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More Interactions Present in Cation π Systems

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Abstract: *Cation π interactions arises from Non-covalent interactions in chemistry and biology in which an aromatic face of the ring binds with a cation. The cation….π interaction plays an important role in the field of molecular recognition in biological receptors. Conventionally,quadrupolar interactions are involved to give 1:1 Cation… π complexes.Different types of non-covalent interactions are present in cation πsystems.Orbital interactions observed in cation-π systems,which makes the non covalent interactions easier.Orgin of dipole interactions and dipole moments like Quadruple moments, binds these type of systems.These complexes has many applications in drug design, supramolecular complexes like crown ethers, calixarenes,spherands,podants etc.Cation πinteractions are the most important one among non-covalent interactions. This work describes various electron rich cation π complexes such as Hexamethylbenzene….2Li+Hexamethylbenzene…..2Na+, Hexamethylbenzene ….2K+,Hexahydroxybenzene…2 Li+,Hexahydroxybenzene…..2Na+,Hexahydroxybenzene…..2K+, Hexamethoxybenzene …..2Li+,Hexamethoxybenzene….2Na+,Hexamethoxybenzene….2K+, Hexaaminobenzene. …..2Li+,Hexaaminobenzene…..2Na+,Hexaminobenzene….2K+ are taken into study.Binding energies are calculated using DFT method and CAM-B3LYP/6-31+G(d,p) basis set in Gaussian 09. Formerly 1:1 cation-π complexes are there.Inorder to get 2:1 complexes we can give the two cations in a single step or in a two step reaction.The binding energies are calculated for all the complexes.One observation is that the binding energy decrease with increase in size of the cation.Secondly when a strong donor group like amino group is present in the benzene ring, highly stable 2:1 cation complexes.Out of all the complexes fprmed,Hexaaminobenzene….2Li+ in single step addition is found to be more stable than benzene….2Li+. An Aromatic ring binds with one cation and forms an Aromatic cation complex.Then the second cation attaches to the opposite side of the Aromatic ring. The third method involves the binding of two cations simultaneously to the aromatic ring. Binding energy ΔE is plotted along the y axis and atomic mass is plotted along the x axis, obtained a straight line graph. On plotting metal ions along the x axis and binding energies ΔE along the y axis, obtained a straight line. Potential energy profile for cation π complexes can be obtained. For a single cation at large separations from the ring,these complexes show asymptotically correct negligible binding energies. This is a potential energy profile at CAM-B3LYP/6-31+G(d,p) for cation π complexes. The behaviour of Hexaaminobenzene to form 2:1 cation π complexes with Li cation and yet remains aromatic has applications in 1-dimensional materials and in molecular electronics or organic semiconductors.*

Keywords: Binding energy, DFT,Potential energy profile, CAM-B3LYP,Cationπ Surface, polarisation

I. INTRODUCTION

Density functional theory DFT is a quantum mechanical method in physics and chemistry to explore the electronic structure of many-body systems, including atoms,molecules and solids.It is known for its accuracy and computational efficiency. It is based on Hohenberg-Kohn theorm that the ground state properties of a many-electron system can be particularly determined by its electron density rather than its many-body wavefunction.It is used for studying the properties of materials at the atomic and molecular scale.The Kohn-Sham equations makes DFT into computational model by treating an interacting system of electrons as non-interacting particles in an effective potential, which describes many-body electron interactions through exchange-correlation functional. The main function of DFT is

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approximating the exchange-correlation(XC) functional, which includes electron-electron interactions,their mutual repulsion and Pauli's exclusion principle.A large number of approximations have been developed to explain this. Key approximations include Local density Approximation(LDA),Generalised Gradient Approximation(GGA),Hybrid functionals etc. B3LYP is one of the most important hybrid functional. CAM-B3LYP is an important method among Density functional theory(DFT). It is Coloumb Attenuating method and is a hybrid exchange correlation functional.It includes B3LYP functional and long-range correction.This correction is used to analyse cation π interactions and other interactions like dispersion interaction, charge transfer etc.It is used to identify cation π complexes such as benzene……$2M^+$, hexamethylbenzene……..$2M^+$, hexahydroxybenzene…..$2M^+$,hexamethoxybenzene….$2M^+$, hexaaminobenzene…..$2M^+$ where M is a metal cation like Lithium,Sodium or Potassium. CAM-B3LYP functional includes 0.19 Hartree Fock plus 0.81 Becke 1988 exchange interaction at short range and 0.65 HF plus 0.35 B88 at long range.The intermediate region is indicated through the standard error function with parameter 0.33. CAM-B3LYP has many applications in protein ligand interactions, supramolecular chemistry and in podants,spherands,calixarenes etc.

B3LYP couldn't explain excited states,particularly for charge transfer and long-range interactions,polarizability of long chains,excitations using time dependent theory TD-DFT for Rydberg states. To overcome these difficulties, CAM-B3LYP was introduced. CAM-B3LYP includes long range correction describe charge-transfer excited states. CAM-B3LYP is an useful tool in explaining organic molecules and excited state properties. CAM-B3LYP can be used along with TD-DFT,which explains excited state exchange-correlation potential. CAM-B3LYP can be used to identify molecular excitons and aggregates.Solvent effects, Solvatochromic shifts, fluorescence and solvent-dependent reactivity are associated with CAM-B3LYP. At long range, the exchange potential behaves as $-0.2r^{-1}$, instead of the exact value $-r^{-1}$. Tsuneda and co-workers found out that

$\frac{1}{r_{12}} = \frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\mathrm{erf}(\mu r_{12})}{r_{12}}$ where the first term accounts for short-range interaction and the second term accounts for the long range

interaction. Coulomb-attenuating method with three parameters is given by

$\frac{1}{r_{12}} = \frac{1-\alpha+\beta\ \mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\alpha+\beta\ \mathrm{erf}(\mu r_{12})}{r_{12}}$ where the relations $0 \leq \alpha + \beta \leq 1,\ 0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$ should be satisfied. The parameter α

deals with the incorporation of HF exchange contribution over the whole range by a factor of α and the parameter β indicates to incorporate the DFT counterpart over the whole range by a factor of 1- $(\alpha + \beta)$.

Mixing of the orbitals take place in CAM-B3LYP. Mixing of s orbitals and p orbitals takes place and local minimum structures are obtained. CAM B3LYP includes many type of interactions like dispersion forces. CAM-B3LYP is the most important in forming molecular structures. CAM-B3LYP paves a way for the doping of cations like Li^+,Na^+,K^+ with various π surfaces of benzene and substituted benzene complexes. The substituted groups are -CH3group, -OH group, -OCH3 group and -NH2 group. These non covalent interactions involve the mixing of orbital interactions in b3lyp and in cam-b3lyp. The charge transfer component and Quadrupolar moment plays an important role in forming new molecular structural complexes. Local minimal structures can be obtained from these type of calculations.The host and guest interactions can also be seen here.

Various structural complexes are taken into study.Lithium ion doped hexahydroxybenzene cation π structure, Sodium ion doped hexahydroxybenzene cation πstructure, Potassium ion doped hexahydroxybenzene cation π structure,Lithium ion doped hexamethoxybenzene cation π structure, Sodium ion doped hexamethoxybenzene cation π structure, Potassium ion doped hexamethoxybenzene cation π structure, Lithium ion doped Hexaminobenzene cation π structure, Sodium ion doped Hexaminobenzene cation π structure , Potassium ion doped Hexaminobenzene cation π are some of the systems that are discussed.

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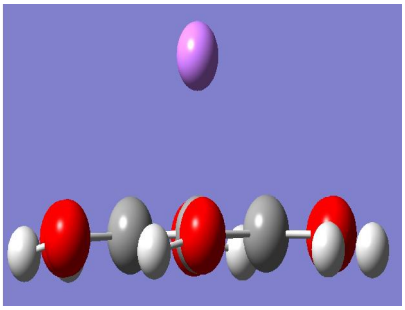
II. METHODOLOGY

The cation π interaction arises from the electrostatic interaction of a cation with the face of a π system.The intial work was done by Kebarle in 1981.He found out that the interaction energy of K^+….water is -18kcal/mol where as K^+……benzene is -19kcal/mol.Benzene stabilizes K^+ ions better in the gas phase than water. Kebarle explained that the interacting geometry involves the ion interacting with the quadropole moment of benzene. This work includes the computational modelling of certain electron rich systems to identify the nature of the interaction[23,24,25]. Calculations were performed to produce cation…….π complexes on benzene and substituted benzenes using hybrid density functional method CAM-B3LYP in Gaussian09 . All calculations were done using CAM-B3LYP method and 6-31+G(d,p) basis-set.[1](’Lee et al., 1988). All imaginary frequency structures and transition states were computed in this method[1](’ Abraham, 2022). Confirmational search for the lowest energy structures led to several possible symmetries for the molecules particularly in orientation of the electron releasing groups and those reported here are of the lowest energy[2](’ Hariharan & ’Pople, 1973).

In hexahydroxybenzene or benzenehexol molecule, when two cations are added separately it forms hexahydroxybenzene……$2Li^+$and the reaction is endothermic. When two cations are added in a single step ,it also forms hexahydroxybenzene……$2Li^+$ structure and remains endothermicBut these complexes are less stable when compared to hexaminobenzene$2Li^+$,hexamethylbenzene$2Li^+$ and hexamethoxybenzene$2Li^+$



Scheme1: Structure of Hexahydroxybenzene…….Li^+ in Gaussian09

The change in internal energy of this system is positive. The free energy of binding of one cation with the aromatic ring is always negative and more for electron releasing systems like methyl group, hydroxyl group, ester group and amino group etc. The calculated binding energies are in good agreement with the experimentally determined values obtained by collision induced dissociation[4](’Zhao et al., 2006).The calculated values are -39.1,-25.0,-34.1,-43.3kcal/mol respectively.Similarly electron releasing groups like $-CH_3$ -OH, $-OCH_3$, $--NH_2$ can be taken into study. These electron releasing groups when attached to the benzene ring,and cation like Li^+,Na^+,K^+will attach, in single step addition and multistep addition forms dication-π complexes.The free energy is also negative for highly electron donating groups like hexamethyl benzene, hexamethoxybenzene and hexaminobenzene etc.

In hexamethylbenzene, the binding energy calculated using CAM-B3LYP[3](’Allouche, 2011) for the formation of monocation complex is found to be -39.1kcal/mol.The bsse corrected value is -38.4kcal/mol.The bsse corrected value is less stable than without bsse correction. When two cations are added separately,it forms Hexamethylbenzene…$2Li^+$ and the reaction is enothermic.When the two cations are added in a single step method, the reaction is exothermic and dication complex is formed.Binding energy is calculated using CAM-B3LYP functional and 6-31+G(d,p) basis set which shows difference between energy of benzene cation complex and sum of energy of hexamethylbenzene and cation M^+. This cation doped polyacene is more stable than hexamethylbenzene or cation M^+.Addition of two cations in single step addition and in a multistep addition forms hexamethylbenzene…..$2Li^+$ complexes.These calculations have demonstrated that these electron donating groups stabilize cation-π complexes.Strong donor groups in the aromatic ring facilitates charge transfer interactions.

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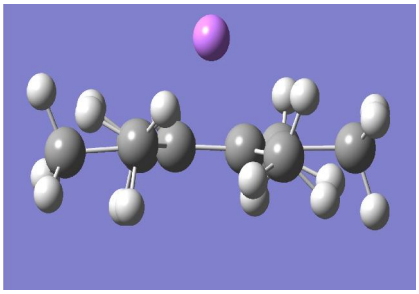
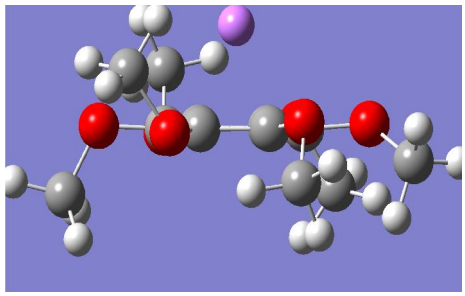


Scheme2: Structure of Hexamethylbenzene…….Li^+ in Gaussian09

In hexamethoxybenzene structure, above benzene ring with six -OCH3 groups a cation like Lithium, Sodium or Potassium is located at a distance of 2.5 A° units above plane of molecule and binding energy is calculated using CAM-B3LYP functional[4](' Zhao & ' Truhlar, 2008) and 6-31+G(d,p) basis set which shows difference between hexamethoxybenzene metal ion complex and sum of energy of hexamethoxybenzene and cation M^+.Binding energy decreases as size of cation increases as Li^+> Na^+>K^+[4]('Jissy et al., 2011). The cations are added separately in multistep addition to form hexamethylbenzene…$2Li^+$,the reaction is endothermic.The free energy of the system is positive. Binding energy is calculated as the difference between energy of hexahydoxybenzene dication complex and sum of energy of hexahydroxy benzene monocation π complex and cation M^+.Third method is to attaching two cations, either Lithium or Sodium or Potassium simultaneously to both faces of the aromatic ring ,the reaction is exothermic and binding energy is calculated using CAM-B3LYP/6-31+G(d,p)basis set[7]('Velde te et al., 2001) and is the difference between energy of hexahydroxybenzene dication complex and sum of energy of benzene system and the two cations.Binding energies of cation π complexes are determined and its stable values are obtained.When binding energy decreases in cation π complexes, reaction rate k increases and has applications in computing rate of reactions and in thermodynamic properties of chemical reaction. These interactions involves the mixing of atomic orbitals to form molecular orbitals[7]('Jose & 'Datta, 2011).



Scheme3: Structure of Hexamethoxylbenzene…….Li^+ in Gaussian09

Table 1. CAM-B3LYP Binding Energies ΔE for monocation and dication complexes

CAM-B3LYP Binding EnergiesΔE in kcal/mol							
Complexes		Benzene-BenzeneM$^+$		BenzeneM$^+$-Benzene2M$^+$		Benzene-Benzene2M$^+$	
		Without BSSE	With BSSE	Without BSSE	With BSSE	Without BSSE	With BSSE
1.	**Hexamethylbenz……2Li$^+$**	-39.1	-38.4	55.1	55.6	-10.2	-6.4
2.	**Hexamethylbenz…….2Na$^+$**	-33.8	-32.4	42.8	44.0	9.01	11.0
3.	**Hexamethylbenz…….2K$^+$**	-27.4	-26.7	36.8	37.5	9.5	10.6
4.	**Hexahydroxybenz……2Li$^+$**	-25.0	-23.9	68.2	68.9	16	19
5.	**Hexahydroxybenz……2Na$^+$**	-25.4	-24.1	Cation-	Cation-	Cation-	Cation-

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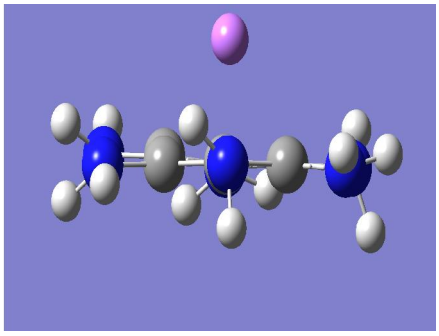
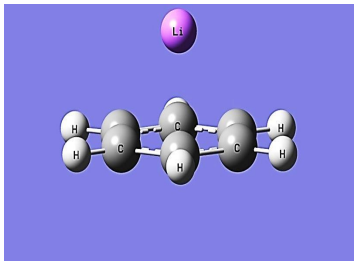
				lone pair	lone pair	lone pair	lone pair
6.	**Hexahydroxybenz……2K$^+$**	-22.1	-21.3	Not Binding	Not Binding	Not Binding	Not Binding
7.	**Hexamethoxybenz…..2Li$^+$**	-34.1	-33.3	56.2	56.9	-1.0	-0.7
8.	**Hexamethoxybenz…2Na$^+$**	-33.1	-31.7	Cation lone pair	Cation lone pair	Cation lone pair	Cation lone pair
9.	**Hexamethoxybenz…..2K$^+$**	Cation lone pair	Cation lone pair	Cation lone pair	Cation lone pair	Cation lone pair	Cation lone pair
10.	**Hexaaminobenz…….2Li$^+$**	-43.3	-42.3	51.2	51.9	-19.9	-18
11.	**Hexaaminobenz…….2Na$^+$**	-33.8	-32.3	Cation lone pair	Cation lone pair	Cation lone pair	Cation lone pair
12.	**Hexaaminobenz……..2K$^+$**	-27.6	-26.6	Cation lone pair	Cation lone pair	Cation lone pair	Cation lone pair

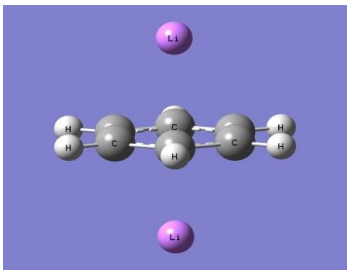
When the aromatic ring binds with one cation, the change in internal energy can be negative and more for highly electron rich systems like hexaminobenzene,hexamethylbenzene and hexamethoxybenzene.The calculated binding energies are in good agreement with the experimentally determined values obtained by collision induced dissociation(CID)[5](’Lopez et al., 2011).For example, the experimental binding energies for the monocation complexes of lithium,sodium and potassium with benzene are-25.9kcal/mol, -25.5kcal/mol,-21.5kcal/mol respectively while the calculated BSSE corrected CAM-B3LYP/6-31+G(d,p) values are-25.4kcal/mol,-25.1kcal.mol,-21.2kcal.mol.From the table it is evident that the importance of dispersion forces in cation π complexes are significant[6](’Forster & ’ Weinhold, 1980).For all the systems binding energies for the aromatic systems follow the order Ar-Li$^+$>Ar-Na$^+$Ar-K$^+$ which is due to the decreasing extent of charge transfer from the π system to the cation[7](’Krapp et al., 2006).



Scheme4: Structure of Hexaaminobenzene…….Li$^+$ in Gaussian09



Scheme5: Structure of benzene…….Li$^+$ in Gaussian09



Scheme6: Structure of benzene….2Li$^+$ in Gaussian09

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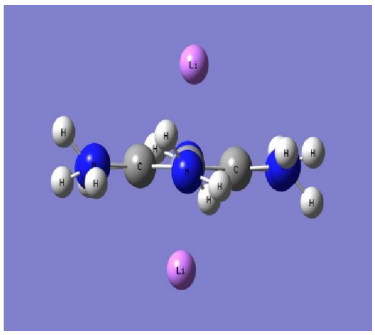

Scheme 7 : Structure of Hexaaminobenzene……2Li$^+$ in Gaussian09

When a second cation is placed on the opposite side the change in internal energy is positive[8](’Schleyer et al., 1996).In hexahydroxybenzene…..2K$^+$, the dication complex is not even a local minimum.In hexahydroxybenzene…..2K+, it will not form any monocation or dication complexes, instead not binding structures are observed.For larger cation like Na$^+$ and K$^+$, the dication complex is converted into cation lone pair complexes.These cation

lone pair complexes are observed in Hexaaminobenzene, Hexahydroxybenzene and inHexamethoxybenzene. In hexamethoxybenzene…..K$^+$, not even a single optimized structure can be found, all are cation lone pair forming structures[7](’Velde te et al., 2001).

Addition of two cations simultaneously to the aromatic ring, the change in internal energy is negative for Hexaaminobenzene ,Hexamethoxylbenzene and Hexamethylbenzene.These three aromatic complexes formed the strongest monocation π complexes[9](’Jerome, 2004).

III. RESULTS

3.1 Binding Energies and Atomic masses

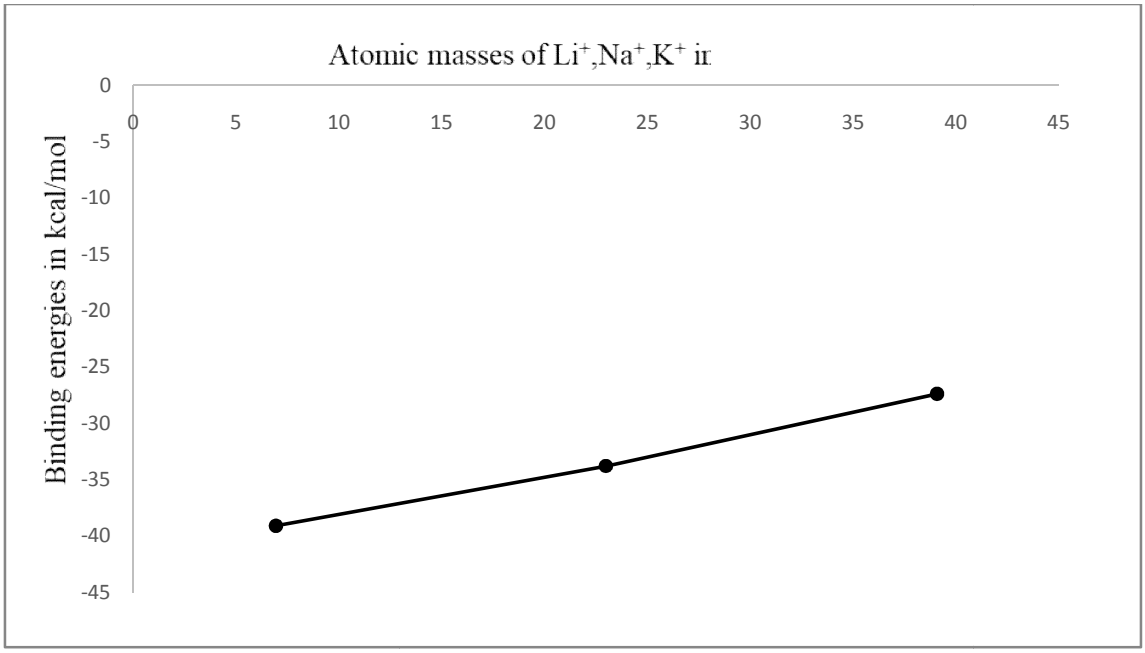

Figure1:Potential energy Profile of Binding Energies in kcal/mol and Atomic masses of metal cations

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On plotting atomic masses of Li^+,Na^+ and K^+along the x axis and binding energies in kcal/mol along the y axis a straight line graph is obtained.Binding energy decreases as size of cation increases.In Hexamethylbenzene……Li^+, the binding energy is found to be
-39.1kcal/mol. Sodium doping on hexamethyl benzene produces a binding energy of
-33.8 kcal/mol. Potassium ion binds with hexamethyl benzene and the resultant binding energy is -27.4kcal/mol.Thus binding energy decreases as atomic mass increases. It is observed that the binding energy is more negative for Lithium doped cation π complexes and is more stable[10](’Scott et al., 1936).

3.2 Binding energies and Metal cations Li^+,Na^+ and K^+

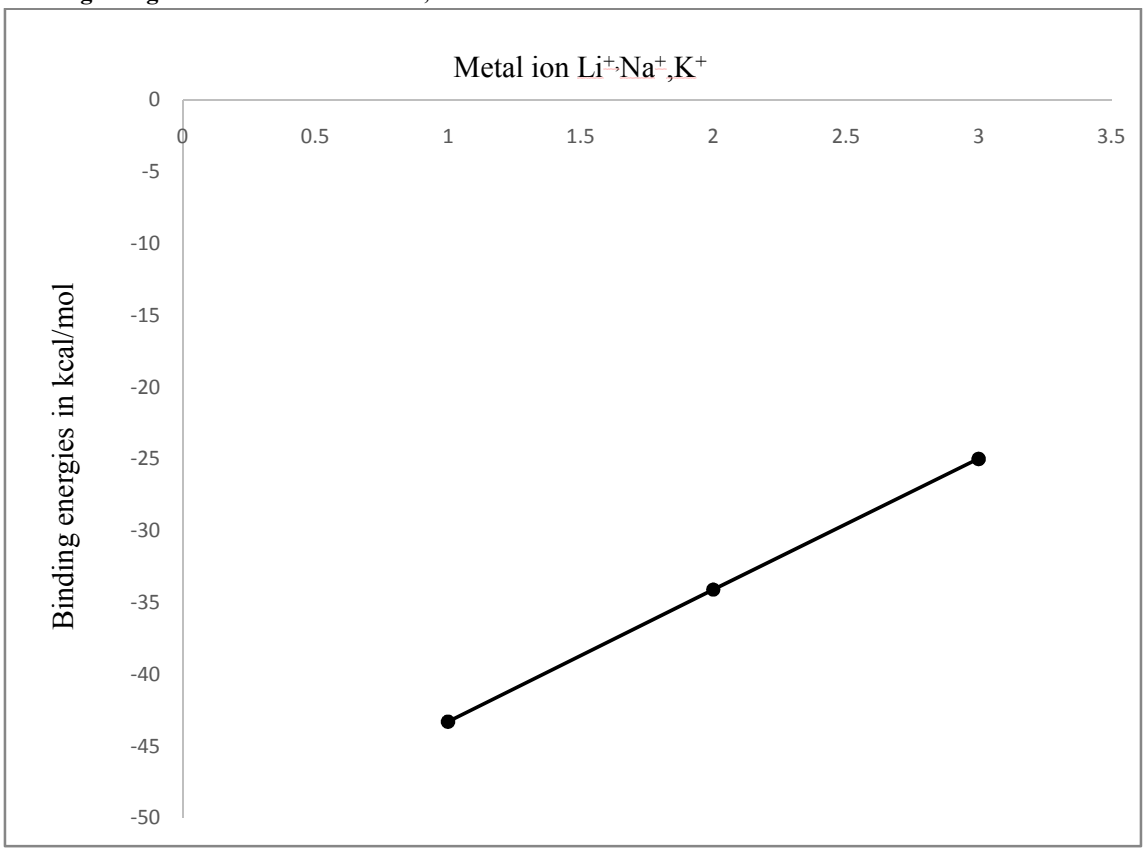

Figure2:Potential energy Profile of Binding Energies in kcal/mol and Metal cations

On plotting the different metal ions along the x axis and binding energies in kcal/mol along the y axis, straight line graph is obtained.In hexaaminobenzene…Li^+ the binding energy is found to be -43.3kcal/mol.In hexamethoxyl benzene….Li^+ the binding energy is -34.1kcal/mol and In hexahydroxy benzene….Li^+ the binding energy is -25kcal/mol.Here binding energy is maximum for hexaaminobenzene…..Li^+ and least for hexahydroxybenzene….Li^+[18-22]. Binding energy varies as hexaaminobenzene…Li^+> Hexamethoxybenzene…Li^+>hexahydroxybenzene ..Li^+. Electrostatic polarisation exists between cation and the π system and binding energy increases as Li^+>Na^+>K^+[11](’Lipkin et al., 1953).

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3.3 Binding Energies and Internuclear Distance in Hexaaminobenzene complexes

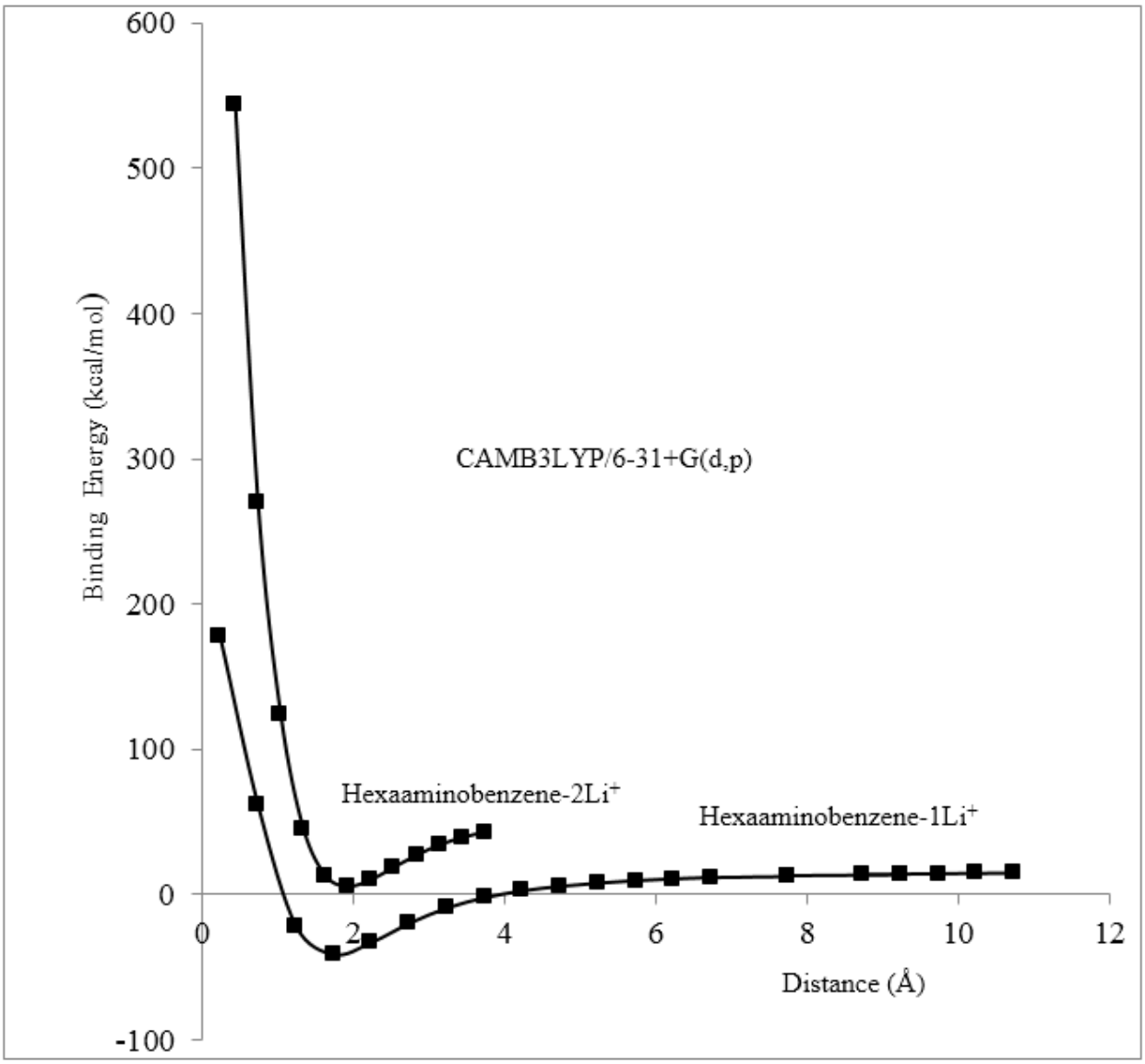

Figure3:Potential energy Profile of HexaaminobenzeneLi$^+$ and Hexaaminobenzene2Li$^+$

The above graph is a potential energy profile of Hexaaminobenzene….Li$^+$ and Hexaaminobenzene……2Li$^+$ monocation and dication complexes using CAM-B3LYP /6-31+G(d,p)[16](’de Hoog et al., 2004).From the plot it is clear that HexaaminobenzeneLi$^+$ is more stable than Hexaaminobenzene 2Li$^+$.Among the systems taken into study, Hexaaminobenzene…….Li$^+$ shows the highest binding energy and gives a value of -43.3kcal/mol. Li$^+$ is the most suitable metal ion for binding. This complex also gives bsse corrected values[17].In Hexaaminobenzene…….Li$^+$ the binding energy is more stable than bsse corrected binding energy value[15](’Quinonero et al., 2002).

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3.4 Binding Energies and Monocation Complexes

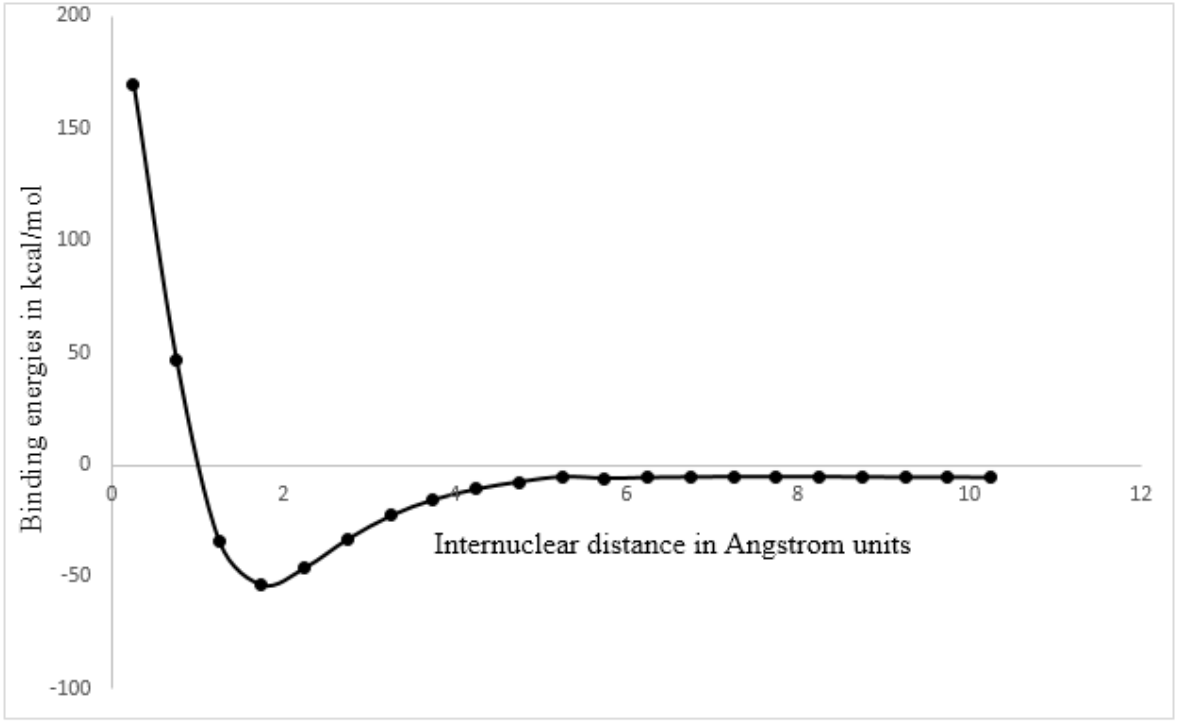

Figure4:Potential energy Profile of monocation π complex.

The potential energy profile for cation π complexes are shown in the figure.For a single cation at large distance 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 cation π complexes[26][12](’Paul et al., 1956).A similar profile at b3lyp/6-31+ G(d,p)does not shows proper asymptotic nature at large d. Interestingly these cation π complexes show a repulsive plot at such large distance.The origin of repulsion is due to the Coulombic attraction between negative and positive charge.In cation π complexes even though a metastable local minimal structure exists at d=2.2Angstrom units,the potential energy surface has no limits[26][13](’Scott, 1939).These complexes show stable binding energy regions for d=1.6A°-2.6A°.Such a stable phase across 1 A° in the potential energy profile is favourable as crystallization conditions or steric crowding of side groups can rarely lead to expansion or contraction of distances greater than 1 A° from equilibrium position[14](’Sunner et al., 1981).

IV. CONCLUSIONS

Density functional theory DFT is an important method of computational chemistry and materials science, exploring the electronic structure of systems with varying complexities.Hybrid functionals particularly range-separated functionals like CAM-B3LYP

has performed limitations in traditional methods particularly for excited states and long-range interactions .CAM-B3LYP can explain excited states,non-covalent interactions and excitonic processes, CAM-B3LYP has become a useful tool for a wide range of systems, from organic molecules to condensed phases.CAM-B3LYP has applications in charge-transfer excited states,Conjugated organic molecules,Time-Dependent DFT(TD-DFT),Molecular Excitons and Aggregates,Solvent Effects etc. Cation π interaction have now been explained in a wide range of areas.Fundamental gas-phase studies both experimental and theoretical, highlights the cation π interaction to be among the strongest of non-covalent binding forces.In the course of this study,we have calculated a detailed analysis of the interaction

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energies.This study produces information in crystal packing and transport of ions in biological systems.The interaction energies of cation π complexes and cation lone pair systems can be observed from the table. Among the cation-π systems introduced using CAM-B3LYP discussed above, Hexaaminobenzene…..Li^+ is the most stable. When a strong donor group like amino group is present in the benzene ring, highly stable 2:1 cation complexes.Out of all the complexes fprmed,Hexaaminobenzene….$2Li^+$ in single step addition is found to be more stable.This study has application in 1-dimensional materials and in molecular electronics or organic semiconductors. The potential energy profiles of monocation and dication systems are discussed.These systems have application in drug delivery and in supramolecular chemistry. These interactions are used to identify cation-π complexes such as hexamethylbenzene…..$2Li^+$, hexahydroxybenzene…$2Li^+$ hexamethoxybenzene…$2Li^+$, hexaaminobenzene….$2Li^+$. .Calixarenes,spherands,podants are other applications of cation πcomplexes.

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