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## Halogens in Competition: Electronic Structure of Mixed Dihalobenzenes

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Received: December 11, 2004; In Final Form: February 17, 2005

The electronic structure of all isomeric dihalobenzenes  $C_6H_4XY$  ( $X, Y = Cl, Br, I$ ) has been investigated by HeI/HeII photoelectron spectroscopy, Green's functions calculations, and comparison with the spectra of related dihalobenzenes  $C_6H_4X_2$  ( $X = Cl, Br, I$ ). The careful analysis of measured  $\pi$  orbital and halogen lone pair ionization energies enabled us to describe substituent effects in terms of resonance, inductive, steric, and spin–orbit coupling interactions.

## Introduction

The reactivity of substituted benzene derivatives has been extensively studied and has led to the notion of the substituent effect (SE). The overall SE can be conceptually partitioned into electronic, steric, and solvent contributions. In this work we focus on the electronic substituent effect only. However, even the electronic SE alone, studied in mono- and disubstituted molecules, has proven difficult to describe quantitatively.<sup>1,2</sup> We hope to further our understanding of SE by investigating how the topology of substitution and polarity of the substituent affect the molecular electronic structure. Substituted benzenes are a convenient test case, because of the great diversity of isomers which are available for experimental study. The molecular descriptor which is closely related to the electronic substituent effect is the ionization energy. This energy can be accurately measured by photoelectron spectroscopy (UPS).

The study of electronic structure and thus of electronic substituent effects can also be performed by theoretical methods such as DFT. DiLabio et al.<sup>3</sup> used DFT calculations to obtain the first ionization energies of 55 para- and meta-disubstituted benzenes. The first ionization energy corresponds to ionization from the  $\pi_3$  orbital (HOMO). The substituent groups in their study were electron-withdrawing (EW) and electron-donating (ED) types. The SE magnitude was measured by calculating the difference between the first ionization energy ( $\Delta E_i$ ) of a particular substituted benzene and that of the parent benzene molecule. The most important question addressed in DiLabio's work was whether the substituent effects are additive and how the presence (or absence) of additivity can be explained.

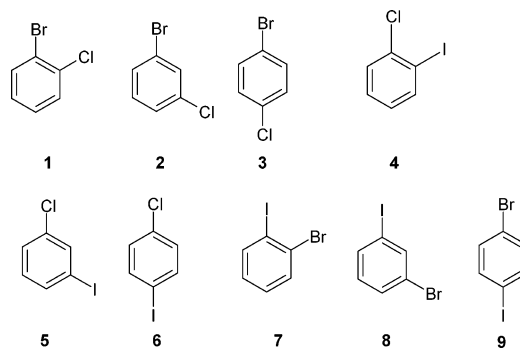
We shall summarize the conclusions of DiLabio et al.<sup>3</sup> regarding EW substituents, because they are relevant to our work which involves two halogen, i.e., EW, substituents. The substituent effects of EW groups are based on deshielding caused by  $\sigma$ -inductive effects. The deshielding leads to a lower energy (contraction) of ring  $\pi$  orbitals. The magnitude of SE in disubstituted benzenes can be quantified by a quadratic expression which relates  $\Delta E_i$  of disubstituted and  $\Delta E_i$  of monosubstituted benzenes. The authors' prediction for polysubstituted

benzenes was that although analysis similar to that of disubstituted derivatives may be possible, the orbital mixing effects may cause "saturation" and hence pronounced nonadditivity of substituent effects. DiLabio et al.<sup>3</sup> have predicted that saturation effects should be observable in benzene derivatives containing more than two ED groups.

The aim of this work is to describe the photoelectron spectroscopic study of mixed dihalobenzenes  $C_6H_4XY$  ( $X, Y = Cl, Br, I$ ) to improve our understanding of SE. The UPS method enables us to investigate not only the changes taking place in the first ionization energies as DiLabio et al. did, but changes in halogen lone pair ionizations as well. Why have we limited our study to halogen substituents? One of the reasons is that halogen lone pair bands (unlike bands related to orbitals localized on other types of substituents) are easily identifiable in the spectra due to their profile and intensity. This allows accurate measurement of their ionization and orbital energies. The halogen lone pair ionizations are very sensitive internal probes for substituent effects.

## Experimental and Theoretical Methods

Compounds **1–9** were purchased from Acros Organics NV and Fluka AG and used without further purification after confirmation of their identity by measuring NMR and mass spectra.



The sample inlet temperatures were in the range 40–60 °C. These temperatures were necessary to obtain sufficient vapor pressures in the ionization region.

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The HeI/HeII photoelectron spectra of **1–9** were recorded on a Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe or Ar gas which was added to the sample flow. The spectral resolution of HeI and HeII spectra was 25 and 70 meV, respectively, when measured as the full width at half-maximum (fwhm) of the  $3p^{-1} \ ^2P_{3/2} \text{Ar}^+ \leftarrow \text{Ar} (^1S_0)$  line. The resolution in the HeII spectra was always inferior to that of HeI, which implies that some bands that are well resolved in HeI may become unresolved in the corresponding HeII spectrum. Therefore, measured relative band intensities and intensity ratios sometimes refer to the combined intensity of two poorly resolved bands rather than to the intensity of a single band.

The spectral bands were, when necessary for intensity measurements, simulated by asymmetric Gaussian profiles.<sup>4</sup> This allowed the deconvolution and estimation of the band intensity to be made. Baseline corrections were also employed. Baseline parameters were determined from the data near the baseline and the exponential form of the baseline function (i.e., band intensity  $\approx 1/E_k$ , where  $E_k$  is the photoelectron kinetic energy). This baseline function was recommended by the manufacturer of the spectrometer. The assignment of the spectra of large molecules can often be facilitated by measuring relative band intensities at various photon energies. The empirical relative intensity of each resolved band in the 7–12 eV region of the HeI or HeII spectrum was normalized to the first band. The ratios of normalized relative HeII and HeI intensities were then used to calculate  $RI_{\text{exp}} = \sigma_i^{\text{HeII}} / \sigma_i^{\text{HeI}}$  (Table 1). The band normalization was necessary, because absolute band intensities could not be measured. Band intensities of halogen lone pair ionizations depend strongly on the photon energy. In particular, relative intensities of bromine, chlorine, and iodine lone pair bands decrease significantly on going from HeI to HeII radiation. Such changes are caused by variations of atomic photoionization cross-sections and are well substantiated by theoretical<sup>5</sup> and UPS<sup>6</sup> studies. These known intensity variations have often been used as an important assignment aid.

The quantum chemical calculations were performed with the Gaussian 03 program.<sup>7</sup> The full geometry optimization and natural population analysis (NPA) were performed using the DFT method at the B3LYP/6-31G\* level. Subsequently, single-point Green's function (OVGF) type calculations implemented in the Gaussian program were performed to obtain ionization energies, using the 6-311G(d,p) basis set for all atoms except for I, for which a relativistic basis set was used.<sup>8</sup> GF calculations with the same basis sets as in our work were used successfully to assign the spectra of monohalobenzenes.<sup>9</sup>

## Results and Discussion

The investigation of substituent effects is our primary aim, but to be able to perform the analysis, we must first have reliable assignments of the spectra. Therefore, the first part of our discussion describes the analysis of photoelectron spectra.

**Spectral Assignment.** The HeI/HeII photoelectron spectra of **1–9** are shown in Figures 1–5. To obtain reliable assignments, we combined the empirical arguments (relative band intensities, band profiles, comparison with the assigned spectra of corresponding mono- and dihalobenzenes, HeI/HeII dependence of band intensities) with theoretical methods (GF calculations). The band profile provides insight into the nature of the orbital from which ionization takes place; a sharp, narrow band often corresponds to an ionization from a strongly localized, nonbonding orbital as suggested by the Franck–Condon principle. Furthermore, halogen lone pair bands show particularly

**TABLE 1: Vertical Ionization Energies ( $E_i \pm 0.05$  eV), Empirically Derived Band Assignments (MO), Calculated Ionization Energies (GF/eV), and Experimental Ratios of Relative HeII/HeI Band Intensities ( $RI$ )<sup>a–c</sup>**

compd	vand	$E_i$	MO type	GF	RI
<b>1</b>	X	(9.04) 9.15	$\pi_3$ (a'')	9.13	1.0
	A	9.57	$\pi_2$ (a'')	9.53	1.0
	B	10.63	$n_{\text{Br}}$ (a')	10.28	0.32
	C, D	(11.35)	$n_{\text{Br}}$ (a')	11.21	0.47
		11.57	$n_{\text{Cl}}$ (a')	11.40	
<b>2</b>	E	12.03	$n_{\text{Cl}}$ (a'')	11.82	0.38
	X	9.25	$\pi_3$ (a'')	9.20	1.0
	A	9.65	$\pi_2$ (a'')	9.63	1.0
	B	(10.8)	$n_{\text{Br}}$ (a')	10.53	0.30
	C	(11.2)	$n_{\text{Br}}$ (a'')	11.00	0.30
<b>3</b>	D	11.56	$n_{\text{Cl}}$ (a')	11.34	0.30
	E	12.4	$n_{\text{Cl}}$ (a'')	12.21	
	X	8.95	$\pi_3$ (b <sub>1</sub> )	9.0	1.0
	A	(9.84) 9.96	$\pi_2$ (a <sub>2</sub> )	9.97	1.13
	B	(10.8)	$n_{\text{Br}}$ (b <sub>2</sub> )	10.52	0.25
<b>4</b>	C	11.1	$n_{\text{Br}}$ (b <sub>1</sub> )	10.78	0.25
	D	11.53	$n_{\text{Cl}}$ (b <sub>2</sub> )	11.33	0.17
	E	12.55	$n_{\text{Cl}}$ (b <sub>1</sub> )	12.32	
	X	8.80	$\pi_3 + n_1$ (a'')	8.67	1.0
	A	9.35	$\pi_2$ (a'')	9.13	1.0
<b>5</b>	B	9.75	$n_1$ (a')	9.31	0.41
	C	10.65	$n_1 + \pi$ (a'')	10.39	0.75
	D	11.45	$n_{\text{Cl}}$ (a')	10.88	
	E	11.80	$n_{\text{Cl}}$ (a'')	11.32	
	X	8.90	$\pi_3 + n_1$ (a'')	8.74	1.0
<b>6</b>	A	9.45	$\pi_2$ (a'')	9.30	1.0
	B	9.95	$n_1$ (a')	9.60	0.42
	C	10.65	$n_1 + \pi$ (a'')	10.39	0.55
	D	11.40	$n_{\text{Cl}}$ (a')	11.50	0.35
	E	(12.0)	$n_{\text{Cl}}$ (a'')	12.08	
<b>7</b>	X	8.77	$\pi_3 + n_1$ (b <sub>1</sub> )	8.64	1.0
	A	(9.7)	$n_1$ (b <sub>2</sub> )	9.29	0.78
	B	9.8	$\pi_2$ (a <sub>2</sub> )	9.91	0.78
	C	10.48	$n_1 + \pi$ (b <sub>1</sub> )	10.00	0.42
	D	11.47	$n_{\text{Cl}}$ (b <sub>2</sub> )	11.31	0.40
<b>8</b>	E	11.9	$n_{\text{Cl}}$ (b <sub>1</sub> )	11.87	
	X	8.80	$\pi_3 + n_1$ (a'')	8.67	1.0
	A	9.30	$\pi_2$ (a'')	9.13	1.0
	B	9.65	$n_1$ (a')	9.31	0.40
	C	10.65	$n_1 + \pi$ (a'')	10.39	0.51
<b>9</b>	D	10.95	$n_{\text{Br}}$ (a')	10.88	0.51
	E	11.35	$n_{\text{Br}}$ (a'')	11.32	0.51
	X	8.9	$\pi_3 + n_1$ (a'')	8.72	1.0
	A	9.40	$\pi_2$ (a'')	9.22	1.0
	B	9.96	$n_1$ (a'')	9.58	0.32
<b>9</b>	C	10.58	$n_1 + \pi$ (a')	10.33	0.39
	D	10.89	$n_{\text{Br}}$ (a'')	10.75	0.39
	E	11.55	$n_{\text{Br}}$ (a')	11.53	
	X	8.75	$\pi_3 + n_1$ (b <sub>1</sub> )	8.55	1.0
	A, B	9.8	$n_1, \pi_2$ (b <sub>2</sub> + a <sub>2</sub> )	9.58, 9.65	1.15
<b>9</b>	C	10.4	$n_1 + \pi$ (b <sub>1</sub> )	10.00	0.42
	D	10.80	$n_{\text{Br}}$ (b <sub>2</sub> )	10.77	
	E	11.60	$n_{\text{Br}}$ (b <sub>1</sub> )	11.63	

<sup>a</sup> Adiabatic ionization energies are given in parentheses and have an uncertainty of 0.03 eV. <sup>b</sup> The bands were simulated by asymmetric Gaussian band shapes as suggested in ref 4, and the variable bandwidths were in the range 0.1–0.3 eV. <sup>c</sup> Where adiabatic energies only are given, they are the same as the band maxima, which in other cases correspond to vertical ionization energies.

pronounced intensity changes with photon energy. However, not all halogen lone pairs 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.<sup>5</sup> Also, halogen lone pair bands sometimes overlap with other  $\pi$  and  $\sigma$  orbital ionizations, which may mask the expected intensity changes. The correlation with reliably assigned spectra of corresponding monohalobenzenes thus becomes necessary.

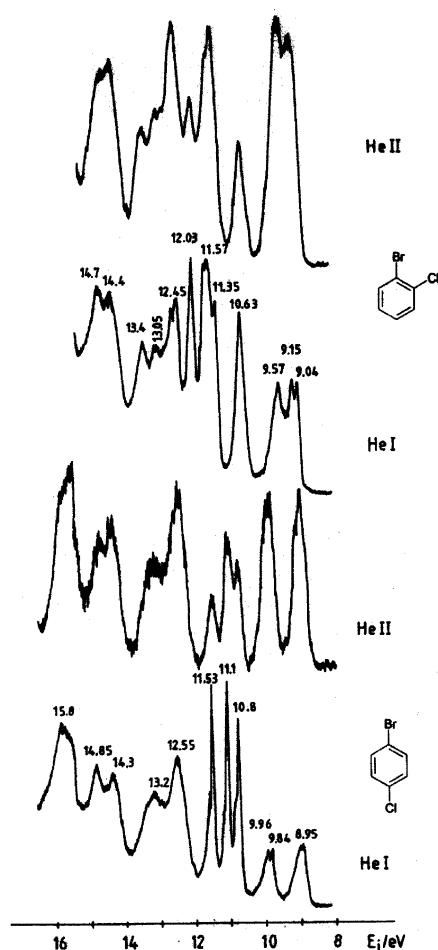


Figure 1. Photoelectron spectra of **1** (top) and **3** (bottom).

The assignments of the spectra of **1–9** are given in Table 1, and we shall briefly describe how they were arrived at. We compared the spectra of **1–9** with the spectra of monohalobenzenes which were carefully assigned by using the Penning ionization method (PIES).<sup>9</sup> Each  $C_6H_4XY$  spectrum was compared with the spectra of  $C_6H_5X$  and  $C_6H_5Y$ . We have also compared the spectra of  $C_6H_4XY$  with the assigned spectra of corresponding isomeric diiodo-,<sup>10</sup> dibromo-,<sup>11</sup> and dichlorobenzenes<sup>12</sup> to confirm the assignments. The combined use of empirical and theoretical methods suggests that the first two bands (X, A) which have the lowest ionization energies arise from ionization of  $\pi_3$  and  $\pi_2$  orbitals, i.e., HOMO and SHOMO. The only exceptions occur in the spectra of **6** and **9**, where the second band comprises two ionizations: from  $\pi_2$  and the in-plane iodine lone pair  $n_{II}$ . The two orbitals are thus quasi-degenerate. The next four bands (B–E) can be attributed to four halogen lone pairs  $n_X$ : two lying in-plane ( $n_{II}$ ) and two out-of-plane ( $n_{\perp}$ ) with the ring. Calculated orbital and GF energies, HeI/HeII intensity variations, and comparison with the spectra of other halobenzenes strongly support this assignment. The last of the four halogen bands (E) does not show the expected variation in HeI/HeII intensity. This may be due to the band overlap between E and neighboring  $\sigma$ -ionizations and to the reduced halogen lone pair character pertaining to the E band itself. The latter effect is due to mixing of halogen  $np$  and  $\pi_1$  orbitals. At this point we amend the assignments made previously regarding mixed fluorodihalobenzenes<sup>13</sup> which were arrived at on the basis of semiempirical calculations. In the previous report<sup>13</sup> the alternative assignment which places the E band at higher ionization energy was considered unlikely.

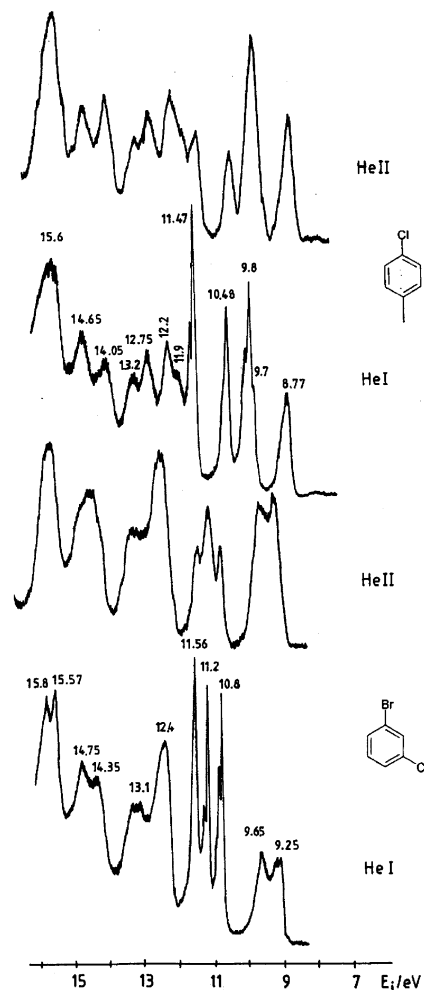
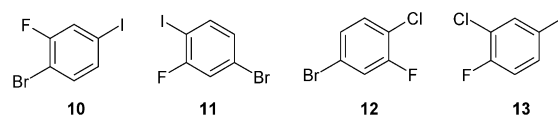


Figure 2. Photoelectron spectra of **6** (top) and **2** (bottom).

However, we now consider that the E band should be associated with the peaks at 11.83, 11.70, 12.73, and 12.19 eV in the spectra of **10–13**, respectively.

The amended assignment becomes consistent with the results reported in this work, as it must be in view of the very similar appearance of spectra of **9**, **3**, and **5** vs **10–13**, respectively.



**Substituent Effects.** In this work we are interested in the complex interplay of inductive (I-effect), resonance (R-effect), and spin–orbit coupling (SOC) effects in dihalobenzenes as monitored by measured ionization energies pertaining to well-resolved  $\pi$  and lone pair bands. The three effects operate simultaneously (antagonistically) to generate the observed energy level pattern as was pointed out a long time ago.<sup>14,15</sup> From the point of view of substituent effects, each halogen can be classified as both a  $\pi$ -donor and a  $\sigma$ -acceptor.<sup>16</sup> However, relative donor/acceptor strengths for individual halogens will be different; e.g., chlorine is a stronger  $\sigma$ -acceptor than  $\pi$ -donor, while exactly the opposite is true for iodine, as suggested by PIES results. Also, NPA analysis suggests that there is less net electron density transferred between chlorine and the ring compared to between iodine and the ring (Table 2). The R-effect introduces conjugative mixing between out-of-plane halogen lone pairs ( $n_{\perp}$ ) and  $\pi_3$ ,  $\pi_2$ , and  $\pi_1$  orbitals of benzene. However,

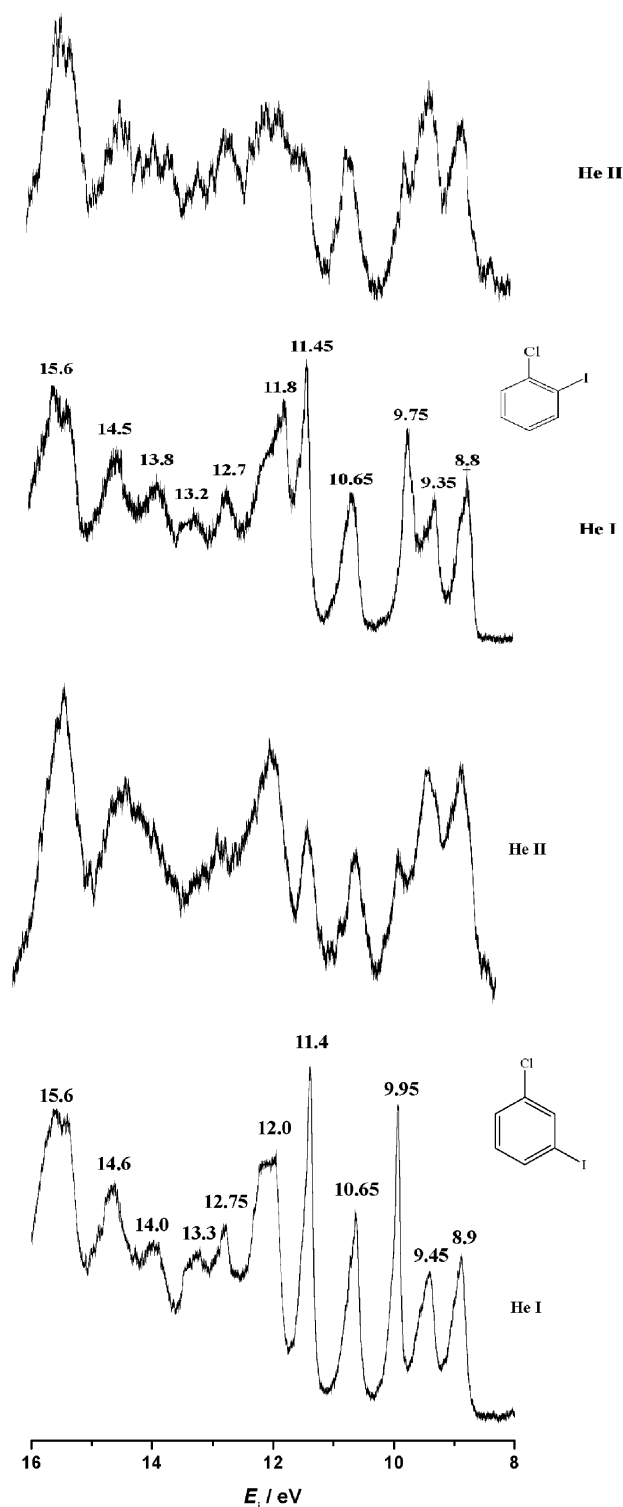


Figure 3. Photoelectron spectra of 4 (top) and 5 (bottom).

we do not classify  $n_{\perp}$  orbitals as “ $\pi$  orbitals”. This is because the  $n_{\perp}$  orbitals retain enough of their distinct character as was demonstrated by a recent PIES study of monohalobenzenes.<sup>9</sup> The comment about orbital character is based on the variations of Penning ionization cross-sections (as a function of the kinetic energy of metastable He\* atoms) for out-of-plane lone pairs vs  $\pi_3$  and  $\pi_2$  orbitals. The authors of the PIES study have therefore retained the conventional  $n_{\perp}$ ,  $n_{\parallel}$ , and  $\pi$  notation, which we adopted in this work. However, according to the PIES study conjugation of an out-of-plane lone pair with  $\pi$  orbitals is strongest for iodine, which we emphasize in Table 1.

The assumptions regarding SOC are given below.

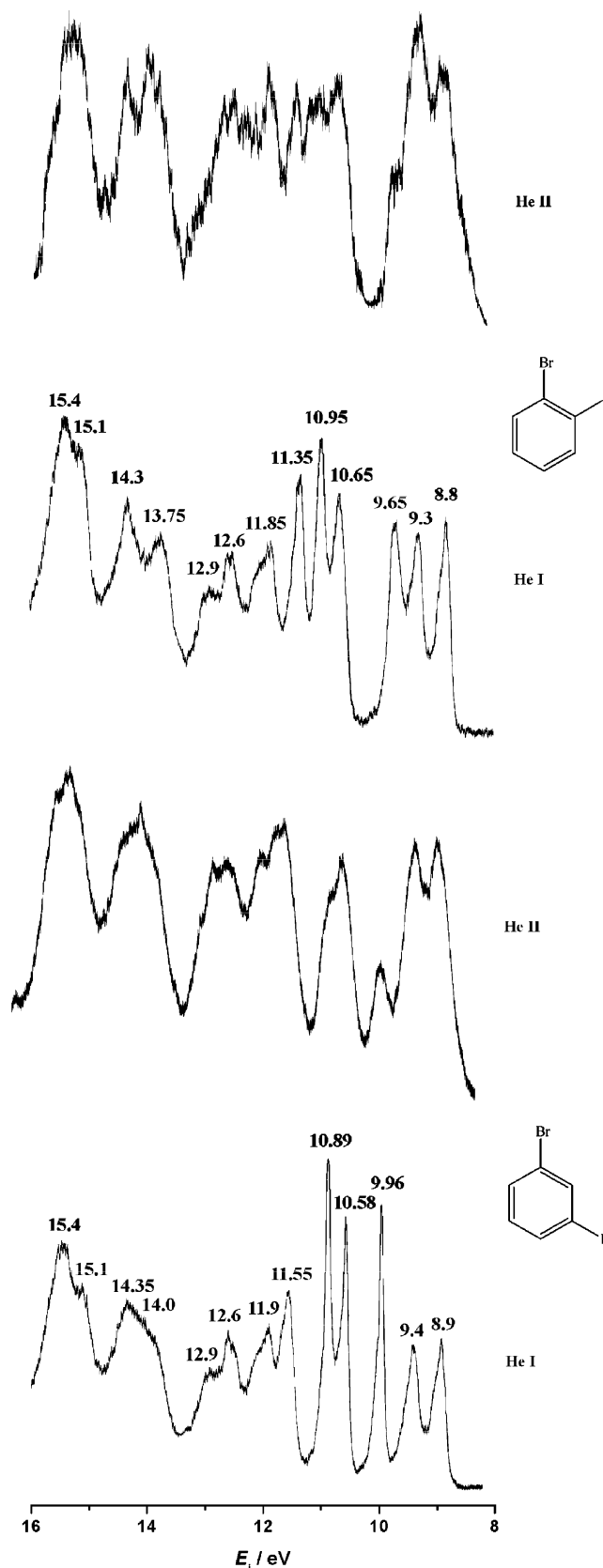


Figure 4. Photoelectron spectra of 7 (top) and 8 (bottom).

(1) The lone pair ionization bands of bromine and iodine are split into pairs by SOC, but the magnitude of the effect is insufficient to obliterate the validity of the in-plane and out-of-plane description. In other words, the SOC does not require the use of double groups for describing and classifying lone pair ionizations as is the case in haloethynes.<sup>14</sup>



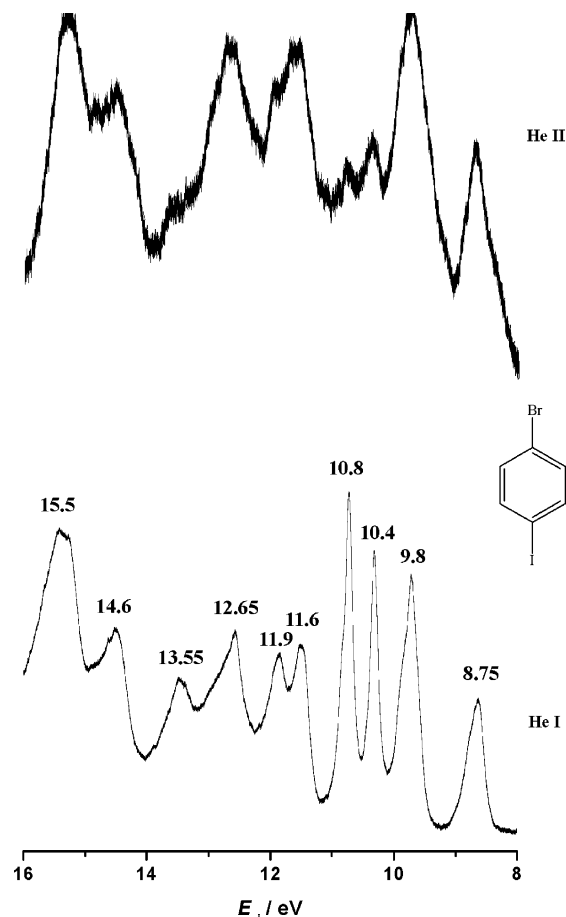


Figure 5. Photoelectron spectra of **9**.

(2) SOC affects bromine and iodine lone pairs, but not chlorine lone pairs or  $\pi$  orbitals. SOC has the same magnitude in all  $C_6H_4XY$  isomers.

We have calculated the following descriptors of substituent effects,  $\Delta n = n(\text{II}) - n(\perp)$ ,  $\Delta\pi = \pi_3 - \pi_2$ ,  $\langle\pi\rangle = 1/2(\pi_3 + \pi_2)$ ,  $\langle n \rangle = 1/2[n(\text{II}) - n(\perp)]$ , from pertinent ionization energies and listed them in Table 2.

The R-effect involves conjugation between  $n_\perp$  and  $\pi$  orbitals. The consequence of this interaction between two fully occupied

orbitals is the destabilization of the  $\pi$  orbital (decrease in ionization energy) and stabilization of the  $n_\perp$  orbital (increase in ionization energy).

The I-effect involves electron density transfer toward halogen (either from the  $\pi$  system or within the C–X bond). As a result the ring becomes more positive and the halogen atom more negative. This leads to stabilization of MOs of benzene and destabilization of halogen lone pairs. It is for this reason that, e.g.,  $\langle\pi\rangle$  values in bromochlorobenzenes are lower than in benzene itself (Table 2). The R-effect and I-effect are antagonistic and induce opposite changes in orbital energy levels as indicated in Table 3. The I-effect does not (in the first approximation) affect  $\Delta n$  values, but it does affect  $\Delta\pi$ . Since electronegativities of Cl, Br, and I decrease along the sequence  $\text{Cl} > \text{Br} > \text{I}$ , one may expect “competition” for electron density to take place. This is indeed the case as can be seen, for example, by comparing average  $\langle n_{\text{Cl}} \rangle$  values in all bromochloro- and chloriodobenzenes. The value for the former group is 11.94 eV and for the latter 11.67 eV. This illustrates how the chlorine atoms gain extra electron density from the less electronegative iodine and become destabilized as a result. The consequences of various substituent effects are summarized qualitatively in Table 3.

To unravel contributions of different substituent effects, we first analyze how  $\langle n \rangle$  and/or  $\Delta n$  values vary in different  $C_6H_4XY$  molecules. We compare  $\langle n \rangle$  and/or  $\Delta n$  in  $C_6H_4XY$  with reference to  $\langle n \rangle$  and  $\Delta n$  values in  $C_6H_5X$  and thus obviate the need to include the SOC effect explicitly. The graphical representation of ongoing interactions between lone pairs on halogen atoms X and Y is given in Scheme 2. Halogen X is more electronegative than halogen Y.

“In” and “out” signify in-plane and out-of-plane halogen lone pairs. Black arrows in Scheme 2 indicate mutual interaction (repulsion) of out-of-plane lone pairs localized on halogens X and Y which takes place via the  $\pi$  system. White arrows indicate possible through-space repulsion of in-plane lone pairs situated on halogens in the 1,2-positions.

The results show that there are two major types of variations in  $\langle n \rangle$  and  $\Delta n$  values. In the first case, which is the most common,  $\langle n \rangle$  or  $\Delta n$  values in  $C_6H_4XY$  increase relative to those in  $C_6H_5X$  and  $C_6H_5Y$ . Table 3 suggests that when  $\langle n \rangle$  or  $\Delta n$  increases for both halogens, the R-effect predominates over the

TABLE 2: Selected Energy Level Separations (eV) and Partial Charges ( $q$ ) in Halobenzenes

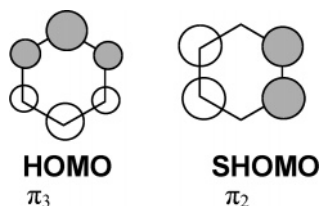
XY	$\langle\pi\rangle$	$\Delta\pi_{3-2}$	$\langle n_{\text{Br}} \rangle$ ( $q_{\text{Br}}$ )	$\Delta n_{\text{Br}}$	$\langle n_{\text{Cl}} \rangle$ ( $q_{\text{Cl}}$ )	$\Delta n_{\text{Cl}}$	$\langle n_{\text{I}} \rangle$ ( $q_{\text{I}}$ )	$\Delta n_{\text{I}}$
$C_6H_6$	9.25	0						
$C_6H_5\text{Br}$	9.31	0.64	10.92	0.60				
$C_6H_5\text{Cl}$	9.36	0.57			11.49	0.36		
$C_6H_5\text{I}$	9.11	0.71					10.15	0.81
1,2-Cl	9.36	0.56						
1,2-Br	9.24	0.50						
1,2-I	9.03	0.76						
1,2-BrCl	9.36	0.42	10.99 (0.090)	0.72	11.8 (0.024)	0.46		
1,2-BrI	9.05	0.50	11.15 (0.092)	0.40			10.15 (0.167)	1.0
1,2-ClI	9.08	0.55			11.63 (0.025)	0.35	10.20 (0.168)	0.90
1,3-Cl	9.42	0.56						
1,3-Br	9.31	0.52						
1,3-I	8.92	0.38						
1,3-BrCl	9.45	0.40	11.00 (0.068)	0.40	11.98 (0.005)	0.84		
1,3-BrI	9.15	0.50	11.22 (0.072)	0.66			10.27 (0.145)	0.62
1,3-ClI	9.18	0.55			11.70 (0.007)	0.60	10.30 (0.144)	0.70
1,4-Cl	9.41	0.87						
1,4-Br	9.35	0.90						
1,4-I	9.16	1.22						
1,4-BrCl	9.40	0.89	10.95 (0.064)	0.30	12.04 (0.002)	1.02		
1,4-BrI	9.28	1.05	11.20 (0.069)	0.80			10.10 (0.143)	0.60
1,4-ClI	9.23	0.93			11.69 (0.004)	0.43	10.14 (0.141)	0.68

TABLE 3: Substituent Effects Operating in Halobenzenes<sup>a</sup>

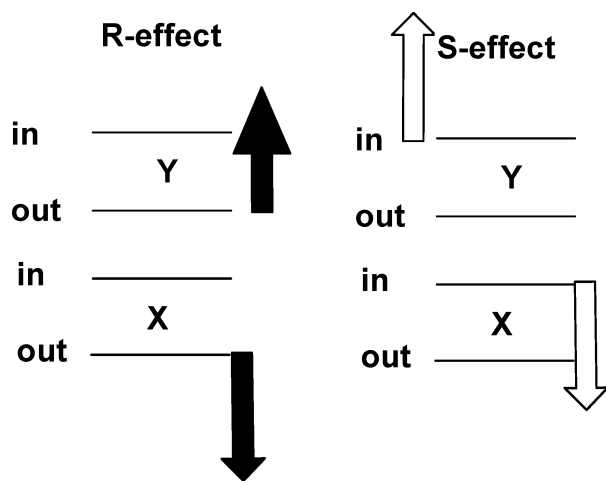
effect	$\langle\pi\rangle$	$\Delta\pi$	$\langle n\rangle$	$\Delta n$
R	<	>	>	>
I	>	<	<	$\approx$
SOC	$\approx$	$\approx$	$\approx$	>

<sup>a</sup> The symbols “>” and “<” designate an increase or a decrease in the ionization energy values of the orbitals due to the particular effect; “ $\approx$ ” designates no significant change due to the effect.

## SCHEME 1



## SCHEME 2



inductive one. In the second case, the increase takes place for the more electronegative of the two halogens, while a decrease is evident for the less electronegative halogen (e.g., in 1,4- $C_6H_4XY$  derivatives). The rationalization of this observation can be outlined by considering the shapes of the HOMO and SHOMO (Scheme 1).

In 1,4-dihalobenzenes the halogen lone pairs are strongly conjugated with the  $\pi_3$  orbital whose  $\pi$  electron density is very high at both the 1- and 4-positions. (The conjugation is not possible for the  $\pi_2$  orbital due to the position of the nodal plane.) The consequence is that X and Y lone pairs ( $n_\perp$ ) interact strongly via the  $\pi_3$  orbital relay, and as a result two  $n_\perp$  orbitals “repel” each other. This “repulsion” leads to a decrease in  $\langle n\rangle$  and  $\Delta n$  values for the less electronegative halogen and to an increase for the more electronegative one. In the 1,2- and 1,3- $C_6H_4XY$  derivatives on the other hand interhalogen interaction via  $\pi$  orbitals is weaker due to the fact that  $\pi$  electron densities at one of the 1,2- or 1,3-positions is either small or equal to zero. In 1,2- $C_6H_4ClI$  and 1,2- $C_6H_4BrI$  the trend is reversed; i.e., the  $\Delta n$  value increases for the less electronegative halogen and decreases for the more electronegative one. This can be rationalized by additional through-space repulsion (S-effect) between in-plane lone pairs of halogens in the neighboring 1,2-positions (Scheme 2). The absence of this effect in 1,2- $C_6H_4ClBr$  and its presence in 1,2- $C_6H_4BrI$  and 1,2- $C_6H_4ClI$  suggest that a large iodine atom is necessary for such repulsions. Similar repulsive through-space interaction was observed in 1,2-diiodobenzene some time ago.<sup>10</sup>

We consider next the behavior of  $\langle\pi\rangle$  and  $\Delta\pi$  values in  $C_6H_4XY$  derivatives (Table 2). The references for comparison are now  $\langle\pi\rangle$  and  $\Delta\pi$  values in  $C_6H_4X_2$  and  $C_6H_4Y_2$ .  $\langle\pi\rangle$  and  $\Delta\pi$  values for  $C_6H_4XY$  are either well within the range spanned by the reference points (i.e., well within  $C_6H_4X_2 \leftrightarrow C_6H_4Y_2$ ) or fall toward one of the boundaries of that range. Thus, the observation of  $\langle\pi\rangle$  and  $\Delta\pi$  values can tell us which halogen (X or Y) governs net ring-halogen interactions. For example, in  $C_6H_4ClBr$  isomers the  $\langle\pi\rangle$  values fall close to those of the corresponding  $C_6H_4Cl_2$  rather than  $C_6H_4Br_2$  isomer. This indicates that chlorine is the “dominant” halogen. In  $C_6H_4ClI$  and  $C_6H_4BrI$  isomers on the other hand,  $\langle\pi\rangle$  and  $\Delta\pi$  values are well within the  $C_6H_4X_2 \leftrightarrow C_6H_4Y_2$  range, so both halogens appear to participate equally in ring-halogen interactions. This effect is often found in 1,2- and 1,3-isomers. It can be attributed to the fact that the  $\pi$  orbital electron density at the ring site where one of the halogens is attached is much smaller than the density at the attachment site of the other halogen (Scheme 1).

## Summary

We have discussed the interplay of substituent effects in dihalobenzenes. The set of accurately measured ionization energies provides detailed insight into the nature and relative magnitude of the substituent effects in benzenes.<sup>16</sup> This empirically derived information complements the analysis based on theoretical calculations<sup>1,3</sup> which was focused on a single numerical descriptor (energy, electron density, or first ionization energy). For a molecule with two or more substituents, reliance on an empirically derived set of descriptor values, rather than on a single value of a single descriptor, may be necessary to account for the complexity of the effects.

**Supporting Information Available:** Coordinates of optimized geometries and total energies for mixed halobenzenes (PDF, DOC). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Bohm, S.; Exner, O. *J. Mol. Struct.: THEOCHEM* **2004**, 682, 171.
- (2) Domingo, L. R.; Perez, P.; Contreras, R. *J. Org. Chem.* **2003**, 68, 6060.
- (3) DiLabio, G. A.; Pratt, D. A.; Wright, J. S. *J. Org. Chem.* **2000**, 65, 2195.
- (4) Lichtenberger, D. L.; Copenhaver, A. S. *J. Electron Spectrosc. Relat. Phenom.* **1990**, 50, 335.
- (5) Yeh, J. *J. Atomic Calculation of Photoionization Cross-sections and Asymmetry Parameters*; Gordon and Breach: Langhorne, PA, 1993.
- (6) Padden Metzker, J. K.; Gruhn, N. E.; Lichtenberger, D. L. *J. Phys. Chem. A* **2002**, 106, 9999.
- (7) Gaussian 03, Revision B2: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.
- (8) Dolg, M. *Mol. Phys.* **1996**, 88, 1645.
- (9) Imura, K.; Kishimoto, N.; Ohno, K. *J. Phys. Chem. A* **2001**, 105, 4189.
- (10) Cvitaš, T.; Gusten, H.; Klasinc, L. *J. Chem. Soc., Perkin Trans. 2* **1977**, 962.
- (11) Cvitaš, T.; Klasinc, L. *Croat. Chem. Acta* **1977**, 50, 291.
- (12) Rušćić, B.; Klasinc, L.; Wolf, A.; Knop, J. V. *J. Phys. Chem.* **1981**, 85, 1486.
- (13) Novak, I.; Potts, A. W. *J. Phys. Chem. A* **1998**, 102, 3532.

(14) (a) Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* **1970**, 53, 331. (b) Haink, H. J.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* **1970**, 53, 1073.

(15) Brogli, F.; Heilbronner, E. *Helv. Chim. Acta* **1971**, 54, 1423.

(16) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, 16, 1.