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A theoretical study on halogen-π interactions: X-C_2-Y…C_8H_8 complexes

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ABSTRACT

M06-2X functional was employed to study halogen-π interactions in X-C_2-Y…C_8H_8 complexes (X, Y=H, F, Cl, and Br). In fact, interactions of mono- or di-halogenated acetylenes and planar cyclooctatetraene as an anti-aromatic π system were considered. Relationship between binding energies of the complexes and charge transfer effects was investigated. Also, electronic charge density values were calculated using atoms in molecules (AIM) method to connect properties of bond, ring, and cage critical points (BCPs, RCPs, and CCPs) to binding energies of the mentioned complexes. Size of halogen atoms has a role on strength of halogen-π interactions. Decrease of electronic charge density values at BCPs and CCPs of the complexes and increase of alteration of these values at RCPs is relatively consistent with increase of binding energies. Electron-withdrawing nature of Br atom leads to inverse charge transfer in some complexes.

Description of halogen-π interactions on an anti-aromatic ring help to design new molecular systems with unique properties for crystal engineering.

Keywords: M06-2X; halogen-π; cyclooctatetraene; charge transfer; AIM

1. INTRODUCTION

The nature of C-X…Y halogen bonded interactions (X= Cl, Br, and I) is an interesting subject matter for chemists and biochemists [1-3]. Specially, essential roles have been assigned for interactions of halogen atoms with aromatic amino acid side chains [4, 5]. Muzangwa et al. investigated π-stacking, CH-π, and halogen bonding interactions in halobenzene clusters [6]. Evaluation of the strength of halogen bonding interactions is an effort to recognize nature of these noncovalent bondings using experimental and theoretical methods [7]. Recently, halogen bonded molecular systems have been considered in some studies [8-17]. Substituent effects on halogen-π interactions were reported by some authors [18]. Also, Christofer S. Tautermann and coworkers examined halogen-π interactions in dispersion dominated systems [19]. Moreover, noncovalent interactions involving halogen-π ones have been studied in Bromobenzene- and mixed Bromobenzene-benzene clusters [20]. Indeed, weak C-X…π halogen bonded complexes which π systems involve ethene and propene have been previously studied [21].

To the best of our knowledge π systems of the halogen bonded complexes in many studies are aromatic rings. In the present

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work, planar cyclooctatetraene (C_8H_8) was chosen as an anti-aromatic ring to investigate halogen-π interactions of mono- and di-halogenated acetylenes on this π system (see scheme 1).

2. COMPUTATIONAL METHODS

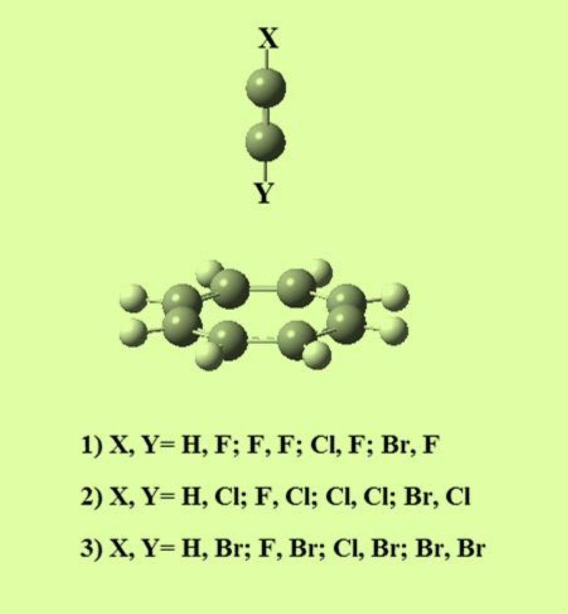
Structures of all monomers and complexes were optimized with Gaussian 09 program package [22] at the M06-2X/6-311++G(d,p) level of theory. The M06-2x functional has good performance for electronic Rydberg and charge transfer excitations [23]. Also, binding energies (-ΔE) of all complexes were calculated with correction for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise procedure [24]. The topological properties of electronic charge densities have been designed by the atoms in molecules (AIM) method using AIM2000 [25] program.

3. RESULTS AND DISCUSSION

3.1. Energy data and charge transfer study

Typical structure of X-C_2-Y…C_8H_8 complexes is shown in scheme 1.

All theoretical results regard the mentioned complexes are listed in Table 1. As can be seen, binding energies of the complexes involve mono- and di-brominated acetylenes are larger than those other ones. Thus, nature of halogen atoms has a role on strength of halogen-π interactions in these complexes. Results indicate that charge transfer (CT) is occurred from X-C_2-Y to C_8H_8 in theX-C_2-Y…C_8H_8 complexes with the exception of complexes involve mono- and di-brominated acetylenes which Br atom interacts with π system of anti-aromatic molecule C_8H_8. It seems that electron-withdrawing nature of Br atom leads to positive charge on molecule C_8H_8 in the later complexes. However, highest CT is occurred in complexes involve mono- and di-Chlorinated acetylenes.



Scheme 1. Presentation of X-C_2-Y…C_8H_8 complexes together with X and Y atoms.

3.2. AIM analyses

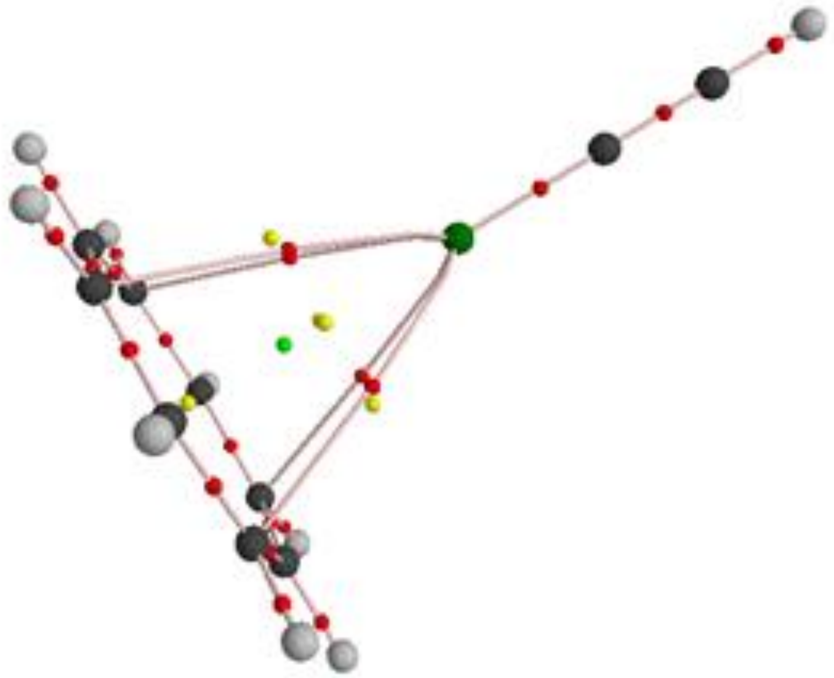
The topological properties of electronic charge densities have been calculated by AIM method. A typical molecular graph of the X-C_2-Y…C_8H_8 complexes is shown in scheme 2 for presentation of positions of critical points and bond paths.

Results show that complex formation lead to increase of electronic charge density values at ring critical points (ρ_{RCP}) of the X-C_2-Y…C_8H_8 complexes in comparison to isolated C_8H_8 (The ρ_{RCP} value at center of isolated C_8H_8 is 4.431×10^{-2} au). Also, increase of $\Delta\rho_{RCP}$ values is relatively accompanied by increase of binding energies of the complexes. Moreover, decrease of ρ_{CCP} in the X-C_2-Y…C_8H_8 complexes is somewhat accompanied by increase of binding energies. As can be observed in Fig. 1, decrease of sum of electronic charge density values at bond critical points ($\sum\rho_{BCP}$) which are formed between halogenated acetylenes and carbon atoms of molecule C_8H_8 in the X-C_2-Y…C_8H_8 complexes is followed by increase of binding energies.

Table 1. Binding energies of the complexes in kcal mol^{-1}, charge of molecule C_8H_8 in complexes in e, and electronic charge densities at critical points in au

Complex	**-$^a\Delta E$**	**-$^b\Delta E$**	**CT**	**$\rho_{RCP}\times10^3$**	**$\rho_{CCP}\times10^3$**	**$\sum\rho_{BCP}\times10^2$**
HC_2F	1.52	1.03	-0.011	4.521	2.883	2.349
HC_2Cl	3.19	2.53	-0.097	4.570	2.520	2.040
HC_2Br	3.67	3.39	0.002	4.554	2.754	1.348
FC_2F	3.44	1.05	-0.025	4.517	2.911	2.392
ClC_2F	1.66	1.13	-0.023	4.526	2.893	2.357
BrC_2F	1.67	1.15	-0.020	4.525	2.891	2.354
FC_2Cl	3.26	2.56	-0.105	4.568	2.525	2.047
ClC_2Cl	3.38	2.65	-0.123	4.574	2.558	2.065
BrC_2Cl	3.43	2.70	-0.117	4.574	2.552	2.059
FC_2Br	3.75	3.45	0.004	4.554	2.774	1.365
ClC_2Br	3.86	3.56	0.023	4.557	2.785	1.367
BrC_2Br	3.79	3.48	0.022	4.564	2.694	1.352

^{a} and ^{b} refer to the binding energies without and with BSSE correction, respectively.



Scheme 2. Typical molecular graph of the X-C_2-Y…C_8H_8 complexes designed by AIM200 software.

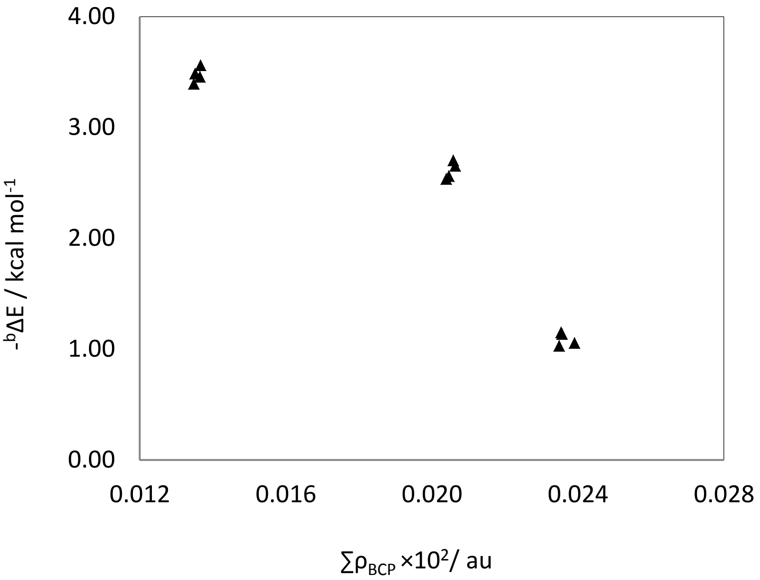


Figure 1. Relationship between binding energies of the complexes and electronic charge density values at BCPs.

As was said, decrease of electronic charge density values at BCPs and CCPs of the complexes is relatively consistent with increase of binding energies. In contrast, increase of $\Delta\rho_{RCP}$ values is in harmony with increase of binding energies. This result implies that alteration of electronic charge density values at RCPs during formation of the complexes has an important effect on magnitude of the binding energy values.

4. CONCLUSIONS

Size of halogen atoms has a role on strength of halogen-π interactions in the X-C_2-Y…C_8H_8 complexes. Electron-withdrawing nature of Br atom leads to positive charge on molecule C_8H_8 in the complexes involve mono- and di-brominated acetylenes which Br atom interacts with π system of this anti-aromatic ring. Decrease of electronic charge density values at BCPs and CCPs is consistent with increase of binding energies of the complexes. Increase of $\Delta\rho_{RCP}$ values has a central role on strength of the binding in the X-C_2-Y…C_8H_8 complexes.

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REFERENCES

[1] M.R. Scholfield, C.M.V. Zanden, M. Carter, P. S. Ho, Protein Sci. 22 (2013) 139.
[2] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, Angew. Chem. Int. Ed. 47 (2008) 6114.
[3] F. Meyer, P. Dubois, Cryst. Eng. Comm. 15 (2013) 3058.
[4] R. Wilcken, M. O. Zimmermann, A. Lange, A. C. Joerger, F. M. Boeckler, J. Med. Chem. 56 (2013) 1363.
[5] Y. Lu, Y. Wang, W. Zhu, Phys. Chem. Chem. Phys. 12 (2010) 4543.
[6] L. Muzangwa, S. Nyambo, B. Uhler, S. A. Reid, J. Chem. Phys. 137 (2012) 184307.
[7] P. Politzer, Halogen Bonding: Fundamentals and Applications,

Structure and Bonding, Springer, NewYork, 2008.

[8] R. Bertani, P. Sgarbossa, A. Venzo, F. Lelj, M. Amati, G. Resnati, T. Pilati, P. Metrangolo, G. Terraneo, Coor. Chem. Rev. 254 (2010) 677.

[9] G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, M. Sansotera, G. Terraneo, Chem. Soc. Rev. 39 (2010) 3772.

[10] P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, Acc. Chem. Res. 38 (2005) 386.

[11] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, Angew. Chem., Int. Ed. 47 (2008) 6114.

[12] Y. X. Lu, J. W. Zou, Y. H. Wang, Y. J. Jiang, Q. S. Yu, J. Phys. Chem. A 111 (2007) 10781.

[13] L. Cheng, M. Y. Wang, Z. J. Wu, Z. M. Su, J. Comput. Chem. 28 (2007) 2190.

[14] Y. X. Lu, J. W. Zou, Y. H. Wang, Q. S. Yu, Chem. Phys. 334 (2007) 1.

[15] B. K. Liu, B. X. Wang, Y. Q. Wang, L. Wang, Chem. Phys. Lett. 477 (2009) 266.

[16] P. Politzer, J. S. Murray, T. Clark, Phys. Chem. Chem. Phys. 12 (2010) 7748.

[17] E. Parisini, P. Metrangolo, T. Pilati, G. Resnati, G. Terraneo, Chem. Soc. Rev. 40 (2011) 2267.

[18] Y. X. Lu, J. W. Zou, Y. H. Wang, Q. S. Yu, Int. J. Quant. Chem. 107 (2007) 1479.

[19] H. G. Wallnoefer, Th. Fox, K. R. Liedl, Ch. S. Tautermann, Phys. Chem. Chem. Phys. 12 (2010) 1494.

[20] S. A. Reid, S. Nyambo, L. Muzangwa, B. Uhler, *J. Phys. Chem. A* 117 (2013) 13556.

[21] Q. J. Shen, X. Pang, X. R. Zhao, H. Y. Gao, H. L. Sun, W. J. Jin, Cryst. Eng. Comm. 14 (2012) 5027.

[22] M.J. Frisch, et al. Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.

[23] N. Mardirossian, J. A. Parkhill, M. Head-Gordon, Phys. Chem. Chem. Phys. 13 (2011) 19325.

[24] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.

[25] R.F.W. Bader, Atoms in Moleculs: A Quantum Theory, Oxford University Press, Oxford, 1990.