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Substituent Effects in Mixed Trihalobenzenes

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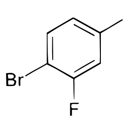
High-resolution He I and He II photoelectron spectra of four mixed trihalobenzenes C_6H_3FXY (X, Y = Cl, Br, I) were recorded. Their electronic structure is discussed with special emphasis on the heavy halogen−aromatic ring interactions. The orbital interactions in the title compounds are more pronounced than those in the compounds of the type $C_6H_4X_2$ (X = Br, I), because of the lower symmetry of the former.

Introduction

The influence of substituents on the structure and reactivity of organic compounds is one of the most widely studied problems in physical organic chemistry. The mechanism of substituent effect (SE) can be analyzed via three components: substituent (the source of perturbation), molecular framework (relay for the perturbation), and reaction site (detector of the perturbation).[1] Two types of SE are usually distinguished: *resonance* and *inductive*, although the quantitative basis for such subdivision is still being debated.[2] Besides, *steric* properties (spatial extent) of the substituent may also play a part in chemical reactivity. Most SE originate from the perturbation in the molecule's electronic structure, and it is this perturbation which subsequently influences reaction rates and equilibria. SE can be studied by spectroscopic, thermodynamic, or kinetic methods. Because many SE have their origin in the electronic structure variations, the electronic structure of substituted molecules had been widely investigated by UV photoelectron spectroscopy (UPS). The archetypal molecular framework for all SE studies, whether spectroscopic, thermodynamic, or kinetic, is benzene. A large amount of UPS data was reported on substituted benzenes and especially halobenzenes. Halogen substituents are stereochemically simple (i.e., monatomic), and halobenzenes provide an ideal case for studying certain aspects of SE, e.g., the importance of atomic number (relativistic effect), substituent position, and resonance/inductive distinction. Some of the UPS studies on halobenzenes were summarized by Wittel and Bock.[3] None of the previous studies[4−8] included molecules that contain three different types of halogens, C_6H_3XYZ. The electronic structure of such molecules can be expected to be complex, partly because low symmetry (C_s point group) allows many orbital interactions to take place and partly because different halogens will induce different perturbations in the electronic structure of the aromatic ring. However, precisely because of their complexity, the electronic structure of C_6H_3XYZ can be used to test and expand our understanding of SE. In this work, we report UPS of the following trihalobenzenes:



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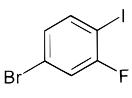

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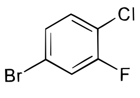

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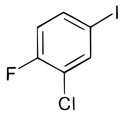

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Experimental and Theoretical Methods

The sample compounds were purchased from Acros Organics (a subsidiary of Fisher Scientific) and after checking their melting points were used without further purification. The photoelectron spectra have been recorded on a substantially modified Perkin-Elmer PS 16./18 spectrometer. He I spectra were recorded with analyzer pass energy of 2 eV, resulting in resolution of around 15 meV in expanded spectra. He I spectra were calibrated using known peaks in the spectra of CH_3I and Ar, while He II calibration was achieved using He $1s^{-1}$ peaks observed in the spectra. He II spectra were recorded with a pass energy of 10 eV to give adequate signal and a resolution of around 70 meV. The $\tilde{X}$ bands were also recorded using either the Ar I (11.828 eV) emission line or the H Lyα line (10.199 eV) emission lines. Because these lines lie close to the ionization energy of the $\tilde{X}$ state, they give a high photoionization signal, and the fact that the retardation required for 2 eV pass operation is considerably reduced in the spectrometer used results in better resolved spectra. Thus, signal and resolution were both improved and well-resolved vibrational structure was obtained (see Table 1).

AM1 calculations were performed by HyperChem program package[9] with full geometry optimization. The AM1 method was chosen instead of the more sophisticated density functional theory (DFT) for the reasons of computational cost. Halobenzenes contain heavy atoms for which relativistic basis sets need to be used. The calculation with such basis sets is costly due to the need for using numerical derivatives in order to obtain force constants. The AM1 harmonic frequencies were scaled by the recommended factor of 0.9532.[10] The calculations were useful mainly for identifying the modes giving rise to the vibrational fine structure, because a reliable assignment can be achieved on the basis of empirical arguments. The title molecules have 30 normal modes, 21 of which are totally symmetric (a'). In ions of C_s symmetry no degenerate modes are present so only totally symmetric modes (a') need to be considered. Even with this simplification the modes are complex, comprising a combination of different bond oscillations with significant amplitudes. The AM1 calculations were thus necessary.

However, the eigenvalues were not tabulated because they do not provide new information but only help with a qualitative description of MO localization properties.

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TABLE 1: Vertical Ionization Energies (IE ± 0.01 eV), Band Assignments, and Vibrational Frequencies (ν) for Halobenzenes[a–e]

molecule	band	IE (eV)	assign	ν_{ion} ± 20 cm^{-1}	ν_{mol}[b] (cm^{-1}) mode
1	$\tilde{X}$	8.86[d]	$\pi_3 - n_X$	185	132 $\delta_{CBr} + \delta_{CI}$
				1400	1487 $\delta_{CF} + \delta_{ring}$
	$\tilde{A}$	9.66	$\pi_2 - n_X$		
	$\tilde{B}$	10.01	n_I (a″)		
	$\tilde{C}$	10.52[d]	n_I (a′)	780	715 δ_{ring}
				320	387 $\nu_{CI} + \nu_{CBr}$
	$\tilde{D} + \tilde{E}$	10.95	n_{Br} (a′ + a″)	980	937 $\nu_{CF} + \delta_{ring}$
2	$\tilde{X}$	8.83	$\pi_3 - n_X$	1110	1075.8[c] δ_{CH}
				180	214 $\delta_{CBr} + \delta_{CF}$
	$\tilde{A}$	9.68	$\pi_2 - n_X$		
	$\tilde{B}$	10.00	n_I (a″)		
	$\tilde{C}$	10.54[d]	n_I (a′)	1020	1075.8[c]
				390	389 $\nu_{CBr} + \nu_{CI}$
	$\tilde{D} + \tilde{E}$	10.95[d]	n_{Br} (a′ + a″)	840	869.0[c]
3	$\tilde{X}$	9.07	$\pi_3 - n_X$	1180	1193 $\nu_{CCl} + \delta_{ring}$
				260	272 $\nu_{CBr} + \nu_{CCl}$
	$\tilde{A}$	9.85	$\pi_2 - n_X$	1140	1116 δ_{CH}
	$\tilde{B}$	10.93[d]	n_{Br} (a′)	800	933 $\nu_{CF} + \delta_{ring}$
				550	599 $\nu_{CCl} + \delta_{ring}$
	$\tilde{C}$	11.23[d]	n_{Br} (a″)		
	$\tilde{D} + \tilde{E}$	11.74[d]	n_{Cl} (a′+ a″)	910	933
4	$\tilde{X}$	8.91[d]	$\pi_3 - n_X$	1100	1215 $\nu_{CX} + \delta_{ring}$
				250	241 $\nu_{CI} + \delta_{CCl}$
	$\tilde{A}$	9.62[d]	$\pi_2 - n_X$	1140	1215
	$\tilde{B}$	10.08	n_I (a′)	680	777 $\nu_{CCl} + \delta_{ring}$
	$\tilde{C}$	10.68[d]	n_I (a″)	710	777
	$\tilde{D} + \tilde{E}$	11.62[d]	n_{Br} (a′ + a″)	745	777
				420	527 δ_{CCF}

[a] IUPAC notation is used to designate ionic states ($\tilde{X}-\tilde{F}$) and *yz* was the molecular plane. [b] Scaled AM1 values are listed because of the lack of experimental values. [c] *The Aldrich Library of FTIR Spectra*, 1st ed.; Aldrich Chemical Co.: St. Louis, MO, 1989; Vol. 3, p 926. [d] Adiabatic IE. [e] Vibrational assignments assume that frequencies for the cation are close to molecular frequencies for nonbonding ionizations.

Results and Discussion

The photoelectron spectra of the title compounds are shown in Figures 1–4. They were assigned on the basis of empirical arguments: comparison with the UPS deduced energy levels of related halobenzenes (Figure 5) and He I/He II relative intensity variations. The empirical arguments were used in preference to AM1 calculations. The preference is due to the approximations inherent in both the AM1 method and Koopmans' theorem. These approximations tend to make assignments unreliable when the eigenvalues are separated by <0.5 eV. Our analysis is based instead on the Gelius model[11] and the calculated atomic photoionization cross sections.[12] The two approaches combined together, allow the meaningful interpretation of observed He I/He II intensity variations. The ratios of He II/He I atomic photoionization cross sections are 0.307, 0.905, 0.046, 0.062, and 0.098 for C 2p^{-1}, F 2p^{-1}, Cl 3p^{-1}, Br 4p^{-1}, and I 5p^{-1} ionizations, respectively. The numerical values suggest that relative band intensities of all halogen *n*p^{-1} ionizations should decrease compared to bands from π-orbital ionizations. The only exceptions are molecular orbitals with F 2p character; their band intensities should increase. The region between 8 and 12 eV is the most interesting one in each spectrum. It contains two bands due to π-orbital ionizations (a″ symmetry) and four bands corresponding to halogen *n*p^{-1} ionizations (a′ and a″ symmetry). The π bands are related to the e_{1g} π band in benzene which is split upon symmetry change from D_{6h} to C_s. Each halogen atom contains two lone pairs (*n*p orbitals), one being localized in-plane (a′ symmetry) and the other out-of-plane (a″ symmetry). Only the latter can interact with π-orbitals of the aromatic ring. The halogen lone pair bands can be easily recognized by their sharp profiles and also by a decrease in relative intensity on going from He I to He II radiation. The assignment of halogen *n*p^{-1} ionizations is aided by knowing that ionization energies (IE) increase along the sequence I 5p < Br 4p < Cl 3p. A single band at approximately 14.5 eV shows a distinct intensity enhancement and can be attributed to F 2p^{-1} ionizations. Taking all these arguments into consideration, the general assignment of all spectra can be readily completed (Table 1, Figure 5). Many bands exhibit vibrational fine structure, and the relevant frequencies are summarized in Table 1. However, the spectra

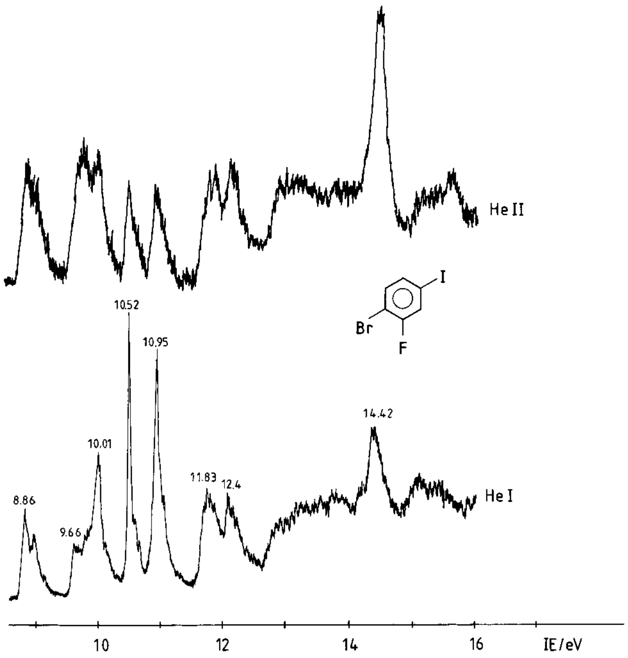

Figure 1. He I and He II photoelectron spectra of 1-bromo-2-fluoro-4-iodobenzene.

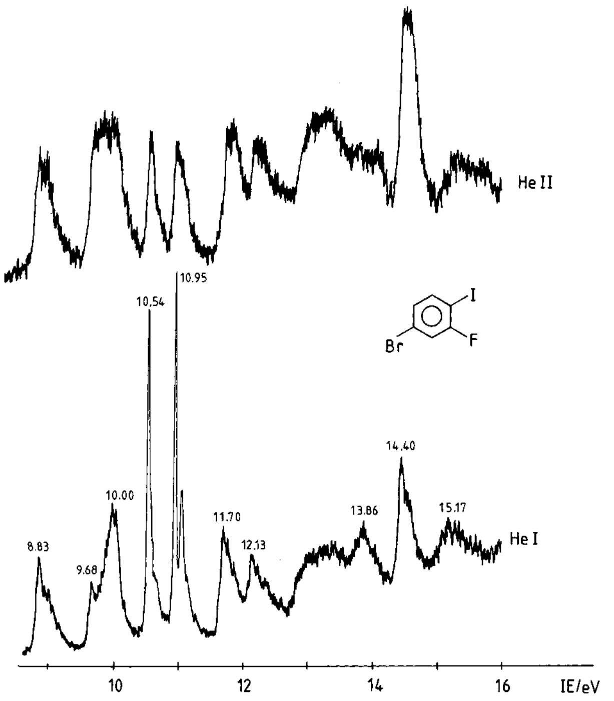

Figure 2. He I and He II photoelectron spectra of 1-bromo-3-fluoro-4-iodobenzene.

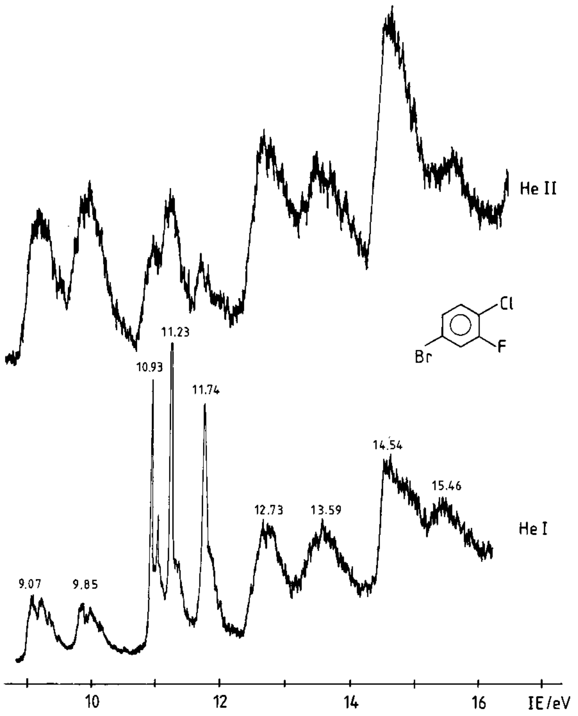

Figure 3. He I and He II photoelectron spectra of 1-bromo-3-fluoro-4-chlorobenzene.

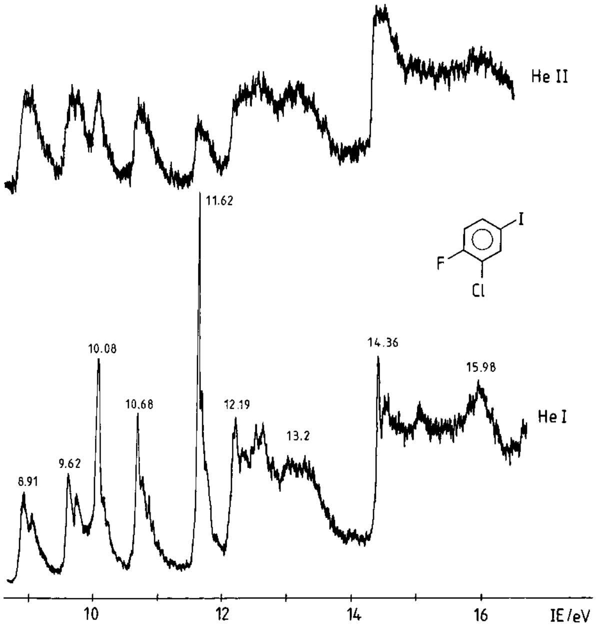

Figure 4. He I and He II photoelectron spectra of 1-fluoro-2-chloro-4-iodobenzene.

provide a very detailed insight into the orbital interactions and SE which we shall discuss in the following paragraphs.

Most useful information comes from the analysis of halogen $n\mathrm{p}^{-1}$ band profiles and ionization energies. As mentioned earlier, halogen $n\mathrm{p}^{-1}$ bands (excluding deep-lying F $2\mathrm{p}^{-1}$ bands) are sharp and well-defined and thus represent ideal probes for monitoring orbital interactions. In heavy halogens (bromine and iodine) the energies of $n\mathrm{p}^{-1}$ bands differ by the extent of spin−orbit coupling (SOC) which has average values of 0.35 and 0.54 eV for Br 4p and I 5p ionizations, respectively.[13] A deviation from these values and/or the broadening of band profiles can be rationalized in terms of π−np orbital interactions of suitable (a″) symmetry.

The inspection of spectra of **1** and **2** reveal some interesting effects. The relative position of F atom does not alter the spectra significantly, which is in keeping with its predominantly inductive role as a substituent. However, broadening of $\tilde{B}$ band (I $5\mathrm{p}^{-1}$) occurs on going from **1** to **2**. A possible rationalization in terms of Coulombic effect can be outlined as follows. The $\tilde{B}$ ionic state contains an electron hole (a trough in electron density) which is located mainly on I atom. The presence of a strong negative charge density (F atom) in the vicinity of the hole as in the case in **2** may destabilize the hole, shorten its lifetime, and cause band broadening. In **1** the F atom is further removed from the trough, and its Coulombic influence diminished. Why is then the broadening of $\tilde{D}$ bands (Br $4\mathrm{p}^{-1}$) not observed in spectra of **1**? The reason may be sought in the lower polarizability (higher electronegativity) of the bromine atom. Alternatively, ion **2** can be expected to have rather different equilibrium geometry than the parent molecule. This can be due to steric and Coulombic interactions between positively charged iodine and the neighboring fluorine with high electron affinity. The change in equilibrium geometry of ion **2** can lead to broadening of the Franck−Condon envelope for the $\tilde{B}$ band.

Coulombic effects are superimposed on the general broadening of the $\tilde{B}$ band (compared to the $\tilde{C}$ band) in **1** and **2**. The broadening is caused by interaction between out-of-plane I 5p and ring π-orbitals. Further evidence of significant π−np interactions can be found in the fact that Br $4\mathrm{p}^{-1}$ bands in **1** and **2** are not visibly split by SOC, but the 0.3 eV splitting is observable in **3**. An alternative assignment of UPS of **1** and **2** is possible in which one assigns Br $4\mathrm{p}^{-1}$ ionizations to bands at 10.95 and 11.70 (11.83) eV. However, this assignment would require an unusually large Br 4p splitting of ≥ 0.8 eV compared to the standard SOC value of 0.31 eV. This seems unlikely in view of the fact that the SOC splitting of I $5\mathrm{p}^{-1}$ bands is close to the standard 0.54 eV value. Furthermore, such an assignment is not supported by He I/He II spectra which show that the relative intensity of the 11.70 (11.83) eV bands does not decrease at higher photon energy which would be expected of Br $4\mathrm{p}^{-1}$ ionization.

Finally, π/np mixing is also suggested by the relative intensities of $\tilde{X}$ and $\tilde{A}$ bands in He I and He II spectra. The relative intensity of the $\tilde{A}$ band increases compared to $\tilde{X}$, upon increasing photon energy in **1**−**3,** while in **4** a weak opposite trend is observed. This can be explained by localization properties of benzene's HOMO π-orbitals. When Cl, Br, or I atoms are in the para position, they will mix with only one of the two π-orbitals (the other has a nodal plane passing through para positions). This is manifested in different photoionization cross sections and intensities for $\tilde{X}$ and $\tilde{A}$ bands. However, when halogens are in meta positions, their np orbitals interact with both ring π-orbitals. This leads to a very small variation in photoionization cross sections and subsequent negligible variation in He I/He II band intensities. Bouguerne et al.[14] have suggested on the basis of the UPS data for 1-bromo-2-iodoethane, that bromine has "molecular" and iodine "atomic" character. While this assertion is true for alkanes, where only through-bond halogen−halogen interactions are active, it ceases to be so in CHClBrI[15] or halobenzenes.

Another interesting problem concerns the question of which halogen substituent (chloro, bromo, or iodo) interacts most strongly with the aromatic ring. All halogens can be expected to perturb the aromatic ring inductively according to their electron affinities. However, as Figure 5 demonstrates, the effect on π-ionization energies is virtually independent of the

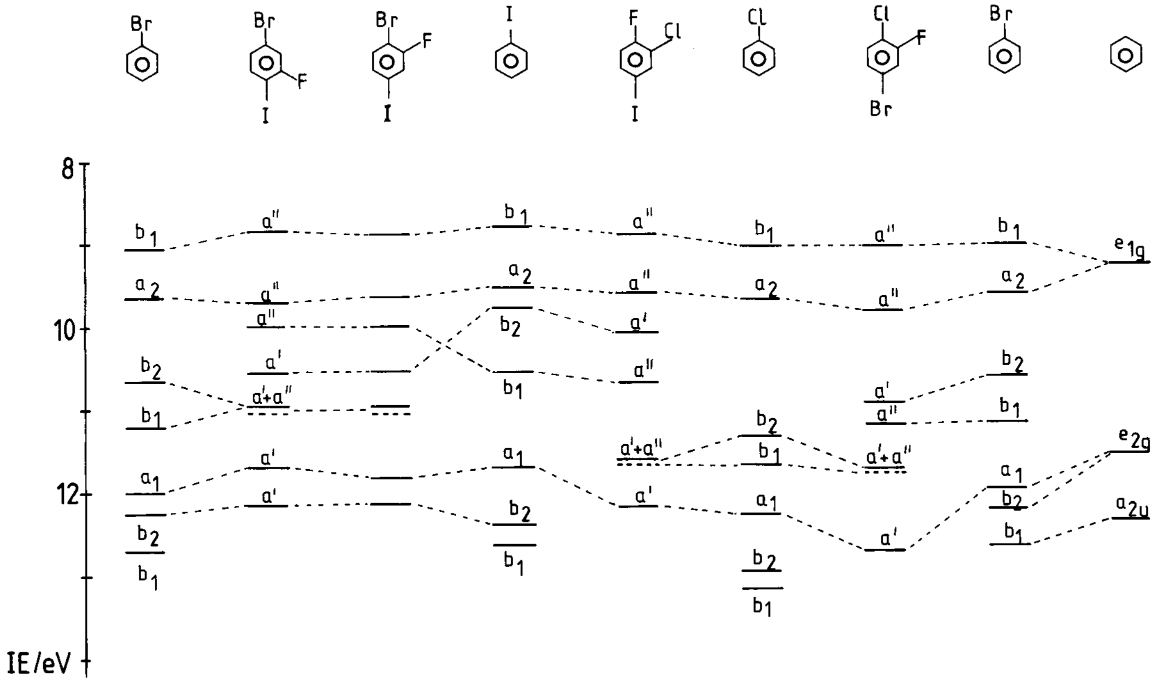

Figure 5. Energy level diagram of benzene and halobenzenes.

halogen type. Is the reason for the insensitivity a combination (cancellation?) of inductive and resonance effects?

The UPS data may help to answer the question. The SE of halogen can be estimated by using perturbation theory (up to second order) and the observed π-ionization energy shifts. Although a reasonably successful theoretical framework had been formulated for IE shifts,[3] it does not include iodine atoms and neglects the interactions with deep-lying π_1-orbital. An alternative, empirical approach relies on the comparison of band profiles and intensities of halogen $n\mathrm{p}^{-1}$ bands within a series of isomeric halobenzenes. We shall discuss this approach next.

The UPS database is not quite satisfactory because most data refer to halobenzenes with at most two different types of halogens, or to compounds of high molecular symmetry. The high symmetry restricts possible orbital interactions and thus is not suitable for the study of SE effects by UPS. When the molecules studied did contain two different halogens,[4] one of them was fluorine which perturbs the aromatic ring only inductively. The UPS spectra of C_6H_5X (X = Cl, Br, I) show only small differences between halogen $n\mathrm{p}^{-1}$ bandwidths.[8] The spectra of perfluro derivatives C_6F_5X suggest[7b] (on the basis of bandwidth analysis) that bromine interacts more strongly with the aromatic ring than chloro or iodo substituents. Our results clearly show that the Cl $3\mathrm{p}^{-1}$ bandwidth is virtually the same in UPS of **3** and **4**. This can be regarded as an indication that the chloro substituent perturbs the aromatic system in the least. I $5\mathrm{p}^{-1}$ bands in **1** and **2** show considerable differences in both intensity and width, more so than Br $4\mathrm{p}^{-1}$. This would indicate that iodine interacts more strongly than bromine with the benzene ring, which is exactly the opposite effect from the one observed by Bouguerne et al.[14] Why? The main reason could be due to the outermost π-orbitals which are closer in energy to I 5p than to Br 4p orbitals. The I 5p$-\pi$ interactions are thus stronger than Br 4p$-\pi$. Br 4p orbitals interact preferably with deep-lying π_1- or various σ-orbitals. Another interesting question concerns the relativistic effects on the electronic structure. To answer this question, one may of course perform relativistic MO calculations which are computationally demanding even with effective core potential basis (see section on experimental and theoretical methods). The other approach is to consider qualitative symmetry arguments. Relativistic effects can be described by going from the C_s point group which has $a' + a''$ representations to the corresponding double group which has only a single representation $e_{1/2}$. This implies that in the extreme of strongly relativistic case σ/π distinction would become meaningless. UPS data point out that σ/π separation is maintained, because for example the halogen $n\mathrm{p}^{-1}$ bands retain distinctly different bandwidths depending on whether they correspond to in-plane or out-of-plane halogen np orbitals. This type of argument would not be valid for halobenzenes which contain heavy (relativistic) halogens but have high molecular symmetry (e.g., p-$C_6H_4I_2$ with D_{2h} symmetry). The reason is that the corresponding double group still contains two different irreducible representations ($e_{g/2}$, $e_{u/2}$). This condition ensures σ/π separation on symmetry grounds.

We have pointed out earlier, on the basis of bandwidths, that considerable np$-\pi$ and np$-n$p interactions take place. Vibrational fine structure analysis (Table 1) supports this assertion. For instance, the vibrational modes appearing in π^{-1} bands have strong C$-$X stretching contributions. Furthermore, the modes present in halogen $n\mathrm{p}^{-1}$ bands are described as linear combinations of C$-$X and C$-$Y stretching or bending modes, where X,Y are different halogens.

Conclusion

The concepts of SE and electron delocalization have been discussed most often from theoretical aspects using various bond or electron localization algorithms. Experimental approaches to the same problem utilize bond lengths. (See recent discussion about the "nonsequitur" between π-conjugation and delocalization.[16]) The use of UPS data to understand these concepts is less common, and our work provides new, experimental information for such analysis.

Our data show several important trends concerning SE and orbital interactions: The benzene ring is a much more efficient relay for transmission of substituent effects than an alkane chain or even a through-space (TS) mechanism. This conclusion is independent of theoretical algorithms and approximations embedded in MO methods. Comparison of halogen $n\mathrm{p}^{-1}$ ionizations in our spectra with those in haloalkanes[13] demonstrates that halogen−halogen np−np interactions in haloalkanes are much weaker than in halobenzenes. Even when a TS mechanism is available to halogen lone pairs as is the case in CHClBrI,[15] the np−np interactions are still weaker than in halobenzenes.

A further study of the remaining mixed halobenzenes may reveal more details about the subtle interplay of different aspects of SE. Also, the rich vibrational fine structure observed in our spectra can be used for testing the performance of DFT methods. Such methods are gaining in popularity due to their low computational costs. However, as the very recent results have pointed out,[17] their performance and reliability for ions, especially those containing heavy atoms (relativistic effects), are suspect or unknown.

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