI} is the angle of C2C1I, C2C1I for *cis m*-IC₆H₄NCS, and C2C1I for *p*-IC₆H₄NCS.
[c]For *o*-IC₆H₄NCS, α_{CCNC} is the angle of C3C2NC7, C2C3NC7 for *cis m*-IC₆H₄NCS, and C3C4NC7 for *p*-IC₆H₄NCS.
[d]Onda JMS, 1976 [46].
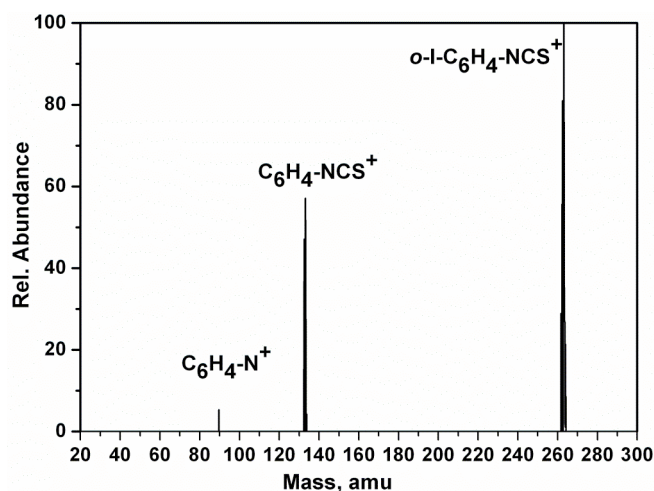[e]Jaman SA, 1985 [44].

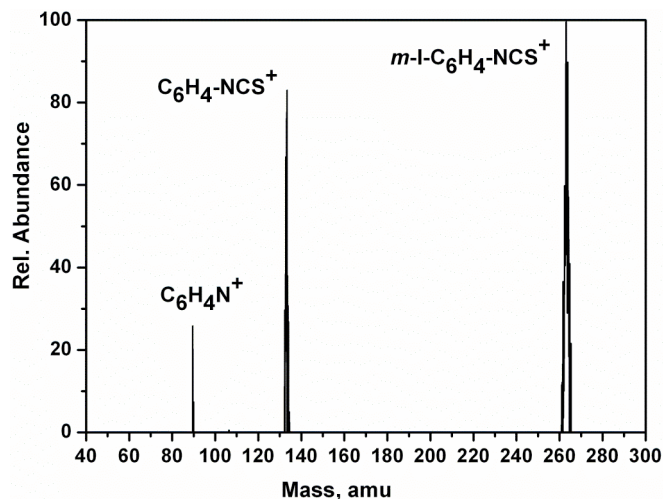**Fig. (4).** Photoionization mass spectra of *o*-iodophenyl isothiocyanate.

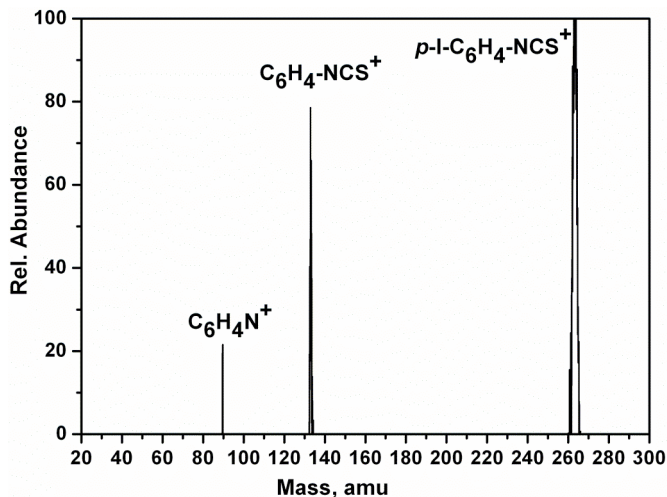**Fig. (5).** Photoionization mass spectra of *m*-iodophenyl isothiocyanate.

Fig. (6). Photoionization mass spectra of *p*-iodophenyl isothiocyanate.

Franck-Condon principle. However, not all halogen lone pair bands display intensity changes of the same magnitude. This is due to different amounts of halogen character in such orbitals and to different atomic photoionization cross-sections for different halogens [50]. Also, halogen lone pair bands sometimes overlap with other electrons on π orbital ionizations which may mask the expected intensity changes. The correlation with reliably assigned spectra of corresponding mono and dihalobenzenes thus becomes necessary [51].

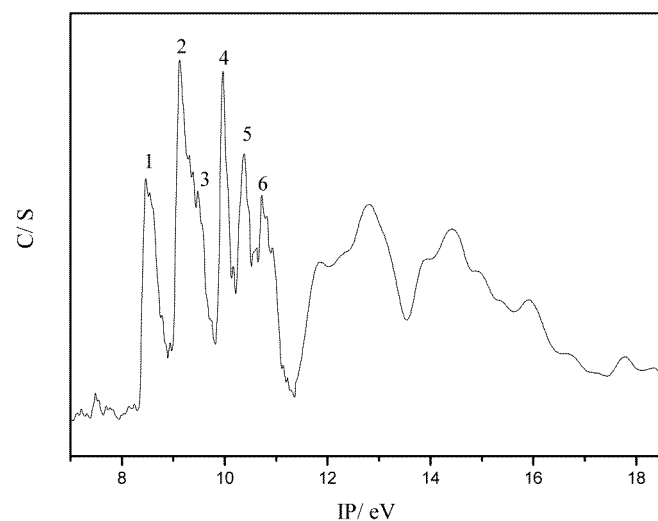The HeI ultraviolet photoelectron spectra of *o*-, *m*-, and *p*-iodophenyl isothiocyanates are shown in Figs. (**7-9**).

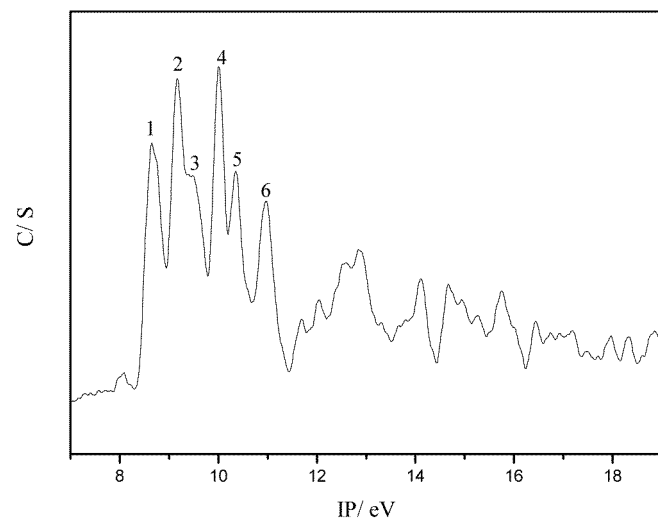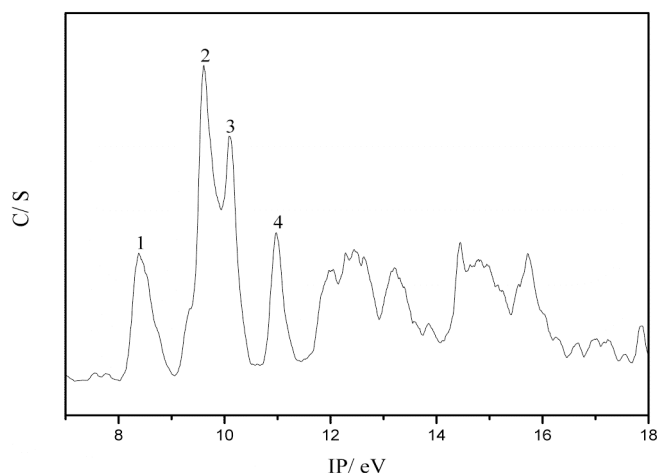**Fig. (7).** HeI photoelectron spectrum of *o*-iodophenyl isothiocyanate.

Fig. (8). HeI photoelectron spectrum of *m*-iodophenyl isothiocyanate.

As clearly seen in the photoelectron spectra, they commonly show several lower energy bands in the region from 7 eV to 12 eV with the strongest band being the second lowest energy one. The experimental and calculated ionization energies as well as the molecular orbital characters of *o*-, *m*-, and *p*-iodophenyl isothiocyanates are listed in Tables **3-5**.

Fig. (9). HeI photoelectron spectrum of *p*-iodophenyl isothiocyanate.

The experimental vertical ionization potentials of iodophenyl isothiocyanates were obtained from the observed photoelectron spectra. In order to assign the photoelectron spectra bands, the vertical ionization energies were calculated with OVGF method, based on the geometry optimized at the DFT and ab initio levels of theory. Tables **3-5** list the experimental and theoretical vertical ionization potentials and MO characters for *o*-, *m*-, and *p*- iodophenyl isothiocy-

anates. The theoretical ionization potentials are in good agreement with the experimental ionization potentials.

By combining empirical arguments (relative band intensities, band profiles, comparison with the assigned spectra of similar compounds) and theoretical method (OVGF calculations), we can develop reliable assignments of bands in the photoelectron spectra. Figs. (**10-12**) show the shapes of the occupied molecular orbitals of *o*-, *m*-, and *p*-iodophenyl isothiocyanates.

Certain common features can be traced throughout the photoelectron spectra of benzene derivatives. Benzene itself has, in its photoelectron spectrum, a lowest-energy band centered at 9.25 eV corresponding to the removal of electron of $1e_{1g}(\pi)$ orbital [52]. In substituted benzenes, the first band, i.e., the one which in benzene is at 9.25 eV, is still apparent, but frequently it is broadened (e.g., as in C_6H_5F [53] and $C_6H_5CH_3$ [54]) or split into two components (e.g., as in C_6H_5I [55], $C_6H_5NH_2$ [56], and C_6H_5OH [52]). These peaks are derived from the ionization of electrons mainly localized on lone pair-type orbitals.

The assignment of the spectrum of *o*-iodophenyl isothiocyanate is given in Table **3**. We have compared it with the spectra of C_6H_5I [55] and C_6H_5NCS [30] to support the assignments. The correlation diagram for the orbital energies of these compounds is shown in Fig. (**13**).

Table 3.   Experimental and Calculated Vertical Ionization Potentials and MO Characters for *o*-Iodophenyl Isothiocyanate

Band	Experimental IPs (eV)	Calculated IPs [a] (eV)		MO	Characters[b]
		B3LYP	**MP2**		
1	8.60	8.64	8.60	(14a")	π_3
2	9.12	9.24	9.16	(13a")	π_2
3	9.47	9.38	9.45	(47a')	n_S
4	9.96	9.91	10.04	(46a')	$n_{\parallel}$
5	10.37	10.43	10.45	(12a")	π_{NCS}
6	10.72	10.81	10.76	(11a")	$n_{\perp}$

[a]OVGF calculation at the 6-311++G** basis set level.
[b]The symbol $n_{\parallel}$ or $n_{\perp}$ indicates the orbital predominantly due to the iodine 5p orbital distributed parallel or perpendicular to the benzene ring.

Table 4.   Experimental and Calculated Vertical Ionization Potentials and MO Characters for *m*-Iodophenyl Isothiocyanate

Band	Experimental IPs (eV)	Calculated IPs [a] (eV)		MO	Characters[b]
		B3LYP	**MP2**		
1	8.65	8.72	8.69	(14a")	π_3
2	9.16	9.26	9.19	(13a")	π_2
3	9.47	9.55	9.82	(47a')	n_S
4	10.00	9.93	9.93	(46a')	$n_{\parallel}$
5	10.34	10.33	10.31	(12a")	π_{NCS}
6	10.96	11.00	11.00	(11a")	$n_{\perp}$

[a]OVGF calculation at the 6-311++G** basis set level.
[b]The symbol $n_{\parallel}$ or $n_{\perp}$ indicates the orbital predominantly due to the iodine 5p orbital distributed parallel or perpendicular to the benzene ring.

Table 5.   Experimental and Calculated Vertical Ionization Potentials and MO Characters for *p*-Iodophenyl Isothiocyanate

Band	Experimental IPs (eV)	Calculated IPs [a] (eV)		MO	Characters[b]
		B3LYP	MP2		
1	8.38	8.54	8.49	(14a")	π_3
2	9.61	9.55	9.73	(13a")	π_2
		9.71	9.84	(47a')	n_S
		9.90	9.88	(46a')	$n_{\parallel}$
3	10.09	9.98	9.89	(12a")	π_{NCS}
4	10.98	11.08	11.08	(11a")	$n_{\perp}$

[a]OVGF calculation at the 6-311++G** basis set level.
[b]The symbol $n_{\parallel}$ or $n_{\perp}$ indicates the orbital predominantly due to the iodine 5p orbital distributed parallel or perpendicular to the benzene ring.

The combined use of empirical and theoretical methods suggests that the low-energy bands 1, 2, 5 and 6 correspond to the ionization of electrons from π_3 (type a"), π_2 (type a"), π_{NCS} (type a"), n (type 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 ， the iodine lone pair (n) and the π orbitals of NCS group. As is clearly shown in Fig. (**10**), the first, second, fifth, and sixth highest occupied orbitals are delocalized over among the benzene ring, the iodine atom and the NCS group, while the third and the fourth highest occupied nonbonding n_S and n_I orbitals remain localized on the S atom of NCS group and iodine atom, respectively.

In the spectra of monohalogenbenzenes, there are two bands due to halogen lone pairs. The reason is that the in-plane ($n_{\parallel}$) and out-of-plane ($n_{\perp}$) halogen orbitals interact to different extent with the benzene σ- and π-electron systems.

The $n_{\perp}$ orbital, perpendicular to the C-halogen bond and the plane of benzene ring, would be expected to overlap more effectively with the benzene π orbital than the $n_{\parallel}$ orbital. Therefore, the $n_{\perp}$ electrons would have higher ionization potential than the $n_{\parallel}$ electrons. Furthermore, since the $n_{\parallel}$ orbital is not effectively shielded by the benzene ring, it can give a narrow and sharp band in the photoelectron spectra. From the band position and profile, we can assign the fourth and sixth bands to the $n_{\parallel}$ and $n_{\perp}$ orbitals, respectively.

The assigned orbitals are expected to appear in the 8-12eV region as the comparison with the spectra of related molecules−alkyl pseudohalides [57], and halobenzenes [58-60] —demonstrates. The bands with energies > 12 eV overlap strongly in the spectra due to the high density of ionic states and cannot be reliably assigned. They will not be discussed further in this work.

(61)   **(60)**   **(59)**

(58)   **(57)**   **(56)**
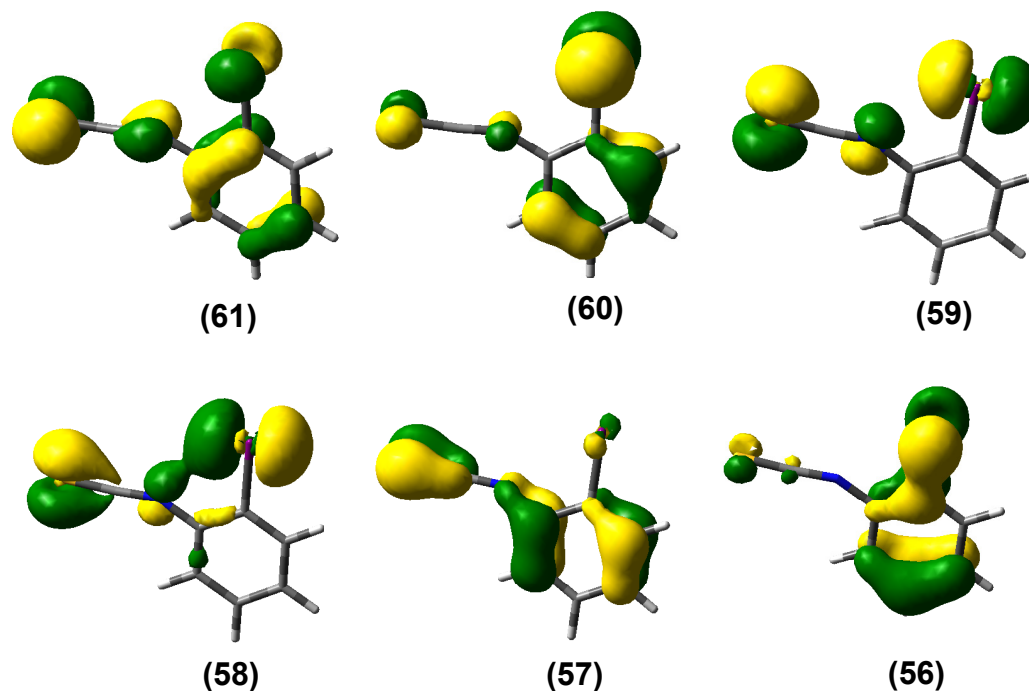
Fig. (10). Characters of the first six occupied molecular orbitals for *o*-iodophenyl isothiocyanate.
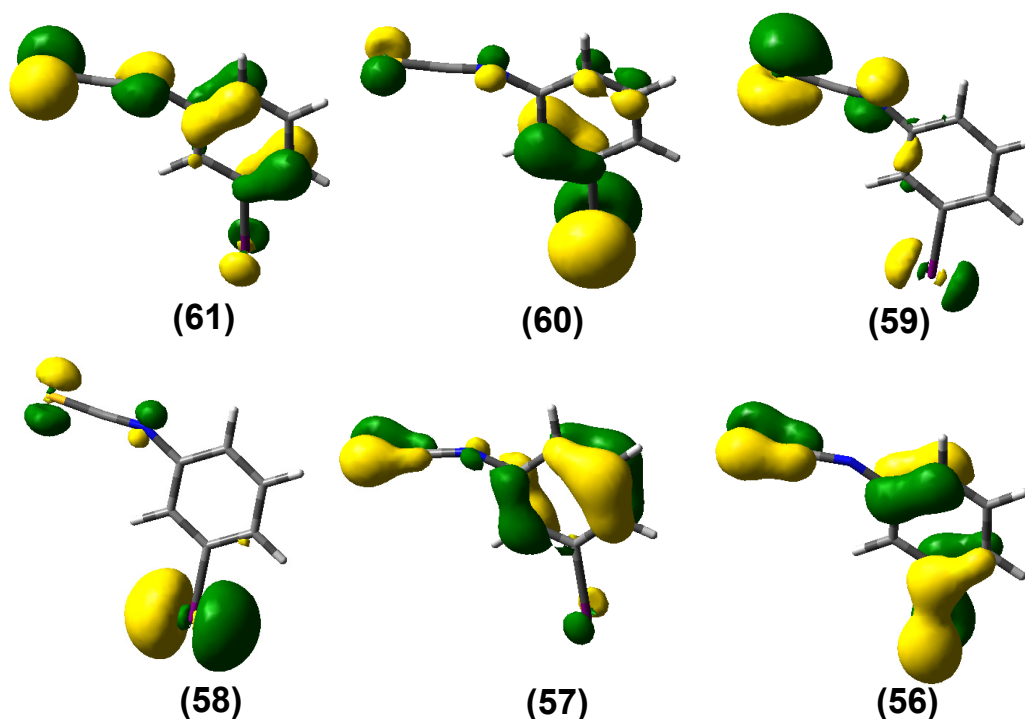
Fig. (11). Characters of the first six occupied molecular orbitals for *m*-iodophenyl isothiocyanate.
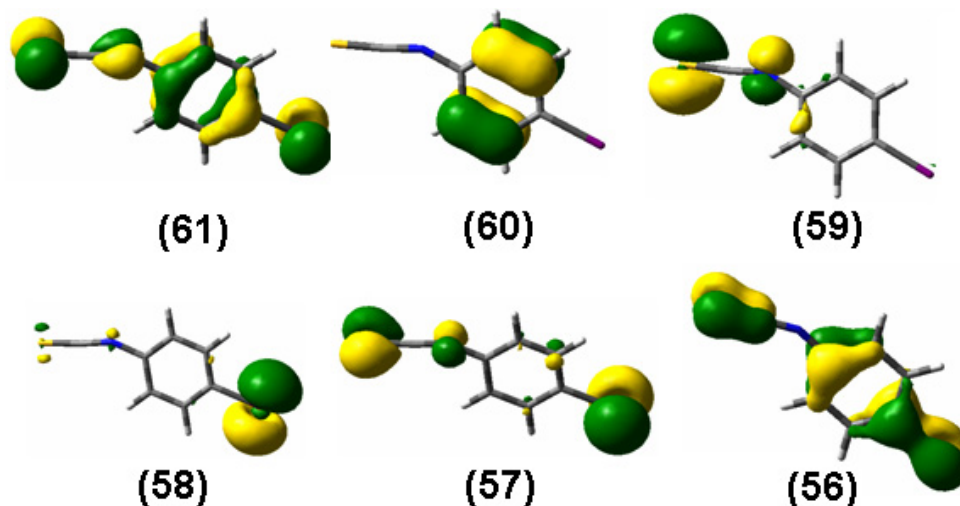

Fig. (12). Characters of the first six occupied molecular orbitals for *p*-iodophenyl isothiocyanate.

The assignments of the spectra of *m*- and *p*-iodophenyl isothiocyanates are carried out as in the case of *o*-phenyl isothiocyanate and are indicated in Fig. (**13**). Changes of relative substituent positions on the ring produce shifts of ionization potentials but no change in their relative order. As analyzed above, bands 1-6 of *m*-iodophenyl isothiocyanate are assigned to the π_3, π_2, n_S, $n_\parallel$, π_{NCS}, $n_\perp$ orbitals. Bands 1-4 of *m*-iodophenyl isothiocyanate are assigned to the π_3, the overlap of π_2, n_S and $n_\parallel$ orbitals, π_{NCS}, and $n_\perp$ orbitals. All the π_3, π_2, $n_\perp$ and π_{NCS} orbitals can be identified as the combination of a π orbital of the benzene ring, an out-of-plane iodine lone pair electron and a π orbital of the NCS group. The π_3 and π_2 orbital electrons are mainly localized on the benzene ring, while the $n_\perp$ orbital is mainly localized on the iodine lone pair, the π_{NCS} orbital mainly on the NCS group.

Substituent Effects and Chemical Reactivity

In this work we describe the interplay of substituent effects as represented by ionization energies pertaining to well resolved π and lone pair electrons bands, especially the relative chemical reactivity of NCS group.

From the point of view of substituent effects, each halogen can be classified as both π–donor and σ–acceptor [61]. However, relative donor/acceptor strengths of individual halogens will be different, e.g., chlorine is stronger σ–
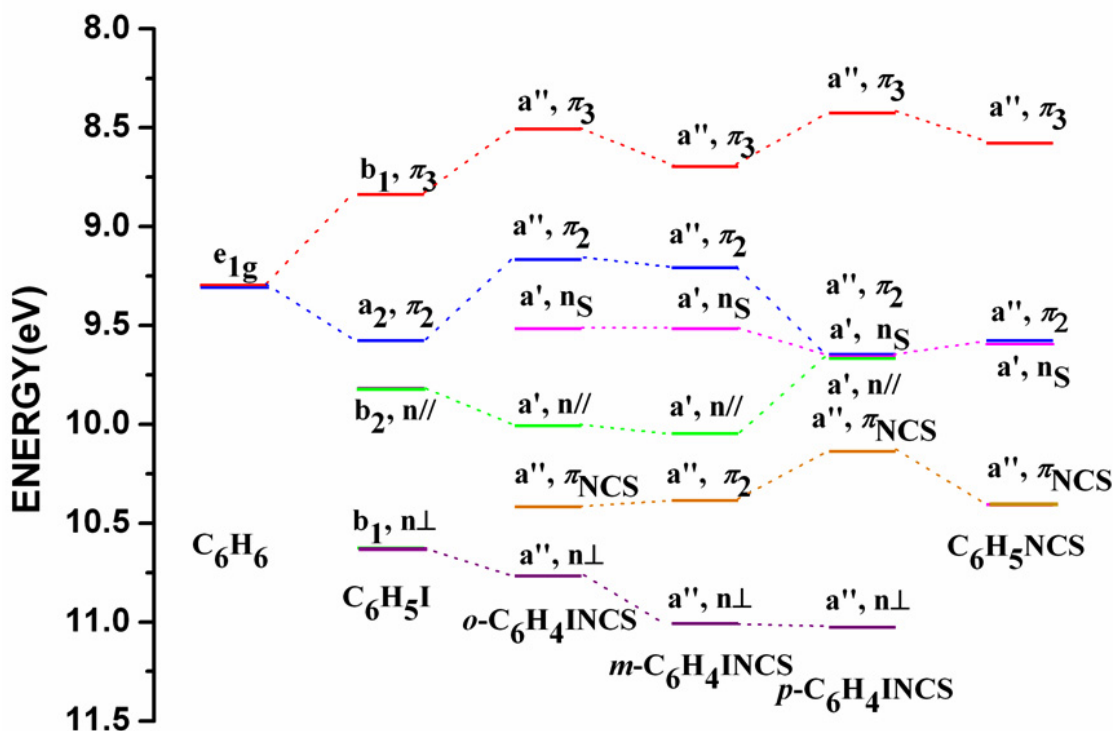
Fig. (13). Correlation diagram of the experimentally determined vertical ionization potentials for benzene, iodobenzene, phenyl isothiocyanate and iodophenyl isothiocyanates.

acceptor than π–donor, while exactly opposite is true for iodine.

Substituent effects can be quantified by introducing the following descriptors from pertinent ionization potential.

Resonance effect (R-effect) involves conjugation among iodine $n\perp$ lone pair electron, NCS π_{NCS} orbitals and benzene π orbitals electrons. These three orbitals interact with each other and leads to destabilization of benzene π orbitals electrons (decrease in ionization energy) and concomitant stabilization of iodine $n\perp$ lone pair electron (increase in ionization energy) as shown in the Fig. (**13**).

π_3 orbital has high π-electron density at *para* positions while π_2 orbital has high π-electron density at *ortho* positions [51]. In *o*-iodophenyl isothiocyanate, there are two substituents at *ortho* positions. Therefore, we can expect that π_2 in *o*-iodophenyl isothiocyanate shall be the most conjugatively destabilized of the three iodophenyl isothiocyanates, as is indeed observed. While in *p*-iodophenyl isothiocyanate, there are two substituents at *para* positions which can be expected that π_3 shall be the most conjugatively destabilized of the three iodophenyl isothiocyanate, as is indeed observed.

It is interesting that $n_\parallel$ of *o*-iodophenyl isothiocyanate is more destabilization than that of *m*-iodophenyl isothiocyanate. This can be attributed to the interaction between the positive charge of the N atom of the NCS group and the negative charge of the I atom (Table **1**) at the *ortho* position shown in Fig. (**10**).

The important information about aromatic pseudohalides concerns the interaction between ring π-orbitals and NCS group. Neijzen compared the photoelectron spectra of aromatic isothiocyanates [29] with their alkyl analogues. The relevant NCS bands in alkyl derivatives are sharper than in aromatic ones, which indicates the strong orbital mixing/interaction between ring π-orbitals and NCS group. We can see that the ionization energy of π_{NCS} in iodophenyl isothiocyanates is lower than C_6H_5NCS. This is an indication that the electron donating iodine substituent reduces the stability of NCS group which is then followed by the reduction of measured ionization energy of π_{NCS} orbitals electrons. Moreover, the π_{NCS} orbital in *p*-iodophenyl isothiocyanate is the lowest stable, this may be due to iodine is a π–donor while NCS group is a weak π–acceptor, and the effects is the most prominence when I atom and NCS group at *para* position.

The chemical reactivity of the NCS group is based on the nucleophilic attack on the electron deficient carbon which can be rationalized by simple resonance structures: R-N=C=S↔R-N$^-$-C$^+$=S↔R-N=C$^+$-S$^-$ [2]. According to the analysis of photoelectron spectra of three iodophenyl isothiocyanates, the ionization energy of π_{NCS} orbital electrons of *p*-iodophenyl isothiocyanate is the lowest (destabilization), while the ionization energy of π_{NCS} orbital electrons of *o*- and *m*-iodophenyl isothiocyanate are similar to that of phenyl isothiocyanate. This may indicate that the chemical reactivity of *p*-iodophenyl isothiocyanate is the highest. In Tian's work [24], the yield of *p*-iodophenyl isothiocyanate is the highest when *o*-, *m*- and *p*-iodophenyl isothiocyanate react with the aminophenol.

CONCLUSION

HeI ultraviolet photoelectron spectra were measured to study the electronic structures of iodophenyl isothiocyanates. On the basis of the empirical arguments (relative band intensities, band profiles, and comparison with the assigned spectra of corresponding compounds) and theoretical method (OVGF calculations), the observed bands in the photoelectron spectra were assigned. The substituent effects of iodophenyl isothiocyanates were discussed through the careful analysis of ionization potentials corresponding to π and n orbitals. This is essential for the reliable assignments of the observed photoelectron spectra. Owing to the effects of the iodine atom and the NCS group, the first ionization potentials of iodophenyl isothiocyanates are lower than that of iodobenzene and phenyl isothiocyanate. The energetic order of the first six MOs is $\pi_3 > \pi_2 > n_S > n_\parallel > \pi_{NCS} > n\perp$. The energy and electron density of the topmost occupied moledcular orbitals of iodophenyl isothiocyanates have been analyzed. It has been found that the ionization energy of π_{NCS} orbital electrons in *p*-iodophenyl isothiocyanate is the lowest of three iodophenyl isothiocyanates, which indicates the chemical reactivity of *p*-iodophenyl isothiocyanate is the highest.

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