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Noncovalent interaction or chemical bonding between alkaline earth cations and benzene? A quantum chemistry study using MP2 and density-functional theory methods

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Abstract

Calculations on alkaline earth metal ion–benzene complexes were performed using the density-functional theory (DFT) B3LYP and ab initio MP2 methods. They showed that the interaction is very strong, of the order of magnitude of a normal chemical bond. Electrostatic interaction is not the dominant component, and both charge transfer and induction make a significant contribution. Analysis of molecular orbital interactions indicated that binding of the alkaline earth metal ions to benzene may be attributed to s– π and p– π interactions, which are significantly stronger than those between alkali cations and benzene. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Experimental and theoretical studies in recent years have clearly demonstrated that cation– π interactions play an important role in diverse chemical and biological processes [1]. The cation– π

interaction has also been invoked to rationalize specific drug–receptor interactions [2,3], and to design both novel receptor binding pockets and more potent ligands [4–6]. It is also recognized as contributing significantly to protein [7–10] and DNA stability [10,11]. Both experimental and theoretical studies have been carried out on cation– π interactions, and have provided valuable insights into their nature [1,12]. Although experimental measurements should provide unambiguous data, theoretical methods have been demonstrated to be powerful tools for studying

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such interactions at the atomic and electronic levels, and have proved capable of accurately predicting binding energies. Hence, quantum chemical methods are now widely accepted as being complementary to experimental measurements on cation– π systems. Wouters [13] recently presented experimental evidence for a cation– π interaction between a sodium cation and a tryptophan indole ring in hen egg white lysozyme. The metal ion– π interaction within proteins thus appears to resemble metal ion interactions with small aromatic molecules, and can, accordingly, be modeled similarly employing quantum chemical methods.

In most previous investigations of cation– π interactions, much effort have been devoted to monovalent cations, such as ammonium, quaternary ammonium and alkali metal ions, while less attention was paid to divalent ions. To the best of our knowledge, only Choi et al. [5] have made calculations for the interaction of alkaline earth metal ions interacting with aromatics, but their objective was the design of novel ionophores, making use of the cation– π interaction, rather than attempting to understand its physical basis. Cation– π interactions involving divalent cations appear to play a significant role in a number of biological systems. Thus, a tryptophan residue controls blockade and permeation of Mg^{2+} in the selectivity filter of the *N*-methyl-D-aspartate receptor [15]. Divalent metal cation– π interactions have been suggested to be involved in DNA bending, DNA-protein recognition, base-flipping, RNA folding and catalysis [11]. Furthermore, evidence has been presented for a cation– π interaction of an Mg^{2+} ion with HIV integrase [14]. Accordingly, we performed a quantum chemistry investigation on models of complexes of benzene with the alkaline earth metal ions, Be^{2+} , Mg^{2+} and Ca^{2+} .

2. Methods

Based on our experience in performing calculations on alkali cation–benzene complexes [16], we adopted a geometry with C_{6v} symmetry for all three complexes, with the ions being located exactly above the center of the benzene ring (Fig. 1).

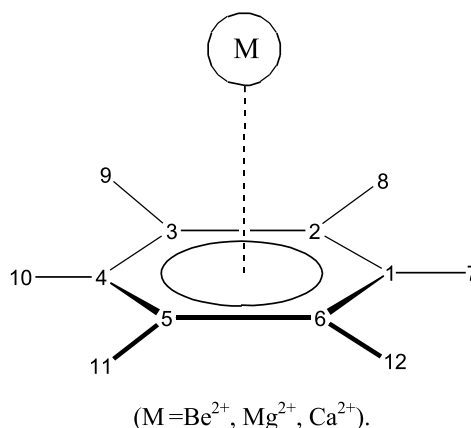


Fig. 1. Initial geometry of the alkaline earth cation–benzene complexes.

It has been proposed that the MP2 method with 6-31G** basis sets is a reliable method for studying cation– π interactions [1]. However, our earlier study suggested that the density-functional theory (DFT) method, B3LYP, with 6-31G* basis sets, would utilize computational resources more sparingly, would speed up the calculations and, above all, provide precise results comparable to those generated by MP2 method [16–18]. So as to establish the validity of future use of the B3LYP/6-31G* method for larger systems, in the present study we employed both methods for purposes of comparison.

Full geometry optimizations were performed on the three initial geometries, using GAUSSIAN 98 package [19]. Frequency calculations were then performed to verify the stability of the optimized structures, as well as to produce a series of thermodynamic parameters. The enthalpy change was calculated based on the raw SCF energy from geometry optimization, and the thermal energy from the frequency computation. In order to obtain more reliable energies, basis sets superposition error (BSSE) corrections were also taken into account. In addition, the common practice of running a high-level single-point energy calculation at the geometry computed by use of a cheaper method is as effective as performing all calculations at the higher level of theory. Thus, using the optimized geometries produced by the MP2/6-31G** method, we carried out the single-point

energy calculations and BSSE corrections using the MP2/6-311+G** method, and using the optimized geometries of the B3LYP/6-31G* method, we carried out the single-point energy calculations and BSSE corrections at the B3LYP/6-311+G(3df,2p) level. All calculations were performed on an SGI Power Challenge R10000 supercomputer.

3. Results and discussion

3.1. Optimized structures

All frequency calculations for the three optimized geometries gave no imaginary frequencies, suggesting that they are all true energy minimum structures. Some important structural parameters of the optimized complexes (C_{6v}) and of free benzene are summarized in Table 1. It can be seen that the distances of the ions to the center of benzene ring calculated by B3LYP/6-31G* are 1.293, 1.948, and 2.458 Å for the Be^{2+} -benzene, Mg^{2+} -benzene, and Ca^{2+} -benzene complexes, respectively, values very close to those calculated by Choi et al. [5] using the same theoretical method. In addition, the results produced by B3LYP/6-31G* are in excellent agreement with those calculated by the MP2/6-31G** method (Table 1), suggesting that there would be no significant differences if the optimized structures

were generated by the B3LYP/6-31G* rather than by the MP2/6-31G** method. It is also apparent that obviously that the calculated distances between the ions and the benzene ring are rather small, comparable to the lengths of normal chemical bonds, suggesting that the interaction between alkaline earth cations and benzene is very strong.

With increasing ion size, the distance between the metal ion and the centroid of the benzene becomes greater (Table 1). However, complexation results in elongation of the C–C bonds relative to benzene itself. The effect is greatest in the Be^{2+} -benzene complex, in which the C–C bond length is increased by 0.027 Å, the corresponding values for the Mg^{2+} -benzene and Ca^{2+} -benzene complexes being 0.022 and 0.014 Å, respectively. This elongation indicates a weakening of the strength of the C–C bond. However, no significant change is observed in the lengths of the C–H bonds. In all three cases, the presence of the cation results in the hydrogens bending out of the plane of the benzene ring. Unlike for the alkali metal ion-benzene complexes [21], the out-of-plane orientations of the hydrogens are not in the same direction. In the Ca^{2+} -benzene complex, the hydrogen atoms move away from the metal ion, in the Mg^{2+} complex, they are nearly coplanar with the carbons, and in the Be^{2+} complex, they move slightly to the same side as the ion (Table 1). The reasons for these differences remain to be clarified.

Table 1

Principal structural parameters for the Be^{2+} -, Mg^{2+} - and Ca^{2+} -benzene complexes and for free benzene (where B3LYP represents the B3LYP/6-31G* level of theory, and MP2 represents the MP2/6-31G** level)

Structural parameter	Be^{2+} -benzene		Mg^{2+} -benzene		Ca^{2+} -benzene		Benzene	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
R_{C-C} (Å)	1.423	1.423	1.419	1.418	1.411	1.410	1.397	1.396
R_{C-H} (Å)	1.089	1.086	1.088	1.085	1.088	1.084	1.087	1.083
R_{M-C} (Å)	1.923	1.912	2.411	2.420	2.835	2.882		
$R_{M-center}^a$ (Å)	1.293	1.293	1.948	1.957	2.458	2.486		
$R_{M-center}^b$ (Å)	1.292		1.948		2.426 ^c			
$A_{M-center-H}$ (°)	88.24	88.21	90.58	90.66	91.25	91.48		
$A_{H7-C1-C2}$ (°)	119.92	119.91	119.99	119.98	119.96	119.93	120.00	120.00
$D_{H7-C1-C2-C3}$ (°)	175.30	175.01	178.46	177.74	176.70	175.64	180.00	180.00

^a $R_{M-center}$ is the distance from the ion to the centroid of the benzene molecule.

^b See [5], B3LYP/6-31G* method results.

^c B3LYP/6-31G* result [5], the 6-31G* quality (AhlrshsPVD2+1d function) basis set was used for Ca^{2+} , and the 6-31G* basis set for C and H.

3.2. Binding energies

The thermodynamic parameters for each complex obtained by the two theoretical methods are listed in Table 2. No comparable experimental values have yet been reported. The association energies calculated by Choi et al. [5] for the Be^{2+} , Mg^{2+} and Ca^{2+} complexes are -237.5 , -124.1 and -72.3 kcal/mol, respectively. These values are very similar to our corresponding uncorrected values for ΔH , -236.49 , -124.58 and -72.40 kcal/mol, at the same theoretical level (Table 2). The raw binding energy values, ΔE_{scf} s, calculated using B3LYP, are slightly larger than those obtained using MP2/6-31G**, suggesting that the diffusion effect [20] is not important in these systems. With the introduction of the diffuse functions and triple split basis sets, ΔE_{scf} decreased significantly for both the Be^{2+} and Mg^{2+} complexes, by ca. 4–11 kcal/mol. But the introduction of the diffuse functions and triple split basis sets increased the binding energies for the Ca^{2+} complex. With regard to correction of the binding energies, we observed that the values of BSSE produced by the DFT method are very small; consequently, there

are no significant differences between the corrected and uncorrected energies (Table 2). Thus, using this method, we can get relatively accurate results without BSSE corrections, whereas the BSSEs are much larger when using the MP2 method. For the Be^{2+} –benzene complex, the BSSE is as large as 10.72 kcal/mol at the MP2/6-31G** level, and 7.45 kcal/mol at the MP2/6-311+G** level. Accordingly, BSSE correction is necessary for obtaining accurate binding energies when using the MP2 method. Adding diffuse functions and triple split basis sets results in a decrease in the BSSE correction. Thus, running a high-level single-point energy calculation at a geometry computed using a cheaper method may be a good choice for obtaining accurate energy values. Table 2 shows that, in general, the calculated binding energies produced by the DFT method are in good agreement with those obtained using the MP2 method. The binding energies for the alkaline earth metal ions complexing with benzene are much greater than those for the Li^+ – and Na^+ –benzene complexes [16,21,22], approaching the strengths of chemical bonds. For Be^{2+} –benzene, the computed binding enthalpy is about -220 and -230 kcal/mol for the

Table 2
Energy parameters of alkaline earth and alkali cations complexed with benzene

Energies (kcal. mol ⁻¹)	Be^{2+} –benzene		Mg^{2+} –benzene		Ca^{2+} –benzene		Li^+ –benzene ^a		Na^+ –benzene ^a	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
ΔE_{scf}	-237.85	-235.39	-125.25	-120.35	-73.02	-67.06	-42.34	-42.49	-28.48	-28.65
ΔE_{therm}	1.95	2.57	1.26	2.60	1.21	1.35	1.58	1.842	1.23	1.47
BSSE	2.13	10.72	2.73	8.22	2.41	4.34	2.5	6.27	2.09	5.14
ΔH	-236.49	-233.39	-124.58	-118.34	-72.4	-66.3	-41.35	-41.24	-27.84	-27.77
ΔH_{cor}	-234.36	-222.69	-121.85	-110.12	-69.99	-61.96	-38.85	-34.97	-25.75	-22.63
$\Delta E_{\text{scf}}^{\text{b}}$	-230.93	-224.71	-121.4	-112.89	-82.33	-75.97				
BSSE ^b	0.78	7.45	1	4.76	0.58	3.29				
$H_{\text{cor}}^{\text{c}}$	-228.79	-215.28	-119.73	-106.12	-81.13	-71.92				
$\Delta E_{\text{scf}}-\text{H}_2\text{O}^{\text{d}}$	-155.6	-150.2	-90.9	-86.1	-60.2	-57.7				
E_{binding}	-237.5 ^e		-124.1 ^e		-72.3 ^f		-38.3 ^g		-28.0 ^h	

^a B3LYP/6-31G* results [16], MP2/6-31G** results were calculated based on those of MP2/6-31G*.

^b BSSE of the B3LYP/6-311+G(3df,2p) and MP2/6-311+G** results, respectively.

^c Binding energies calculated using the thermal energy correction of B3LYP/6-31G* and MP2/6-31G** results, respectively, and the SCF energies and BSSEs of B3LYP/6-311+G(3df,2p) and MP2/6-311+G**, respectively.

^d The SCF binding energy values for interaction of alkaline earth cations with water.

^e See [5], B3LYP/6-31G* results.

^f B3LYP/6-31G* result [5], the 6-31G* quality (AhlrshsPVD2+1d function) basis set was used for Ca^{2+} , and the 6-31G* basis set used for C and H.

^g Experimental value [23].

^h Experimental value [24].

MP2 and DFT methods, respectively, both values being much higher than for many chemical bonds. Therefore, in energetic terms, the interaction between the alkaline earth metal ions and benzene may be considered as a chemical bond.

Many chemical processes, and the vast majority of biological processes, take place in aqueous media. It thus seemed of interest to compare the hydration energies of the alkaline earth ions under consideration with their binding energies to benzene. Therefore, the hydration energies of Be^{2+} , Mg^{2+} and Ca^{2+} were calculated at the same levels of theory as for their interaction with benzene, and are also shown in Table 2. It can be seen that the binding of all three ions to benzene is much stronger than with water, suggesting that they can overcome the bounding of water molecules, and preferentially bind to π systems under aqueous conditions in biological systems.

3.3. Charge transfer

Charge transfer in the alkaline earth ion–benzene complexes, and donation of electron density from the ring to the cations (Table 3) is significantly greater than observed for the Na^+ – and Li^+ –benzene complexes [21]. Thus, using B3LYP, 1.43 unit electrons transfer from benzene to Be^{2+} (the corresponding value for MP2 being 1.41), 1.07 from benzene to Mg^{2+} (MP2: 1.01), and 0.51 from benzene to Ca^{2+} (MP2: 0.46). Taking the data in Tables 2 and 3 together, it appears that greater charge transfer results in a stronger cation– π interaction. This is shown directly in Fig. 2, which plots transferred charge vs both the raw (uncor-

rected) and corrected binding enthalpies. In our earlier study [16], we did not report MP2/6-31G** binding energies for the Li^+ – and Na^+ –benzene complexes. Therefore, based on the results of MP2/6-31G*, we reoptimized the geometries and calculated the binding enthalpies at the level of MP2/6-31G** (Table 2). The correlation coefficient, R^2 , between the transferred charge and the binding energy is 0.9253 for the uncorrected binding enthalpies of the DFT result (MP2: 0.9423), and 0.9256 (MP2: 0.9377) for the corrected energies, suggesting that charge transfer plays an important role in these cation– π systems.

3.4. Mulliken bonding population (MBP)

The MBPs of the cation–benzene complexes are summarized in Table 4. The MBPs of the C–C bonds in the three complexes all decreased compared to free benzene, consistent both with the decrease in the charge on the carbon atoms (Table 3), and the increase in the C–C bond lengths (Table 1). Compared to free benzene, only slight changes occurred in the MBP of the C–H bonds in the complexes (Table 4). Among the complexes, the MBP between Be^{2+} and the carbon atoms is the largest, 0.1120 for the DFT result and 0.1124 for the MP2 result. The corresponding values for the Mg^{2+} complex are 0.0940 and 0.0919 for DFT and MP2, respectively, and for the Ca^{2+} complex, only 0.0579 and 0.0502. The total MBP between the ions and the six carbons are either larger than or similar to the magnitudes of the MBPs of the C–C and C–H bonds (Table 4), once again demonstrating that the interaction is very strong.

Table 3
Mulliken and CHelpG atomic charges of the cation–benzene complexes and of free benzene^a

Molecule	Q_C /Mulliken		Q_H /Mulliken		Q_M /Mulliken		Q_M /CHelpG	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
Be^{2+} –benzene	–0.0830	–0.0930	0.3213	0.3276	0.5707	0.5919	0.7897	0.7871
Mg^{2+} –benzene	–0.1125	–0.1285	0.2903	0.2964	0.9333	0.9925	1.2087	1.2335
Ca^{2+} –benzene	–0.1792	–0.1940	0.2641	0.2708	1.4910	1.5391		
Li^+ –benzene ^b	–0.1247	–0.1476	0.2213	0.2303	0.4209	0.5037	0.6074	0.6161
Na^+ –benzene ^b	–0.1458	–0.1674	0.2040	0.2155	0.6512	0.7115	0.7197	0.7269
Benzene	–0.1285	–0.1484	0.1285	0.1484				

^a Q_C , Q_H and Q_M represent the charges of the carbon atoms, the hydrogen atoms and the cations, respectively.

^b From [16].

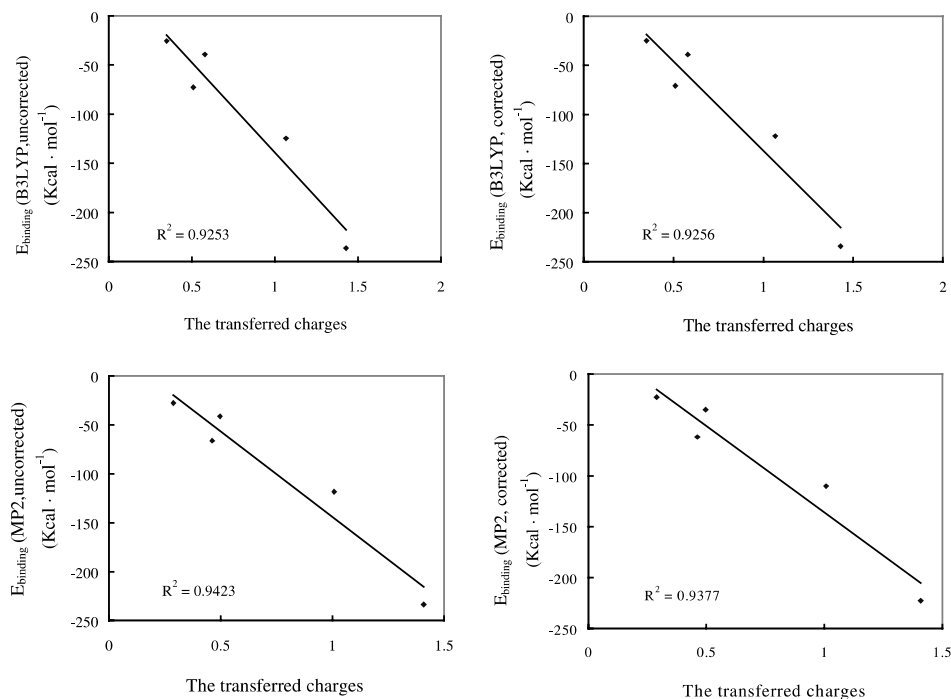


Fig. 2. Relationship between transferred charge and the binding energy.

3.5. Electrostatic and induction interactions

As discussed above, in energetic terms the interaction between the alkaline earth metal ions and benzene may be considered as a chemical bond. In order to better understand its nature, we performed electrostatic interaction calculations on the M–benzene complexes (where M = Li⁺, Na⁺, Be²⁺, Mg²⁺, Ca²⁺) using a point-charge model with CHelpG charges [25] at the B3LYP/6-31G* level. Radius information for Ca²⁺ is not included in the GAUSSIAN program. Since, however, for systems with less charge transfer, the Mul-

liken charge is not very different from the ChelpG charge (Table 3), we used it instead of the ChelpG charge for the Ca²⁺–benzene. The calculations of electrostatic energies were performed as described earlier [26]. The calculated results are shown in Table 5. Since electrostatic interaction energies generated using the point-charge model are not always reliable, we recalculated them using version 3.2 of the ORIENT program developed by Stone [27], in which a precise distributed multipoles model is employed.

Table 5 shows that our calculated values for alkali metal ions are in good agreement with those

Table 4
MBPs of the alkaline earth cation–benzene complexes and of free benzene

MBP	Be ²⁺ –benzene		Mg ²⁺ –benzene		Ca ²⁺ –benzene		Benzene	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
C–C	0.4148	0.4316	0.4316	0.4487	0.4772	0.4898	0.5515	0.5526
C–H	0.3658	0.3836	0.3753	0.3941	0.3748	0.3957	0.3589	0.3947
Cation–C	0.1120	0.1124	0.0940	0.0919	0.0579	0.0502		
Cation–benzene ^a	0.6720	0.6744	0.5640	0.5514	0.3274	0.3012		

^a The total MBP between the cation and the carbons of benzene.

Table 5
Electrostatic interaction energies and induction energies of the complexes

Complex	$E_{\text{ele}}^{\text{a}}$	$E_{\text{ele}}^{\text{b}}$	$E_{\text{ele}}^{\text{c}}$	E_{ind}	$E_{\text{ind}}^{\text{c}}$	H_{corr}
Li^+ -benzene	-17.83	-18.55	-18.7	-46.25	-46.9	-38.85
Be^{2+} -benzene	-36.21	-35.35		-468.26		-234.36
Na^+ -benzene	-15.62	-14.56	-14.8	-22.41	-21.0	-25.75
Mg^{2+} -benzene	-47.69	-37.43		-165.03		-121.85
K^+ -benzene	-12.98 ^d	-10.74	-11.9	-11.71	-12.8	-15.45
Ca^{2+} -benzene	-41.81 ^d	-28.45		-79.97		-69.99

^a CHelpG charge results.

^b Results calculated by ORIENT 3.2.

^c See [28].

^d Mulliken charge results.

of Tsuzuki [28]. Furthermore, the results produced using the simple ChelpG point-charge model are, in general, in agreement with those obtained using the ORIENT program. From the data in Table 5, we can estimate that the electrostatic interaction energy accounts for 15% of the total binding energy for the Be^{2+} -benzene complex, 31–39% for the Mg^{2+} complex, 48% for the Li^+ complex, 41–60% for the Ca^{2+} complex, and ca. 60% for the Na^+ complex. Thus, for all three alkaline earth cation complexes, the binding energies are not dominated by the electrostatic interaction. We conjecture that some other interactions may make an important contribution to the strong interaction seen in the Be^{2+} and Mg^{2+} complexes, which may provide new insights into the nature of the cation- π interaction.

The data of Tsuzuki et al. [28] showed that the induction energy plays an important role in the Li^+ - and Na^+ -benzene complexes. Therefore, induction interactions for the various cation- π systems were calculated using the distributed polarizabilities model encoded in ORIENT version 3.2 [28], based on the geometries of B3LYP/6-31G*. The results obtained are displayed in Table 5. The induction energies calculated for the Li^+ and Na^+ complexes are in good agreement with the values of Tsuzuki et al. [28] (Table 5). The small differences between our values and theirs originate in differences in the structural geometries derived from the different theoretical methods employed. The induction energies calculated for that of Be^{2+} , Mg^{2+} and Ca^{2+} complexes are -468.3, -165.0 and -80 kcal/mol, respectively.

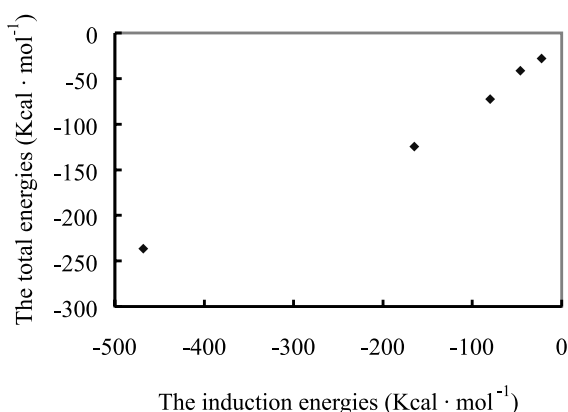


Fig. 3. Relationship between induction energy and total energy.

Thus, the contribution from induction to the attraction between the alkaline earth cations and benzene is much larger than the electrostatic interaction, whereas for the alkali cation-benzene systems the two are rather similar. In addition, the induction interaction energies correlate well with the total binding energies (Fig. 3), indicating that the binding energies with benzene of the cations studied are proportional to induction interactions.

3.6. Molecular orbital analysis

As distinct from transition metal ions, the alkaline earth metal ions have no d electrons; thus, they should not be able to form coordinate complexes with aromatics like the transition me-

tal ions. As discussed above, both the binding energies and the bond lengths suggest that the alkaline earth metal ions form a chemical bond with the benzene ring (Tables 2 and 4). In order to explore the interaction further, we analyzed the molecular orbitals of both the alkaline earth ion–benzene complexes and the alkali ion–benzene complexes. Herein, we treat only the Be^{2+} –benzene and Li^+ –benzene complexes as representative cases. It appears that benzene uses mainly the π orbitals, a_{2u} and e_{1g} , to interact with the 2s and 2p orbitals of Be^{2+} and Li^+ , respectively, generating three bonding orbitals a_1 and e_1 (degenerate orbitals) and three antibonding orbitals a_1^* and e_1^* (degenerate orbitals). Schematic diagrams of the orbital interactions are presented in Fig. 4, and the contributions of the atomic orbitals to the molecular orbitals are listed in Table 6. Atomic charge calculations show that the electrons of benzene transfer toward the cations (Table 3), indicating that the frontier orbitals of benzene, a_{2u} and e_{1g} , serve as the electron-donors, and the s and p orbitals of the cations as the electron acceptors. Based on the symmetry of the orbitals,

the a_{2u} orbital of benzene interacts mainly with the 2s orbital of Li^+ and Be^{2+} to form a_1 and a_1^* orbitals, and the two degenerate orbitals of benzene, e_{1g} , interact with $2p_x$ and $2p_y$ orbitals of the cations, to form, respectively, e_1 and e_1^* orbitals (Fig. 4). The $2p_z$ orbital of the cations can also interact with the a_{2u} orbital of benzene. However, the orbital coefficients indicate that its contribution is less significant than that of the 2s orbitals (Table 6). The contour maps of the molecular orbitals of Be^{2+} –benzene and Li^+ –benzene complexes are presented in Fig. 4, which also indicates that the a_1 and a_1^* orbitals make mainly π –s interactions, while the e_1 and e_1^* orbitals make mainly π –p interactions. In addition, in the Be^{2+} complex, π –s and π –p interactions are more significant than in the Li^+ complex (Table 6 and Fig. 4).

4. Conclusion

Our study on the cation– π interaction of alkaline earth ions with benzene, for Be^{2+} , Mg^{2+} and

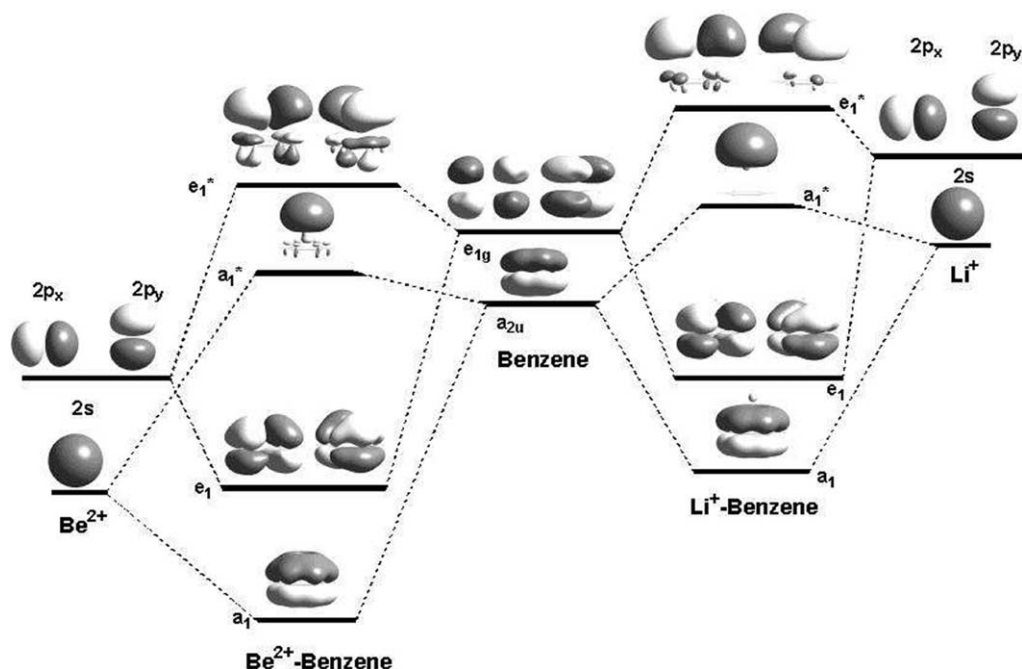


Fig. 4. Schematic representations of the orbital interactions in the Be^{2+} – and Li^+ –benzene complexes.

Table 6

Relevant molecular orbital energies and contributions of atomic orbitals to the molecular orbitals of the Be^{2+} -benzene and Li^+ -benzene complexes (B3LYP/6-31G* results)

Orbital interaction	MO	E. level (a.u.)	Cation orbitals (%)				Carbon orbital (%)		
			s	p_x	p_y	p_z	s	p_z	
Be^{2+}	p- π	e_1^*	-0.3100	58.51	11.66		8.45	16.43	
	p- π	e_1^*	-0.3100	11.66	58.51		8.45	16.43	
	s- π	a_1^*	-0.4860	70.91		20.18	1.50	6.05	
	p- π	e_1	-0.7310		1.97	12.56	2.60	79.34	
	p- π	e_1	-0.7310		12.56	1.97	2.60	79.34	
	s- π	a_1	-0.8413	18.34			2.08	3.09	72.69
Li^+	p- π	e_1^*	-0.1209		1.04	77.81	9.37	5.83	
	p- π	e_1^*	-0.1209		77.81	1.04	9.37	5.83	
	s- π	a_1^*	-0.1899	79.95			13.82	2.65	2.14
	p- π	e_1	-0.4604		2.75	2.86	0.46	92.94	
	p- π	e_1	-0.4604		2.86	2.75	0.46	92.94	
	s- π	a_1	-0.5735	9.48			7.08	1.43	81.12

Ca^{2+} , shows that the interaction is very strong, and that charge transfer and induction effects both play a significant role. The electrostatic interaction energies are, however, smaller than the induction energies, which play a dominant role. Molecular orbital interaction analysis shows that the metal ions bond with benzene via s- π and p- π interactions. The bond lengths and bonding energies, especially for the Be^{2+} and Mg^{2+} complexes, are comparable to those of normal chemical bonds.

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