Structure of the Benzene···ICl Complex: A UVPES and ab Initio Molecular Orbital Study[†]

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UVPES studies and ab initio and DFT computations have been done on the benzene···ICl complex; electron spectral data and computed orbital energies show that donor orbitals are stabilized and acceptor orbitals are destabilized due to complexation. Calculations predict an oblique structure for the complex in which the interacting site is a C═C bond center in the donor and iodine atom in the acceptor, in full agreement with earlier experimental reports. BSSE-corrected binding energies closely match the enthalpy of complexation reported, and the NBO analysis clearly reveals the involvement of the π orbital of benzene and the σ^* orbital of ICl in the complex.

Introduction

Benzene forms weak intermolecular complexes with small molecules such as HF, HCl, Cl_2, Br_2, I_2, and H_2O, and the structure of these complexes has been a fascinating problem for over 50 years. Several experimental techniques[1−10] and theoretical methods[11−17] have been employed to investigate the energetics and structure of such complexes. While experimental studies have been conducted in condensed phases where complexes of different stoichiometries could exist, theoretical predictions have been made for isolated 1:1 complexes. Later, complexes isolated in a nitrogen matrix at 20 K were studied;[6,7] in this study, though, the matrix will have its effect on the complex structure, the influence is milder, and the complexes will be chiefly of 1:1 type.

Complexes of benzene with proton donors such as HF, HCl, and H_2O are mainly stabilized by hydrogen-bonding interactions, and they have been thoroughly studied. Benzene−halogen complexes are of donor−acceptor type, where π electrons of benzene are accepted into the σ^* orbital of halogens. These complexes have been well-known for a long time, but there are only few experimental[1−9,18] and theoretical reports[11−15] on them. Although such complexes appear to be very simple, their structure is still a matter of controversy. The small molecule, a halogen or an interhalogen as the case may be, can approach the benzene ring in different ways, leading to several stable conformations, namely, resting, axial, oblique, and so on. As π electrons of benzene lie above and below the ring plane, the approach of the halogen toward benzene in the ring plane is not favorable. This has been found to be true from electrostatic potential map of benzene as well as from the fact that there was no noticable steric inhibition of complex formation as the extent of methylation of the benzene ring increased.[19] Such different orientational possibilities result in a potential energy surface (PES) with several minima and saddles, and further these stationary points vary only very little in energy as the interaction is very weak. Mulliken[1,11] first proposed, on the basis of orbital symmetry argument and maximum Coulomb interaction, that the resting geometry was more stable than axial. In the resting geometry the halogen molecule is lying parallel to the benzene ring, and in the axial geometry the halogen molecule aligns with the C_6 axis of the benzene ring. The axial model was rejected, as it involved a lot of charge separation. Later Mulliken[12] suggested an oblique structure for the benzene−chlorine complex with one chlorine above one C═C bond. Hassel and Strømme[4] from the X-ray studies of benzene complexes with Cl_2 and Br_2 and Ferguson[5] from IR studies of benzene complexes with Br_2 and I_2 strongly argued for the axial structure for 1:1 benzene−halogen complexes. Fredin and Nelander[6,7] studied the IR spectra of benzene complexes with Cl_2, Br_2, I_2, and ICl in a nitrogen matrix at 20 K and UV spectrum of the benzene−iodine complex in a nitrogen matrix and concluded that the benzene−iodine complex has axial geometry, while all other halogen complexes have oblique structure with the halogen molecule mainly interacting with one of the C═C double bonds. Their argument mainly relied on the activity of the most forbidden fundamentals in the IR spectra of the complexes. Engdahl and Nelander[8] analyzed the IR and visible spectra of the benzene−iodine complex in solid matrixes and confirmed the axial structure for the complex.

Iodine monochloride is the strongest acceptor of the halogen/interhalogen group, and the iodine atom is the best coordination site for an electron donor, as chlorine is substantially more electronegative than iodine.[3] UV,[2,19] IR,[6] X-ray,[3] and thermochemical[20] studies of the benzene···ICl complex have been done, and all of them point out that this complex is the strongest among the benzene−halogen/interhalogen complexes known and in the complex ICl takes up unsymmetrical orientation with the iodine atom near the donor. A report[6] on the benzene···ICl complex in a nitrogen matrix at 20 K suggests two possible conformers for the complex. Despite the several reports mentioned above, the structure of the benzene···ICl complex still remains inconclusive, and therefore we investigate the energetics, structure, and interaction at the orbital level of this complex using UVPES and ab initio MO calculations. This is the first theoretical report on the benzene···ICl complex, and for the first time electron spectroscopy is used to study a benzene−interhalogen complex. Ultraviolet photoelectron spectroscopy (UVPES) is a powerful tool to study weakly bound complexes in the gas phase,[21,22] but none of the investigations

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reported so far on benzene−halogen complexes, barring a recent report by us on the benzene−bromine complex,[9] have employed this technique. UVPES could give electron states of the complex and monomers, and therefore it could reveal the nature of interactions in the complex at the orbital level. UVPES in conjunction with results from molecular orbital (MO) calculations provides experimentally based pictures of valence orbital structures in the complex.[23] MO calculations provide information about the nature of bonding in the complex, the complexation energy, the amount of charge transfer from donor to acceptor, and so forth, and thus would be helpful to look at the interactions at the orbital level.

Experimental and Computational Details

Ultraviolet photoelectron spectroscopic measurements have been carried out employing a home-built spectrometer[24] consisting of a He I UV lamp, a 3-mm-diameter collision chamber, and a channeltron electron multiplier. Differential pumping allowed for operation of the He I lamp at 1.5 Torr, a sample pressure of 0.1−0.5 Torr, and a pressure of 5×10^{-5} Torr in the rest of the spectrometer. The resolution of the spectrometer is 60 meV at 6.06 eV (KE). Freshly distilled benzene and ICl have been taken in glass ampules and connected to the spectrometer by a variable leak valve. First, monomer spectra of benzene and ICl have been independantly obtained. The complex sample has been prepared in a glass vacuum system by co-condensation of the donor, and the acceptor in a glass bulb fitted with a Teflon valve. The glass bulb is gently warmed to about 50 °C and admitted into the spectrometer by means of a needle valve. Initially, the UVPES of only the benzene molecule has been observed. After, excess donor has been removed by continuous pumping, photoelectron spectra of both the monomers and the complex have appeared. Spectra have been recorded a number of times to establish the peak positions.

All computations have been performed with the Gaussian 94W program[25] implemented on a Pentium computer. As the resting geometry of the complex has already been ruled out from earlier studies on benzene−halogen complexes, we have considered only axial, oblique, and other possible models. Totally five geometries have been considered; C_{6v} complex (structure i in Figure 1) and four C_s complexes (structures ii−v in Figure 1). In the C_{6v} structure ICl aligns with the C_6 axis, and in C_s complexes described in Figure 1 (ii−v) ICl moves in a mirror plane that bisects the benzene ring and passes either through a pair of opposite carbon carbon bonds (ii and iii) or through a pair of opposite carbon atoms (iv and v). The geometries of the complexes have been fully optimized both at the Hartree−Fock (HF) level and with Moller−Plesset perturbation at the second term level (MP2) and also using density functional theory (DFT) with hybrid functionals within symmetry constraints. For all proposed geometries HF level calculations have been done with the 3-21G* basis set[26] (split valence and d functions added to I and Cl) and the LANL2DZ (D95 on first-row atoms,[27] Los Alamos ECP plus DZ on I and Cl[28]) basis, and MP2 calculations have been done with the 3-21G* basis set alone. DFT calculations have been done with the exchange potential of Becke and the correlation functional of Lee, Yang, and Parr (B3LYP) and the 3-21G* basis set. For structures iii and v calculations at the HF and MP2 levels with larger basis sets, denoted here as HW1 and HW2, have been performed additionally. By HW1 and HW2 we mean respectively 6-31G* and 6-311G* basis sets for the first-row and second-row atoms and the effective core potential of Hay and Wadt[28] for the iodine atom. Frequency calculations have been done to characterize the stationary points obtained through HF/3-21G* and B3LYP/3-21G* optimizations. The binding energies of the complex at different conformations have been corrected for basis set superposition error (BSSE). BSSE has been calculated using the counterpoise method[29] and applying a modification[30] that takes into consideration the energy effect due to the change of the monomer geometries upon complexation. Natural bond orbital (NBO) analysis[31] has been carried out for the selected stable conformations (iii and v) with the 3-21G* basis set at all the levels mentioned above.

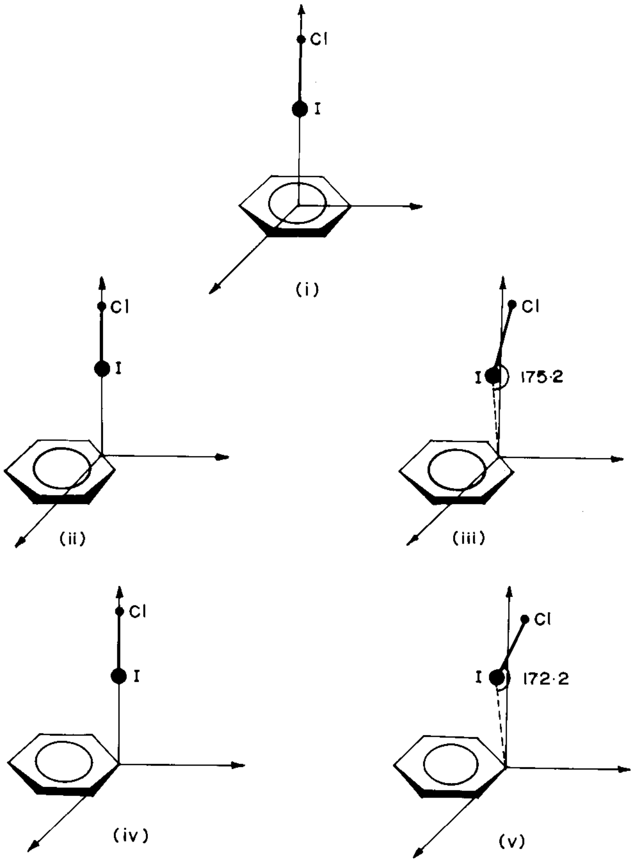

Figure 1. Different possible orientations of the benzene···ICl complex.

Results and Discussion

The interaction energies of the complex calculated at various levels, BSSE, counterpoise-corrected complex binding energies, and the number of imaginary frequencies obtained for each structure of the benzene···ICl complex at selected levels are presented in Table 1. Selected structural parameters of the monomers and the complex (structures iii and v) are given in Table 2. For the discussion of structural parameters, orbital occupancies, and orbital energies of the complexes and monomers, results from all electron basis set (3-21G*) calculations alone have been considered. Occupancies of the interacting orbitals, quantum of charge transferred, and the second-order perturbation energy lowering due to the interaction of the donor and the acceptor orbitals $\Delta E^{(2)}$ calculated at various levels are summarized in Table 3. Computed orbital energies $(-\epsilon)$ at various levels and the vertical ionization energies (I) obtained from UVPES are presented in Table 4. In Figure 1 various structures (i−v) of the benzene···ICl complex are shown. In Figure 2 the He I photoelectron spectra of benzne, ICl, and their complexes are shown.

He I Spectra of the Benzene···ICl Complex

He I photoelectron spectra of benzene, ICl, and their complex show the following: ICl exhibits features at 10.2, 10.8, 12.65,

TABLE 1: Complexation Energies ΔE_b, BSSE, Counterpoise-Corrected Interaction Energies ΔE_b^{cp} (kcal/mol), and Number of Imaginary Frequencies (n_i) for the Benzene···ICl Complex

		structure		
level	parameter	I	iii	v
HF/3-21G*	ΔE_b	3.43	4.17	4.17
	BSSE	1.74	2.12	2.14
	ΔE_b^{cp}	1.69	2.05	2.03
	n_i	2	1	0
DFT/3-21G*	ΔE_b	3.69	6.61	6.51
	BSSE	2.60	3.97	4.03
	ΔE_b^{cp}	1.09	2.64	2.48
	n_i	2	0	0
MP2/3-21G*	ΔE_b	6.01	8.05	8.05
	BSSE	3.49	4.86	4.88
	ΔE_b^{cp}	2.52	3.19	3.17
HF/LANL2DZ	ΔE_b	1.66	1.98	1.98
	BSSE	0.09	0.19	0.19
	ΔE_b^{cp}	1.57	1.79	1.79
HF/HW1	ΔE_b		2.81	2.82
	BSSE		0.74	0.75
	ΔE_b^{cp}		2.07	2.07
HF/HW2	ΔE_b		2.36	2.36
	BSSE		0.39	0.40
	ΔE_b^{cp}		1.97	1.96
MP2/HW1	ΔE_b		7.44	7.43
	BSSE		2.53	2.54
	ΔE_b^{cp}		4.91	4.89
MP2/HW2	ΔE_b		7.26	7.25
	BSSE		2.63	2.64
	ΔE_b^{cp}		4.63	4.61

TABLE 2: Selected Structural Parameters for the Monomer (ICl) and Complexes iii and v Calculated at Various Levels. Values Given in Parentheses Are for Structure v

molecule	parameter[a]	HF/3-21G*	DFT/3-21G*	MP2/3-21G*
ICl	R_{ICl}[b]	2.358	2.387	2.373
benzene···ICl	R_{ICl}	2.372	2.428	2.402
		(2.372)	(2.428)	(2.401)
	$R_{X\cdots I}$[c]	3.362	3.011	3.027
		(3.349)	(2.989)	(3.018)
	$\theta_{X\cdots I-Cl}$[c]	175.2	174.6	177.5
		(172.2)	(172.4)	(174.3)

[a] Bond lengths in angstroms and bond angles in degrees. [b] Experimental ICl bond length is 2.321 Å (ref: Robert, E. W. Jr.; William, W. C., III. *J. Chem. Phys.* **1980**, *72*, 4946). [c] X denotes the center of the C=C bond in iii and the carbon atom in v.

and 14.2 eV. The first two peaks are due to the spin−orbit split π molecular orbitals of iodine. The next peak at 12.65 eV corresponds to the π molecular orbital of chlorine, and the remaining peak at 14.2 eV corresponds to the σ molecular orbital of ICl. Benzene has a characteristic band at 9.25 eV due to the ionization of the $\pi_{C=C}$ MO, which is doubly degenerate. The second peak at 11.53 eV is from the σ_{C-H} MO, which is also doubly degenerate. The remaining peaks at 12.23, 13.72, and 14.49 eV correspond to $\pi_{C=C}$, σ_{C-H}, and σ_{C-C} MOs, respectively. These values match well with those reported in the literature.[32] The photoelectron spectrum of the complex shown in Figure 2 is different from that of benzene and ICl with additional peaks at 9.50, 9.75, 10.40, 11.75, and 12.5 eV. The presence of both monomer and complex peaks in the complex spectra is the proof for the existence of the complex in equilibrium with the monomers. Ab initio MO calculations have been used to assign these peaks and to understand the nature of interactions in the intermolecular complex.

Potential Energy Surface

Benzene forms a weak intermolecular charge-transfer complex with ICl in which π electrons of benzene are donated into the σ^* orbital of ICl. Theoretically there are many orientational possibilities for the monomers in the complex. As the complexation involves π orbitals of benzene and the σ^* orbital of ICl, the approach of ICl has to be naturally from above, with the iodine atom pointing vertically downward toward the benzene plane. In such an approach ICl can point toward the ring center (axial) or a bond center or a carbon atom. In each of these approaches the ICl can take up a vertical or oblique orientation. Besides these, there are other structures, namely, resting model, and so forth, and they are discounted as less favorable on the basis of electrostatics. The potential energy surface (PES) of the benzene···ICl complex has been scanned choosing the above six structures. Calculations show that there are three stationary points on the PES corresponding to structures I, iii, and v. The structure with oblique orientation of ICl on the C_6 axis of benzene converged on structure i, and the structures ii and iv converged on structures iii and v, respectively. Frequency calculations at the Hartree−Fock level show that the axial structure i is a second-order saddle, the struture iii has one imaginary frequency (9.37 cm^{-1}), and only v is the stable structure (Table 1). As the imaginary frequency for structure iii was too low and its interaction energy was the highest, the frequency calculations were done at the B3LYP/3-21G* level to check if structure iii is really a first-order saddle. DFT calculations revealed that it is a minimum. From the complexation energies (Table 1) one can conclude that the bond-center-oriented structure (iii) is more stable than the atom-center-oriented structure (v). This is in total agreement with the structure reported by Fredin and Nelander[6] on the basis of the IR spectral studies of the benzene···ICl complex in a nitrogen matrix at 20 K. They have ruled out the axial structure (i) on the basis of the fact that almost all the fundamental vibrations of benzene appeared in the complex, and this could be a result of lowering of symmetry on complexation. They further stated

TABLE 3: Natural Bond Orbital Analysis for the Benzene···ICl Complex

			occupancy (au)		$\Delta E^{(2)}$ (kcal/mol)
molecule	level	q_{CT}	$\pi_{C=C}$	σ^*(ICl)	$\pi_{C=C}$, σ^*(ICl)
benzene···ICl (iii)	HF/3-21G*	0.023	1.667, 1.663, 1.663	0.022	5.35
	DFT/3-21G*	0.079	1.630, 1.664, 1.664	0.090	12.14
	MP2/3-21G*	0.048	1.658, 1.665, 1.665	0.051	13.59
benzene···ICl (v)	HF/3-21G*	0.024	1.662, 1.660, 1.655	0.023	4.29, 0.44
	DFT/3-21G*	0.083	1.629, 1.653, 1.642	0.091	9.36, 0.47
	MP2/3-21G*	0.049	1.651, 1.648, 1.656	0.051	10.72, 0.84
benzene	HF/3-21G*		1.666		
	DFT/3-21G*		1.666		
	MP2/3-21G*		1.666		
ICl	HF/3-21G*			0.001	
	DFT/3-21G*			0.000	
	MP2/3-21G*			0.001	

TABLE 4: Vertical Ionization Energies, Calculated Orbital Energies, and Assignments of Benzene, ICl, and the Complex

	$-\epsilon$ (eV)			
molecule	HF/3-21G*	MP2/3-21G*	*I* (eV)	assignment
benzene	9.22	9.12	9.25	$\pi_{C=C}$
	13.37	13.32	11.53	σ_{C-H}
	13.83	13.59	12.23	$\pi_{C=C}$
	16.12	15.97	13.72	σ_{C-H}
	16.99	16.75	14.49	σ_{C-C}
ICl	10.45	10.47	10.20, 10.80	n_{π}(I)
	13.81	13.76	12.65	n_{π}(Cl)
	14.27	14.21	14.20	σ_{I-Cl}
benzene···ICl[a]	9.55, 9.68 (9.55, 9.68)	9.37, 9.65 (9.38, 9.65)	9.50	$\pi_{C=C}$
	10.11, 10.24 (10.11, 10.23)	10.04, 10.37 (10.04, 10.34)	9.75, 10.40	n_{π}(I)
	13.30, 13.31 (13.29, 13.30)	12.93, 12.95 (12.93, 12.95)	12.50	n_{π}(Cl)
	13.85, 13.87 (13.85, 13.87)	13.96, 14.00 (13.96, 14.01)	11.75	σ_{C-H}

[a] Orbital energies are given in the format iii (v).

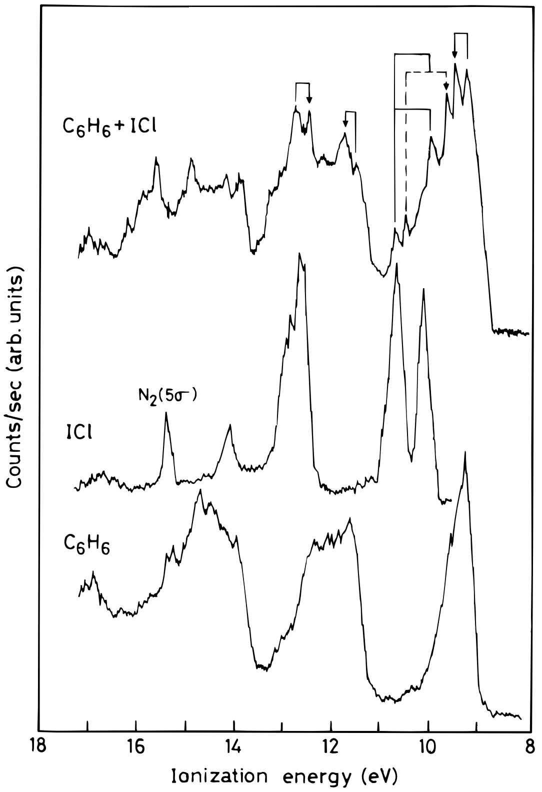

Figure 2. He I photoelectron spectra of benzene, ICl, and the benzene···ICl complex. Features due to the complex are marked by arrows.

that the ICl stretching region showed evidence for two isomeric 1:1 complexes. On this basis the authors suggested two possible oblique structures: one in which the symmetry plane passes through a pair of opposite C−C bonds and another in which the symmetry plane passes through a pair of opposite carbon atoms. Considering the symmetry elements of the active fundamentals, they concluded that ICl interacts mainly with one of the C═C bonds of the benzene ring. Our calculations also predict that only the two oblique structures are stable, and between the two, the bond-oblique structure iii is the most stable one, in full conformity with the above experimental facts. As structure v differs very little in energy over iii, both are considered for further analysis. For the same reason, computations have been done for these forms at the HF and MP2 levels with two higher level basis sets, HW1 and HW2, additionally.

Energetics and Structure

Complex binding energies listed in Table 1 show that the 3-21G* basis set overestimates it, but reasonable binding energies are obtained once the BSSE corrections are included. BSSE is found to be less for the LANL2DZ basis as well as for the HW1 and HW2 basis at the HF level. The LANL2DZ basis at the HF level gives lower binding energy compared to the 3-21G* basis. Corrected binding energies for structure iii are marginally higher over those of v, and in some cases, namely, HF/LANL2DZ and HF/HW1, both have exactly the same energy. The difference in the binding energy is the highest at the DFT level. Corrected binding energies of structures iii and v at the HF level appear to lie very closely, with the LANL2DZ value lying slightly lower. Inclusion of correlation corrections at the MP2 level shoots up the binding energy. DFT calculations with the B3LYP functional/3-21G* basis give 2.64 kcal/mol as the binding energy for structure iii, which exactly matches the experimental value of the enthalpy of complexation for the benzene···ICl complex, 2.53 ± 0.1 kcal/mol, reported by Drepaul and co-workers.[20] The benzene···ICl complex is also found to be stronger than the benzene···Br_2 complex, for which the enthalpy of formation is reported as 1.86 kcal/mol.[20]

On complexation, geometrical parameters of benzene are not altered much except small changes due to lowering of symmetry of the benzene from D_{6h} to C_s. Notable changes have been observed in the ICl unit, and the relevent parameters are listed in Table 2. As one would normally expect, the ICl bond undergoes elongation. The ICl bond lengths are almost the same in structures iii and v. MP2 and DFT calculations predict more weakening of the ICl bond over the HF calculation. As the interaction site X is a bond center in iii and a carbon atom in v, $R_{X\cdots I}$ and $\theta_{X\cdots I-Cl}$ values vary considerably for iii and v. Both MP2 and DFT calculations predict a closer $R_{X\cdots I}$ distance than the HF calculation, and this trend closely parallels the trend observed in binding energy. The X···I distance is shorter and the X···I−Cl angle is lower for iii than for v at all levels, and this is due to the fact that one carbon atom is directly involved in the interaction in structure v while the interaction is shared by two carbon atoms forming the C═C bond in iii.

Analysis of Interactions

Further understanding of the nature of interactions in the complex can be made by examining the shifts in the orbital energies and a change in the orbital occupancies of frontier molecular orbitals on complexation. NBO analysis is a powerful tool for obtaining such information and is used here. NBO analysis has been done on the optimized geometries of the complex for structures iii and v with the 3-21G* basis set at all the levels, and the data are presented in Table 3. The orbital occupancies and the $\Delta E^{(2)}$ values clearly indicate that the π orbital of benzene ($\pi_{C=C}$) and the antibonding orbital (σ^*) of ICl are mainly involved in the charge-transfer interaction. On complexation occupancies of the π orbitals of benzene decrease while those of the σ^* orbital of ICl increase, indicating charge transfer from benzene to ICl. q_{CT} values clearly show the quantum of charge transferred and are characteristic of a weak intermolecular charge-transfer complex. q_{CT} values and occupancy of the σ^* orbital of ICl are much closer for structures iii and v, while the occupancy of the π orbital changes slightly though. This is due to the fact that the donor interaction site varies in iii and v; it is a bond center in iii and an atom in v. In iii only one of the π orbitals of the benzene is involved, and therefore the occupancy of this interacting orbital is different from the other two. The picture is slightly different in the case of structure v, where the interacting site is a carbon atom. In this case one π bond is closer to the interacting site, while the other two π bonds are slightly farther and are not equidistant from the interaction site. This leads to a situation where one π bond is strongly interacting, another weakly interacting, and the third one very weakly interacting. This can be clearly seen from the three different π orbital occupancy values. $\Delta E^{(2)}$ values also indicate the dominant participation of a single π-bond orbital in structure iii and differential participation of two π orbitals in structure v. NBO analysis data at the MP2 and DFT levels predict the interaction to be relatively stronger, and this is in tune with the trend predicted in binding energy by all the methods employed.

The photoelectron spectra of the monomers and the complex give a clear picture of the electronic structure of the complex. The observed photoelectron spectra have been interpreted using ab initio orbital energies in conjunction with Koopmans' theorem.[33] Table 4 lists the computed orbital energies and vertical ionization energies obtained from UVPES. DFT orbital energies have not been compared here, as it is still not clear if DFT orbital energies could be compared in Koopmans' sense. However, Nyulászi and Veszprémi[34] have used DFT methods to assign photoelectron spectral peaks; they have not directly compared the DFT orbital energies, but they have calculated the ionization energies by computing the energies of the neutral molecules and their positive ions. The ordering of orbital energies calculated at the other two levels is consistent with the experimental ordering, although agreement in absolute values is good for ICl and moderate for benzene and the complex. Complex peaks are assigned as follows. The first peak at 9.50 eV corresponds to the $\pi_{C=C}$ orbital of benzene, and the next lying peaks at 9.75 and 10.4 eV are spin−orbit split n_π orbitals of iodine in the ICl unit. The peak at 11.75 corresponds to σ_{C-H} of benzene. The peak at 12.5 eV is due to the n_π orbital of the chlorine atom of ICl. Both orbital energies and vertical ionization energies show that, as expected, complexation stabilized the frontier MOs of the donor benzene by about 0.25 eV and destabilized those of acceptor ICl by about 0.4 eV. Complexation lowers the symmetry, and as a consequence the degeneracy of the π orbitals is lifted, as can be seen from the computed orbital energies.

Conclusions

UVPES studies and ab initio computations show that benzene forms a weak charge-transfer complex with ICl, and in the complex π electrons of benzene are donated into the σ^* orbital of ICl. Full geometry optimization at the HF/3-21G*, HF/LANL2DZ, MP2/3-21G*, and B3LYP/3-21G* levels reveals that there are three stationary points in the PES: one axial and two oblique structures. Frequency calculations at the HF/3-21G* and B3LYP/3-21G* levels confirm that the axial structure is a second-order saddle and other two are stable structures. BSSE-corrected complex binding energies of the stable structures reveal that the bond-oblique structure has the highest binding energy. Calculations with higher basis sets, HW1 and HW2, at HF and MP2 levels performed on oblique structures also confirm this. This is in excellent agreement with the available experimental reports based on IR spectral studies on the complex isolated in a nitrogen matrix at 20 K. MP2 and DFT calculations predict a stronger interaction in the complex. Complexation leads to lengthening of the ICl bond and lowers the symmetry; acceptor orbitals are destabilized and donor orbitals are stabilized. NBO analysis clearly shows that occupancies of benzene π orbitals decrease while that of σ^* of ICl increases, and this indicates the involvement of these orbitals in complexation.

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