

Inverse halogen bonds intermolecular interactions

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Received 15 November 2010; Accepted (in revised version) 13 December 2010
Published Online 28 March 2011

Abstract. A new number of inverse halogen bonds (IXBs) intermolecular interaction system of $Y-F \cdots DB_2$ ($D=C, N, O$ or S ; $B=O$ and S ; $Y=Cl$) have been investigated at B3LYP/6-311++g(d, p) computational level. According to the BSSE corrected interaction energy, it can be concluded that the stability of the five IXBs complexes of the $ClF \cdots DB_2$ system increases in the order of $ClF \cdots CS_2 < ClF \cdots CO_2 < ClF \cdots NO_2 < ClF \cdots O_3 < ClF \cdots SO_2$. Comparing the ClF monomer with ClF moiety of the complexes, the chemical shifts of F atoms all increased by a certain degree and presented a trend to downfield. This indicates that the electrons flow from ClF to DB_2 ($D=C, N, O$ or S ; $B=O$ or S) and the IXBs form between ClF and DB_2 .

PACS: 34.20.b, 31.15.ae

Key words: intermolecular interactions, inverse halogen bonds, electron density topological properties

1 Introduction

Intermolecular interaction plays an important role in the fields of physics, biology, chemistry and materials science. It has captured the interest of chemists for a long time and reports about its theory and experiment have been well presented [1–7]. It has been found that a lot of physical and chemical phenomena are closely related to the intermolecular weak interactions including hydrogen bond [8–10], π -cation [11], halogen bond (XB) [12–16], lithium bond [17–19], etc. Among these intermolecular interactions studied, halogen bond is an earlier and more extensively studied ones, and it is an interesting interaction analogous to hydrogen bond [20]. Halogen bonding is the noncovalent interaction between halogen atoms (Lewis acids) and neutral or anionic Lewis bases [21]. Most published works of XB are of

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the type $D \cdots X-Y$ ($Y=C, N$ or halogen) in which X , the situs of electron acceptor, is Lewis acid ($X=Cl, Br, I$ or F), and D ($D=O, S, N$ or π electron system), the situs of electron donor, is Lewis base.



Figure 1: The electron transfer directions.

In the XB aforementioned, the D ($D=O, S, N$ or π electron system) atom plays the role of electron donor for the XB systems, and X ($X=Cl, Br, I$ or F) atom plays the role of electron acceptor (Fig. 1(a)). Our question is if there is an inverse electron transfer direction in some special $D \cdots X-Y$ systems? To answer this question, we propose to study a new class of unconventional XB where the halogen atom will provide electrons and another non-halogen atom will accept them (inverse halogen bond (IXB), Fig. 1(b)). The term IXB is used for defining any noncovalent interaction involving halogens as electron donors.

Recently, the inverse hydrogen bonds (IHBs) between XeH_2 and hydride and fluoride derivatives of Li, Be, Na and Mg have been studied theoretically [22]. So, we are interested in knowing if there are any IXBs interactions, and how the interactions take place. And we consider a particular set of molecules formed by “donors” and “acceptors” of electrons as shown in Table 1, where F atoms in $Cl-F$ is electronically rich enough to provide electrons in the formation of a IXB, and D atoms in DB_2 ($D=C, N, O$ or $S, B=O$ or S) with electronically poor property are the halogen bond electron acceptors. Thus, given the absence of both experimental and theoretical studies on the inverse halogen bonds interactions of DB_2 with ClF , the present study reports the results of a DFT-B3LYP theoretical study on the nature of the mentioned interaction. In order to compare, the normal XBs, the $CH_3F \cdots DB_2$ ($D=C, N, O$ or $S; B=O$ or S) systems are also calculated.

2 Method and results

All possible geometries obtained by a full optimization on the surface of inverse halogen-bonded and normal halogen-bonded systems obtained at the B3LYP/6-311++g (*d,p*) computational level are depicted in Fig. 2. The equilibrium geometries of $ClF \cdots CS_2$ and $H_3C \cdots O_3$ were confirmed to be transition states by analytical frequency computations, and the other equilibrium geometries as minima. Some of the key geometrical parameters optimized for these complexes, stretching frequencies and interaction energies (δE_{CP}) with basis set superposition error (BSSE) corrections are gathered in Table 1.

It is found that for the $Cl-F \cdots DB_2$ and $H_3C-F \cdots DB_2$ systems the $Cl-F$ or $C-F$ bonds length (R) are elongated due to the formation of the inverse or normal halogen bonds. For the normal XBs of $H_3C-F \cdots DB_2$ system, this bond elongation leads to a red shift of the $C-F$ stretching

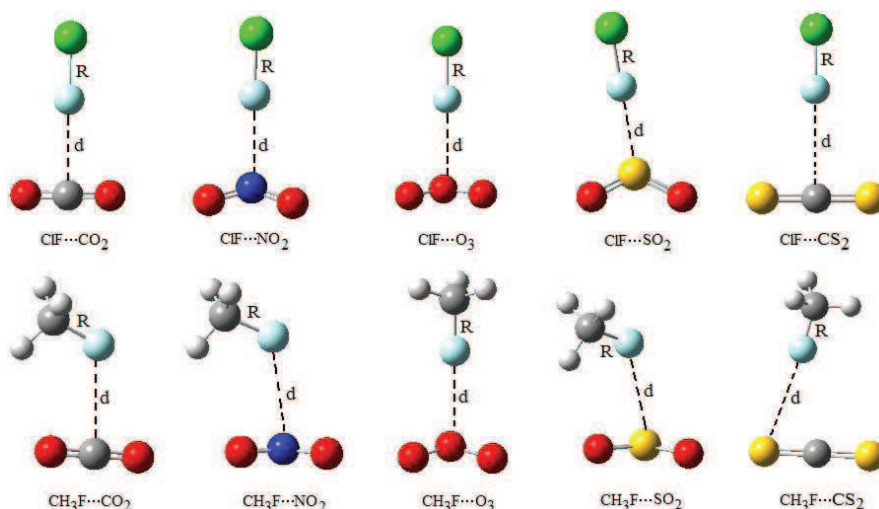


Figure 2: Geometries of the IXBs complexes (upper) and normal XBs (lower) calculated at B3LYP/6-311++g (d, p) computational levels.

Table 1: Bond lengths(\AA), stretching frequencies (ν , cm^{-1}) and interaction energies (ΔE , $\text{kJ}\cdot\text{mol}^{-1}$) of Y-F...DB₂ (D=C, N, O and S; B=O and S; Y=Cl and CH₃) at B3LYP/6-311++g (d, p) computational level.

Y-F	DB ₂	d	R	ΔR	ν	$\Delta\nu$	ΔE	BSSE	ΔE_{CP}
Cl-F	-	-	1.6788	-	739.69	-	-	-	-
	CO ₂	3.1101	1.6792	0.0004	741.73	+2.04	-2.10	+0.81	-1.29
	NO ₂	2.9268	1.6802	0.0014	737.24	-2.45	-2.73	+1.39	-1.34
	O ₃	2.97376	1.6792	0.0004	742.19	+2.50	-3.89	+2.39	-1.50
	SO ₂	3.04820	1.6825	0.0037	731.61	-8.08	-5.24	+1.94	-3.30
	CS ₂	3.62681	1.6789	0.0001	739.96	+0.27	-0.45	+0.56	+0.11
H ₃ C-F	-	-	1.3955	-	1033.40	-	-	-	-
	CO ₂	2.8835	1.4009	0.0054	1020.09	-13.31	-6.08	+0.11	-5.97
	NO ₂	2.9230	1.3998	0.0043	1022.45	-10.95	-5.48	+0.18	-5.30
	O ₃	2.8479	1.3985	0.0030	1025.86	-7.54	-6.27	+1.54	-4.73
	SO ₂	2.8575	1.4074	0.0119	1001.58	-31.82	-13.77	+1.83	-11.94
	CS ₂	3.9180	1.3954	0.0001	1032.96	-0.44	+0.07	-0.33	-0.26

frequency, and the maximum red-shifted value is 31.82 cm^{-1} for the $\text{H}_3\text{C-F}\cdots\text{SO}_2$ among the five complexes. However, in the case of the IXBs of $\text{Cl-F}\cdots\text{DB}_2$ system, the shifting tendency is not so clear, except for in $\text{Cl-F}\cdots\text{SO}_2$ and $\text{Cl-F}\cdots\text{NO}_2$ complexes, a weak un-normal blue shift of Cl-F stretching frequency was obtained with the Cl-F bond elongation. So, for the inverse halogen bond systems, the relation between the length variation of electron donor and its stretching frequency shift is complicated and different from the conventional halogen bond

system (Fig. 1(a)). [23] In addition, it is reported [24] that van der Waals radii of F, N, O and S atoms are 1.47, 1.55, 1.52 and 1.80 Å, respectively. And the van der Waals radii of C atom is 1.70 Å. Seen from Table 1, it is clear that, except for the complex related to CS₂, which could not be exactly regarded as IXB non-covalent interaction, these inverse halogen bonds non-covalent distances $d(\text{F}\cdots\text{D})$ are shorter than the sum of the relevant atomic van der Waals radii of F and D atoms. Further more, It should be noticed that the bond angles of Cl-F-D are all 180° in Cl-F \cdots DB₂ system, however, the feature of bond angles of C-F-D in normal XBs of H₃C-F \cdots DB₂ system are not so all.

The interaction energies data without (ΔE) and with (ΔE_{cp}) BSSE correction shown in Table 1 indicate that the electron donors, ClF and H₃CF are both weakly bound to DB₂, the electron acceptors. Especially, the interaction energies in ClF \cdots CS₂ and H₃CF \cdots CS₂ are close to null. Over all, the interaction energies of H₃CF \cdots DB₂ of the normal XBs system are larger than that of ClF \cdots DB₂ of the IXBs systems. The interaction energies with BSSE correction (ΔE_{cp}) is high to $-11.94 \text{ kJ}\cdot\text{mol}^{-1}$ between H₃CF and SO₂. It is easy find that the interaction energies are higher when SO₂ as the electron acceptor in ClF \cdots DB₂ system or H₃C-F \cdots DB₂ system. Here, according to the BSSE corrected interaction energy (ΔE_{CP}) calculated at B3LYP/6-311++g (*d,p*) level listed in Table 2, we can conclude that the stability of the five IXBs complexes of the ClF \cdots DB₂ system increases in the order of ClF \cdots CS₂ < ClF \cdots CO₂ \approx ClF \cdots NO₂ < ClF \cdots O₃ < ClF \cdots SO₂, that of H₃CF \cdots DB₂ system with normal XBs increases in the order of H₃CF \cdots CS₂ < H₃CF \cdots O₃ < H₃CF \cdots NO₂ < H₃CF \cdots CO₂ < H₃CF \cdots SO₂.

Table 2: Variations of the chemical shifts (δ , ppm) of F atoms upon complexation at the B3LYP/6-311++g (*d, p*) computational level.

Complexes \rightarrow Atoms \downarrow	ClF \cdots CO ₂	ClF \cdots NO ₂	ClF \cdots O ₃	ClF \cdots SO ₂	H ₃ CF \cdots CO ₂	H ₃ CF \cdots NO ₂	H ₃ CF \cdots O ₃	H ₃ CF \cdots SO ₂
F(620.8,460.0) ^a	627.2	627.2	631.8	634.4	455.0	455.2	455.0	440.0
Δ_F ^b	6.4	6.4	11.0	13.6	-5.0	-5.2	-5.0	-20.0

^a The absolute chemical shift of F atom in ClF is 620.8 ppm, and that of F atom in CH₃F is 460.0 ppm.

^b The variations of the chemical shift, $\Delta_F = \delta_{\text{complex}} - \delta_{\text{monomer}}$.

The electrons transfer direction is intensively related to the chemical shift. Variations of the chemical shifts (δ , ppm) of F atoms upon complexation at the B3LYP/6-311++g (*d, p*) computational level are listed in Table 2. Comparing the ClF monomer with ClF fragment of the complexes, the chemical shifts of F atoms in complexes all increased by a certain degree and presented a trend to downfield. This indicates that the electrons flow from ClF to DB₂ (D=C, N, O or S; B=O or S). It is thus clear that the IXBs formed between ClF and DB₂. On the contrary, comparing the H₃CF monomer with H₃CF moiety of the complexes, the chemical shifts of F atoms all decreased by a certain degree and presented a trend to upfield. This indicates that the electrons flow from H₃CF to DB₂ (D=C, N, O or S; B=O or S). So, the normal XBs formed between H₃CF and DB₂.

A topological analysis of the electron density was performed using Bader's theory of atom-in-molecules (AIM). Table 3 lists the electron density (ρ) at inverse halogen bond critical points (BCP) and its Laplacian of electron density ($\rho_{(r)}$) and ellipticities (ϵ). λ_i ($\lambda_1, \lambda_2, \lambda_3$)

listed in Table 3 are the eigenvalues of the electron density Hessian matrix, and $\nabla^2\rho(r) = \lambda_1 + \lambda_2 + \lambda_3$. From Table 3, we can see $\lambda_1 < 0$, $\lambda_2 < 0$, $\lambda_3 > 0$ in each complex, according to Bader's theory, [25] they can be labeled as (3, -1), this can indicate the presence of bond critical points (BCP) between the F atom and the D (D=C, N, O and S) atom. For example, for the F...S inverse halogen bond in ClF...SO₂, its $\rho(r)$ is 0.0081 a.u., and its $\nabla^2\rho(r)$ is 0.0334 a.u., respectively. It is noted that for H₃CF...CS₂ normal XB complex BCP located between F atom and S atom instead of F atom and C atom, this is probably the steric restriction of the two S atoms. As some examples, the electron density maps obtained for the IXBs of ClF...SO₂ and ClF...CS₂, and normal XBs of H₃CF...NO₂ and H₃CF...O₃ are shown in Fig. 3. Similar interactions of electrostatic nature have been described in the XeH₂...Na₂F₂ inverse hydrogen bond system. [8] The characteristics of the BCPs between the F atom and D (D=C, N, O and S) atom present small values of ρ and positive values of $\nabla^2\rho(r)$, this indicates that the charge density is in radiation at BCP and the inverse halogen bonds have more ionic property.

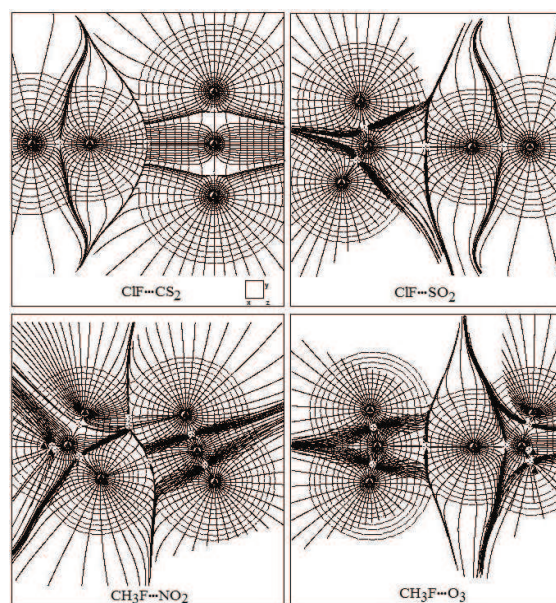


Figure 3: Electron density map of the partial IXBs complexes. Crosses (+) and triangles (▲) indicate the position of the bond and atomic critical points.

In order to further investigate the property of the IXBs in the present study, the ellipticities that are the measurement of σ or π property for the interacting atoms are given. The smaller value of ellipticity, the stronger σ property is, and otherwise the stronger π property is. The ellipticities of IXBs critical points in ClF...CS₂ and ClF...CO₂ are obviously larger than those of in the others IXBs complexes, and these of normal XBs critical points in H₃CF...CO₂ and H₃CF...CS₂ are also obviously larger than those of in the others normal XBs complexes. So

the covalent content of the IXBs of ClF...CS₂ and ClF...CO₂ complexes would mainly represent π property, and the same characteristic to the normal XBs systems of H₃CF...CO₂ and H₃CF...CS₂.

Table 3: The electron density topological properties at the IXB' critical points of the ten complexes.

Compound	Atom	$\rho(r)$	λ_1	λ_2	λ_3	$\nabla^2\rho(r)$	Ellipticity	Type
ClF...CO ₂	F...C	0.0036	-0.0028	-0.0009	0.0234	0.0197	2.1871	BCP
ClF...NO ₂	F...N	0.0059	-0.0047	-0.0046	0.0359	0.0266	0.0083	BCP
ClF...O ₃	F...O	0.0047	-0.0038	-0.0035	0.0303	0.0230	0.0957	BCP
ClF...SO ₂	F...S	0.0081	-0.0065	-0.0063	0.0462	0.0334	0.0446	BCP
ClF...CS ₂	F...C	0.0017	-0.0010	-0.0002	0.0093	0.0081	2.9122	BCP
H ₃ CF...CO ₂	F...C	0.0078	-0.0070	-0.0034	0.0459	0.0355	1.0712	BCP
H ₃ CF...NO ₂	F...N	0.0071	-0.0060	-0.0043	0.0416	0.0313	0.3947	BCP
H ₃ CF...O ₃	F...O	0.0067	-0.0055	-0.0052	0.0422	0.0315	0.0541	BCP
H ₃ CF...SO ₂	F...S	0.0137	-0.0119	-0.0114	0.0716	0.0483	0.0456	BCP
H ₃ CF...CS ₂	F...S	0.0015	-0.0009	-0.0003	0.0085	0.0073	1.4887	BCP

3 Conclusions

The inverse halogen bonds (IXBs) intermolecular interaction system of Y-F...DB₂ (D=C, N, O or S; B=O and S; Y=Cl) have been investigated at B3LYP/6-311++g (*d*, *p*) computational level. According to the BSSE corrected interaction energy (ΔE_{CP}), the stability of the five IXBs complexes of the ClF...DB₂ system increases in the order of ClF...CS₂ < ClF...CO₂ \approx ClF...NO₂ < ClF...O₃ < ClF...SO₂. Comparing the ClF monomer with ClF moiety of the complexes, the chemical shifts of F atoms all increased by a certain degree and presented a trend to downfield which indicates that the electrons flow from ClF to DB₂ (D=C, N, O or S; B=O or S) and the IXBs form between ClF and DB₂ when IXB complexes formed. The calculation on electron density topology properties indicates that the IXB interaction is mainly electrostatic, that is, IXB has more ionic property than covalent property.

Acknowledgments. This project is supported by "Qing Lan" Talent Engineering Funds of Tianshui Normal University and the National Natural Science Foundation of China under Grant No. 51063006.

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