A Study on the π Bond of Benzene and Hydrogen Chloride Interaction†

Jie Yang[*], Shaobo Li, Benhong Yang, Guoquan Shao and Qiyi Yin

Department of Chemical and Materials Engineering, Hefei University (Nanyanhu Campus), Jin Xiu Avenue, Economic Technology Development Zone, Hefei 230603, , Anhui Province, P.R. China

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

We applied *ab initio* theoretical studies on the complex of C_6H_6 and n(HCl), formed by X-H⋯π bond complexes. 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-p VTZ level. The results demonstrated that C_6H_6⋯n HCl (n = 1 to 12), with increasing hydrogen chloride number, the binding energy of complex present in the overall increasing trend, however, the π bond of C_6H_6⋯$(HCl)_n$ at least interact to 12 hydrogen chloride to formation of X-H⋯π bond complexes.

Key Words: Weak intermolecular interaction, X-H⋯π Interaction, Hydrogen chloride, Benzene.

INTRODUCTION

Benzene is the most simple aromatic ring the π monomer and a typical of the highly delocalized π-type electron donor. Rozas *et al.*[1] use the MP2 and B3LYP methods to study the interaction of benzene and hydrogen halide, Tinghua *et al.* proposed the vertical point benzene ring center and with C_{6V} symmetry structure inconsistent[1-3]. Williams *et al.*[4] reported spectrum of experimental values consistent. Kim comparative study of the interaction between benzene and hydrogen halide, higher basis set level optimization had been stable configurations inclination[5] and the use of symmetry-adapted perturbation theory (SAPT) binding energy were energy decomposition analysis. The results show that the X-H⋯π interaction energy of the electrostatic interaction is the main attraction and dispersion and induction can be very important to the formation of X-H⋯π bond reveals the essential characteristics of the X-H⋯π bond energy component[6]. Huang *et al.*[7] were amended and extended Legon's theory, in particular, to analyze the complexes formed by the aromatic heterocyclic interact with Lewis acid system, studies have shown that, for the hetero atom-X-H⋯π interactions the essence is the result of joint action by the role of electrostatic and orbital. After that we study the periodicity of the X-H⋯π bond complexes interaction in the last year[8]. In conclusion, the study of the interaction of benzene with hydrogen halide is more extensive, however, the maximum capacity of both interactions has never reported.

EXPERIMENTAL

As the interaction of C_6H_6 and HCl is a weak interaction, requiring a higher accuracy of calculation, in the case of considering the amount of computation and calculation accuracy, we using the MP2 method in this paper to study the interaction of C_6H_6 and HCl. 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.

As from the π bond upper and lower interface of the C_6H_6 molecule, we can add the HCl molecules point to the midpoint of carbon-carbon double bonds in the benzene ring. For this based on the p bond of benzene ring the electronic distribution characteristics to build C_6H_6⋯nHCl formed complex system (Fig. 1).

RESULTS AND DISCUSSION

Structural optimization: The addition of HCl and C_6H_6 interaction needs to consume a large amount of computing resources, taking into account the actual calculation conditions and the machine, and other factors, the calculation and analysis of the complex system in the meantime, C_6H_6⋯n HCl (n = 12). The monomer and the formation of C_6H_6⋯n HCl complex geometry optimization carried out in MP2/cc-pVTZ levels; the structural parameters as shown in Table-1.

TABLE-2
INTERACTION ENERGIES OF $C_6H_6\cdots nHCl$ (n = 1, 2, 3, 6, 12)

Complex	E (Hartree)	ΔE (kcal/mol)	ΔE^{CP} (kcal/mol)	$\Delta_2 E^{CP}_{\pi\text{-}nHCl}$ (kcal/mol)	BSSE (kcal/mol)
$C_6H_6\cdots HCl$	-692.068934	-5.744	-4.697	-4.697	1.047
$C_6H_6\cdots 2HCl$	-1152.392422	-10.989	-9.382	-9.213	1.607
$C_6H_6\cdots 3HCl$	-1612.708096	-11.331	-8.899	-10.272	2.432
$C_6H_6\cdots 6HCl$	-2993.657254	-13.698	-11.714	-17.419	1.984
$C_6H_6\cdots 12HCl$	-5755.565130	-24.430	-23.410	-30.169	1.020
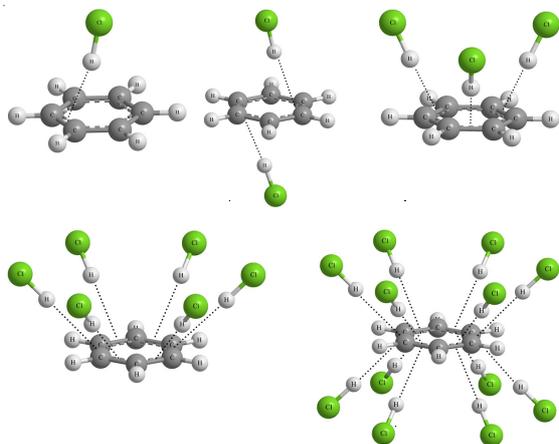
Fig. 1. Structure of model $C_6H_6\cdots n$ HCl (n = 1, 2, 3, 6, 12)

TABLE-1
GEOMETRICAL PARAMETERS FOR THE $C_6H_6\cdots nHCl$ COMPLEX

Complex	$R^a_{H\text{-}C}$ /Å	$R^a_{C\text{-}C}$ /Å	$R^a_{H\text{-}Cl}$ /Å	$R^a_{(Cl)H\text{-}\pi}$/Å	$R^a_{Cl\text{-}\pi}$/Å
$C_6H_6\cdots HCl$	1.081	1.395	1.281	2.406	3.667
$C_6H_6\cdots 2HCl$	1.081	1.395	1.278	2.412	3.681
$C_6H_6\cdots 3HCl$	1.082	1.396	1.278	2.369	3.603
$C_6H_6\cdots 6HCl$	1.082	1.397	1.274	2.645	3.695
$C_6H_6\cdots 12HCl$	1.083	1.399	1.273	2.921	3.705

$^a R_{(Cl)H\text{-}\pi}$ R $_{Cl\text{-}\pi}$ representing HCl in the HCl atom to the distance of C-C bond; $R_{H\text{-}C}$, $R_{C\text{-}C}$, $R_{H\text{-}Cl}$ represent the bond lengths of C-C, C-H in the C_6H_6 and HCl

From the optimized balanced stable structure of $C_6H_6\cdots nHCl$ composite, by comparing the configuration $C_6H_6\cdots n$ HCl (n = 1, 2, 3, 6, 12) to optimize the resultant structure are maintained when the construct symmetry structure. Wherein, the stable structure of $C_6H_6\cdots n$ HCl (n = 1, 2) complexes is that HCl offset vertical benzene plane C_6 axis tilting point on the benzene ring carbon-carbon bond; Cl-H point to the midpoint of the carbon-carbon bond in the optimization of $C_6H_6\cdots n$ HCl composite.

By complex geometrical structure parameters (Table-1) showed that due to the X-H$\cdots\pi$ bond of $C_6H_6\cdots n$ HCl complex major role in the highly delocalized of the carbon-carbon bond in the benzene ring, carbon-carbon of the benzene ring bond length $R_{C\text{-}C}$ and $R_{H\text{-}C}$ bond length does not change, $R_{H\text{-}Cl}$ bond length almost unchang; $R_{Cl\text{-}\pi}$, bond length almost no change in $C_6H_6\cdots n$ HCl (n = 1, 2), however, when n = 12, the bond length of the longest. When n ≥ 3, there is a more significant increase $R_{(Cl)H\text{-}\pi}$. Main reason is that HCl intermolecular repulsion in the limited space and caused of the smaller inclination angle between nHCl and benzene ring in $C_6H_6\cdots nHCl$ complex.

Energy calculation and comparation: $C_6H_6\cdots nHCl$ 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. The results are follows as Table-2.

From Table-2, the unit $(HCl)_n$(n=1-12) and C_6H_6 interaction generated strong binding energy and with the number of nHCl (n ≤ 12) molecules increasing, which the interaction energy show the general trend of increasing, meanwhile the total binding energy ΔE_{Total}, ΔE^{CP}_{Total} also be increasing. $\Delta_2 E^{CP}$ π-nHCl represent that multiple-HCl molecules composed of the unit $(HCl)_n$ inteact with the π system C_6H_6 to formed π$\cdots(HX)_n$ interaction energy by BSSE correction.

By $\Delta_2 E^{CP}_{\pi\text{-}nHCl}$, ΔE^{CP}_{Total} two parameters: at n ≤ 3, $\Delta_2 E^{CP}_{\pi\text{-}nHCl}$ closer with ΔE^{CP}_{Total}, that is to say, the interaction energy of C_6H_6 and $(HCl)_n$ of $\Delta_2 E^{CP}_{\pi\text{-}nHCl}$ roles in total interaction energy percentage of dominant proportion of ΔE^{CP}, however the interaction between the HCl molecules role in total interaction energy is relatively small. Meanwhile, with increase the number of nHCl(n ≥ 3) molecule, the energy of $\Delta_2 E^{CP}_{\pi\text{-}nHCl}$, ΔE^{CP}, the interaction energy between the HCl molecules are significantly increased and the amplitude of increase did not of convergence, two binding energy of ΔE^{CP} and $\Delta_2 E^{CP}_{\pi\text{-}nHCl}$ are difference more obvious; when n = 12, the difference between the two binding energy up to maximum 6.760 Kcal/mol, which the interaction between the HCl molecule also reaches a maximum.

From the composite structure of the formation of $C_6H_6\cdots n$ HCl (n ≤ 12) and the π-bond in the distribution characteristics of electrons, X-H$\cdots\pi$ bond formed by the track direction of the benzene molecule geometric space constraints of smaller, thus, from the π bond maximum effect capacity of C_6H_6 molecule interact with multiple-HCl has not reached the limits.

Conclusion

Application of *ab initio* theory of the p bond of C_6H_6 and HCl to the formation of the $C_6H_6\cdots n$ HCl (n ≤ 12) complex system, geometry and binding energy are described and analyzed. The π bond C_6H_6 molecule at least interacting with 12HCl to formation of the X-H$\cdots\pi$ bond complex.

REFERENCES

1. I. Rozas, I. Alkorta and J. Elguero, *J. Phys. Chem. A*, **101**, 9457 (1997).
2. T.H. Tang, W.J. Hu and Y.P. Cui, *J. Mol. Struct (Theochem.)*, **207**, 319 (1990).
3. A.C. Legon and P. Ottavia, *Phys. Chem. Chem. Phys.*, **4**, 4103 (2002).
4. F.A. Baiocchi, J.H. Williams and W. Klemoerer, *J. Phys. Chem.*, **87**, 2079 (1983).
5. P. Tarakeshwar, S.J. Lee, J.Y. Lee and K.S. Kim, *J. Chem. Phys.*, **108**, 7217 (1998).
6. P. Tarakeshwar, H.S. Choi and K.S. Kim, *J. Am. Chem. Soc.*, **123**, 3323 (2001).
7. D.-M. Huang, Y.-B. Wang, L.M. Visco and F.-M. Tao, *Chem. Phys. Lett.*, **407**, 222 (2005).
8. J. Yang, S.B. Li, B.H. Yang and G.Q. Shao, *Asian J. Chem.*, **24**, 4038 (2012).