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The Influence of Cation-π Interactions on the Strength and Nature of Intramolecular O···H Hydrogen Bond in Orthohydroxy Benzaldehyde Compound

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The influence of cation-π interactions on the strength and the nature of intramolecular O···H hydrogen bond has been investigated by quantum chemical calculations in orthohydroxy benzaldehyde (HBA) compound. *Ab initio* calculations have been performed at MP2/6-311++G** level of theory. Vibrational frequencies and physical properties such as chemical potential and chemical hardness of these compounds have been systematically explored. The natural bond orbital (NBO) analysis and the Bader's quantum theory of atoms in molecules (QTAIMs) have also been used to elucidate the characteristic the interaction of these complexes. The intramolecular O···H hydrogen bond has been categorized from weak to medium in the investigated systems. The results obtained from the calculations and topological parameters derived from the Bader theory suggest that the strongest interaction and the highest electron density at BCP (bond critical point) are related to the Be^{2+}-HBA complex. The HOMO-LUMO energy has also been evaluated. The calculated highest occupied molecular orbital (MO) and lowest unoccupied MO energies show that charge transfer occurs within the molecule. Furthermore, numerous correlations between topological, geometrical and energetic parameters have been found.

Keywords: Cation-π, Hydrogen bond, *Ab initio*, QTAIM, NBO

INTRODUCTION

Understanding the noncovalent interactions and the interplay among them are of pivotal importance to the development of fields such as supramolecular chemistry and molecular recognition [1]. Interactions involving aromatic rings are crucial binding forces in both chemical and biological systems [1]. For instance, cation-π bonding is an important and widely recognized noncovalent interaction that involves aromatic rings [2]. Numerous studies have reported the occurrence of cation-π interactions in protein structures, [3] protein-ligand [4] and protein-DNA [5] complexes. The cation-π interaction is dominated by electrostatic and ion-induced polarization terms [6]. The nature of the electrostatic term can be rationalized by means of the permanent quadrupole moment of the arene. The hydrogen bond interaction is mainly dominated by the electrostatic effects (dipole-dipole interactions) [6].

According to Vijay and Sastry, when the noncovalent interactions operate simultaneously and mutually enhance the strength of each other, they are termed as acting cooperatively [7]. In other words, the difference between the total complexation energy (the difference in the energy of the complex and that of the monomers) and sum of the individual interaction energies can be defined as cooperativity energy (negative) or anti-cooperativity energy (positive). It indicates how the noncovalent interactions influence each other. It is very important to understand molecular aggregation and is currently a topic of wide ranging interest [8]. In 2005, Mignon et al. investigated the interplay between π-π stacking and hydrogen bonding related to the nucleic acids [8]. In 2008, Vijay *et al.* reported the strong cooperativity between cation-π interaction involving alkali and alkaline earth metal ions and π-π, and hydrogen bonding interactions [8]. In 2010, they performed

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*Corresponding author. E-mail: az_khanmohammadi@yahoo.com systematic quantum chemical studies to estimate the effects of cation-π and π-π interaction on each other in cation-π-π systems. The results indicated a notable increase of 2-5 kcal mol^{-1} in the π-π interaction energy in the presence of the cations and the cation-π interaction energy is also enhanced in the presence of π···π interaction [8]. Recently, the interplay between anion-π and π-π interactions has been investigated with experimental and theoretical methods [9]. It was demonstrated that there is a strong synergetic effect between anion-π and π-π interactions in complexes where both interactions coexist. Very recently, the interplay between cation-π and hydrogen bonding interactions has also been studied in different systems with quantum chemical calculations [9]. A large synergetic effect is present in complexes where cation-π and hydrogen bonding interactions coexist. This effect is helpful for understanding some biological processes where the interplay between two interactions exists.

The present communication is directed to investigate the orthohydroxy benzaldehyde interactions with some mono and divalent metal cations, namely Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} and Ca^{2+}. The main objective of this article is not only to determine the effects of cation-π interactions on the nature and strength of intramolecular O···H hydrogen bond, but also to gain further insight into the effect of mentioned interactions on the geometrical parameters, binding energies, topological properties and population analyses of the formed complexes. To this end, *ab initio* calculations are accompanied by the AIM and NBO analyses. To gain further insight, we present a comprehensive analysis of these interactions on HOMO-LUMO data in the studied complexes.

METHODS

All calculations have been performed with the Gaussian 03 program [10]. These complexes have been optimized at the MP2/6-311++G** level of theory. The complexation energies have been corrected for the basis set superposition error by the Boys-Bernardi counterpoise technique [11]. The procedure for obtaining these energies is as follows:

$$\Delta E_{ion\text{-}\pi} = E_{ion\text{-}HBA} - (E_{ion} + E_{HBA}) \qquad (1)$$

The vibrational frequencies have been calculated at the MP2/6-311++G** level on the optimized geometries. The topological electron charge density has been analyzed by the atoms in molecules (AIMs) method [12], using the AIM2000 program [13] on the obtained wave functions at the MP2/6-311++G** level. Also, the population analysis has been performed by the natural bond orbital (NBO) method [14] on the optimized structures using NBO program [15] under Gaussian 03 program package. The molecular orbital (MO) calculations such as HOMO-LUMO are also performed on all complexes.

RESULTS AND DISCUSSION

Cation-π Interaction

The complexes have been illustrated according to the position of the cations (M) on the orthohydroxy benzaldehyde ring (Fig. 1). The calculations suggest that the size of cation and the nature of π-system (HBA) are two influential factors that affect the nature of interaction. In the current investigation, the interactions are classified into two different types. Theoretical evidences have been used to demonstrate different natures for the interaction of HBA with the alkali-metal cations and the alkaline-earth cations. However, because the aim of this section is investigation of the cation-π interaction effects on some structural and electronic properties of HBA ring, all ions are located along the main symmetry axis (C_2v) in the selected structures.

As presented in Table 1, the absolute values of complexation energy ($|\Delta E_{ion\text{-}\pi}|$) for divalent ions ($Be^{2+}$, Mg^{2+} and Ca^{2+}) is greater than those for monovalent ions. For each ion group (alkali or alkaline-earth), the dependence between $|\Delta E_{ion\text{-}\pi}|$ and $d_{ion\text{-}\pi}$ (the distance between the ion and the center of aromatic ring) should separately be considered. A reverse relationship is found between $|\Delta E_{ion\text{-}\pi}|$ values and $d_{ion\text{-}\pi}$. Furthermore, as shown in Table S1 (Supporting Information), complexation changes the geometrical parameters of HBA molecule. Theoretical results show that the greatest $|\Delta E_{ion\text{-}\pi}|$ value corresponds to the longest C-C bond ($d_{C\text{-}C}$) in the studied complexes. In isolated HBA, the HOC, OCC and CCCC angles (θ_{HOC}, θ_{OCC} and φ_{CCCC}) are equal to 106.7°, 124.3° and 0.0°, respectively. The $\theta_{HOC}/\theta_{OCC}$ increases/decreases with increasing $|\Delta E_{ion\text{-}\pi}|$ in the investigated complexes. Furthermore, the obtained results

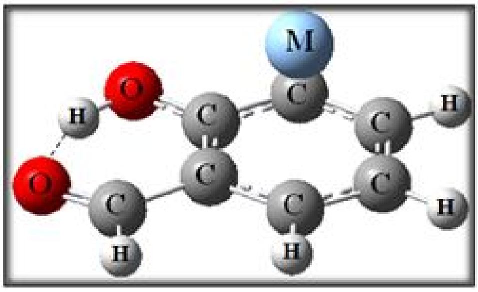

Fig. 1. The investigated complexes: The complexes of ion···HBA derivatives. M = Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} and Ca^{2+}.

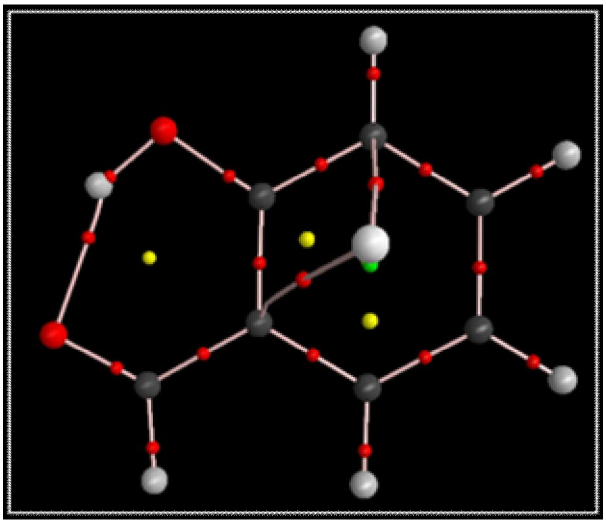

Fig. 2. Schematic representation of distribution of critical points in Be^{2+}-HBA complex. Small red spheres, small yellow spheres, small green sphere and lines represent bond critical points (BCPs), ring critical points (RCPs), cage critical point (CCP), and bond paths, respectively (Color figure online).

how that the distance between the ions and C atoms is not identical in the analyzed complexes. Thus, the HBA ring is not flat in these complexes ($\varphi_{CCCC} \neq 0.0°$). Results of theoretical calculations on the Be^{2+} complex show that the increase of $|\Delta E_{ion\text{-}\pi}|$ value is accompanied with increasing φ_{CCCC}.

The Bader's theory [12] is a powerful tool not only to characterize the electronic properties of the considered species but also to have a better understanding of the nature of the intermolecular interactions. The characteristic of the electron density at the bond critical point (ρ_{BCP}) and its laplacian ($\nabla^2\rho_{BCP}$) reveal the nature of the interaction. A large ρ_{BCP} can be ascribed to a concentrated electronic charge ($\nabla^2\rho_{BCP} < 0$). A small ρ_{BCP} can be attributed to a depletion of the electronic charge in the internuclear region ($\nabla^2\rho_{BCP} > 0$). The former case is an indication of sharing of the covalent bond. The latter is observed for interactions between the closed shell systems such as ionic interactions, van der walls interactions or H-bonds [16,17]. Figure 2 presents a molecular graph of a typical complex analyzed in this manuscript. The BCP is made between metals and each C atom of HBA in the studied complexes.

The decreased electron density, ρ, is found to be in the order $K^+ > Na^+ > Li^+$ for the corresponding alkali complexes (Table 2). The obtained results show that the smallest value of ρ at the BCP is found for the biggest cation that leads to the largest equilibrium distance of the cation-π and weakest interaction energy and *vice versa*. This likely reflects the strength of cation-π interaction. Calculations show the same results for alkaline-earth complexes. For the M^+-HBA complexes, as the size of the cation increases, the values of Laplacian become smaller (Table 2). Interestingly, a good linear relationship is observed between the complexation energies ($|\Delta E_{ion-\pi}|$) and the electron densities (ρ_{ion-C}), and the correlation coefficient R is equal to 0.988 at MP2/6-311++G** level of theory. Thus, the values of ρ_{ion-C} could be useful to characterize the nature and strength of ion-π interactions in the complexes. A positive value of laplacian of ρ at various BCPs of cation-ligand bonds ($\nabla^2\rho_{ion-C}$) indicates that these interactions are electrostatic in nature (see Table 2). Moreover, a comparison of the values of ρ at the C-C (ρ_{C-C}) and C-H (ρ_{C-H}) BCPs within the formed complexes, demonstrates significant changes during the interactions. The results presented in Table 2 indicate that the increase in the $|\Delta E_{ion-\pi}|$ of complexes is in agreement with the decrease of the ρ_{C-C}. Based on the results, the BCP of C-H bond is also increased with the cation-π interactions (see Table 2). Furthermore, our theoretical results show that the relationship between the ρ_{C-C} and ρ_{C-H} values and their corresponding bond lengths is reversed.

Natural bond orbital analysis emphasizes on the role of intermolecular orbital interaction in the complex, particularly charge transfer. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic importance by second-order perturbation theory. The results of second-order perturbation theory analysis at MP2/6-311++G** level of theory are collected in Table 3. The charge transfer energies reported in Table 3 are related to the dominant interaction which is between π-electrons of donor species and LP* of the cations ($\pi_{C-C} \rightarrow LP^*_{cation}$). Table 3 shows that the greatest value of $E^{(2)}$ is achieved for the Be^{2+} complex, while the smallest values of $E^{(2)}$ belongs to the K^+ complex. The obtained results show that the stronger interaction leads to lower occupation number of π_{C-C}. The results of calculation also reveal that, the $E^{(2)}$ values for HBA complexes with divalent ions are larger than those with monovalent ions, indicating that the cation-π interactions are stronger in these complexes. It is interesting to note that the obtained results at the NBO basis are completely in accordance with the results obtained in the AIM framework. In cation-π interaction, the large variation of electron density at the C-C bond critical point of π-system can be justified by large value of charge transfer from $\pi_{(C-C)}$ to LP* of the cation. Therefore, our theoretical results show that the observed trend in the energies of these interactions ($E^{(2)}$) is in agreement with $|\Delta E_{ion-\pi}|$ and ρ_{ion-C} parameters (Tables 1 and 2). The obtained data also demonstrate that the charge transfer for alkaline-earth metal complexes is more considerable than that for alkali-metal complexes (Table 3). The net charge transfer is evaluated to be from π_{C-C} to the cation by 6.36, 2.17 and 1.12 kcalmol^{-1} for the Li^+, Na^+ and K^+ complexes, respectively, indicating that the smaller cation with more charge allows the cation to more effectively withdraw electron density from the π-system, increasing the charge transfer. The same behavior is observed for the cation-π interactions in alkaline-earth metal complexes. These results are in accordance with the geometries and analyses of the binding energies as well as our investigation on the cation-π interactions between the HBA system and cations.

The charge transfers ($\Delta q_{(CT1)}$) for the investigated complexes are reported in Table 4. The transferred charge between the HBA ring and a cation during complexation could be easily determined as the difference of charges between free cation and complexed cation. As obviously seen in Table 4, the charge transfer for these complexes, gives the smallest values for K^+ complex and the largest values for Be^{2+} complex. The size or the charge density on metal indicates that these complexes are largely electrostatic in nature. The greater charge density of the smaller metal leads to the more charge transfer of cation-ligand interaction in the system.

The influence of ion-π interactions on the occupation numbers of Lp_O and Val_O has also been investigated. In isolated HBA, the Lp_O and Val_O occupancies are equal to 1.9809 e and 6.6659 e, respectively. The obtained results show that the Lp_O and Val_O occupation numbers are

Table 1. The Complexation Energies ($\Delta E_{ion\text{-}\pi}$ in kJ mol^{-1}) and Stretching Frequencies (υ, in cm^{-1}) of Ion-π and OH Group Calculated at the MP2/6-311++G** Level of Theory

	$\Delta E_{ion\text{-}\pi}$	$\upsilon_{(O\text{-}H)}$	$\upsilon_{(O...H)}$	$\upsilon_{(ion\text{-}\pi)}$
HBA	-	3549.74	257.47	-
Li^+	-104.17	3503.04	255.62	373.28
Na^+	-55.23	3512.36	259.60	174.34
K^+	-45.08	3521.12	272.00	80.14
Be^{2+}	-876.36	3332.73	242.58	632.85
Mg^{2+}	-415.42	3386.46	245.68	353.18
Ca^{2+}	-269.37	3459.27	268.89	233.19

Table 2. Selected Topological Parameters of Investigated Complexes (in a.u.) and Complexation Energy (ΔE in kJ mol^{-1}) Calculated at MP2/6-311++G** Level

	$\rho_{C\text{-}C}$	$\rho_{C\text{-}H}$	$\rho_{O\text{-}H}$	$\rho_{O...H}$	$\nabla^2\rho_{O...H}$	$\rho_{ion\text{-}C}$	$\nabla^2\rho_{ion\text{-}C}$	$H_{O...H}$	ΔE
Li^+	0.3049	0.2892	0.3382	0.0359	0.1344	0.0174	0.0950	-3E-07	-44.12
Na^+	0.3065	0.2884	0.3396	0.0359	0.1347	0.0101	0.0414	-6E-06	-44.23
K^+	0.3074	0.2881	0.3404	0.0358	0.1345	0.0088	0.0345	3E-05	-44.05
Be^{2+}	0.2932	0.2904	0.3202	0.0375	0.1348	0.0602	0.2210	-0.0008	-46.23
Mg^{2+}	0.2966	0.2900	0.3262	0.0375	0.1364	0.0274	0.1314	-0.0007	-46.60
Ca^{2+}	0.3006	0.2893	0.3300	0.0371	0.1361	0.0208	0.0762	-0.0005	-45.96

diminished by the cation-π interactions. The hybridization of Lp_O corresponding to sp^n is investigated in complexes. The s character of this orbital is increased in the presence of cations. These changes are enhanced with increasing $|\Delta E_{ion\text{-}\pi}|$, $\rho_{ion\text{-}C}$ and $E^{(2)}$ values. The change of charge on the O atom of HBA complexes (q_O) has been investigated by NBO method (see Table 4). The obtained results show that cation-π interactions reduce $|q_O|$. Also for these interactions, the maximum $|\Delta E_{ion\text{-}\pi}|$ value corresponds to the highest charge transfer ($\Delta q_{(CT1)}$) upon complexation and *vice versa*. This may mean that the charge transfer roughly corresponds to the strength of ion-π interaction.

The Influence of Ion-π Interactions on the O···H H-Bond

In this section, the influence of cation-π interactions on the HBA intramolecular H-bond, shown in Fig. 1, has been investigated. During full geometry optimization, this structure does not change for alkali and alkaline-earth complexes. In the studied complexes, it is observed that the equilibrium distances of the cation-π and O···H interactions for divalent ions become shorter compared to monovalent

Table 3. $E^{(2)}$ Corresponds to Charge Transfer between $\pi_{(C\text{-}C)}$ and LP^*_{cation} and the Oxygen Lone Pair and σ*O-H Antibond (in kcal mol^{-1}) and Occupation Numbers (ON) of Mentioned Orbitals Computed at the MP2/6-311++G** Level of Theory

			Occupancy			
	LPO → σ*O-H	$\pi_{C\text{–}C} \rightarrow LP^*_{cation}$	LPO	$\pi_{C\text{-}C}$	σ*O-H	LP^*_{cation}
Li^+	3.46	6.36	1.9801	1.6829	0.0298	0.0405
Na^+	3.32	2.17	1.9802	1.6968	0.0297	0.0133
K^+	3.22	1.12	1.9803	1.6971	0.0296	0.0057
Be^{2+}	4.47	62.84	1.9783	1.5905	0.0328	0.1839
Mg^{2+}	4.33	22.45	1.9785	1.6480	0.0327	0.0798
Ca^{2+}	4.03	10.32	1.9791	1.6894	0.0318	0.0407

Table 4. The Results of Natural Bond Orbital Analysis and the Charge Transfers (Δq_{CT} in e) at MP2/6-311++G** Level of Theory

	Occ Val_O	S (%)	q_O	$\Delta q_{(CT1)}$ $\pi_{C\text{–}C} \rightarrow LP^*_{cation}$	$\Delta q_{(CT2)}$ LPO → σ*O-H
HBA	6.6659	58.26	-0.256	-	-
Li^+	6.5947	58.49	-0.314	0.479	-0.058
Na^+	6.6113	58.41	-0.330	0.164	-0.074
K^+	6.6205	58.39	-0.337	0.015	-0.081
Be^{2+}	6.5078	58.88	-0.217	1.443	0.039
Mg^{2+}	6.5373	58.70	-0.249	1.000	0.007
Ca^{2+}	6.5556	58.63	-0.266	0.394	-0.01

ions ($R_{cation\text{-}\pi}$ = 1.326, 1.975 and 2.373 and $R_{O\cdots H}$ = 1.766, 1.766 and 1.772 Å in the presence of Be^{2+}, Mg^{2+} and Ca^{2+} cations, respectively), indicating that both interactions become stronger in these complexes. However, the obtained results in this study show that the smallest distances correspond to the Be^{2+} cation. Whereas the ultimate aim of this work is to compare the influences of cation-π interactions on O¨H H-bond, we only concentrate on the complex geometries which optimized in fixed $d_{ion\text{-}\pi}$ (that obtained at previous section). It is observed from Table 2 that the absolute values of complexation energy (|ΔE|) in divalent are greater than those in monovalent complexes. The H¨A (A is proton acceptor) distance is often treated as a rough measure of the strength of H-bond [18]. The O¨H distance ($d_{O\cdots H}$) increase/decrease in the presence of monovalent/divalent complexes. Results of theoretical

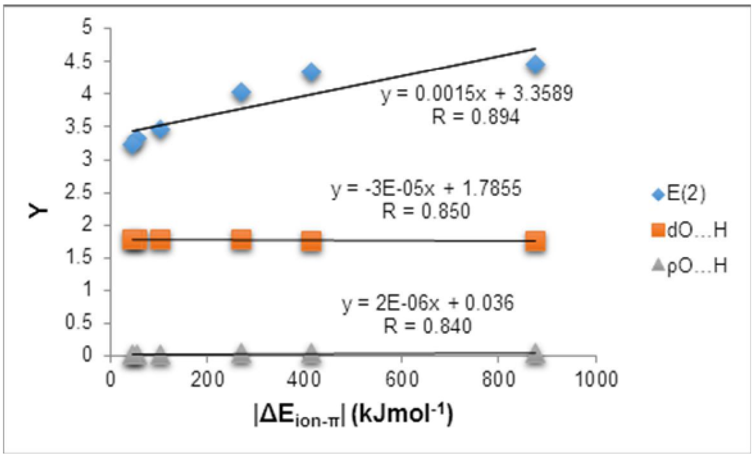

Fig. 3. The dO$^{\cdots}$H and ρO$^{\cdots}$H values and the $E^{(2)}$ value of LPO → σ*O-H interaction *vs.* $|\Delta E_{ion\text{-}\pi}|$.

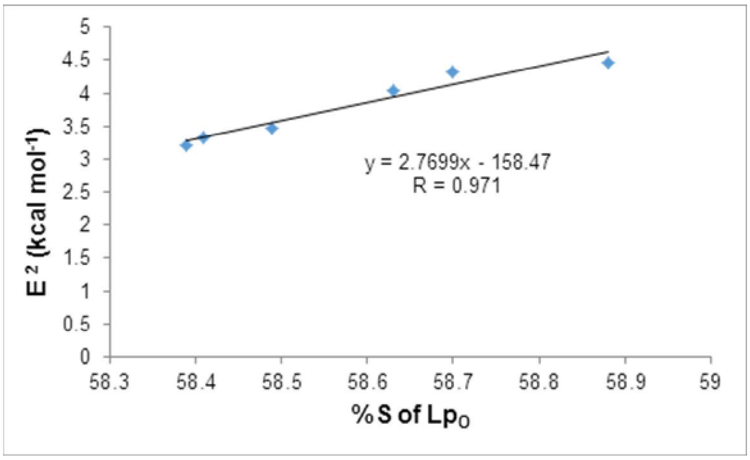

Fig. 4. The $E^{(2)}$ value of LPO → σ*O-H interaction *vs.* %S of Lp_O.

calculations on the Be^{2+} complex show that the $d_{O\ldots H}$ value is the smallest in comparison with the other complexes, which confirm that the hydrogen bond (H-bond) in this complex is stronger than the others. The obtained results also show that a meaningful relationship is not found between |ΔE| and $d_{O\ldots H}$ in the studied complexes. As shown in Tables 1 and S1 (Supporting Information), the $d_{O\ldots H}$ values presented here may be compared with $|\Delta E_{ion\text{-}\pi}|$. The increase in $|\Delta E_{ion\text{-}\pi}|$ is accompanied with decreasing $d_{O\ldots H}$ in these complexes. This relationship is shown in Fig. 3. In isolated HBA, the OH bond length (dO-H) is equal to 0.978 Å. The elongation of OH bond length is observed due to the formation of intramolecular hydrogen bond. The longest $d_{O\text{-}H}$ is accompanied with the shortest $d_{O\ldots H}$ and *vice versa*. The dependence of $d_{O\ldots H}$ to ion-π interaction can also be explained using q_O. The increasing $d_{O\ldots H}$ in the studied complexes may be due to the decrease of q_O in the presence of cations (see Tables S1 and 4).

Topological criteria are also proposed to detect the existence of H-bond [19,20]. The BCPs of the O$^{\cdots}$H interaction are found and the features of them are analyzed since it is well-known that characteristics of BCPs, such as the electron densities, their Laplacians, and the energetic properties (H_{BCP}) of BCPs, allow us to categorize interactions, and these topological parameters are also treated as criteria for the H-bond strength [21,22]. Rozas *et al*. have classified H-bonds according to their strength [23]. Weak H-bonds show both $\nabla^2 \rho_{BCP}$ and H_{BCP} values positive; for medium H-bonds $\nabla^2\rho_{BCP} > 0$ and $H_{BCP} < 0$ and also for strong H-bonds the $\nabla^2\rho_{BCP}$ as well as H_{BCP} are negative. As observed in Tables 1 and 2, the maximum value of $\rho_{O\cdots H}$ is accompanied with the highest and lowest $|\Delta E_{ion\text{-}\pi}|$ in divalent and monovalent complexes, respectively. This result can be supported by more $\rho_{O\cdots H}$ and $|\Delta E_{ion\text{-}\pi}|$ values in the Be^{2+} cation with respect to the other cations in the related complexes. This relationship is shown in Fig. 3. Furthermore, Our theoretical results reveal that the studied systems are characterized by the positive $\nabla^2\rho_{O\cdots H}$ and negative $H_{O\cdots H}$ showing that they may be classified as medium H-bonds (except for K^+ complex). However, in K^+ complex, the $\nabla^2\rho_{O\cdots H}$ and $H_{O\cdots H}$ values are positive, which means that H-bond is weak in this complex. Herein, the O$^{\cdots}$H interactions ranging from weak to medium H-bonds are observed. Numerous works indicated that the shorter atom-atom contact, which may be the rough measure of interaction strength, corresponds to the greater ρ at the related BCP [24-26]. This relationship is found between $\rho_{O\cdots H}$ and $d_{O\cdots H}$. In agreement with the changes of $d_{O\text{-}H}$, the ρ value at BCP of OH bond ($\rho_{O\text{-}H}$) in divalent ones is less than that in monovalent complexes.

To gain more insight into the influence of ion-π interactions on O$^{\cdots}$H H-bond, the NBO analysis has been performed on the investigated complexes. The NBO calculations show that the most important donor–acceptor interaction in HBA complex is $Lp_O \rightarrow \sigma^*_{O\text{-}H}$. The energy value of this interaction $E^{(2)}$ increases with increasing $|\Delta E_{ion\text{-}\pi}|$ in the studied complexes (see Fig. 3). A linear relationship is also observed between $\rho_{O\cdots H}$ and $E^{(2)}$ values. The trend in the $E^{(2)}$ values is different from the Lp_O occupancy in ion-HBA complexes. As seen in Table 3, the greater Lp_O occupancy corresponds to the lowest $E^{(2)}$ value and *vice versa*. The trend in the $E^{(2)}$ value is in accordance with the hybridization of Lp_O in ion-HBA complexes. As stated in the previous section, s character of sp^n increases by cations interaction. This relationship is shown in Fig. 4.

The increase of s character is accompanied with withdrawing the electrons and decreasing the Lewis base (O atom) properties of HBA. Also for these interactions, the maximum $E^{(2)}$ value corresponds to the highest charge transfer ($\Delta q_{(CT2)}$) upon complexation and *vice versa* (see Table 4). Theoretical results show that the occupation number of σ*O-H increases by LpO → σ*OH interaction, causing the elongation of O-H bond.

The frequency stretching modes (υ) corresponding to the O-H$^{\cdots}$O H-bond have also been displayed in Table 1. The $\upsilon_{O\cdots H}$ is amplified/diminished by the monovalent/divalent interaction. This parameter decrease with increasing the $E^{(2)}$ and $\rho_{O\cdots H}$ values. As shown in Fig. 5, these relationships are also confirmed for vibrational parameters of O-H ($\upsilon_{O\text{-}H}$). In isolated HBA molecule, the $\upsilon_{O\text{-}H}$ value is equal to 3549.74 Hz. The obtained results show that the elongation of O-H bond upon complexation leads to red-shift in the stretching mode. Hence, they behave in a similar way as proper H-bonded systems [27].

HOMO-LUMO Analysis

The most important frontier molecular orbitals (FMOs) such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play a crucial role in the chemical stability of the molecule [28]. The HOMO represents the ability to donate an electron and LUMO as an electron acceptor represents the ability to accept an electron. The energy gap between HOMO and LUMO ($\Delta E_{H\text{-}L}$) also determines the chemical reactivity, optical polarizability and chemical hardness–softness of the molecule [29]. In the present study, the HOMO and LUMO energies are predicted at MP2 method with 6-311++G** basis set (see Table 5). Figure 6 shows the energy levels of HOMO and LUMO orbitals for the Be^{2+} complex. Our calculated results show that the energy gap values in monovalent ions (Li^+, Na^+ and K^+) of the studied complexes are computed 5.40, 5.33 and 2.94 eV, respectively, whereas these values for divalent ions (Be^{2+}, Mg^{2+} and Ca^{2+}) are 5.36, 5.19 and 2.38 eV, respectively.

The frontier orbitals have been drawn to understand the bonding scheme of Be^{2+}-HBA complex. The positive phase is red and the negative one is green. As can be seen in Fig. 6, the HOMO of Be^{2+}-HBA complex is localized mainly on the ring and C=O and O-H groups. It also shows the antibonding character of C-H bond. There is no electronic

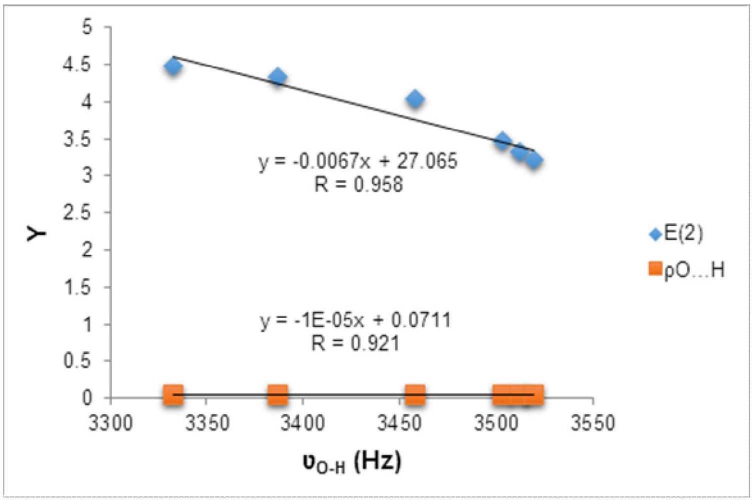

Fig. 5. The $E^{(2)}$ value of LPO → σ*O-H interaction and $\rho_{O\ldots H}$ *vs*. $\upsilon_{O\text{-}H}$.

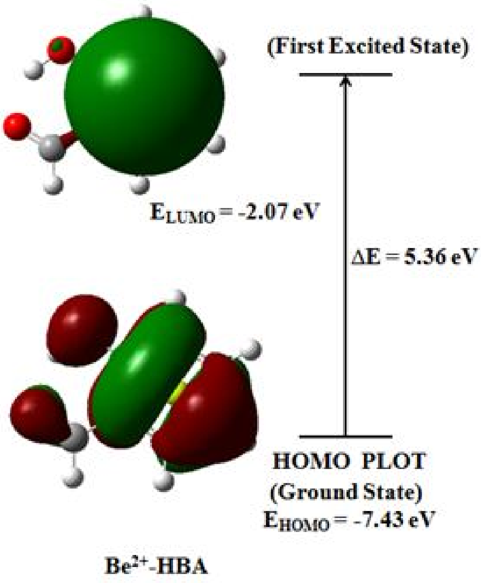

Fig. 6. HOMO and LUMO of Be^{2+}-HBA complex as obtained with MP2/6-311++G** level of theory.

projection over the C-H group. By contrast, the LUMO of π nature (*i.e.* benzene ring) of this complex is delocalized over the whole C-C bonds. As clearly seen in Fig. 6, the LUMO of Be^{2+} complex has an antibonding character over the C=O, C-H and O-H bonds.

The chemical hardness and electronic chemical potential have been calculated using the HOMO and LUMO orbital energies at MP2/6-311++G** level of theory using the following approximate expression:

$$\mu = \frac{(\varepsilon_{LUMO} + \varepsilon_{HOMO})}{2} \qquad (1)$$

$$\eta = \frac{(\varepsilon_{LUMO} + \varepsilon_{HOMO})}{2} \qquad (2)$$

where μ is the chemical potential (the negative of the

Table 5. Values of the HOMO and LUMO Energies, the Molecular Orbital Energy Gap ($\Delta E_{H\text{-}L}$), Chemical Hardness (η) and Chemical Potential (μ) in Terms of eV, Calculated at the MP2/6-311++G** Level of Theory

	E_{HOMO}	E_{LUMO}	$\Delta E_{H\text{-}L}$	η	μ
HBA	-8.969	-5.093	3.876	1.938	-7.031
Li^+	-7.351	-1.955	5.396	2.698	-4.653
Na^+	-7.315	-1.986	5.329	2.664	-4.651
K^+	-8.041	-5.096	2.944	1.472	-6.568
Be^{2+}	-7.428	-2.073	5.355	2.677	-4.750
Mg^{2+}	-7.393	-2.199	5.194	2.597	-4.796
Ca^{2+}	-7.479	-5.095	2.384	1.192	-6.287

electronegativity), and η is the hardness [30,31]. The chemical hardness and softness of a molecule is a good indicator of the chemical stability of a molecule. The molecules having large energy gap are known as hard and molecules having a small energy gap are known as soft molecules. The soft molecules are more polarizable than the hard ones because they need small energy to excitation. Chemical hardness and electronic chemical potential values of species are given in Table 5. One can relate the stability of the molecule to hardness, which means that the molecule with the least HOMO-LUMO gap means it is more reactive. Chemical hardness of the Li^+ complex is greater than the other complexes, which indicates that this complex is more stable than the others. Also, from the calculations, we conclude that the Ca^{2+} complex taken for investigation belongs to the soft material. From Table 5, it can be seen that chemical potential of the Na^+ complex is greater than that for the other complexes. Our findings confirm that in most cases, the values of hardness and chemical potential of the mentioned complexes increase for the monovalent complexes and decrease for the divalent complexes.

CONCLUSIONS

We have analyzed HBA H-bonded system in the presence of cation-π interaction. It is found that unlike $d_{O\cdots H}$, $\rho_{O\cdots H}$ and $E^{(2)}$ values of $Lp_O \rightarrow \sigma^*_{OH}$ interaction increase in the presence of cation-π. The order of $E^{(2)}$ is in accordance with the hybridization of Lp_O in ion-HBA complexes. It is observed that s character of sp^n increases by cation interactions. The increase of s character is accompanied with withdrawing electrons and decreasing the Lewis base (O atom) properties of HBA. Using AIM analysis, one can see that the studied systems are characterized by the positive $\nabla^2\rho_{O\cdots H}$ and negative $H_{O\cdots H}$ showing that they may be classified as medium H-bonds (except for K^+ complex). However, in K^+ complex, the $\nabla^2\rho_{O\cdots H}$ and $H_{O\cdots H}$ values are positive, which means that H-bond is weak in this complex. Optimization results show the elongation of O-H bond, due to complexation, and red shift of stretching mode. Hence, they behave in a similar way as proper H-bonded systems. Furthermore, the obtained results show that chemical hardness of the Li^+ complex is greater than that for the other complexes, indicating that this complex is more stable than the others.

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