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Effect of Counterions on Cation…π Interactions

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Abstract: *Counterions like F^-,Cl^-.Br^-,I^- are introduced into benzene…Li^+, benzene….Na^+ and benzene…K^+ complexes. Addition of these counterions lowers the binding energy of these cation…π systems. The alkali metal cations includingLi$^+$,Na^+ and K^+ and counterions including F^-,Cl^-,Br^-,I^- are considered in the present study usingB3LYP/6-31+G(d,p)basis set. Results show that cation….π interactions are more stable than counter ionic interactions. When counterions like halide ions, sulphate ions and phosphate ions are introduced into a cation….π complex, there observed a decrease in binding energy, which yields valuable information in understanding crystal packing.*

I. Introduction

Benzene can be considered as a planar hexagonal system with delocalized π electron centres above and below the plane . Addition or Interaction of a cation reduces the charge density on the benzene. The cation binds to the π-face of the aromatic. In the initial findings, K^+ interacts with water gives an interaction energy of 18kcal/mol, where as K^+ with benzene it is 19 kcal/mol [1]. Hence the aromatic complexes are more stronger. Both NMe_4^+ and K^+ have similar interaction energies. Electrostatic interaction is the driving force for these interactions.[2]

It is seen that a counterion is the ion ,that accompanies an ionic species inorder to maintain electric neutrality.[3,4,5]. In Sodium chloride(NaCl), the sodium cation is the counterion for the chlorine atom and vice versa. In tight ion pairs, the anion will effect the ability of the cation to participate in cation….π binding. In tetramethylammonium binding with picrate, the binding energy is for picrate is found to be -8.35kcal/mol, in tetramethylammonium chloride, the binding energy for chloride is -4.64kcal/mol. Results shows that cation-π interactions are more stable than counterionic interactions. (Alkali metals> Alkaline earth metals.) When counterions like halogens, sulphates and phosphates are introduced into a cation-π complex, there is a decrease in binding energy.

II. Theory of Cation–π Interactions

Electrostatic model and Quadrople moment are the important factors controlling cation…π Interactions . According to electrostatic model, the positive surface is balanced by negative π-Electrons above and below the plane. A comparison of simple alkali metals binding to Benzene, the trend is $Li^+ > Na^+ > K^+$ gives -37.24kcal/mol, -24.06kcal/mol and -15.23kcal/mol. The more negative the maximum electron charge cloud over the center of the aromatic, cation-π interaction is stronger.

Electrostatic components and dispersive forces are one of the major factor, that controls cation- π interaction. Probably the most important of these for simple systems is the interaction of the ion with the induced dipole in the system. Donor-acceptor and charge- transfer terms along with dispersion forces may also be important.

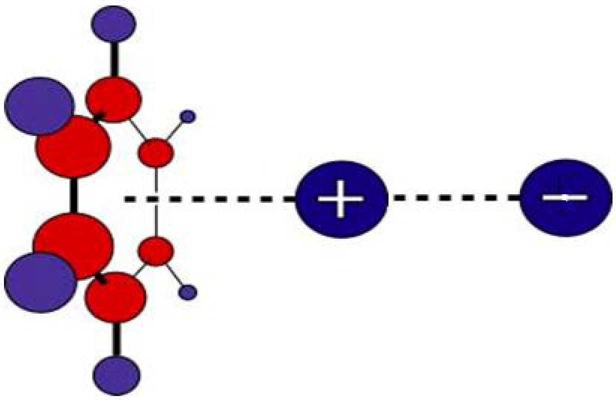
Binding Energy is one of the factor that controls Cation π interaction. It is found that when the binding energy of cation….π system is more negative, it is more stable.The electrostatic forces and dispersion forces are also interesting. The role of an induced dipole in cation binding showed that cyclohexane is better than benzene in this regards it is just that the induced dipole is not enough to make a strong cation binding site.

Concerning the aromatic component, the electrostatic potential surfaces of the aromatic rings of delocalization electron clouds shows trends in cation-π interactions. Variations among the ions are also consistent, in that the cation-π interaction decreases as the ionic radius increases, as expected for an electrostatic model.

Benzene, has no dipole moment, but it does have a substantial, permanent quadrupole moment. A quadrupole can be thought of as two dipoles aligned in such a way so that there is no net dipole. Topologically, quadrupoles are equivalent to dorbitals and the quadrupole in benzene in particular is topologically equivalent to a dz^2 orbital. Thus, there is a permanent, non-spherical charge distribution in benzene, with regions of relative negative and positive charges. Plots of the electrostatic potential surface provide a useful way to visualize the quad-rupole. Just as an ion can be attracted to the appropriate end of a dipole, so can an ion experience a favourable interaction with appropriate regions of a quadrupole. This is an electrostatic interactions ,it requires no adjustment of the electronic distribution around the ion or the molecule. Importantly, there is no a prior reason to expect that such interactions will be inherently weaker when the molecule contributes a quadrupole rather than a dipole.

The usefulness of the quadrupole moment is that it provides an easy way to visualize the charge distribution of aromatics and leads naturally to the expectation of significant electrostatic interactions. It also correctly predicts the preferred geometries of cation-π complexes and other "polar-π" inter- actions.

III. STRUCTURE AND BONDING



IV. CATION…π INTERACTIONS-COUNTERIONIC EFFECT

SO_4^{2-} ion is a counterionic group, it is interacted with the benzene…Li^+ system. It is seen that the cation-π system is interacting with the counterionic system. The sulphur oxygen bond aligned parallel to the carbon hydrogen bond. When benzene…Li^+ system interacts with the counterionic group like SO_4^{2-}system, through non-covalent interaction, there forms interaction energy. This counterionic interactions forms a planar system, where as in Li^+ ion, cation Pi interaction exists.

Six resonances can possible for an sulfate ion. The SO_4^{2-} exists in the resonance forms, where the sulphur-oxygen bond has more energy than the oxygen- oxygen bond. The S-O bond length is 2Angstrom more. Many Interactions are possible in these type of systems. The S-O bond length is 2Angstrom more than O-O bond or S-S bond.

A) Sulfateion (SO_4^{2-})

Sulfate ion (SO_4^{2-}) is the conjugate base of HSO_4^-, which in turn is the conjugate base of H_2SO_4, sulphuric acid. GilbertLewisin1916, in terms of electron octets around each atom, proposed that there is no double bonds but only aformalchargeof2+onthesulphuratom. The apparent contradiction to the shortness of the S-O bond length insulfateion than S-O single bonds can be cleared if one realizes that there are covalent double bonds in the Lew is structure that representbondsthatarestronglypolarizedbymorethan90%towardstheoxygenatom.Ontheotherhand,inthestructurewithanionicbond,thechargeislocalizedasalonepairontheoxygen.

B) Phosphate ion (PO_4^{3-})

The phosphate ion is a polyatomic ion with the empirical formula PO_4^{3-} and a molar mass of 94.97 g/mol. It consists of one central phosphorus atom surrounded by four oxygen atoms in a tetrahedral arrangement. The phosphate ion carries a negative three formal charge and is of the hydrogen phosphate ion, HPO_4^{2-} , which is the conjugate base of

$H_2PO_4^-$, the dihydrogen phosphateion, which in turn is the conjugate base of H^3PO^4, phosphoric acid. A phosphate salt forms when a positively charged ion attaches to the negatively charged oxygen atoms of the ion, forming an ionic compound.

C) Chlorate (ClO_3^-)

The chlorate ion cannot be satisfactorily represented by just one Lewis structure since all the Cl-O bonds are of the same length (1.49 Å) in potassium chlorate and the chlorine atom is hypervalent. Instead, it is often thought of as a hybrid of multiple resonance structures.

V. COUNTERION EFFECT IN CATION-Π SYSTEMS

Counterions like F^-, Cl^-, Br^-, I^-_ are introduced into benzene...Li^+, benzene....Na^+ and benzene...K^+ complexes. Addition of these ions lowers the binding energy. Binding energy shows an increase in the values, from F^- to I^-. Cation-π interaction with counterionic groups are strongly favoured when an anion like I^- is interacting. The binding energy is found to be -25.63kcal/mol. The observed values are found to be -13.98,-15.21,-16.67 and -25.63 kcal/mol.[6,7,8]. Calculations were performed on the interaction between cation…π systems and various anionic groups, which are called counterionic groups, where M+=Li+,Na+,K+ and X=F-,Cl-,Br-.I^-.Calculations were performed using B3LYP version of DFT. 6-31+G(d,p) basis set was employed. Calculations for the lowest energy structures were obtained.

It is observed that the cation…π interaction in benzene…..Li^+, benzene….Na^+, Benzene..K^+ systems are more stronger than counterionic interactions. Electrostatic interaction is the major driving force for benzene…Li^+, Na^+, K^+ complexes where charge transfer decreases in the order K^+>Na^+>Li^+

Benzene……Li+…..		F-Benzene…..Li+……Cl-

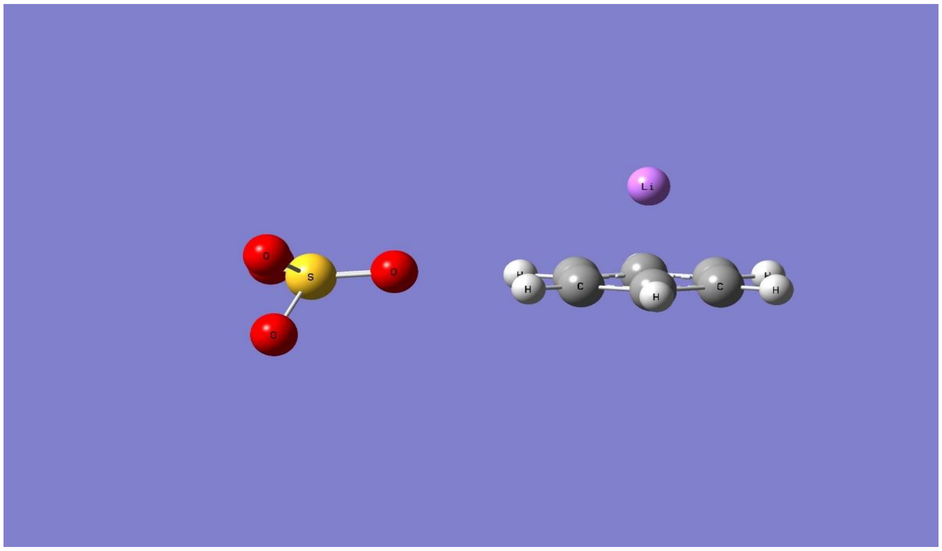
Benzene……Li+……		Br-Benzene…….Li+……I-

Benzene..Li^+halide counterionic systems

Counterionic Systems	ΔE(kcal/mol)	ΔE_{bsse}(kcal/mol)
Benz…..Li^+F^-	-13.98kcal/mol	-11.57kcal/mol
Benz….Li^+Cl^-	-15.21kcal/mol	-13.38kcal/mol
Benz….Li^+Br^-	-16.67kcal/mol	-13.46kcal/mol
Benz…..Li^+I^-	-25.63kcal/mol	-16.42kcal/mol

Binding Energy of Benzene..M^+halide counterionic systems

Counterionic System	**ΔE(kcal/mol)**	**ΔE_{bsse}(kcal/mol)**
Benz….Na^+F^-	-9.76kcal/mol	-9.03kcal/mol
Benz….Na^+Cl^-	-10.64kcal/mol	-9.96kcal/mol
Benz….Na^+Br^-	-13.26kcal/mol	-9.88kcal/mol
Benz…..Na^+I^-	-14.06kcal/mol	-5.84kcal/mol
Benz…..K^+F^-	-6.64kcal/mol	-6.15kcal/mol
Benz….K^+Cl^-	-7.13kcal/mol	-6.41kcal/mol
Benz…..K^+Br^-	-9.27kcal/mol	-6.12kcal/mol
Benz…..K^+I^-	-15.62kcal/mol	-5.41kcal/mol



In benzene.....Li^+ sulfate, there is some interaction energy.(82kcal/mol).There is no such interaction in Na^+ and K^+. In benzene......Li^+ chlorate, there is no binding of chlorate with Li. It is not in Na^+ and K^+. In benzene....Li^+ phosphate, phosphate binds with Li+ and not in Na^+ and K^+.

In Benzene.....Li phosphate , the Li^+ ion binds with central phosphorus atom significantly a Li-P bond, with the Li attached to two oxygen atoms. P=O bond perpendicular to the plane, above the counterionic system. It is similar to a diamond shaped cut. The oxygen-Lithium bond lengths are 2.5 angstroms and 2.4 angstrom. Binding energy is decreased Li^+ above the plane binds to the aromatic ring .It shows a binding energy of 82kcal/mol where as reverse in the case of Na+ and K^+. The counterionic bond is not seen in the benzene....Na+ phosphate. It is not at all binding in K^+.

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VI. CONCLUSION

Cation….π Interaction with counterionic groups are strongly favoured when an anion like I-Is interacting. Among the halide counterions, Benz…M+I- is more stable.ie, Benz…M+I- binds more and is stable as F<Cl<Br<I. Addition of counter ions like halide ions lowers the binding energy of cation…π system. This study yields valuable information in crystal packing[10,11,12] and also in the transport of ions in biological systems[13]

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