More Interactions present in Anion-π systems

DR. SHARON ACHAMMA ABRAHAM
Department of Chemistry, Mar Thoma College Tiruvalla, Kerala

Abstract*— Anion πinteractions is the most important one among Non-covalent interactions. Various anion π complexes such as benzene hexacarboxylic acid…..F$^-$,Benzene hexasulphonic acid…….Cl$^-$, benzene hexacarboxylicacid methylester……Br$^-$, Benzene hexacarboxaldehyde……..I$^-$,Benzene hexaamide………..F$^-$, are taken into study.Binding energies are calculated using DFT method and B3LYP/6-31+G(d,p) basis set. Binding energy is plotted along the y axis and atomic masses is plotted along the x axis, obtained a straight line graph. On plotting substituted groups along the x axis and binding energies along the y axis, obtained a straight line. Potential energy profile for anion π complexes can be obtained. For a single anion at large separations from the ring, these complexes show asymptotically correct negligible binding energies. This is a potential energy profile at m06-2X/6-31+G(d,p) for anion π complexes.

***Index Terms*- Binding energy, DFT, Potential energy profile, B3LYP, Anion π Surface, polarisation.**

I. INTRODUCTION

Anion *π* interactions has been emerging as a new developmental technology in recent area in the field of protein-ligand interactions and in supramolecular complexes. Various types of non-covalent interactions increases in anion *π*systems. Orbital interactions possible in anion-*π* systems, which makes the non covalent interactions easier.Orgin of dipole interactions and dipole moments like Quadruple moments, electrostatic interactions are present in these type of systems. These complexes has many applications in drug design, supramolecular complexes like crown ethers, calixarenes, spherands, podants etc.

Anion *π* interactions paves a way for the doping of anions like F$^-$, Cl$^{-,}$Br$^-$,I$^-$with various *π* surfaces which makes the binding easier. Fluorine doped anion *π* surface, Chlorine doped anion *π* surface , Bromine doped anion *π* surface, Iodine based anion *π* surface,are some of the systems in which the intercalation of anions are under study. These non-covalent interactions involves the mixing of orbital interactions of s orbitals and *p* orbitals in b3lyp and m062x.The charge transfer component and Quadrupolar moments plays an important role in forming new molecular structure complexes. Local minimal structures can be obtained from these type of calculations. The host and guest interactions can also be seen here[1]

II. METHODOLOGY

Consider a series of complexes of various *π* surfaces with anions like
F$^-$, Cl$^-$,Br$^-$,I$^-$ as shown in the table.All the calculations were performed using B3LYP version of DFT which is comprised of Becke's hybrid three parameter functional and the correlational functional of Lee, Yang and Parr. The 6-31+G[d,p] basis set was employed. Confirmational search for the lowest energy structures led to several possible symmetries for the molecules particularly in orientation of the electron withdrawing groups and those reported here are of the lowest energy[2]. Additional frequency calculations were performed to verify all real vibrational frequencies.

Consider hexacarboxylic acid benzene molecule in which the hydrogen atoms are replaced by carboxylic acid groups. This molecule binds with a fluoride anion. Electron withdrawing group like -COOH decreases the electron density on the benzene system and an anion like F$^-$ fluoride anion easily attaches to the *π* surface and becomes more stabilized forming an anion *π*complex[3].

The free energy of binding of one anion with the aromatic ring is always negative and more for electron withdrawing systems like carboxylic acid group,sulfonic acid group, ester group, aldehydic group,amide group etc. The calculated binding energies are in good agreement with the experimentally determined values obtained by collision induced dissociation.The experimentally determined values are -15.2,-12.4,-10.2,-8.5 etc respectively. Similarly electron withdrawing groups like -COOH, SO_3H,$COOCH_3$,CHO,$CONH_2$ can be taken into study. These electron withdrawing groups when attached to the benzene ring,and an anion like F^- ,Cl^-,Br^-,I^- will attach, form anion π complexes.The free energy is also negative for highly electron withdrawing groups like benzene hexacarboxylic acid, benzene hexasulfonic acid,benzene hexacarboxylic acidmethyl ester,benzene hexacarboxaldehyde,benzene hexaamide etc[4,5,6].

	Anion-π complexes	Binding energy in kcal/mol
1.	Benzene hexacarboxylic acid…..F^-	-15.2
2.	Benzene hexasulfonic acid…….Cl^-	-12.4
3.	Benzene hexacarboxylic acid ester……Br^-	-10.2
4.	Benzene hexacarboxaldehyde……..I^-	-8.5
5.	Benzene hexaamide………..F^-	-15.7

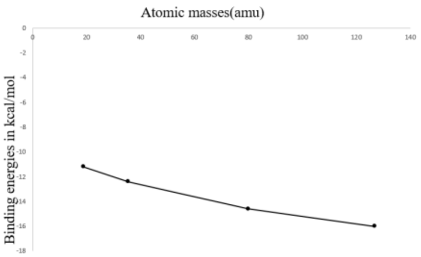
In benzene hexacarboxylic acid, free energy is produced when anion like fluoride is attached. Electron withdrawing group like -COOH withdraws electron from the benzene ring and the free energy of the system is negative. The calculated binding energies are in good agreement with the experimentally determined values obtained by collision induced dissociation. The experimental binding energies for fluoride and chloride ion with benzene are -15.2kcal/mol and-12.4kcal/mol respectively[7,8].The contribution of dispersion forces to the stabilization of anion π complexes is significant.In a benzene ring, six –COOH groups are attached and above the plane of benzene ring, an anion is located at a distance of 4.7A° above plane of molecule and binding energy is calculated using B3LYP functional and 6-31+G(d,p) basis set which shows difference between energy of benzene anion complex and sum of energy of benzene hexacarboxylic acid and anion M^-. This anion doped polyacene is more stable than benzene carboxylic acid or anion M^-.These calculations have demonstrated that these electron withdrawing groups stabilizeanion-π complexes.Less binding energies can be obtained from these complexes.

In benzene hexasulfonic acid……………..Cl^-, the SO_3H group is highly electron withdrawing and the free energy of the system is negative.Then change in internal energy is negative and entropy is positive. Change in internal energy and entropy is negative or Tdelta S is greater than change in internal energy in magnitude. Above benzene ring with six SO_3H groups, an anion is located at a distance of 4.7A° above plane of molecule and binding energy is calculated using B3LYP functional and 6-31+G(d,p) basis set, which shows difference between benzene anion complex and sum of energy of benzene and anion.The binding energy calculated depends upon the benzene anion π complex,benzene and the anion.Confirmational search for the lowest energy structures led to several possible symmetries for the molecules particularly in orientation of the groups attached and those reported are of the lowest energy. The role of dispersion interactions is significant here.

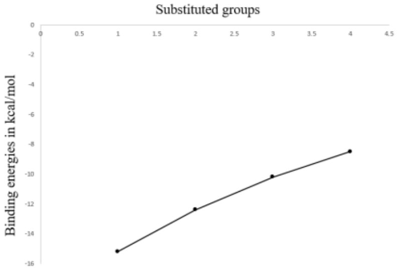
In benzene hexacarboxylic acid ester……..Cl^-, the carboxylic acid ester group is an electron withdrawing group and the system is stabilised by Cl^- situated at the top of the benzene ring. The free energy of the system is also negative. Above benzene ring with six ester groups, anion like Cl^- is located at a distance of 4.7A°above plane of molecule and binding energy is calculated using B3LYP functional and 6-31+G(d,p) basis set, which shows difference between benzene hexacarboxylic acid ester and and sum of energy of benzene and anion. Potential energy surfaces for each of the complexes were analysed as function of the centroid of the ring……anion distance to investigate the range of displacements for which such interactions are stable and also to ascertain the correct dissociative nature of the hybrid functionals at large separations [9,10,11]

In benzenecarboxaldehyde……I^-, the free energy of the system is negative and the system is stabilized by I^- group. Then TΔS is negative and ΔS is positive which makes Δ G negative or ΔH is negative or Δ S is positive.Then the binding energy is negative which can be calculated as the difference between benzene anion π complex and sum of energies of benzene carboxaldehyde and anion M^-.Then the change in internal energy can also be negative[12,13].These anion π systems can compute rate of reactions and studies in thermodynamic properties of chemical reactions. Anions like F^-, Cl^-,Br^-, I^- are introduced into benzene hexacarboxaldehyde complexes. When the free energy of the system is negative, the rate of the reaction can be positive.

In Benzene hexaamide…….F^-, anion like F- is attached 4.7 A° above top of benzene ring and an anion π complex is formed. The free energy of the system is taken as negative. The standard free energy can be calculated from the equation $\Delta G° = -2.303\mathrm{RTlogK}$, where the equilibrium constant K can be calculated. When the π system attaches the anion, free energy is produced and it can be taken as negative. This mechanism for the formation of anion Pi complex is exothermic for Benzene hexaamide……F^-. A second anion is introduced at the opposite side of the benzene ring can also be taken into study.



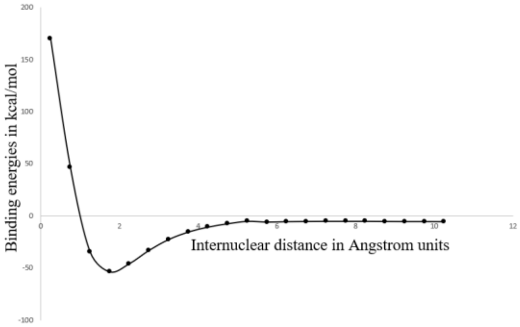
Binding energies are calculated for various anion π complexes.Binding energy is plotted along the y axis and atomic masses is plotted along the x axis. Less binding corresponds to the Iodine doped anion π surface, since polarisation is more. Binding energies decreases as atomic mass increases. Electrostatic polarisation exists between anion and the π system and binding energy increases as F>Cl>Br> I.



On plotting substituted groups along the x axis and binding energies along the y axis, obtained a straight line. Binding energy decreases on according to the substituted groups -COOH, -SO3H,-COOCH3,-CHO etc.

III. RESULTS

Among the systems taken into study,Benzene hexacarboxylic acid……F- shows the highest binding energy and gives a value of -15.2kcal/mol. F^- is the most suitable halogen for binding. This complex also gives bsse corrected values.In Benzene carboxylic acid…….F^-, the binding energy is more stable than bsse corrected binding energy value.



The potential energy profile for anion π complexes are shown in the figure.For a single anion at large separations from the ring, these complexes show asymptotically correct negligible binding energies. This is a potential energy profile at m06-2X/6-31+G(d,p) for anion π complexes.A similar profile at b3lyp/6-31+ G(d,p)does not display a proper asymptotic behaviour at large d. Interestingly these anion π complexes show a repulsive profile at such large distance[14,15,16].The origin of repulsion is traced to the Coulombic attraction between negative and positive charge. For anion π complexes even though a metastable local minimal structure exists at d=2.2Angstrom units,the potential energy surface is unbound.These complexes show stable binding energy regions for d=1.6Angstrom units-2.6Angstrom units.Such a stable phase across 1 A° in the potential energy profile is encouraging as crystallization conditions or steric effects of side groups can rarely lead to expansion or contraction of distances greater than 1 A° from equilibrium position.

CONCLUSION

Anion π interactions are the most prominent non-covalent interactions . These systems have applications in drug design and in supramolecular chemistry. These interactions are used to identify anions such as benzenehexacarboxylicacidF^- .Calixarenes, spherands,podants are other applications of Anion πcomplexes.

REFERENCES

[1] Salonen, L. M.; Ellerman, M.; Diederich, F. Angew. Chem., 123, 4908; (2011) Angew. Chem. Int. Ed., 50, 4808(2011).

[2] (a) Ma, J. C.; Dougherty, D. A. Chem. Rev. 97, 1303(1997,). (b) Gopalan, R. S.; Kulkarni, G. U.; Rao, C. N. R. ChemPhysChem, 1, 127.(2000).

[3] Gallivan, J. P.; Dougherty, D. A.; Proc. Natl. Acad. Sci. USA, 96, 9459 (1999).

[4] Korth, M.; Grimme, S.; Towler, M. D. J. Phys. Chem. A, 115, 11734 (2011).

[5] Estarellas, C.; Bauza, A.; Frontera, A.; Quinonero, D.; Deya, P. M. Phys.Chem. Chem.Phys., 13, 5696.(2011).

[6] Minoux, H.; Chipot, J. J. Am. Chem. Soc. 121, 10366(1999).

[7] Zeng, Y.; Zhu, M.; Meng, L.; Zheng, S. ChemPhysChem, 12, 3584(2011).

[8] Li, R.; Li, Q.; Cheng, J.; Liu, Z.; Li, W. ChemPhysChem, 12, 2289 (2011).

[9] (a) Quinonero, D.; Frontera, A.; Garau, C.; Ballester, P.; Costa, A.; Deya, P. M.; ChemPhysChem, 7, 2487(2006). (b) X. Lucas, A. Frontera, D. Quinonero, P. M. Deya, J. Phys. Chem. A, 114, 1926 (2010).

[10] Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H-J.; Kruger, C. J. Am. Chem. Soc., 105, 5479 (1983).

[11] Li, a.Y.; Zhou, G.; Li, J.; Wu, J.; Gu, B. L.; Duan, W. J. Phys. Chem. C, 115, 7292 (2011).

[12] Wang, L.; Cai, Z.; Wnag, J.; Jing, L.; Luo, G.; Lai, L.; Qin, R.; Gao, Z.; Yu, D.; Li, G.; Mei, W. N.; Sanvito, S. Nano Lett. 8, 3640(2008).

[13] Wang, J.; Zhang, X.; Schleyer, P. v. R.; Chen, Z. J. Chem. Phys., 128, 104706(2008).

[14] Jonas, K.; Russeler, W.; Angermund, K.; Kruger, C. Angew. Chem. 1986, 98, 904; Angew. Chem. Int. Ed., 25, 927(1986).

[15] Bock, H.; Havlas, Z.; Hubmann, K. G.; Holl, S.; Sievert, M. Angew. Chem. Int. Ed, 42, 4385(. 2003).

[16] For a discussion on the limit to the puckering of benzene and yet sustaining aromaticity: A. Datta, S. K. Pati, Chem. Phys. Lett., 433, 67. (2006)