EFFECT OF UNIFORM EXTERNAL ELECTRIC FIELD ON CATION-π INTERACTIONS: A COMPUTATIONAL INVESTIGATION

A Thesis Presented for the
Master of Science in Chemistry,
School of Chemistry and Biochemistry,
Thapar Institute of Engineering and Technology,
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(Deemed to be University)

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Under the guidance of:
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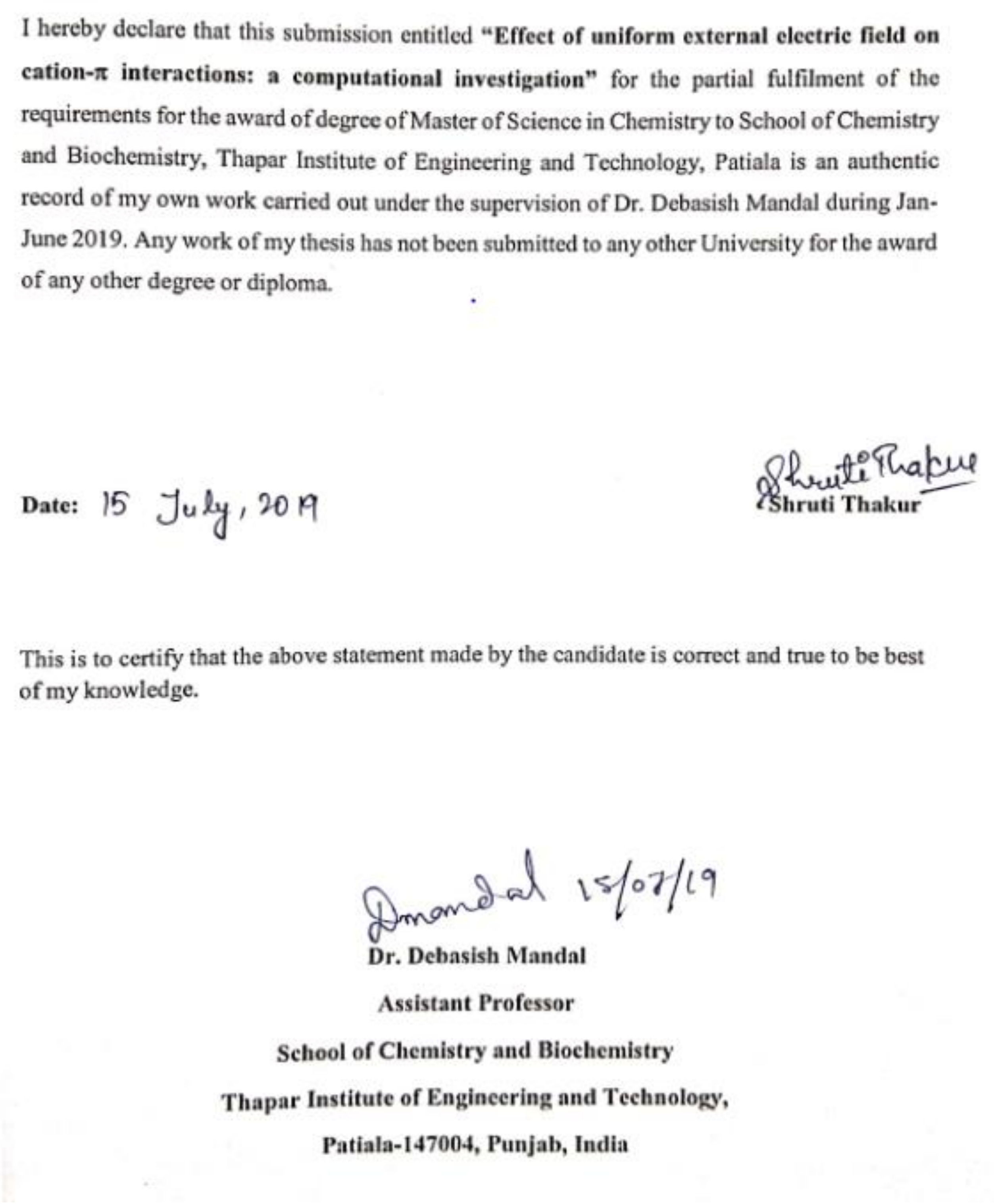
Certificate



I hereby declare that this submission entitled **"Effect of uniform external electric field on cation-π interactions: a computational investigation"** for the partial fulfilment of the requirements for the award of degree of Master of Science in Chemistry to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my own work carried out under the supervision of Dr. Debasish Mandal during Jan-June 2019. Any work of my thesis has not been submitted to any other University for the award of any other degree or diploma.

Shruti Thakur

Date: 15 July, 2019 **Shruti Thakur**

This is to certify that the above statement made by the candidate is correct and true to be best of my knowledge.

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Abstract

Computational investigations were carried out to study the effect of oriented external electric field (OEEF) on the nature of benzene-cation interactions. Density functional (B3LYP, M062X) as well as *ab initio* (MP2) methods were used to optimize the complexes between benzene and cations i.e., Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} and Ca^{2+} subjected to C_6 axis over the ring. This work is based on the investigation of the effect of OEEF on the cation- π interactions exhibited between benzene and various chosen alkali and alkaline earth metal cations. The cation- π interactions in the chosen systems were analysed via various parameters such as variations in interaction energies, dipole moment and the distance of the cation from the centroid of the benzene ring. These factors highlighted the role of suitable direction of OEEF strength in enhancing the operating interactions and its various possible applications.

Extent of OEEF strengths on the chemistry of cation-π interactions was analysed for various systems. The various studied parameters have been found to pointing out to the presence of ‘periodic trends’, signifying the impact of the charges, polarizability, nuclear forces of attraction on the nature of these interactions.

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CHAPTER I

Introduction

The realm of bio-macromolecular structures is administered by covalent and non-covalent interactions in which the latter forms the basis of various biological and biochemical processes. Covalent bonds can be described as the strong interactions of the order of 100-400 kJ/mol responsible for holding the atoms together and thus, providing strong and rigid structural framework and bonding network to the entities. On the other hand, non-covalent interactions are the weaker forces of interactions, generally of the order of strength 1-250 kJ/mol, operating from the vacancies or voids left out in the bonding framework. These do not necessitate the electron sharing as they constitute the wider electromagnetic interaction variations between the participating species. Therefore, they are known as ‘hidden interactions’ working as the ‘determiner of shape and biological activity’ by formation of weaker bonds or interactions between various side groups attached to various chemical entities or protein chains [1] [2].

Non-covalent interactions play a presiding role in various vanguard fields of chemistry and biology. The domain of non-covalent interactions is immense and boundless, covering chemistry, biology and many other disciplines. These interactions govern molecular interactions between various biological molecules and their reciprocity and incorporation in biology and its disciplines rules life. These subsist from the simplest example of existence of liquid phase especially water to the double-helical structure of DNA which form the basis of life. These are the responsible factors for the folding of the protein structures [3] and are essential for analysing and decoding the possible crystal structures of various biomolecules. These also play a major role in enzyme catalysis, material design and biological drug-receptor interactions [4].

These can be categorised into various types: electrostatic, π-effects, van der Waals interactions and the hydrophobic effects. These can be further classified into various classes given as:

1. Electrostatic interactions

   The strength of electrostatic interactions are generally of the order 10-250 kJ/mol. These can be further categorized as ion – ion interactions (~200 kJ/mol), ion – dipole interactions (5-50 kJ/mol), hydrogen bonding (10-65 kJ/mol) and halogen bonding.

2. Van der Waals forces of attraction

   These are quite weak interactions ~ 1-5 kJ/mol. These can be classified as dipole-dipole interactions, dipole-induced dipole interactions and London dispersion forces.

3. π effects or π interactions

   These can be categorized as cation-π, anion-π and π-π interactions generally lying in the range of 0-80 kJ/mol. These interactions are relatively stronger than Van der Waals interactions but weaker than electrostatic interactions.

4. Hydrophobic interactions or Hydrophobic effect

   These are the weakest interactions which are difficult to assess and possesses the energy around 3-12 kJ/mol. Mostly in solvent phase reaction in presence of water, these interactions are found.

Cation-π interactions

In this work we are mainly focused on Cation-π interactions. The interactions between the positive charge of cations and the filled π-orbitals of the unsaturated organic compounds like olefins, aromatic compounds and alkynes are known as cation-π interactions. In recent years, the study of bio-macromolecular structures has led to the recognition of these interactions as a significant tool in molecular recognition, enzyme catalysis and drug-receptor interactions. Cation- π interactions are a general and vital force responsible for stabilising structures, having prime relevance in various physiological processes, structural biology, chemistry and allied domains. These interactions being of electrostatic origin are a consequence of consolidation of solvation effects along with the electrostatic interactions. These have been found to be one of the strongest non-covalent interactions, thus, having a recognizable tendency to significantly affect the surrounding chemical environment [5] [6].

Cation-π interactions lie at the heart of the bio-macromolecular chemistry. The early manifestations were derived from two investigations: scrutiny of high-resolution crystal geometries of proteins by Petsko and Burley showing positively charged amino acids to be located near the centroid of the aromatic amino acids [7] and surveillance of synthesised cyclophane receptors in aqueous media [8]. These investigations aroused the possibility of cation-π interactions. The first plausible computation was done by Kebarle showing predilecting interaction of K^+ ion with benzene as compared with water [9]. Later, Guo and his co-workers computationally founded high binding energies for the Na^+−benzene (−28.0 kcal/mol) and Pb^+−benzene (−26.2 kcal/mol) complexes [10].

These interactions are predominantly embedded in thousands of bio-molecular systems which are hard to overlook due to their acknowledged effect on the neighbourhood environment. Dougherty and co-workers fabricated significant contributions in analysing cation−π interactions in numerous macro cyclic receptors, scrutinizing their possible domain in molecular recognition [11] [12]. From the early research of these interactions in synthetic cyclophane receptors to the molecular design of 'molecular switches' impersonating for metal cations using a 1,3-alternate calix [4] arene cavity [13], numerous significant host-guest complexes have been synthesised based upon the existence of these interactions.

In proteins, tertiary and quaternary structures consisting of numerous peptide chains are held together by their delicate network of these interactions. Computational studies have concluded that for every 77 side -chains, there exists on an average of 1 energetically relevant interaction between cation composed of positively charged amino acid residue and π-cloud of an aromatic amino acid residue [14]. This ratio of number of significant cation-π interactions per aromatic acid residues remains same and does not change with the length and shape of the protein [15]. Olson and co-workers computed that single arginine-tryptophan interaction, provided residues arranged in proper orientation and arena, on the peptide surface leads to the remarkable free energy contribution to stability of the helix formed [16] [17]. Studies revealed that cation-π interactions operating in lysine-tryptophan residues in β-hairpin peptides leads to the folding and significant binding of these peptides with chromodomains [18] [19]. Their significance has further expansion in the functioning of signalling biomolecules and neurotransmitters such as acetylcholine receptors and nicotine acetylcholine receptors which bind to the small cationic molecules, providing an insight of their key roles in drug-receptor interactions [20] [21]. Computational calculations have led to the conclusion that divalent cations are significant in induced sequence-directed DNA bending and RNA folding also [22]. Goldstein et al. founded their domain in substrate and/or transition-state recognition in various enzymes such as phosphatidylinositol-specific phospholipase C in *Staphylococcus* aureus [23]. Phospholipase C catalyzes the hydrolysis of the phosphodiester bond present in phospholipids in order to yield diacylglycerol and the phosphorylated head group which has the tendency to act as a significant constituent of various bio-signalling mechanisms [24].

To study the binding of various cations with aromatic moieties, Sastry and co-workers computationally modelled various systems where regioselectivity character of cation binding and effect of increasing alkyl groups to aromatic moieties were studied [25-26]. The effect of size of the aromatic ring on the cation-π interaction had been studied by experimental and theoretical methods. It has been concluded that the complexes with larger π acceptor molecule exhibit a significant increase in complexation energy, uniformly in cyclic and acyclic systems [27] and alkylation increases the complexation energy [28]. Hassan et al. investigated the effect of ring annellation to benzene on interactions [29].

Substitution effect and inductive effect have been found to influence the cation-π interactions. The magnitude of these interactions depends on the electron density and substituent. The substituent effects occur due to the polarization of the π system [28].

External electric fields have the tendency to bring significant phenomenon to bio-chemical structures by affecting various parameters such as bonds, interacting forces and molecular geometries. Electric fields also influence catalytic systems by altering electronic interactions, promoting electron transfer, oxidation states, thermodynamic and kinetic properties, reaction energies, selectivity etc. [30] [31]. Most of the effects can be described as the 'field-induced stabilization' [32]. These have a great role to play in medicines and biological systems also.

The effect of OEEF on various chemical reactions have been studied. But harnessing its effects in domain of non- covalent interactions is still pending. The effects of OEEF on reactivities, interaction energies, stabilities and distribution of electron density needs to be studied in order to get hold of various biological structures and processes via non-covalent interactions.

In this work, an attempt has been made to study the effect of oriented external electric field on cation-π interactions between alkali and alkaline earth metals with benzene via various parameters e.g., energy, stability, dipole moment, electron density distribution etc.

CHAPTER II

Theoretical Concepts

Computational chemistry can be simply described as the combination of the theoretical chemistry and the computing power of machines and computers. It can be recounted as the 'result or outcome of digital age' as it involves the modern-day technology involved with the computing associated with all sorts of artificial intelligence.

The difficulties in investigating the properties of molecules and their interactions by means of chemical methods make this branch highly significant.

Its major domains of application in chemistry are:

1. Prediction of possible pathways of formation of various compounds i.e., to rule the best mechanism for a chemical reaction out of various possibilities.
2. Designing of molecules which can play an important role as drugs and catalysts and comparison of docking of various ligands through various parameters.
3. Prediction of the variations over time of molecular structures of unknown compounds and their various properties including geometry, bond order, colour and spectra and conformational analysis also.
4. Collecting and storing wide amount of data about various chemical compounds and biomolecules.

Computational quantum chemistry is generally the techniques to solve the Schrödinger equation and analysis of the outcome. The Schrödinger equation is a partial differential equation which forms the basis of quantum mechanics by using concept of energy conservation (Kinetic Energy + Potential Energy = Total Energy) to obtain information about the behaviour and complete description of the electronic structure of a molecule [33].

It can be expressed as:

$$H\psi = E\psi$$

where H = Hamiltonian operator

E = Energy eigenvalue

and ψ = wave-function of the molecule

This time-independent equation can be written for hydrogen atom as:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\mathrm{r}) + V(r)\Psi(\mathrm{r}) = E\Psi(\mathrm{r})$$

Since Schrödinger's equation cannot be completely solved for multi-electron systems, computational methods are used to solve the equation approximately.

Solving Schrödinger equation for molecules can be categorized into three parts:

1. Born-Oppenheimer Approximation

   Born–Oppenheimer approximation [34] is an assumption stating that the nuclear and electronic motions of a molecule can be treated separately as the nuclei can be considered stationary relative to the fast-electronic motion such that wave function for the molecule can be written as:

$$\psi_{\mathrm{total}} = \psi_{\mathrm{electronic}}\ \psi_{\mathrm{nuclear}}$$

2. The Method

   The next significant approximation is the elaboration and construction of ψ in a basis of Slater determinants which can be described as the elementary antisymmetric wave function in agreement with the Pauli's principle.

3. Representation of Slater determinants by molecular orbitals

   The obtained slater determinants are represented by molecular orbitals which are linear combinations of atomic-like-orbital functions.

Basically, there are two major categories of methods involved in the computational quantum chemistry such as Semi-empirical methods and Ab initio methods. These methods are based upon the concepts of quantum mechanics and differ in various approximations involved in the treatment of Schrodinger's equation. The various methods required for this study have been described as:

Hartree-Fock (HF)

It is the computational method based upon the central field approximation which does not takes into account electron correlation for the determination of energy and wave function in the stationary state of the system. Various post-HF methods utilized in this study are:

Ab initio method

This method, directly procured from the theoretical concepts has a tendency to solve the Schrodinger's equation in order to extract utilitarian information such as energy, electron density etc. It does not use any experimental data and is completely dependent on the theoretical concepts. For example: MP2 method.

Moller-Plesset Perturbation theory

Moller-Plesset Perturbation theory is one of the simplest and widely used post-Hartree-Fock ab-initio method utilizing the approximation of correlation energy arising due to electron correlation in molecules. Electron correlation refers to the electronic interactions of a quantum model system. The correlation energy is the measure of the impact on the electronic motion due to the presence of neighbouring electrons [35].

It is an improvisation of Hartree-Fock method by addition of electron correlation via Rayleigh- Schrodinger Perturbation theory (RS-PT) generally considered to the second (MP2), third (MP3) or fourth (MP4) order. The MP corrections in energy are obtained with unperturbed Hamiltonian defined as the shifted Fock operator,

$$\hat{H}_0 \equiv \hat{F} + \langle \Phi_0 | (\hat{H} - \hat{F}) | \Phi_0 \rangle$$

and the correlation potential is the term given to perturbation given by,

$$\hat{F}\Phi_0 \equiv \sum_{k=1}^{N} \hat{f}(k)\Phi_0 = 2\sum_{i=1}^{N/2} \varepsilon_i \Phi_0 .$$

where the normalized Slater determinant Φ_0 is the lowest eigenstate of the Fock operator. Here N is the number of electrons in the molecule (a factor of 2 in the energy arises from the notion that each orbital is occupied by a pair of electrons with opposite spin).

The total electronic energy is given by the sum of Hartree–Fock energy and second-order MP correction:

$$E \approx E_{\mathrm{HF}} + E_{\mathrm{MP2}}.$$

Density Functional Theory (DFT)

Density Functional Theory (DFT) is an advanced level of computational method in which the total energy is expressed in the form of total electron density and no wave function is used to describe the system of atoms or molecules, taking into account electron correlation [34].

Density Functional Theory (DFT) is a computational method in which the energy of the molecule is described as the functional of the electron density. The functional (F) of electron density corresponds to the energy of the molecule [34]:

$$\text{Electron density} = \rho(x, y, z)$$

$$\text{Energy} = F[\rho(x, y, z)]$$

Kohn and Hohenberg gave two principle theorems for density functional theory (DFT), popularly called as the Hohenberg-Kohn theorems. First theorem states that "the full many-particle ground state is a unique functional of n(r), where n(r) represents the electron density at a given position in space." Thus, on solving the Schrodinger equation in order to get the ground-state energy, there exists a link between ground-state energies and their electron densities. The second theorem relates the system's minimal energy with the electron density in order to get the complete results of Schrodinger equation.

B3LYP Method

B3LYP is a hybrid functional consisting of a set of approximations corresponding to the exchange–correlation energy functional where B3 refers to Becke's exchange correlation functional utilizing three variables and LYP is the Lee Yang and Parr correlation functional [36]. It is given by:

$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = E_{\mathrm{x}}^{\mathrm{LDA}} + a_0\left(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{LDA}}\right) + a_{\mathrm{x}}\left(E_{\mathrm{x}}^{\mathrm{GGA}} - E_{\mathrm{x}}^{\mathrm{LDA}}\right) + E_{\mathrm{c}}^{\mathrm{LDA}} + a_{\mathrm{c}}\left(E_{\mathrm{c}}^{\mathrm{GGA}} - E_{\mathrm{c}}^{\mathrm{LDA}}\right),$$

where E_x^{GGA} and E_c^{GGA} are generalized gradient approximations and E_c^{LDA} is local density approximation.

M062x method

M062x is a highly parametrized global hybrid exchange-energy correlation functional lying in the class of Minnesota functionals consisting of 54% HF exchange. This method belongs in M06 suite of functionals based upon GGA DFT approximation in which the energy is dependent on the occupied orbitals through the HF exchange terms and also the non-interacting kinetic energy densities [37].

This functionals is highly recommended for main-group thermochemistry and kinetics investigation and non-covalent interactions.

Basis Set

A basis set is a group of non-orthogonal and one-particle functions which are utilized for fabricating the molecular orbitals and thus, the corresponding wave function. These provide vector representation to wave functions and are expressed as linear combinations comprising of coefficients [33].

6-31g** basis set

It is a split-valence basis set where 6 primitive Gaussians are forming each core atomic orbital basis function with two basis functions consisting of linear combination of 3 and 1 primitive Gaussian functions respectively.

Def2-SVP

Def2-SVP is a basis set where def2 refers to second generation of def basis set and SVP refers to Split valence polarization.

Since, this work includes the application of oriented electric fields, a little idea of the electric filed is necessary. The electric field, by definition, can be described as the electric force divided by unit charge. In laymen terms, it can be described as the expanse or the extent around a charge in which when another charge is placed confronts the influence of the first charge. Mathematically, it is defined as a vector field that identifies every point in space the force acting per unit charge there if an infinitesimal positive test charge was being placed at that point [32]. The expression for the electric field can be obtained from the Coulomb's law as stated below:

According to definition,

$$Force = Electric\ field \times Charge$$

Therefore,

$$Electric\ field = \frac{Force}{Charge}$$

$$\text{Or,}\quad E = \frac{F}{q} = k\,\frac{Q}{r^2}$$

where ‘Q’ and ‘q’ are the magnitude of the two charges and ‘r’ is the distance between them.

where the electric force is measured in Newtons (N) and the charge in Coulombs (C), so that the unit of electric field is N/C or volts/m, where the latter is the SI unit.

And dipole moment can be defined as the described as the product of the distance between the ends of dipole and magnitude of the charges, i.e.,

$$\mu = q \times d$$

where q = magnitude of charges

d = separation between the charges with Debye as SI unit.

For computational investigations, systems consisting of benzene ring and M^+/M^{2+} cations were chosen. The required geometries were optimized using Gaussian 16 [38] software and performed with the above-mentioned methods and corresponding basis sets using the secure shell client. The origin of cartesian axes was then made to coincide with the centroid of benzene ring with one of its axes passing through the centre of the cation, perpendicular to the π- cloud of benzene ring, in order to apply the external electric field.

The external electric field was applied along the axis passing through cation centre. The external field was applied in two possible directions relative to the axis passaging through centroid and metal cation centre, one along the axis and other in opposite direction i.e., in Fz >0 or <0 directions respectively with magnitudes: 0.004, 0.002, -0.006, -0.004, -0.002 a.u. The required optimizations consisting of external electric field were conducted with the same methods and basis sets.

The effects of external electric field were studied on the cation-π interaction prevailing in the system with the help of various parameters such as energy stabilization or destabilization, dipole moment, distance of the cation from the centroid of ring and NBO charges [33].

For investigating the dependency of the stability factor of cation-benzene interaction on external electric field, calculated total interaction energies were corresponding to absence and in presence of external field were compared. The magnitude and dipole moment and distance of the cation from the benzene centroid were determined with the help of Chemcraft software [39].

CHAPTER III

Result and discussion

At first, the interaction energies computed in the presence and absence of OEEF are compared to have an insight into the effect of the orientation of the OEEF on the energy of the complexes under study. A schematic representation of the benzene-cation system has been shown below in the figure 1.

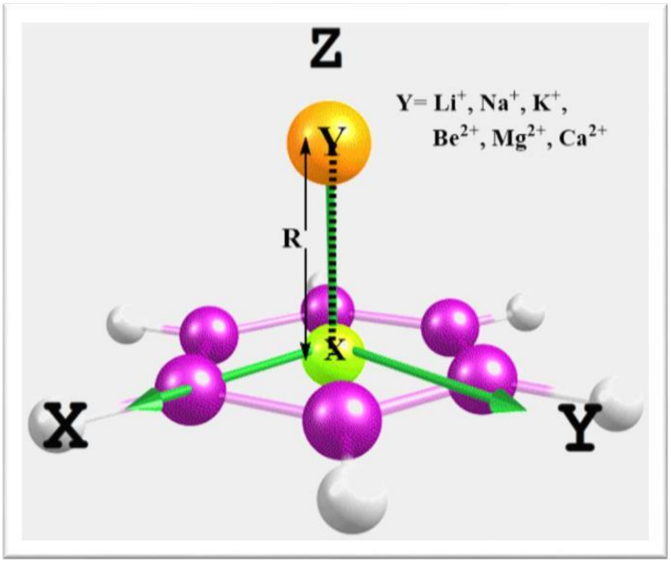

Figure 1: The benzene-cation system with the direction of Cartesian axis. The dummy atom X is placed at the centroid of benzene to direct the eye. The distance of the cation from the dummy atom is represented by 'R'

For benzene–Li^+ complex, the interaction energies at various oriented field magnitudes i.e., -0.006, -0.004, -0.002, 0.004 & 0.002 a.u. are plotted in figure 2. The energy difference is obtained by subtracting the energy of the system without field from that of the system under applied electric field. So, negative energy difference signifies the stabilization whereas positive energy difference signifies destabilization of the system.

Here, the stabilization of the complex is achieved in $F_z < 0$ compare to $F_z = 0$ with the stability of 2.55 kcal/mol on applying -0.002 a.u. It further stabilized in presence of higher field e.g., 5.25 kcal/mol and 8.15 kcal/mol in presence of 0.004 a.u. and -0.006 a.u. In presence of $F_z > 0$ the complex gets destabilized by 2.39 kcal/mol and 4.65 kcal/mol on applying +0.002 a.u. and +0.004 a.u. Consequently, it signifies that the stability of the complex depends on both the orientation and field strength.

The similar results have also been found at two other level of theories presented in figure 2 (A) i.e., Fz > 0.

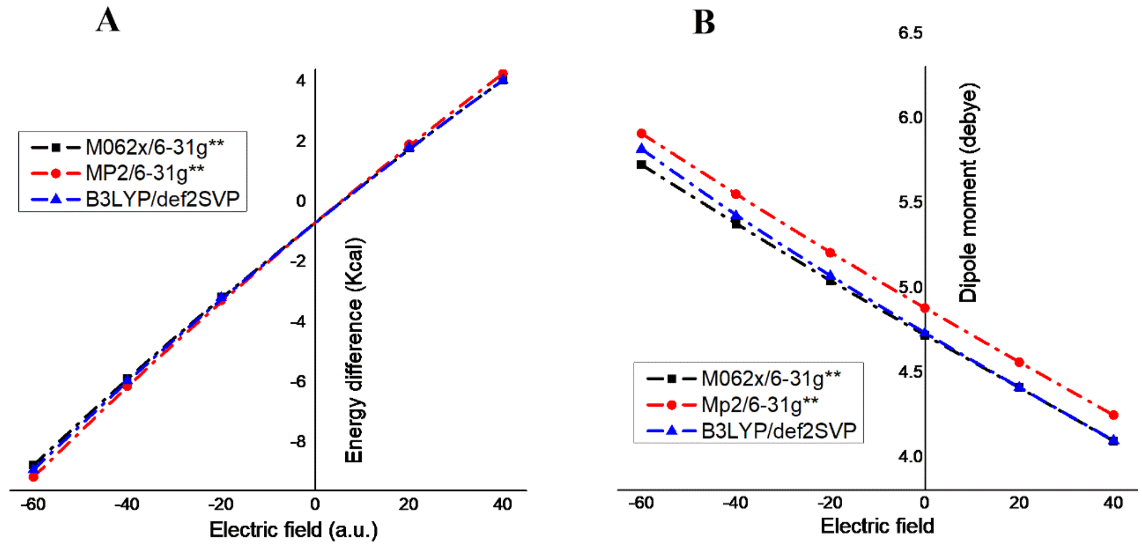

Figure 2: (A) represents the variation of interaction energy and (B) represents the variation of dipole moment with OEEF computed at M062x, MP2 and B3LYP levels of theory in (Bn-Li^+)

The second observation of interest is the distinction of the net dipole moment for benzene-Li^+ system with variation of magnitude and direction of the applied electric field presented in figure 2. The dipole moment in Fz=0 is 4.91 D and it increases in presence of Fz < 0 whereas reduces in presence of Fz >0. It reaches the lowest magnitude of 4.29 D in case of application of +0004 a.u. field strength, to the highest magnitude of 5.92 D in case of -0.006 a.u. on M062x/6-31G** level of theory. The trends have been verified in case of other levels and presented in figure 2 (B).

The most interesting observation obtained is the variation of distance of the cation from π-cloud centroid of benzene ring represented by 'R'. The variation in this case has been found to follow an interesting pattern. Its value increases from 1.87 Å to 1.96 Å with increase in magnitude of field strength in -Z -direction and decreases from the same to 1.82 Å with increasing field strength in +Z – direction as depicted in figure 3 (A).

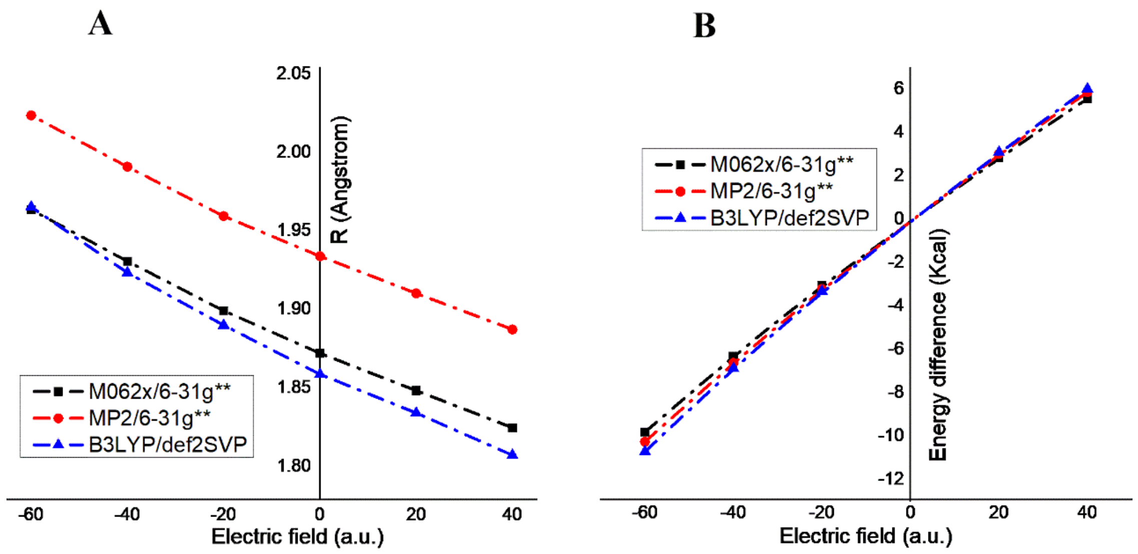

Figure 3: (A) represents the variation of R in Bn-Li$^+$ and (B) represents the variation of interaction energy in Bn-Na$^+$ with OEEF computed at M062x, MP2 and B3LYP levels of theory

Benzene- Na$^+$ complex:

Bn-Na$^+$ behaves almost similar to Bn-Li$^+$ in presence of OEEF but the degree of stabilization or destabilization is found higher for Bn-Na+ complex. In Bn-Na$^+$ system, stabilization of 3.32 kcal/mol occurs on application of electric field of strength -0.002 a.u., -6.88 kcal/mol associated with -0.004 a.u. and -10.72 kcal/mol with field strength of -0.006 a.u. while that of strength +0.002 a.u. causes destabilization of 3.11 kcal/mol and 6.03 kcal/mol in case of +0.004 a.u by M062X level as shown graphically in figure 3 (B). Similar trends have been obtained using the other two levels of theory as shown in the same figure.

Benzene-K$^+$ complex:

The interaction pattern of Bn-K$^+$ is similar to the earlier two complexes. The magnitude of stabilization and destabilization caused by OEEF follows the similar trend as observed above. Here, maximum stabilization of -11.32 kcal/mol is obtained in case of field strength of -0.006 a.u. followed by -7.34 kcal/mol in case of -0.004 a.u. and at last of -3.55 kcal/mol with -0.002 a.u. And destabilization of 6.41 kcal/mol and 3.32 kcal/mol are obtained on applying field strengths of +0.004 and +0.006 a.u. respectively at M062x computational level of theory shown graphically in figure 4 (A). Similar trends obtained at other levels have been shown in the same figure.

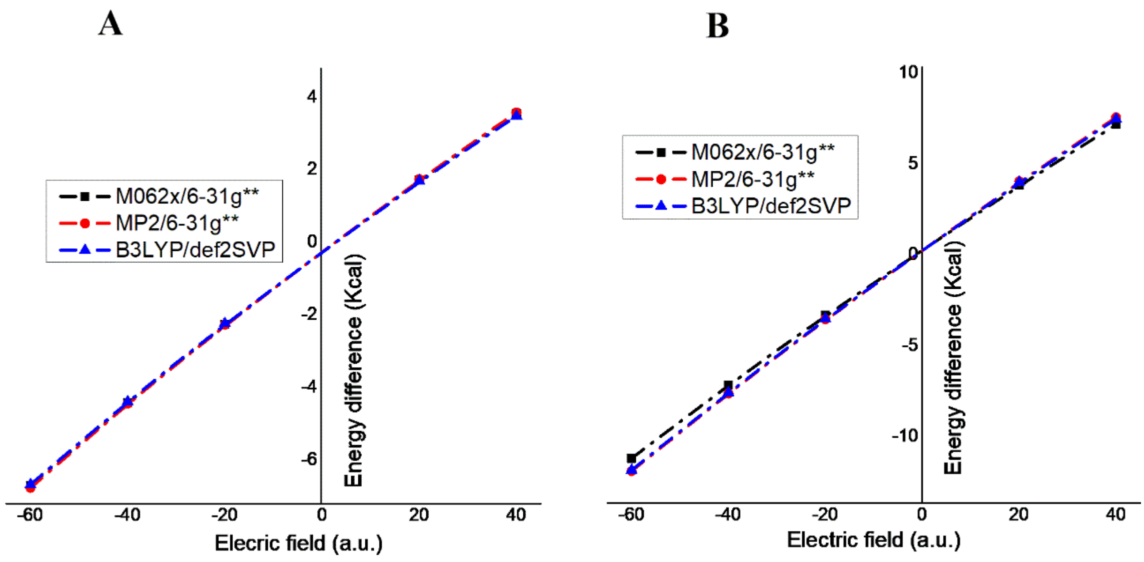

Figure 4: (A) represents the variation of interaction energy in Bn-K^+ and (B) represents its variation in Bn-Be^{2+} with OEEF computed at M062x, MP2 and B3LYP levels of theory

Benzene- Be^{2+} complex:

The above observed trend has been followed by bn-be cation also at all three computational levels of theory. From the state of system without OEEF, the system attains stability of -2.05 kcal/mol, -4.22 kcal/mol and -6.50 kcal/mol with field strengths -0.002 a.u., -0.004 a.u. and -0.06 a.u. respectively. From the same state, it gets destabilized by 1.94 kcal/mol and 3.76 kcal/mol on applying field strengths +0.002 a.u. and +0.004 a.u. respectively at M062x computational level of theory as shown graphically in figure 4 (B).

Benzene- Mg^{2+} complex:

On M062X computational method, stabilizations of -3.67 kcal/mol, -7.51 kcal/mol and -11.54 kcal/mol are obtained at -0.002 a.u., -0.004 a.u. and -0.006 a.u. respectively. Destabilizations of 3.50 kcal/mol and 6.80 kcal/mol are obtained on applying +0.002 a.u. and +0.004 a.u. respectively. Figure 5 (A) shows the graphical representation of obtained trends for various methods.

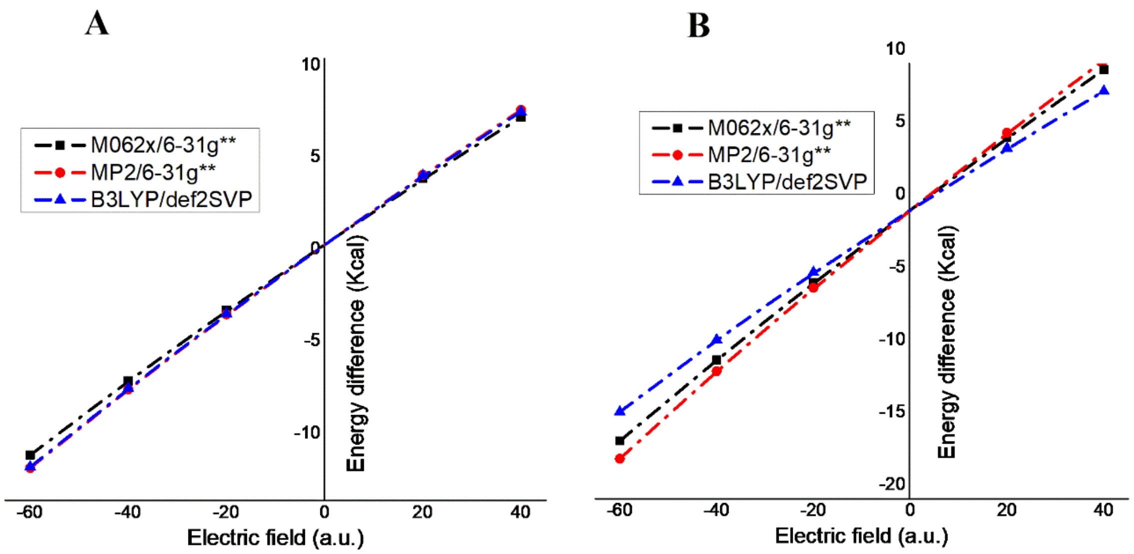

Figure 5: (A) represents the variation of interaction energy in Bn-Mg^{2+} and (B) represents its variation in Bn-Ca^{2+} with OEEF computed at M062x, MP2 and B3LYP levels of theory

Benzene- Ca^{2+} complex:

In this case also, similar trends have been obtained with stabilizations of -5.11 kcal/mol, -10.44 kcal/mol and -16.01 kcal/mol at -0.002 a.u., -0.004 a.u. and -0.006 a.u. field strengths respectively. And destabilizations of 4.89 kcal/mol and 9.57 kcal/mol have been obtained at M062x method with electric field strengths +0.002 a.u. and +0.004 a.u. respectively. MP2 and B3LYP methods have verified the obtained results as shown in figure 5 (B).

Thus, all benzene – cation systems, discussed above follow almost the similar trend of interaction energies having minimum value and maximum stability in the case of highest field strength applied to -Z– direction and maximum energy value and minimum stability is obtained on the application of field strength having highest magnitude in +Z- direction. It can be also stated that stability of the complex is achieved on applying OEEF directed from cation to π-cloud and instability is produced with application of electric field pointed from π- cloud to the cation.

Variation of dipole moment has followed similar patterns for other benzene-cation systems clearly shown by the following figures i.e., figures 6, 7 and 8 (A). It obtains maximum magnitude on application of field strength directed towards the π-cloud from the cation and minimum value when directed from the π-cloud to the cation.

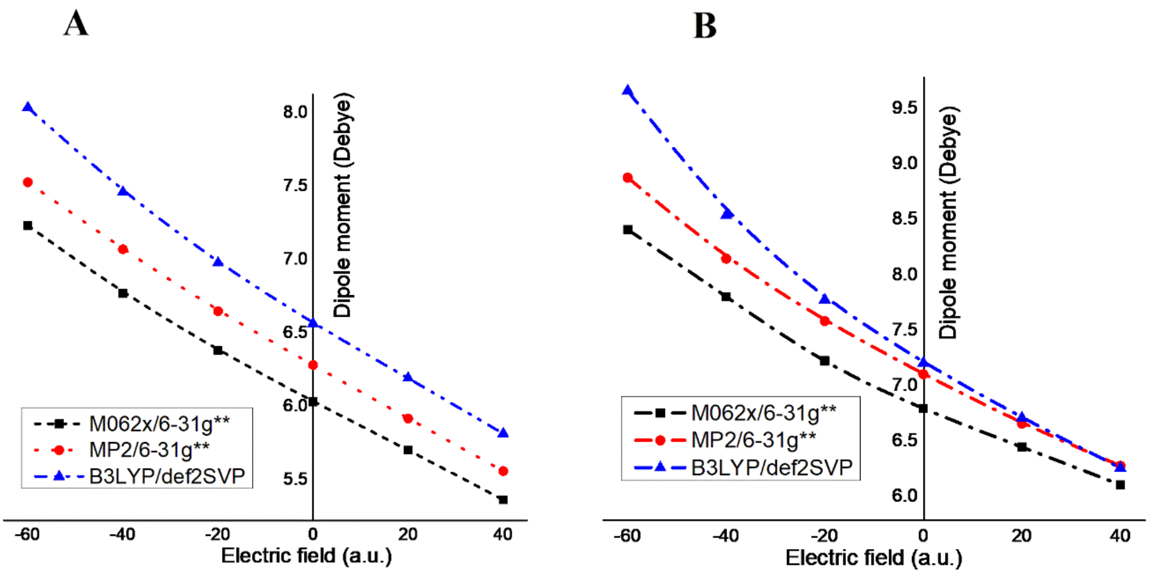

Figure 6: (A) represents the variation of interaction energy in Bn-Na$^+$ and (B) represents its variation in Bn-K$^+$ with OEEF computed at M062x, MP2 and B3LYP levels of theory

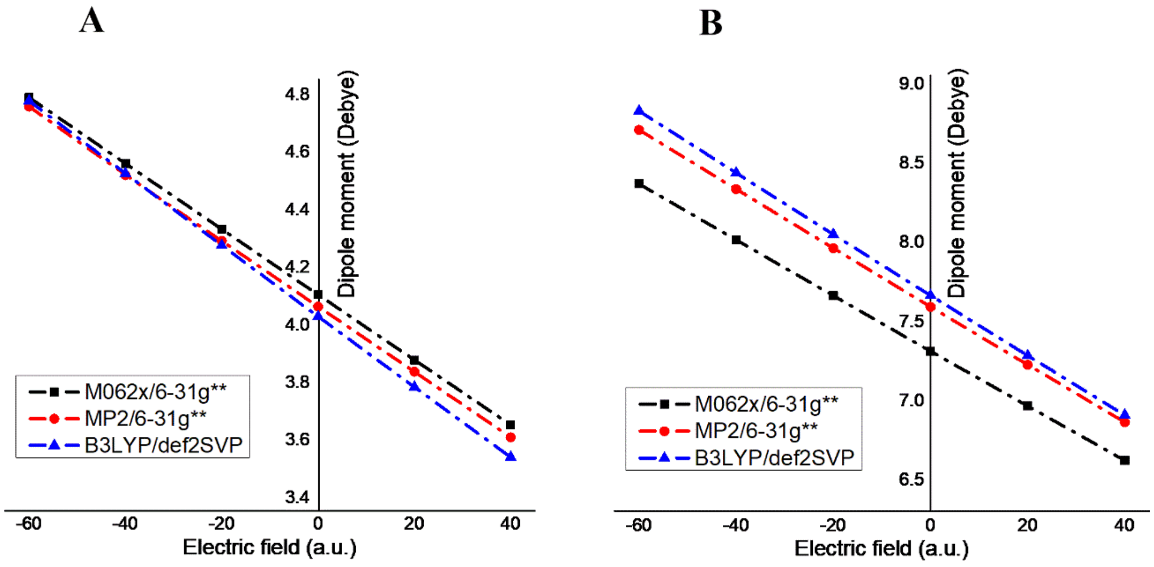

Figure 7: (A) represents the variation of interaction energy in Bn-Be^{2+} and (B) represents its variation in Bn-Mg^{2+} with OEEF computed at M062x, MP2 and B3LYP levels of theory

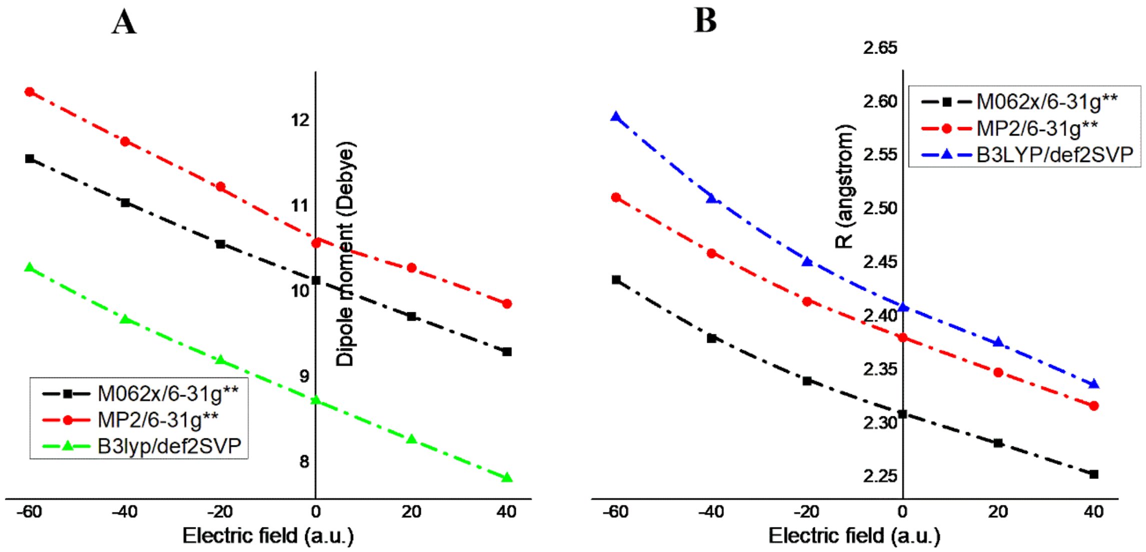

Figure 8: (A) represents the variation of dipole moment in Bn-Ca^{2+} and (B) represents the variation of R in Bn-Na^{+} with OEEF computed at M062x, MP2 and B3LYP levels of theory

All the above figures showing similar patterns of dipole changes with oriented field strengths confirms the presence of same chemistry behind these energy trends.

The following computationally obtained data of variation of R for other benzene-cation systems confirms the earlier described dependence of R on oriented field strengths. Figures 8 (B), 9 and 10 represent the variation of R with OEEF strengths.

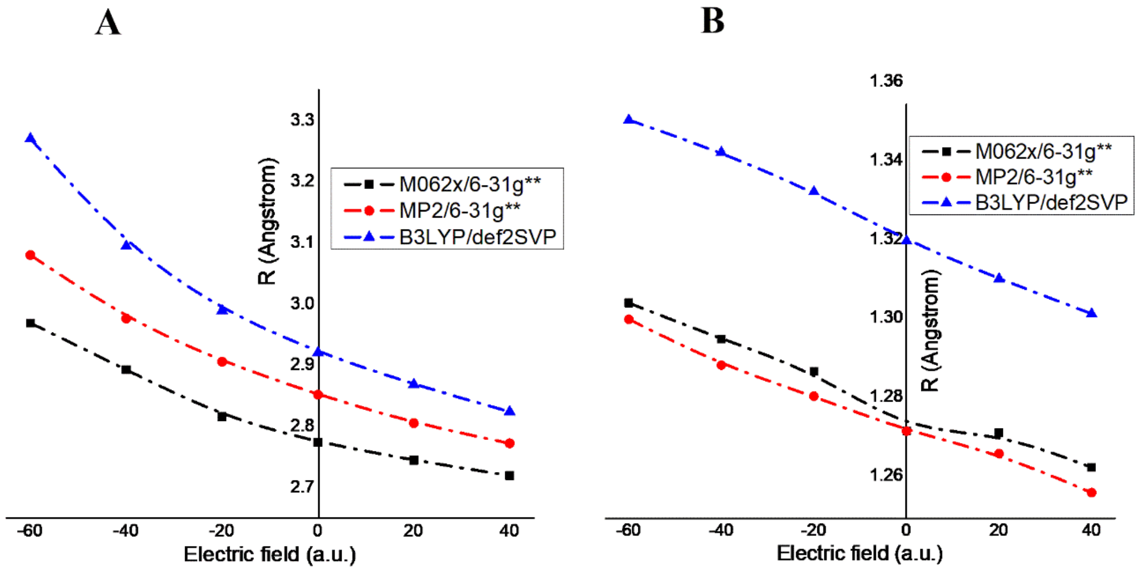

Figure 9:(A) represents the variation of R in Bn-K^{+} and (B) represents its variation in Bn-Be^{2+} with OEEF computed at M062x, MP2 and B3LYP levels of theory

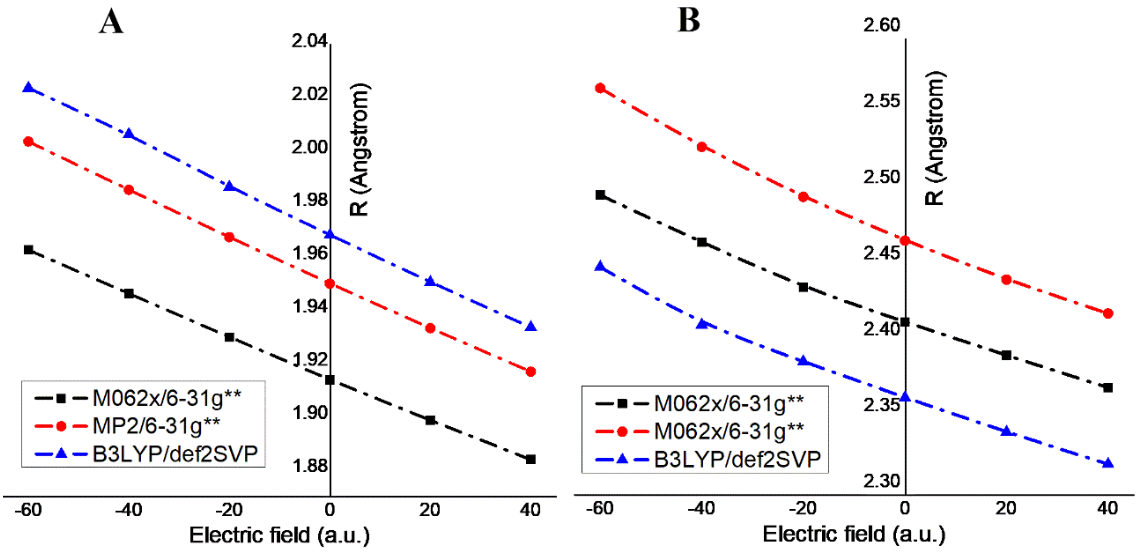

Figure 10:(A) represents the variation of R in Bn-Mg^{2+} and (B) represents its variation in Bn-Ca^{2+} with OEEF computed at M062x, MP2 and B3LYP levels of theory

However, the aforementioned results signify the existence of some factor taking place in the presence of OEEF that is controlling the pattern of interaction. And this factor has been found to be the resultant dipole moment for the system in presence and/or absence of field.

According to chemistry / physics conventions, dipole moment is directed from positive charge to the negative charge as the positive direction. The complex in which there occurs a charge transfer from metal cation to the benzene ring is indicated by a positive dipole moment and opposite direction is represented by negative dipole moment. When the electric field $F_z > 0$ i.e., positive electric field with vector oppositely aligned to the dipole moment vector of the complex, then by vector addition, net dipole moment gets reduced than the original magnitude for the complex. Similarly, on applying $F_z < 0$ i.e., negative electric field, magnitude of net dipole moment increases due to the alignment of electric field vector in the same direction as that of the original dipole moment of the complex. Thus, magnitude of dipole moment increases for -0.002, -0.004 and -0.006 values and decreases for 0.002 and 0,004 a.u. values than that in the absence of electric field.

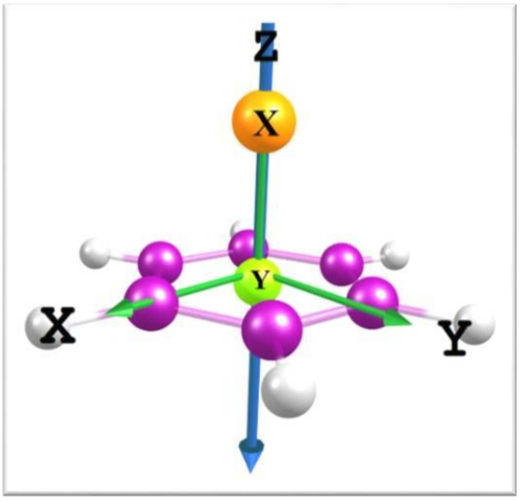

Figure 11: General sketch of System where blue pointer marks the direction of dipole moment

The respective changes in the dipole moment effects the nature of interactions in terms of polarity of the system. As we know, non-zero or increase in dipole moment refers to more polar character than the non-polar character in the case of zero dipole moment. The increase in polar character can be simply described as the existence of stronger attractive interactions or forces on the electrons, followed by slight imbalance in charges. This explains the existence of negative electric field to the system imparts extra stability to it and that of positive electric field leads to some destabilization to it.

Since, significant increase or decrease in magnitude of dipole moment can led to the suitable changes in the magnitudes of ‘q’ and ‘d’ parameters. (However, no significant changes have been observed in the NBO charges.)

But it showed the most unexpected trend of variation of R than the most probable relation of strength of cation-π interaction being inversely related to the distance between the cation and centroid of benzene ring (R), supported by the notion of cation-π interactions being of electrostatic origin. But the strength of the cation-π interactions has been found to increase with the cation-centroid distance and decrease with the decrease in the distance of cation- centroid distance. It can be explained by relating the above described notion of dipole moment. On application of -0.002, -0.004 and -0.006 values of field strength, the linear increase and decrease with 0.002, 0.004 and so on values can be described on basis of patterns obtained in the dipole moment in presence or absence of electric field. As discussed above, the system attains more stability with increase in dipole moment which in turn, leads to the increase in distance i.e., separation between the charges defined as R in this text. This explains the increase in R with increase in dipole moment and stability in case of $F_z < 0$. On similar ground, decrease in 'R' with that in dipole moment and de-stability gets explained in case of external $F_z > 0$.

A relative comparison of all the chosen systems shows that the order of effect of oriented electric fields on the interaction energies of existing interactions lies in the orders:

Bn -Li$^+$ < Bn -Na$^+$ < Bn – K$^+$

And, **Bn -Be^{2+} < Bn -Mg^{2+} < Bn –Ca^{2+}**

Computationally observed data providing evidence for the above observed trend has been graphically represented in figures 12 and 13 (A).

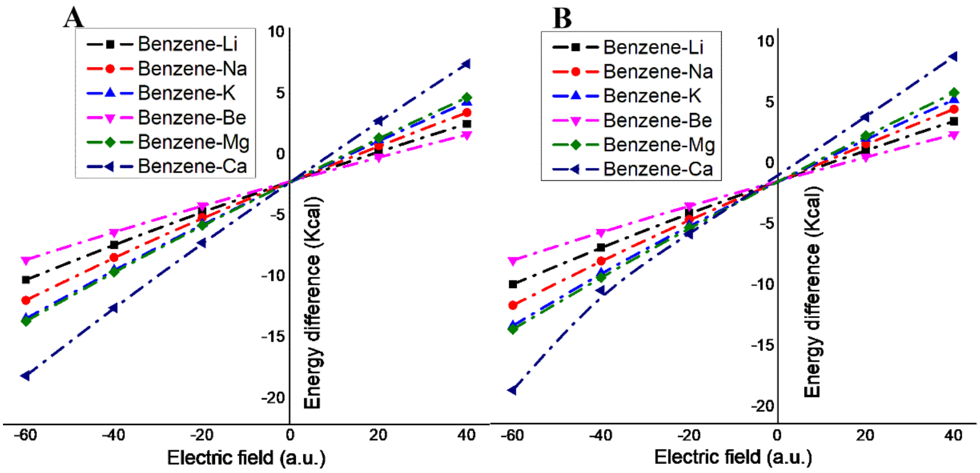

Figure 12: (A) and (B) represents the variation of interaction energy computed at M062x and MP2 levels of theory respectively

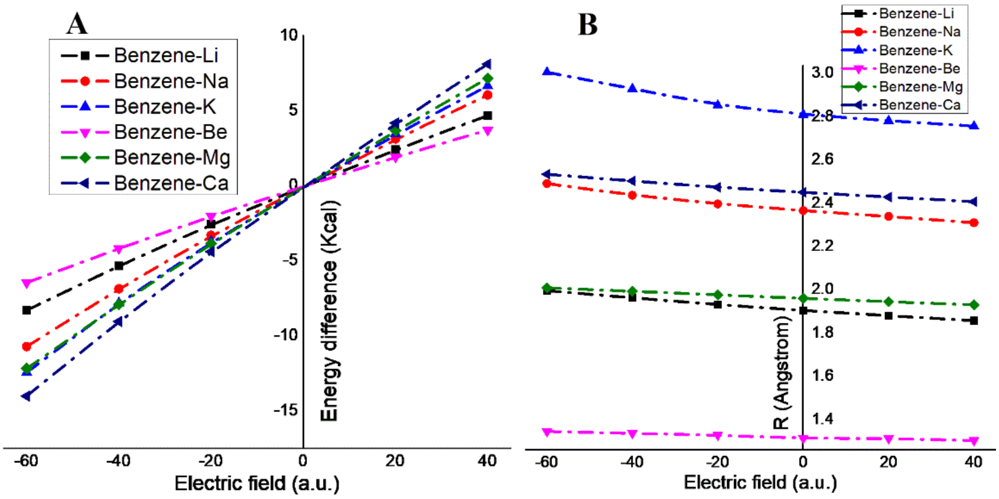

Figure 13: (A) represents the variation of interaction energy and (B) represents the variation of R for various systems with OEEF computed at B3LYP and M062x levels of theory respectively

These trends can be described as the resultant of the extent of polarizability of cations depending upon their charges and cationic radii. More will be the strength of cation to hold its electrons, lesser will be the delocalisation or diffusion of charges by applied field. It can also be described as the effect on the changes in interaction energies.

Incorporating them, we get,

Bn -Be^{2+} < Bn -Li^{+} < Bn -Na^{+} < Bn – K^{+} < Bn -Mg^{2+} < Bn – Ca^{2+}

The variation in the incorporated trend from the expected trend may be due to some unseen differences in the chemistry of cations.

In case of R, the extent of variation due to the effect of oriented field follows the described trend as given below, supported by the observations shown in figures 13 (B) and 14.

Bn-Be^{2+}< Bn-Mg^{2+}< Bn-Ca^{2+}< Bn-Li^{+} < Bn-Na^{+}< Bn-K^{+}

The trends obtained in this parameter can be attributed to the effect of charge on cationic radii. As the cationic radii decreases due to increase in charge, the net potential of oriented fields and dipole vector associated with them decreases due to the stronger nuclear forces operating on the valence electrons in it. So, the maximum displacement of R will be found in the system with cation having least nuclear forces operating on the valence electrons.

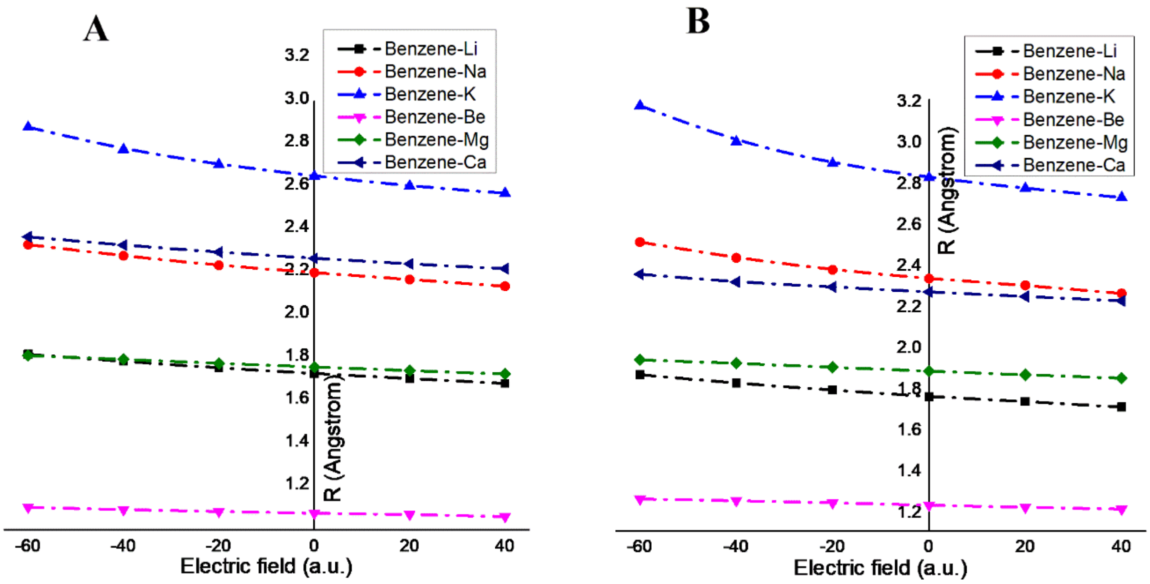

Figure 14: (A) and (B) represents the variation of R with OEEF for various systems computed at MP2 and B3LYP levels of theory respectively

While in the domain of dipole moment, following trend has been obtained:

Bn-Be^{2+}< Bn-Li^{+}< Bn-Mg^{2+}< Bn-Na^{+}< Bn–Ca^{2+}< Bn-K^{+}

This observed trend is the resultant of the last trend discussed above and the corresponding charges and shows the trend among periods, and is maximum for period 3 followed by period 2 and then by period 1 in case of chosen metal cations. The greater change in dipole moment in case of systems containing alkali metal cations than that containing alkaline earth metal cations due to lesser nuclear forces operating on the valence electrons in alkali metal cations due to which oriented fields can affect the electron density distribution and thus, dipole moment associated with them easily.

Computational data supporting this observation has been shown by figures 15 and 16.

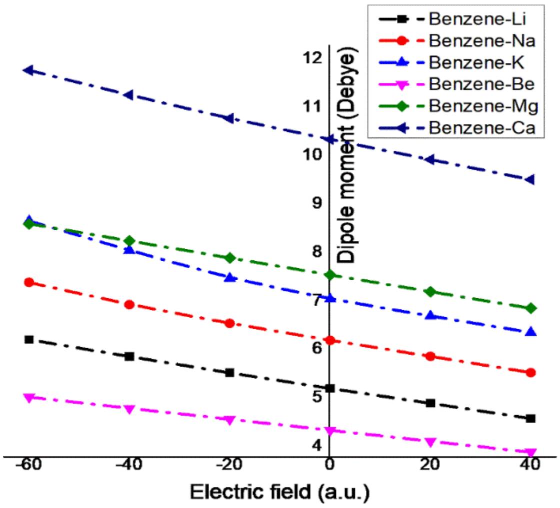

Figure 15 represents the variation of dipole moment with OEEF for various systems computed at M062x level of theory

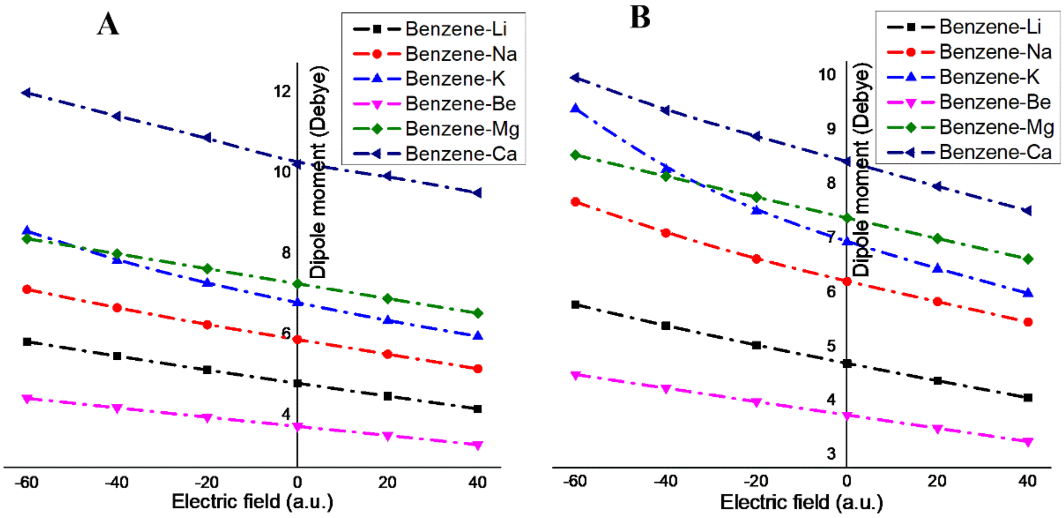

Figure 16: (A) and (B) represents the variation of dipole moment for various systems with OEEF computed at MP2 and B3LYP levels of theory respectively

CHAPTER IV

Conclusion

Oriented external electric fields have directional dependence on the nature of cation-π interactions. Field intensities applied in noble direction of charge transfer tend to stabilize the interactions and those in opposite direction tend to destabilize them. The dipole moment plays a significant role in assigning stability to systems by incorporating the effect of field intensity vector to it. An unexpected trend has been found in the effect of direction of electric field to the distance of cation and centroid of benzene, defying the general approach lying on the electrostatic principles.

Extent of the effect of oriented field strengths on the chemistry of cation-π interactions has been found to be varying in 'periods'. The maximum response in interaction energies in the presence of external fields has been given by period 3 cations in both groups I and II followed by period 2 and then period 1 cations, described as,

$$\mathbf{Bn\text{-}Li^{+} < Bn\text{-}Na^{+} < Bn\text{–}K^{+}}$$

And, $$\mathbf{Bn\text{-}Be^{2+} < Bn\text{-}Mg^{2+} < Bn\text{–}Ca^{2+}}$$

In terms of cation-benzene centroid distance, maximum effect has been shown by alkaline earth metal cations than those of alkali metals, but that also following the above described period trend, i.e.,

$$\mathbf{Bn\text{-}Be^{2+} < Bn\text{-}Mg^{2+} < Bn\text{-}Ca^{2+} < Bn\text{-}Li^{+} < Bn\text{-}Na^{+} < Bn\text{-}K^{+}}$$

The same periodic effect has been found in domain of dipole moment also, as:

$$\mathbf{Bn\text{-}Be^{2+} < Bn\text{-}Li^{+} < Bn\text{-}Mg^{2+} < Bn\text{-}Na^{+} < Bn\text{–}Ca^{2+} < Bn\text{-}K^{+}}$$

All these effects can be attributed to the net possible delocalisation of electron density in the presence of oriented external fields in the by overcoming the effects of nuclear charge, polarizability etc.

CHAPTER V

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