

The Essential Law of π Bond Interaction of $C_2H_2 \cdots n(HX)$

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Abstract:

The current work is mainly focused on the geometrically stable configuration of $\pi \cdots (H-X)$ bond complex, the accurate calculation of the interaction energy of $\pi \cdots (H-X)$ bond, and the study of the essential characteristics of $\pi \cdots (H-X)$ bond such as the electron transfer situation and the analysis of the energy composition of $\pi \cdots (H-X)$ bond. In contrast, the important aspects of the essence of $\pi \cdots (H-X)$ bond in the complex formed by carbon-carbon triple bond ($-C\equiv C-$) and hydrogen halide are discussed at the electronic structure level. However, This paper report on the study of the maximum interaction capacity of π bond of $C_2H_2 \cdots (HX)_n$ ($n=1\sim 8, X=F, Cl, Br, I$) with multiple HX molecules by ab initio theoretical, the results demonstrated that $C_2H_2 \cdots n(HX)$, with increasing halogen atomic number, indicating that $\pi \cdots (H-X)$ bond in $C_2H_2 \cdots nHX$ complex have saturation property, and in the $n=6$ reach saturation state.

Keywords: Hydrogen halide molecules, Saturation, $\pi \cdots (H-X)$ bond, Binding energy.

I. INTRODUCTION

Acetylene, as the simplest monomer of alkynes, is also one of the most typical electron donors of π bond. The interaction between the π bond and a hydrogen halide is a typical $\pi \cdots (H-X)$ interaction. At present, the interaction of π bond in C_2H_2 and hydrogen halide to form $\pi \cdots (H-X)$ bond complex has been widely studied in theory and experiment [1-4]. As early as the 1980s, A-C Legon showed that the $\pi \cdots (H-X)$ bond complex formed by C_2H_2 , HF and HCl had similar T-shape configuration structure, and the results of the experiment and high-precision theoretical calculation were very consistent [1,5]. Dietrich Mootz in 1992 studied on 2-butyne $\cdots 2HCl$, 2-butyne $\cdots HCl$ formed by the interaction of $(Cl-H) \cdots \pi$ hydrogen bond. It is found that both of them can form stable geometry of T-shape, and HCl points vertically to the midpoint of carbon-carbon triple bond ($-C\equiv C-$), especially with two HCl molecules. Two HCl molecules are close to 2-butyne from both sides, forming the T-shape configuration complex [6]. B.G. Oliveira optimised and obtained stable $C_2H_2-2(HF)$ semicircle structure, and carried out the topological analysis. The results indicate that the main component of the complex is $H \cdots \pi$ bond, and

F-H $\cdots$ F-bond interaction results in a stable semi-circular geometry [7]. S J. Grabowski studied C₂H₂ $\cdots$ n (HF) and found that the optimised geometry of the complex showed a semi-circular structure. It was showed that there was a large electron transfer in the complex system, and there were two kinds of hydrogen bonds in the system, and weak C-H $\cdots$ F synergistic effect exists [8].

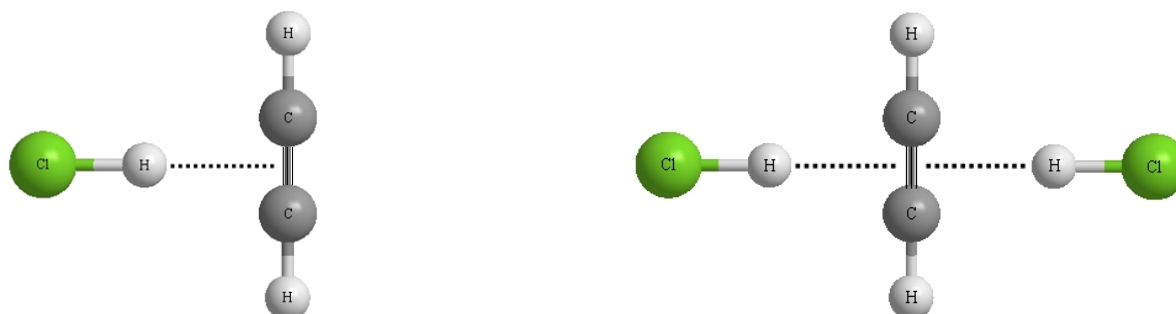
The current work is mainly focused on the geometrically stable configuration of $\pi\cdots$ (H-X) bond complex, the accurate calculation of the interaction energy of $\pi\cdots$ (H-X) bond, and the study of the essential characteristics of $\pi\cdots$ (H-X) bond such as the electron transfer situation and the analysis of the energy composition of $\pi\cdots$ (H-X) bond. In contrast, the important aspects of the essence of $\pi\cdots$ (H-X) bond in the complex formed by carbon-carbon triple bond (-C $\equiv$ C-) and hydrogen halide are discussed at the electronic structure level. However, there is no report on the study of the maximum interaction capacity of π bond with multiple HX molecules.

II. METHODS AND MODELS

MP2 method is used to study the weak interaction C₂H₂ $\cdots$ (HX)_n, and the structural parameters and binding energy of C₂H₂ and hydrogen halide complex are calculated and compared at the level of Dunning correlation consistent basis group. At the same time, the valence electron basis function of the same level is used for heavy elements Br and I in the process of geometric structure optimisation and energy calculation.

All the work and data in this paper are completed in the PC-Linux cluster parallel computing system of Guizhou Key Laboratory of high-performance computational chemistry by using the Gaussian 98 program [9].

Because the π bond of C₂H₂ molecule can interact with multiple hydrogen halides to form (H-X) $\cdots\pi$ bond complex in the straight line around the connecting nucleus, making multiple HX molecules point to the midpoint of (-C $\equiv$ C-) triple bond. To study whether the π bond of the acetylene molecule can reach the maximum interaction capacity of multiple HX molecules, the following seven models of C₂H₂ $\cdots$ n (HX) are constructed: as shown in Fig 1.



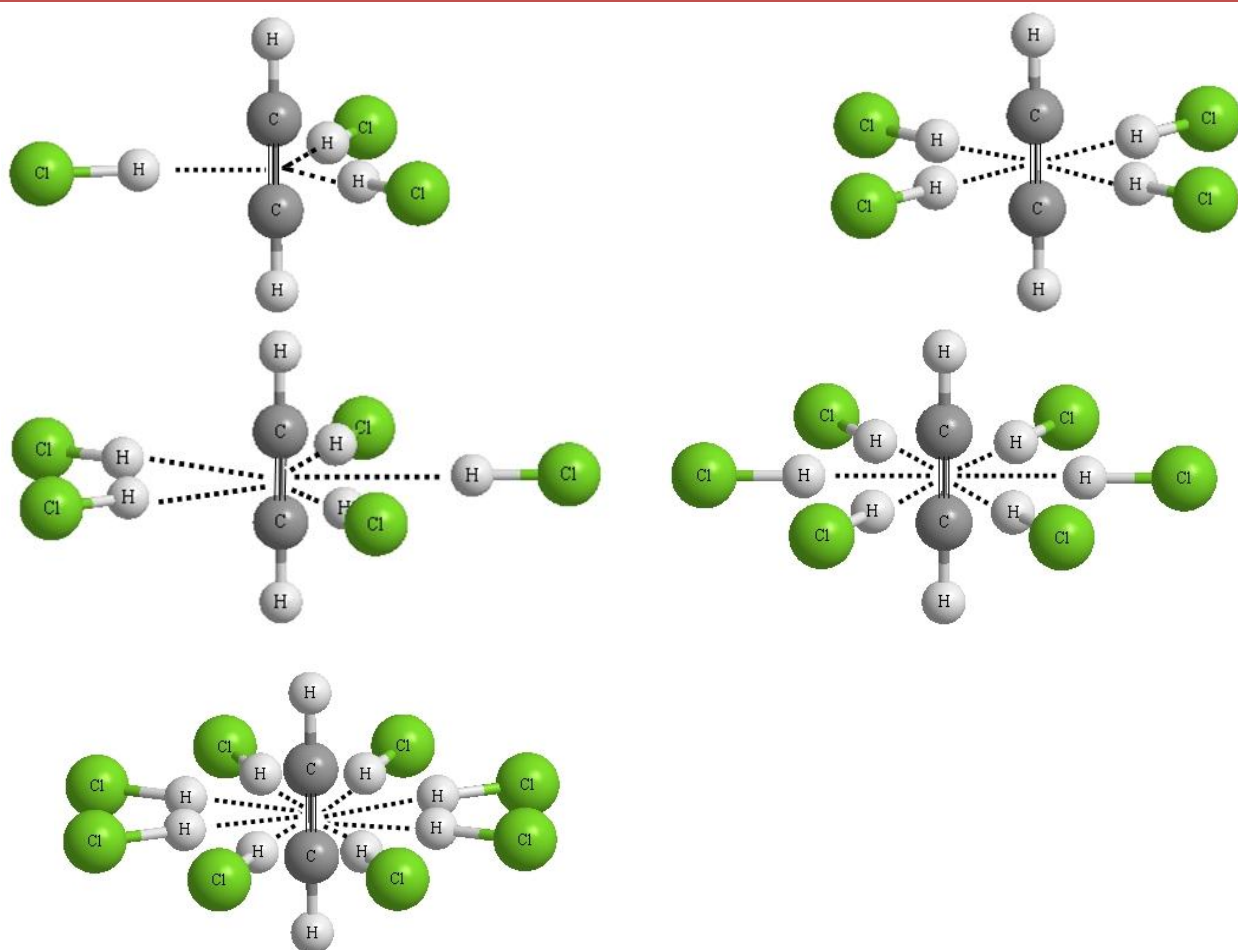


Fig 1: The structure of model $C_2H_2 \cdots nHX$ ($n=1 \sim 8$; $X=Cl$)

III. DATA ANALYSIS

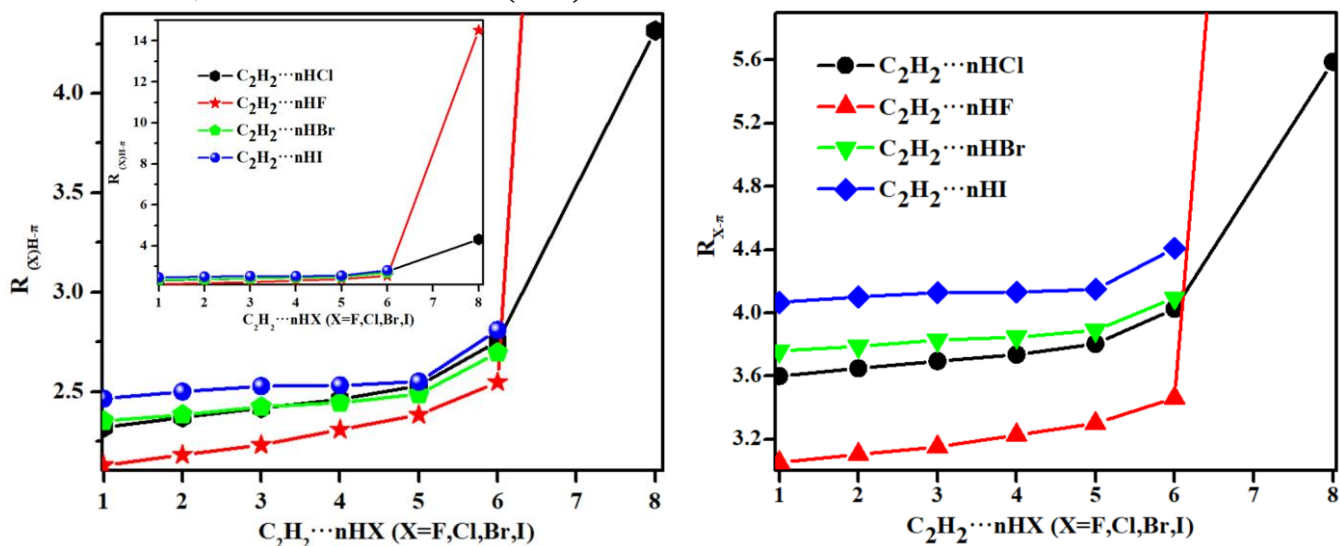
Structure optimization and discussion: at the MP2/cc-pvtz level, the molecular monomer and complex geometry of $C_2H_2 \cdots n(HX)$ system were optimized by full degree of freedom energy gradient, for heavy elements (-PP) was used. The calculation results are as follows:

TABLE I. $C_2H_2 \cdots n(HCl)$ Geometrical Parameters

Complex	$R_{H-C}^a / \text{\AA}$	$R_{C-C}^a / \text{\AA}$	$R_{H-X}^a / \text{\AA}$	$R_{(X)H-\pi}^a / \text{\AA}$	$R_{X-\pi}^a / \text{\AA}$	$\angle XH-\pi^a / ^\circ$
C_2H_2-HCl	1.063	1.213	1.281	2.319	3.600	90.00
C_2H_2-2HCl	1.064	1.214	1.279	2.370	3.649	90.00
C_2H_2-3HCl	1.065	1.215	1.277	2.417	3.695	90.00
C_2H_2-4HCl	1.065	1.215	1.276	2.461	3.737	90.00
C_2H_2-5HCl	1.066	1.216	1.275	2.530	3.804	90.00
C_2H_2-6HCl	1.066	1.216	1.273	2.753	4.026	90.00

C_2H_2-8HCl	1.063	1.213	1.272	4.317	5.589	90.00
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According to TABLE I, for the increase of hydrogen chloride, the bond length of R_{C-C} and R_{H-C} has almost no change, indicating that the formation of $C_2H_2 \cdots nHX$ complex has little effect on the structure of acetylene. By $C_2H_2 \cdots nHCl$, when $n = 8$, R_{H-C} and R_{C-C} are shorter than when $n = 6$, indicating that the π electricity of C_2H_2 increases and the $(H-X) \cdots \pi$ interaction weakens, which is consistent with the calculation results of energy. It can be seen from Fig 2 that for the increase of hydrogen chloride, $R_{(X)H-\pi}$, $R_{X \cdots \pi}$ increase, and the decrease of $(H-X) \cdots \pi$ indicates that the distance between HX in $C_2H_2 \cdots nHX$ and $C \equiv C$ bond in acetylene becomes longer, that is to say, the bond length of $(H-X) \cdots \pi$ bond increases with the increase of n value. It can be seen from the change of geometry that there is an obvious interaction between $C_2H_2 \cdots n(HX)$, and the interaction increases with the increase of n ($n \leq 6$). When $n \leq 6$, the bond length of $R_{X-\pi}$, $R_{(X)H-\pi}$ increases slightly, but when it increases to 8 HX , the bond length increases greatly, which indicates that when $n = 8$, due to the repulsion of HX molecular space, the interaction of $C_2H_2 \cdots n(HX)$ weakens, so that the bond length of $R_{X-\pi}$ becomes longer, especially the $R_{F-\pi}$ bond length of $C_2H_2 \cdots 8(HF)$ complex system has reached 15.43 Å, which further indicates that when $n = 8$, the bond length of the complex system has reached 15.43 Å. The interaction between HF and C_2H_2 is very weak, almost zero, because of the larger molecular radius of HBr and HI , HX has a strong interaction with C_2H_2 on the one hand, and on the other hand, has a suitable space to maintain a stable structure. When it is increased to 8 HX ($x = Br, I$) molecules, it cannot form a stable $(H-X) \cdots \pi$ interaction.



(a) The bond of $C_2H_2 \cdots nHX$ ($R_{(X)H-\pi}$)

(b) The bond of $C_2H_2 \cdots nHX$ ($R_{X-\pi}$)

Fig 2: The bond of $C_2H_2 \cdots nHX$ ($R_{(X)H-\pi}$, $R_{X-\pi}$)

It can be seen from Fig 2 that when the number of $n(HX)$ is the same, the bond length of the complex is as follows: $R_{I-H \cdots \pi} > R_{Br-H \cdots \pi} > R_{Cl-H \cdots \pi} > R_{F-H \cdots \pi}$, indicating that the bond length of $\pi \cdots (H-X)$ formed by the interaction of C_2H_2 and $n(HX)$ presents periodic change. The bond an-

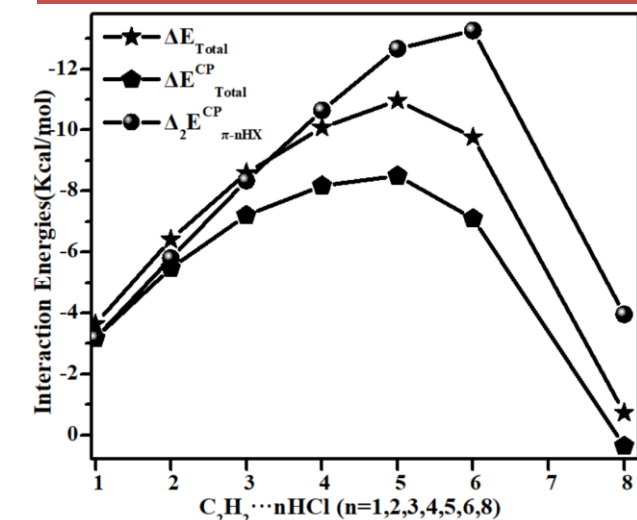
gle $\angle \text{XH}-\pi$ is 90.00° , that is to say, the HX molecule in $\text{C}_2\text{H}_2 \cdots n(\text{HX})$ complex points vertically to π bond, and the $\pi \cdots (\text{H}-\text{X})$ bond in $\text{C}_2\text{H}_2 \cdots n\text{HX}$ presents T-shape stable configuration.

Calculation and comparison of combined energy: Based on the optimised geometry, the binding energy of $\text{C}_2\text{H}_2 \cdots n(\text{HX})$ was calculated by MP2/aug-cc-pVTZ level, and BSSE was corrected by Boys and Bemardi's complete equilibrium correction CP. Similarly, the binding energy of $n\text{HBr}$, $n\text{HI}$ and C_2H_2 composite system was calculated by (-pp) level. The calculation results are as follows:

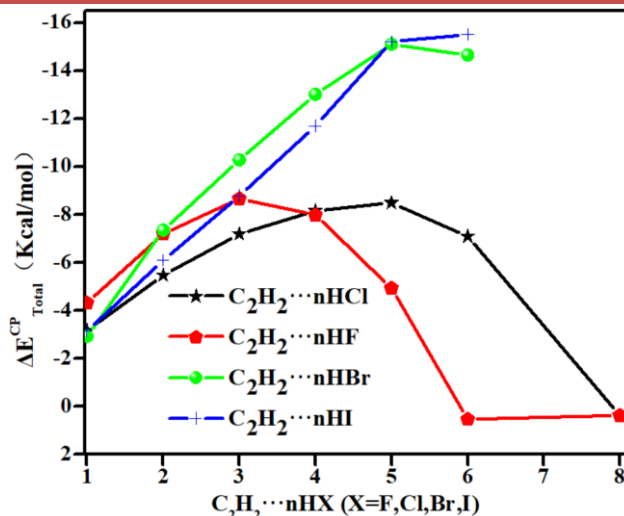
TABLE II. $\text{C}_2\text{H}_2 \cdots n(\text{HCl})$ Interaction Energies

Complex	E (Hartree)	ΔE (kcal/mol)	ΔE^{CP} (kcal/mol)	BSSE (kcal/mol)	$\Delta_2 E^{\text{CP}}_{\pi-n\text{HX}}$ (kcal/mol)
$\text{C}_2\text{H}_2 \cdots \text{HCl}$ 1	-537.48498 3	-3.638	-3.169	0.469	-3.169
$\text{C}_2\text{H}_2 \cdots 2\text{HCl}$ 3	-997.80452 3	-6.407	-5.472	0.935	-5.793
$\text{C}_2\text{H}_2 \cdots 3\text{HCl}$ 36	-1458.1231 36	-8.593	-7.195	1.398	-8.337
$\text{C}_2\text{H}_2 \cdots 4\text{HCl}$ 28	-1918.4406 28	-10.076	-8.169	1.907	-10.639
$\text{C}_2\text{H}_2 \cdots 5\text{HCl}$ 64	-2378.7571 64	-10.959	-8.499	2.460	-12.662
$\text{C}_2\text{H}_2 \cdots 6\text{HCl}$ 89	-2839.0703 89	-9.764	-7.091	2.673	-13.260
$\text{C}_2\text{H}_2 \cdots 8\text{HCl}$ 55	-3759.6862 55	-0.733	0.363	1.096	-3.949

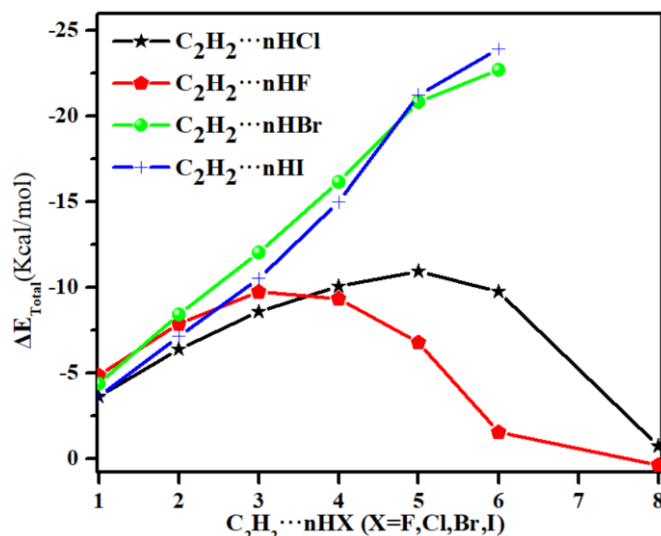
There are $\pi \cdots (\text{H}-\text{X})$ interaction and $n(\text{HX})$ interaction in $\text{C}_2\text{H}_2 \cdots n\text{HX}$ complex. Therefore, to investigate the maximum interaction ability of π bond and $n\text{HX}$ in C_2H_2 , we should consider not only the interaction and spatial structure between $n(\text{HX})$ molecules, but also the $\pi \cdots (\text{H}-\text{X})$ bond formed by $n(\text{HX})$ molecules and π system. $\Delta_2 E^{\text{CP}}_{\pi-n\text{HX}}$ represents the interaction energy of $\pi \cdots (\text{HX})_n$ formed by the unit $(\text{HX})_n$ composed of n halogenated hydrogen molecules corrected by BSSE and $\pi \cdots (\text{HX})_n$ formed by π system.



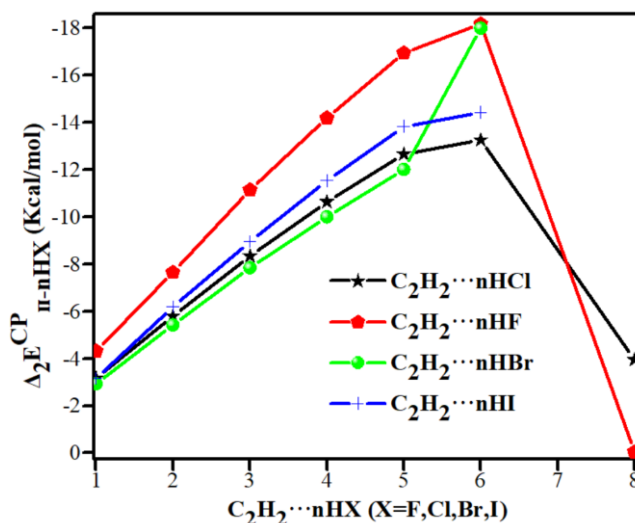
(a): Interaction energies of $C_2H_2 \cdots n(HX)$



(b): ΔE_{Total}^{CP} Interaction energies of $C_2H_2 \cdots n(HX)$



(c): ΔE_{Total} Interaction energies of $C_2H_2 \cdots n(HX)$



(d): $\Delta E_{\pi-nHX}^{CP}$ Interaction energies of $C_2H_2 \cdots n(HX)$

Fig 3: Interaction energies of $C_2H_2 \cdots n(HX)$

From the BSSE value in Table II, as the molecular number n ($n \leq 6$) of HCl increases, it gradually increases to 2.673 kcal/mol, indicating that the overlap error of the base group cannot be ignored. Combined with the calculated values of each binding energy given in Figure 3, it can be concluded that: as the values of $\Delta E_{\pi-nHX}^{CP}$ and ΔE_{Total}^{CP} are very close in general, but with the increase of n value, the difference is more obvious. On the one hand, it shows that the unit $(HX)_n$ and C_2H_2 is dominant in the summation of binding energy. On the other hand, it shows that the interaction between $n(HX)$ molecules cannot be ignored. With the increase of n value, this kind of interaction cannot be ignored. The interaction energy is also increasing. For

$C_2H_2 \cdots n(HX)$ ($x = F, Cl$), the interaction between $(HX)_n$ unit and C_2H_2 produces strong binding energy, which is from -3.169 to -18.179 kcal/mol, and the interaction energy increases with the increase of n ($n \leq 6$). When $n=6$, the interaction energy between the unit $(HX)_6$ and C_2H_2 is the largest, that is, the interaction between them is the strongest at this time, and the system with a large number of π bond attracting hydrogen halide and the strongest attraction ability. When $n=8$, the interaction energy of the unit $(HX)_8$ and C_2H_2 suddenly decreases. Because $R_{X-\pi}$ extends a lot, the distance between two the unit structures is very long. Although it is the system with the most number of π bonds attracting HX at this time, there is only weak interaction energy between them, indicating that the interaction between $(HX)_n$ and C_2H_2 has been limited at this time. When $n=6$, the difference between $\Delta_2E_{\pi-nHX}^{CP}$ and ΔE_{Total}^{CP} are the largest, which indicates that not only the interaction energy between the unit $(HX)_6$ and C_2H_2 is the largest, but also the interaction energy between HX in the unit $(HX)_6$ is the largest at a suitable distance, so the sum-up of the combined energy is mainly determined by the two interactions.

The maximum interaction ability between π bond and a hydrogen halide is determined mainly by the interaction energy $\Delta_2E_{\pi-nHX}^{CP}$ of the unit $(HX)_n$ and C_2H_2 , and the contribution of the interaction between HX molecules to summing up the energy ΔE_{Total}^{CP} is considered. Therefore, for $x=F, Cl$, with the increase of n ($n \leq 6$), $\Delta_2E_{\pi-nHX}^{CP}$ increases continuously. When $n=8$, ΔE_{Total}^{CP} decreases, which indicates that π bond in C_2H_2 molecule can bind to HX, but due to the limitation of its spatial structure, the binding energy ΔE_{Total}^{CP} increases first and then decreases. From the calculation results of binding energy in Figure 3, it can be seen that for $x=Br$, ΔE_{Total}^{CP} is larger than $\Delta_2E_{\pi-nHX}^{CP}$ in the system $x=I$, which may be caused by the strong interaction in $n(HBr)$ and $n(HI)$ units with the increase of atomic radius, which enhances the polarization between molecules, and the mutual attraction between HX molecules. The $\pi \cdots (H-X)$ bonds in $C_2H_2 \cdots 8(HBr)$ and $C_2H_2 \cdots 8(HI)$ with too large radii of Br and I atoms have been seriously deformed and can not form stable T-shaped structures, which shows that when $n = 6$, the maximum interaction ability of π bonds and multiple HX in C_2H_2 molecule has reached the limit.

IV. CONCLUSION

The $X-H \cdots \pi$ bond formed by $n(HX)$ and π bond in C_2H_2 is described and analyzed by ab initio calculation theory. The results show that the parameters of the $\pi \cdots (H-X)$ bond and the complex $C_2H_2 \cdots n(HX)$ system formed by π bond and HX in C_2H_2 are periodic with the increase of halogen atomic number, the binding energy increases when $n \leq 6$, and reaches the maximum when $n=6$. At this time, the maximum interaction ability of π bond in C_2H_2 molecule and multiple hydrogen halides has reached the limit, indicating that π bond in $C_2H_2 \cdots (HX)_n$ complex system can interact with six HX molecules at most to form $\pi \cdots (H-X)$ bond complex. The $\pi \cdots (H-X)$ bond of $C_2H_2 \cdots (HX)_n$ system is saturated and reaches the saturation state when $n=6$.

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