



Interaction of $C_2H_4 \cdots (HX)_3$ ($X = F, Cl, Br, I$) and $C_6H_6 \cdots 3HCl$ †

JIE YANG*, SHAOBO LI, WEIWEI YAO, QIYI YIN, CHANGAN TIAN, JINSONG XIE and JUNSHENG LIU

Department of Chemical and Materials Engineering, Hefei University, JinXiu Avenue Road 99, Economic Technology Development Zone, Hefei 230601, Anhui Province, P.R. China

*Corresponding author: Tel: +86 551 2158510; E-mail: yangjo@hfu.edu.cn

Published online: 10 March 2014;

AJC-14841

We applied *ab initio* theoretical studies on the $X-H \cdots \pi$ bond complexes of $C_2H_4 \cdots 3HX$ ($X = F, Cl, Br, I$) and comparative analysis of the interaction capability of the π bond in the complexes of $C_2H_4 \cdots 3HCl$ and $C_6H_6 \cdots 3HCl$. The results demonstrated that, $C_2H_4 \cdots 3HX$ ($X = F, Cl, Br, I$) with increasing halogen atomic number, the bond length have all increasing. However, the binding energy of complex present in the overall decreasing trend. The corresponding $X-H \cdots \pi$ 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: Intermolecular interaction, π bond, $X-H \cdots \pi$ interaction.

INTRODUCTION

The π bond of the monomer in the interaction with hydrogen halide is a typical mutual $X-H \cdots \pi$ bond. The $X-H \cdots \pi$ bond complexes in the theory and experiment have been more extensively studied¹⁻⁴. There are many reports on the method of calculation of HCl the stable structures and the accurate calculation of the interaction of C_2H_4 and $(HX)_n$ ($X = F, Cl; n = 1-4$) 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. After we have studied the C_2H_4 and $(HX)_n$ ($X = F, Cl, Br, I; n = 1-2$) interact to form the $X-H \cdots \pi$ bond complexes interaction. However, the π bond of $C_2H_4 \cdots 3HX$ 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 $X-H \cdots \pi$ bond interaction $C_2H_4 \cdots 3HX$ complex system structure and binding energy research reports, either no reports on the π bond in $C_2H_4 \cdots 3HCl$ or $C_6H_6 \cdots 3HCl$ complexes system strength of commitment interaction capabilities comparing^{5,6}.

EXPERIMENTAL

We using the MP2 method to study the interaction of $C_2H_4 \cdots 3HX$. 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.

The C_2H_4 molecules, which are 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 $X-H \cdots \pi$ bond complexes. So, we can add hydrogen halide molecule point to the mid-point of carbon-carbon double bonds, for which we constructed $C_2H_4 \cdots 3HX$ to form the composite material system. The structure of $C_2H_4 \cdots 3HX$ complexes shown in Fig. 1.

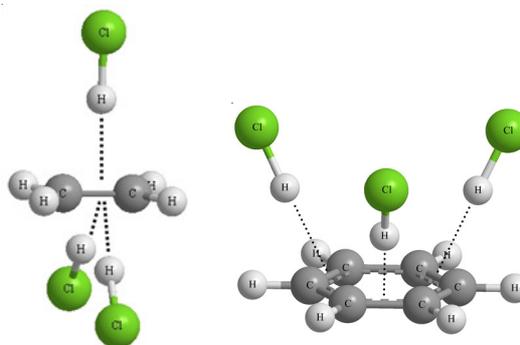


Fig. 1. Structure of model $C_2H_4 \cdots 3HX$ ($X = Cl$) and $C_6H_6 \cdots 3HCl$

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

RESULTS AND DISCUSSION

$C_2H_4 \cdots 3HX$ ($X = F, Cl$) 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 $C_2H_4 \cdots 3HX$ ($X = Br, I$) were geometry optimized at the level of MP2/cc-pVTZ-pp. The results are given in Table-1.

Table-1 clearly showed the complex geometry with the halogen elements in increasing atomic number, R_{C-C} , R_{H-C} bond length of the $C_2H_4 \cdots 3HX$ ($X = F, Cl, Br, I$) complexes is almost unchanged, indicating the formation of complexes $C_2H_4 \cdots 3HX$ in little effect on the structure of ethylene; R_{H-X} , $R_{(X)H-\pi}$, $R_{X \cdots \pi}$ in the $C_2H_4 \cdots 3HX$ complexes increasing greatly, indicating the formation of $X-H \cdots \pi$ hydrogen bond structure of halogenated greater impact; the $X-H \cdots \pi$ interaction weakened, as $R_{I-H \cdots \pi} > R_{Br-H \cdots \pi} > R_{Cl-H \cdots \pi} > R_{F-H \cdots \pi}$, shows C_2H_4 and $3HX$ ($X = F, Cl, Br, I$) interact to form the $X-H \cdots \pi$ bond length periodicity changes, the π bond distance increases and less relevant interactions. All of hydrogen halide molecule vertical point to the π bond, imply that the $X-H \cdots \pi$ bonds in the $C_2H_4 \cdots 3HX$ complexes have shown T-Shape stable structures.

$C_2H_4 \cdots 3HX$ ($X = F, Cl, Br, I$) 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 Bernardi correction BSSE; similarly, HBr, HI and C_2H_4 complexes formed system for binding energy calculations at the MP2/aug-cc-pVTZ-pp level. The results are follows in Table-2.

$\Delta_2 E_{\pi-3HX}^{CP}$ represent that the multiple-HX molecules composed of the unit $(HX)_3$ interact with the π system C_2H_4 , C_6H_6 to formed $\pi \cdots (HX)_3$ interaction energy by BSSE correction. From Table-2, the binding energy ΔE^{CP} of $C_2H_4 \cdots 3HX$ ($X = F, Cl$) is 6.891 Kcal/mol reduced to 6.629 Kcal/mol and for $X = Br, I$, the binding energy ΔE^{CP} from 9.453 Kcal/mol reduced to 8.659 Kcal/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 $(Br-H)_3 \cdots \pi$ and $(I-H)_3 \cdots \pi$, but the overall trends in terms of binding energy.

ΔE and ΔE^{CP} are reduced. The main reason is that: with the atomic number increases, the acidity of hydrogen halides and

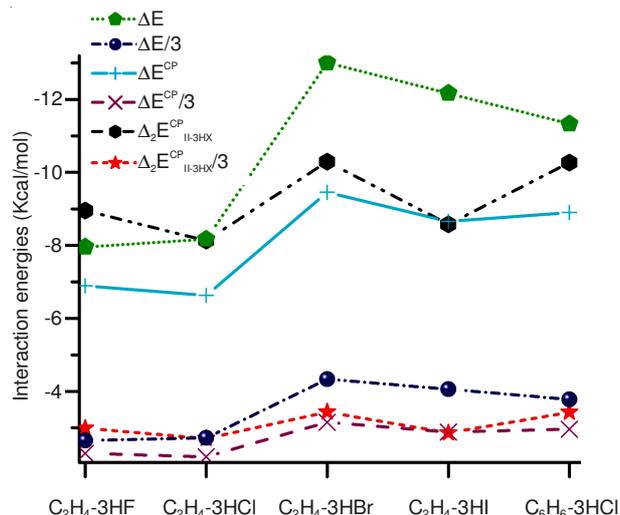


Fig. 2. Interaction energies of $C_2H_4 \cdots 3HX$ ($X = F, Cl, Br, I$) and $C_6H_6 \cdots 3HCl$

the π bond distance of C_2H_4 has increased significantly, leading to reduced interaction energy. The same trend of $\Delta_2 E_{\pi-3HX}^{CP}$ and ΔE^{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.

The π bond of $C_2H_4 \cdots 3HX$ system, in terms of complex geometry and on the binding energy aspects of study, the results show that the compound $C_2H_4 \cdots 3HX$ ($X = F, Cl, Br, I$), 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 three hydrogen halide molecules to formation of the $X-H \cdots \pi$ bond complex.

$C_2H_4 \cdots 3HCl$ with $C_6H_6 \cdots 3HCl$ the binding energy of each π bond bears a comparative analysis of the interaction energy and two π bond system, each ability HCl given a comparative analysis of the interaction: from the Fig. 2, the $\Delta E^{CP}/3$, $\Delta_2 E_{\pi-3HX}^{CP}/3$ of system $C_2H_4 \cdots 3HCl$, $C_6H_6 \cdots 3HCl$ have smaller gap between two data, illustrate two π bond systems given each HCl difference electron interaction capabilities small; for $(HX)_3$ unit and π system interaction energy $\Delta_2 E_{\pi-3HX}^{CP}$, $\Delta_2 E_{\pi-3HX}^{CP}/3$ is, $C_6H_6 \cdots 3HCl$ system than $C_2H_4 \cdots 3HCl$ of $\Delta_2 E_{\pi-3HX}^{CP}$, $\Delta_2 E_{\pi-3HX}^{CP}/3$ slightly bigger, the π bond in the C_6H_6 molecule described bear bigger interaction energy than C_2H_4 interaction; this is

TABLE-1
GEOMETRICAL PARAMETERS FOR THE $C_2H_4 \cdots 3HX$ COMPLEX

Complex	R_{H-C} (Å)	R_{C-C} (Å)	R_{H-X} (Å)	$R_{(X)H-\pi}$ (Å)	$R_{X \cdots \pi}$ (Å)
$C_2H_4 \cdots 3HF$	1.082	1.340	0.920	2.203	3.123
$C_2H_4 \cdots 3HCl$	1.082	1.339	1.279	2.402	3.681
$C_2H_4 \cdots 3HBr$	1.082	1.338	1.407	2.403	3.807
$C_2H_4 \cdots 3HI$	1.081	1.337	1.603	2.515	4.118

TABLE-2
INTERACTION ENERGIES OF $C_2H_4 \cdots 3HX$ ($X = F, Cl, Br, I$)

Complex	E (Hartree)	ΔE (Kcal/mol)	ΔE^{CP} (Kcal/mol)	BSSE (Kcal/mol)	$\Delta_2 E_{\pi-3HX}^{CP}$ (Kcal/mol)
$C_2H_4 \cdots 3HF$	-379.439830	-7.957	-6.891	1.066	-8.955
$C_2H_4 \cdots 3HCl$	-1459.362935	-8.171	-6.629	1.542	-8.131
$C_2H_4 \cdots 3HBr$	-1327.569980	-13.005	-9.453	3.552	-10.297
$C_2H_4 \cdots 3HI$	-964.925956	-12.172	-8.659	3.513	-8.580
$C_6H_6 \cdots 3HCl$	-1612.708096	-11.331	-8.899	2.432	-10.272

mainly due to the C₆H₆ molecule contains three large highly delocalized π bond and C₂H₄ only has one π bond, thus providing the C₆H₆ molecule π bond maximum effect was stronger than C₂H₄ molecule.

ACKNOWLEDGEMENTS

The paper work and data are used Gaussian98 program⁷, in Guizhou Province Key Laboratory of Chemistry of High Performance Computing PC-Linux cluster parallel computing system for completion. Thanks the teachers and staffs of GHPCC. This work was supported by the Natural Science Research Foundation of Hefei University (12KY03ZR), Natural Science Foundation of China (No. 51102073), Natural Science Foundation of Anhui province (No. 10040606Q53, 13080-85QB35), Open Project of Key Laboratory for Ecological-Environment Materials of Jiangsu Province (No. K11031), Natural Science Foundation of Education Department of Anhui Province (KJ2012B154, KJ2013B229), Key Laboratory for

Advanced Technology in Environmental Protection of Jiangsu Province (AE201361) and the College Students' Innovation and Entrepreneurship Training Program of China (No. 201311059013, 201311059014, 201311059015, 201311059016, 201311059050, 201311059054).

REFERENCES

1. A.C. Legon and D.J. Millen, *Farad. Discuss. Chem. Soc.*, **73**, 71 (1982).
2. B.G. Oliveira, R.C.M.U. Araújo, A.B. Carvalho, E.F. Lima, W.L.V. Silva, M.N. Ramos and A.M. Tavares, *J. Mol. Struct. (Theochem)*, **775**, 39 (2006).
3. P. Carcabal, N. Seurre, M. Chevalier, M. Broquier and V. Brenner, *J. Chem. Phys.*, **117**, 1522 (2002).
4. S.J. Grabowski and J. Leszczynski, *Chem. Phys.*, **355**, 169 (2009).
5. J. Yang, S. Li, B. Yang and G. Shao, *Asian J. Chem.*, **23**, 4038 (2012).
6. J. Yang, S. Li, B. Yang, G. Shao and Q. Yin, *Asian J. Chem.*, **25**, 5665 (2013).
7. M.J. Frisch, *et al.*, Gaussian98, Revision (Gaussian, Inc., Pittsburgh, PA (1998)).