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# The Interaction of $C_2H_4\cdots(HX)_n$(n=4,X=F,Cl,Br,I) and $C_6H_6\cdots(HX)_n$(n=12,X=Cl)

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## ABSTRACT

We applied *ab initio* theoretical studies on the X-H···π bond complexes of $C_2H_4\cdots(HX)_n$(n=4,X=F,Cl,Br,I), and comparative analysis of the interaction capability of the π bond in the complexes of $C_2H_4\cdots4HCl$ and $C_6H_6\cdots(HX)_n$(n=12,X=Cl).The results demonstrated that, $C_2H_4\cdots(HX)_n$(n=4,X=F,Cl,Br,I) with increasing halogen atomic number, and the formation of X-H···π hydrogen bond structure of halogenated greater impact, the bond length have increasing in the overall, however, the binding energy of complex present in the overall decreasing trend. The corresponding X-H···π interactions weaken, two kinds of π bond system each HCl given small gap electron interaction capabilities, the π bond in the $C_6H_6$ molecule was stronger in the $C_2H_4$ molecule.

**Keywords:** *Ab initio theoretical, interaction, binding energy, hydrogen halide molecule, optimized geometry.*

## 1. INTRODUCTION

Recent years, there are many reports on the method of calculating the stable structures and the accurate calculation of the interaction of $C_2H_4$ $(HX)_n$(X=F,Cl;n=1-4) energy, and several electron transfer conditions and the electron density maps to analyze the topology, the study found optimized geometry of the resulting complexes are rendered semi-circular structure[1-2]. After we have been studied the $C_2H_4$ and $(HX)_n$(X=F,Cl,Br,I;n=1-3) interact to form the X-H···π bond complexes interaction. However, the π bond of $C_2H_4\cdots4HX$ cyclical variation has never reported. The topic on $C_6H_6\cdots$nHCl(n=1-12) complexes systems based on the research to continue in-depth study, not yet containing X-H···π bond interaction $C_2H_4\cdots4HX$ complex system structure and binding energy research reports, either no reports on the π bond in $C_2H_4\cdots4HCl$ or $C_6H_6\cdots12HCl$ complexes system strength of commitment interaction capabilities comparing[3-5].

## 2. EXPERIMENTAL SECTION

We using the MP2 method to study the interaction of $C_2H_4\cdots4HX$.The $C_2H_4$ molecules, which similar to the geometry of space into the area on the lower interface make them up and down the area, three hydrogen halide molecules may interact with from the π bond upper and lower interface of the $C_2H_4$ to formation of X-H···π bond complexes. So, we can add hydrogen halide molecule point to the mid-point of carbon-carbon double bonds, for which we constructed $C_2H_4\cdots4HX$ to form the composite material system. The structure of $C_2H_4\cdots4HX$ complexes shown in Figure 1:

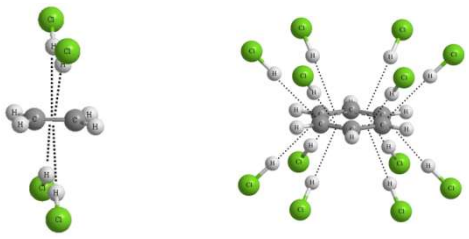

**Figure 1.** The structure of model $C_2H_4\cdots4HX$(X=Cl) and $C_6H_6\cdots12HCl$.

## 3. RESULTS SECTION

$C_2H_4\cdots4HX$(X=F,Cl) 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 $C_2H_4\cdots4HX$(X=Br,I) were geometry optimized at the level of MP2/cc-pVTZ-pp. The results are follows as Table 1.

**Table 1.** Geometrical Parameters for the $C_2H_4\cdots4HX$ complex**.**

| Complex | $R_{H-C}$/Å | $R_{C-C}$/Å | $R_{H-X}$/Å | $R_{(X)H-\pi}$/Å | $R_{X-\pi}$/Å |
|---|---|---|---|---|---|
| $C_2H_4\cdots4HF$ | 1.082 | 1.341 | 0.920 | 2.462 | 3.198 |
| $C_2H_4\cdots4HCl$ | 1.082 | 1.339 | 1.275 | 2.562 | 3.759 |
| $C_2H_4\cdots4HBr$ | 1.082 | 1.339 | 1.403 | 2.516 | 3.889 |
| $C_2H_4\cdots4HI$ | 1.082 | 1.338 | 1.601 | 2.611 | 4.172 |

Table 1 complex geometry can be seen:with the halogen elements in increasing atomic number, $R_{C-C}$, $R_{H-C}$ bond length of the $C_2H_4\cdots4HX$(X=F,Cl,Br,I) complexes is almost unchanged, indicating the formation of complexes $C_2H_4\cdots4HX$ in little effect on the structure of ethylene. $R_{H-X}$, $R_{X\cdots\pi}$ in the $C_2H_4\cdots4HX$ complexes increasing greatly, as $R_{I-H\cdots\pi}>R_{Br-H\cdots\pi}$ , $R_{Cl-H\cdots\pi}>R_{F-H\cdots\pi}$ ,indicating the formation of X-H···π hydrogen bond structure of halogenated greater impact, the X-H···π interaction weakened.

$C_2H_4\cdots4HX$(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, compared with the $C_6H_6\cdots12HCl$. The results are follows as Table 2.

**Table 2.** Interaction energies of $C_2H_4\cdots4HX$(X=F,Cl,Br,I).

| Complex | E (Hartree) | ΔE (Kcal/mol) | $\Delta E^{CP}$ (Kcal/mol) | BSSE (Kcal/mol) | $\Delta_2E^{CP}_{\pi\text{-}nHX}$ (Kcal/mol) |
|---|---|---|---|---|---|
| $C_2H_4\cdots4HF$ | -479.779095 | -6.947 | -5.568 | 1.379 | -10.903 |
| $C_2H_4\cdots4HCl$ | -1919.679574 | -9.118 | -7.083 | 2.035 | -9.763 |
| $C_2H_4\cdots4HBr$ | -1743.957734 | -16.881 | -11.245 | 5.636 | -12.759 |
| $C_2H_4\cdots4HI$ | -1260.433649 | -16.575 | -11.002 | 5.573 | -10.707 |
| $C_6H_6\cdots12HCl$ | -5755.565130 | -24.430 | -23.410 | 1.020 | -30.169 |

$\Delta_2E^{CP}_{\pi\text{-}nHX}$ represent that multiple-HX molecules composed of the unit $(HX)_n$ interact with the π system $C_2H_4$, $C_6H_6$ to formed $\pi\cdots(HX)_n$ interaction energy by BSSE correction. From Table 2,the binding energy $\Delta E^{CP}$ of $C_2H_4\cdots4HX$(X=F,Cl) is 7.083Kcal/mol reduced to 5.568Kcal/mol; and for X=Br,I, the binding energy $\Delta E^{CP}$ from 11.245Kcal/mol reduced to 11.002Kcal/mol; BSSE correction from the relevant items to see, with increasing halogen atomic number, which value are in the overall increasing. 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 $(Br\text{-}H)_4\cdots\pi$ and $(I\text{-}H)_4\cdots\pi$,but the overall trends in terms of binding energy.

ΔE and $\Delta E^{CP}$ are reduced. The mainly reason is that: with the atomic number increases, the acidity of hydrogen halides, and the π bond distance of $C_2H_4$ has increased significantly, leading to reduced interaction energy. The same trend of $\Delta_2E^{CP}_{\pi\text{-}4HX}$ and $\Delta E^{CP}$, the difference between the two instructions shows that two hydrogen halide molecules far apart, so the unit of two hydrogen halide molecules in order to attract the role of dominant.

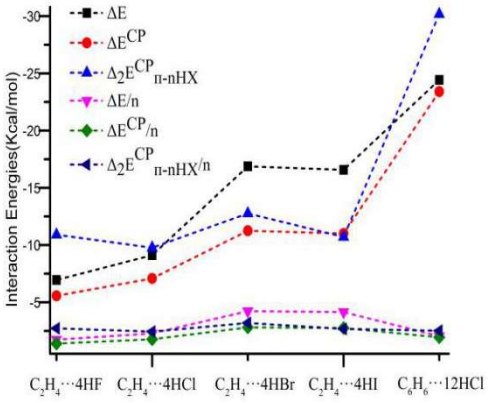


**Figure 2.** The Interaction energies of $C_2H_4\cdots4HX$(X=F,Cl,Br,I) and $C_6H_6\cdots12HCl$.

The π bond of $C_2H_4\cdots4HX$ system, in terms of complex geometry and on the binding energy aspects of study,the results show that the compound $C_2H_4\cdots4HX$ (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. The π bond $C_2H_4$ molecule at least interacting with four hydrogen halide molecules to formation of the X-H···π bond complex.

## 4. CONCLUSIONS

$C_2H_4\cdots4HX$ and $C_6H_6\cdots12HCl$, two π bond system, the binding energy of each π bond bears a comparative analysis of the interaction energy, and each ability HCl given a comparative analysis of the interaction: from the figure 2, the $\Delta E/n$,$\Delta E^{CP}/n$, $\Delta_2E^{CP}_{\pi\text{-}nHX}/n$ of system $C_2H_4\cdots4HX$ (X=F,Cl,Br,I), $C_6H_6\cdots12HCl$ have smaller gap between these data, illustrate two π bond systems given each HCl difference electron interaction capabilities small; for $(HX)_n$ unit and π system interaction energy, $C_6H_6\cdots12HCl$ system than $C_2H_4\cdots4HCl$ of ΔE,$\Delta E^{CP}$, $\Delta_2E^{CP}_{\pi\text{-}nHX}$ of system obviously much bigger, the HCl bond in the $C_6H_6$ molecule described give bigger interaction energy than $C_2H_4$ interaction; this is mainly due to the $C_6H_6$ molecule contains three large highly delocalized π bond, and $C_2H_4$ only has one π bond, thus providing the $C_6H_6$ molecule π bond maximum effect was stronger than $C_2H_4$ molecule.

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