

Study on the π Bond of Small Organic Molecules and Hydrogen Halide Interaction†

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We applied *ab initio* theoretical studies on the complex of C_2H_4 and HX, formed by $X-H\cdots\pi$, respectively. First, the monomers and complex were optimized at the MP2/cc-pVTZ level. Then, we regulated the BSSE and calculated the binding energy of different systems at the same level with the correction of BSSE by using counterpoise method at the MP2/aug-cc-pVTZ level. The results demonstrated that $C_2H_4\cdots HX$ ($X = F, Cl, Br, I$), with increasing halogen atomic number, from HF to HI, the bond length have all increasing, however, the binding energy of complex present in the overall decreasing trend.

Key Words: The weak intermolecular interaction, $X-H\cdots\pi$ interaction, Periodicity.

INTRODUCTION

Ethylene as the carbon-carbon double bonds in the most simple organic molecules and most typical π bond electron donor. The π bond of the monomer in the interaction with the hydrogen halide is a typical mutual $X-H\cdots\pi$ bond. Legon and Millen^{1,2}, by experimental and theoretical studies have shown that C_2H_4 and HF, HCl formation of the $X-H\cdots\pi$ bond complexes have a similar T-shape configuration (H-point to the π system in the center, HX bond π bond to form a vertical point C_{2v} symmetry $X-H\cdots\pi$ interaction structure). Herrebout *et al.*³ reported $C_2H_4\cdots HCl$ with C_{2v} symmetry. Oliveira *et al.*^{4,5} reported $C_2H_4\cdots 2HF$ three-body structure, studies have shown that the main compound is $H\cdots\pi$ bond and $FH\cdots F$ key synergies, leading to its present stable geometry of semi-circular structure. Carcabal *et al.*^{6,7} found that high-precision theoretical calculations and experimental results agree very well and explains the formation of T-shape type $C_2H_4\cdots HCl$ bond energy stronger than $C_2H_2\cdots HCl$ bond energy. Grabowski and others⁸ researchers found that optimizing the system is very complex electron transfer occurs, especially in: $\pi(C=C) \rightarrow \sigma^*(FH)$, $n(F) \rightarrow \sigma^*(FH)$ in the electron transfer is significant.

The $X-H\cdots\pi$ bond complexes in the theory and experiment have been more extensively studied⁹⁻¹¹. Mainly in the method of calculating the stable structures and the accurate calculation of interaction energy and $X-H\cdots\pi$ bond electron transfer and so on. The HX bond interactions with the π system of choice, mainly in the HF, HCl and π bond interaction study more, but

HBr, HI π bond interactions is less reported. It is necessary in the π bond of C_2H_4 and HBr, HI interaction $X-H\cdots\pi$ bond complexes in-depth research, figure out the combination to form complex and precise location of the structure to the system description and analysis of the π bond of C_2H_4 and HX ($X = F, Cl, Br, I$) interact to form the $X-H\cdots\pi$ bond cyclical variation.

EXPERIMENTAL

Research methods: As the interaction of C_2H_4 and HX is a weak interaction, requiring a higher accuracy of calculation, MP2 electron correlation correction methods and calculation results close to advanced methods of QCISD (geometry and energy)¹², so, we using the MP2 method to study the interaction of C_2H_4 and HX. Specifically: use cc-pVTZ basis set for complex geometric structure optimization, then use the aug-cc-pVTZ basis set and apply a balanced correction method to calculate the binding energy of composite system in the optimization and calculation of the heavy elements Br, I valence electrons with the same level of basis functions.

Models: As around the π bond electron cloud of the C_2H_4 molecules, which will contain all of C, H atoms in the same plane is similar to the geometry of space into the area on the lower interface make them up and down the area, HX may in the interface interact with C_2H_4 to formation of $X-H\cdots\pi$ bond complexes. So from the π bond upper and lower interface of the C_2H_4 molecule, we can add the HX molecules point to the mid-point of carbon-carbon double bonds in, for which we

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constructed C_2H_4 and HX ($X = F, Cl, Br, I$) to form the composite material system.

RESULTS AND DISCUSSION

Structural optimization: HF, HCl and C_2H_4 complex systems of molecular geometry of monomer and full freedom to optimize the energy gradient at the MP2/cc-pVTZ levels of theory; similarly, all monomers and complexes of HBr, HI and C_2H_4 were geometry optimized at the level of MP2/cc-pVTZ-pp. The results are follows as Table-1.

TABLE-1
GEOMETRICAL PARAMETERS FOR THE $C_2H_4 \cdots HX$ ($X = F, Cl, Br, I$) COMPLEX AT THE mp2/cc-pVTZ(-pp) LEVEL

Complex	R_{H-C}^a (Å)	R_{C-C}^a (Å)	R_{H-X}^a (Å)	$R_{X(H)-\pi}^a$ (Å)	$R_{X-\pi}^a$ (Å)	$\angle XH-\pi$ π^α (°)
$C_2H_4 \cdots HF$	1.081	1.336	0.926	2.138	3.064	90.00
$C_2H_4 \cdots HCl$	1.081	1.335	1.283	2.325	3.608	90.00
$C_2H_4 \cdots HBr$	1.081	1.335	1.410	2.341	3.751	90.00
$C_2H_4 \cdots HI$	1.081	1.334	1.605	2.461	4.067	90.00

^a $R_{X(H)-\pi}$, $R_{X-\pi}$ representing H, X in the HX atom to the distance of C=C bond; R_{H-C} , R_{C-C} , R_{H-X} represent the bond lengths of C=C, C-H in the C_2H_4 and HX, $\angle XH-\pi$ represents the angle formed by the HX to ethylene.

Table-1 summarized the complex geometry of $C_2H_4 \cdots HX$ ($X = F, Cl, Br, I$), from HF to HI, with the halogen elements in increasing atomic number, R_{C-C} , R_{H-C} bond length is almost unchanged, indicating the formation of complexes $C_2H_4 \cdots HX$ in little effect on the structure of ethylene. Fig. 1 and Table-1 shows that the R_{H-X} , $R_{(X)H-\pi}$, $R_{X-\pi}$ in the $C_2H_4 \cdots HX$ complexes from HF to HI, increasing remarkably, indicating the formation of X-H $\cdots\pi$ hydrogen bond structure of halogenated greater impact. $R_{(X)H-\pi}$ increased, HX to acetylene in the C=C bond distance increases, the X-H $\cdots\pi$ interaction weakened, which is consistent with the results of energy calculations, and comparative analysis of Fig. 1, R_{H-X} , $R_{(X)H-\pi}$ two values can be seen, the same trend, namely X-H $\cdots\pi$ bond interaction between the law as follows: $R_{I-H \cdots \pi} > R_{Br-H \cdots \pi} > R_{Cl-H \cdots \pi} > R_{F-H \cdots \pi}$, shows C_2H_4 and HX ($X = F, Cl, Br, I$) interact to form the X-H $\cdots\pi$ bond length periodicity changes, which major increase in atomic radius with halogen, HX polarization increases, and the role of π bond distance increases and less relevant interactions.

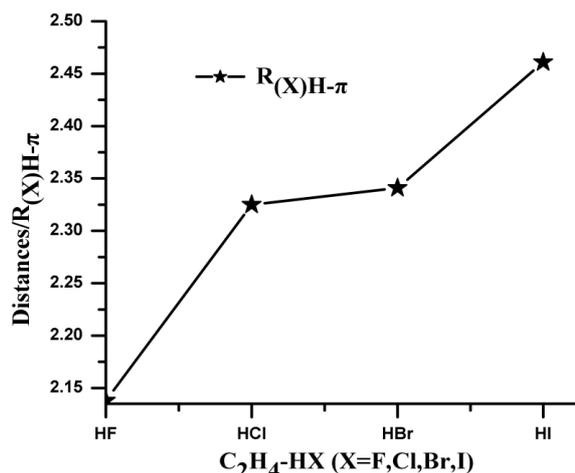
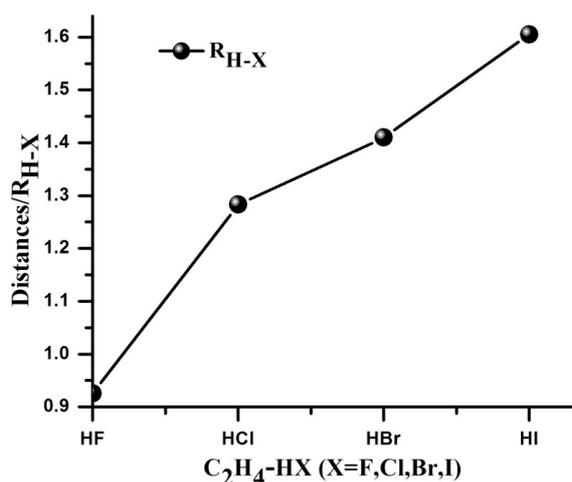


Fig. 1. Bond of $C_2H_4 \cdots HX$ (R_{H-X} , $R_{(X)H-\pi}$)/Å

All X-H ($X = F, Cl, Br, I$) bond in the $C_2H_4 \cdots HX$ complexes point to the π electron center in a straight line, HX molecule vertical point to the π bond, all the X-H $\cdots\pi$ bonds in the $C_2H_4 \cdots HX$ complexes have shown T-shape stable structures.

Energy calculation and comparison: $C_2H_4 \cdots HX$ ($X = F, Cl, Br, I$) on the basis of geometry had been optimized, then the binding energies calculated at the MP2/aug-cc-pVTZ level and with the full balance correction method CP of Boys and Bemardi correction BSSE; similarly, HBr, HI and C_2H_4 complexes formed system for binding energy calculations at the MP2/aug-cc-pVTZ-pp level (Table-2).

TABLE-2
INTERACTION ENERGIES OF $C_2H_4 \cdots HX$ ($X = F, Cl, Br, I$)

Complex	E (Hartree)	ΔE (kcal/mol)	ΔE^{CP} (kcal/mol)	BSSE (kcal/mol)
$C_2H_4 \cdots HF$	-178.753652	-5.177	-4.574	0.603
$C_2H_4 \cdots HCl$	-538.725892	-3.914	-3.377	0.537
$C_2H_4 \cdots HBr$	-494.793820	-4.843	-4.007	0.836
$C_2H_4 \cdots HI$	-373.911642	-4.040	-3.238	0.802

From Table-2 and Fig. 2, the binding energy ΔE^{CP} can be drawn: the binding energy of $C_2H_4 \cdots HX$ ($X = F, Cl$) is 3.377 Kcal/mol increase to 4.574 Kcal/mol; but for $X = Br, I$, the binding energy ΔE^{CP} from 4.007 Kcal/mol reduced to 3.238 Kcal/mol; BSSE correction from the relevant items to see, which value are close. As the heavy elements Br, I used the same level of valence basis functions, does not include the role of inner electrons of heavy elements, resulting in a phenomenon of the large binding energy of Br-H $\cdots\pi$, but the overall trends in terms of binding energy, ΔE and ΔE^{CP} are reduced. $X = F$, when the maximum binding energy value, indicating that the strongest bond of the C_2H_4 interaction with HF at this time; while $X = I$, the minimum binding energy value, indicating that the interaction between the two weakest at this time. The mainly reason is that: from the HF \rightarrow HI, with the atomic number increases, the acidity of hydrogen halides and the role of C_2H_4 in the π bond distance has increased significantly, leading to reduced interaction energy.

In summary, the π bond of C_2H_4 and HX in the formation of X-H $\cdots\pi$ bond system, in terms of complex geometry and on the binding energy aspects of study, with the halogen elements

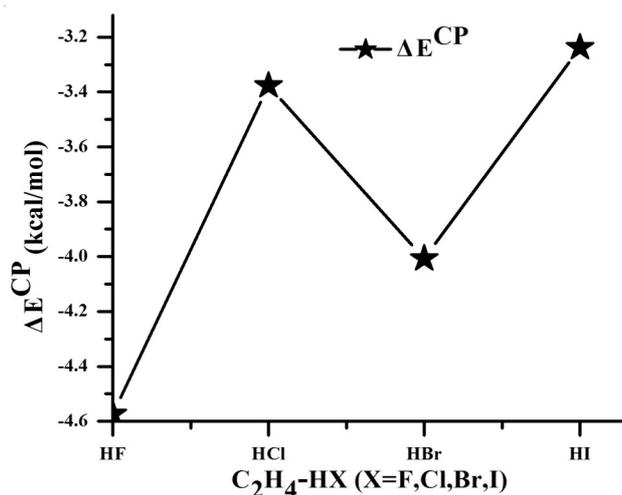


Fig. 2. Interaction energies of C₂H₄...HX (X = F, Cl, Br, I)

in increasing atomic number, the bond lengths show a periodicity increasing, while the binding energy show the general trend of decreasing.

Conclusion

Application of *ab initio* theory of the π bond of C₂H₄ and HX (X = F, Cl, Br, I) the formation of the X-H... π bond complex system are described and analyzed, the results show that the compound C₂H₄...HX (X = F, Cl, Br, I), with increasing halogen atomic number, bond length have also experienced a periodicity increase in binding energy on the whole the general trend showing decreasing.

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