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A THEORETICAL STUDY OF THE INTERACTION BETWEEN $[HB{\equiv}CH]^-$, $[H_2B{=}CH_2]^-$, AND BORATABENZENE ANION WITH ALKALINE AND ALKALINE EARTH METALS: PROPERTIES AND STRUCTURES

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The nature of $[HB{\equiv}CH]^-$, $[H_2B{=}CH_2]^-$, and boratabenzene interactions with alkaline and alkaline earth metals are studied by *ab initio* calculations. The interaction energies are calculated at the B3LYP/6-311++G(*d,p*) level. The calculations suggest that the cation size and charge are two influential factors that affect the nature of the interaction. AIM and NBO analyses of the complexes indicate that the variation of densities and the extent of charge transfers upon complexation correlate well with the obtained interaction energies.

Keywords: metals-π interaction energy, natural bond orbital (NBO), atoms in molecules methodology (AIM).

The cation-π interaction (a noncovalent molecular interaction of an electron-rich π system and the adjacent cation) as a chemical phenomenon has been studied extensively by quantum mechanical *ab initio* calculations. Several theoretical calculations have been reported on the interaction of alkali metal cations with aromatic complexes such as benzene [1—3], pyrole [4], azoles [5, 6], and other aromatic rings [7—11]. Changes in the electron density distribution in both donor and acceptor molecules are one of the consequences of the interaction. This interaction can play a significant role in stabilizing the three- dimensional structure of a protein. A magnificent example is given by the nicotinamide acetylcholine receptor whose molecular recognition mechanism of its substrate acetylcholine (a positively charged molecule) nearly entirely bases on cation-π interaction [12].

The present study is directed to investigate the $[B{\equiv}CH]^-$, $[H_2B{=}CH_2]^-$ and boratabenzene interactions with the alkaline and alkaline earth metals. The main objective is not only to determine the geometrical parameters and the binding strength of the complexes formed but also to gain further insight into the nature of interactions. An analysis of the topology of the electron density obtained from theoretical wave functions using Bader′s theory of atoms in molecules (AIM) provides valuable information on the interaction characteristics.

The method of natural bond orbital (NBO) analysis was also employed to study the intermolecular orbital interactions in the complexes.

CALCULATION METHODS

The structures of the π-systems ($[HB{\equiv}CH]^-$, $[H_2B{=}CH_2]^-$ and $[C_5BH_6]^-$) with alkali and alkaline earth metals are optimized by the B3LYP method, and 6-311++G(*d,p*) is chosen as a basis set.

The optimization was made along with a frequency calculation for each complex to verify that the all geometries are without any imaginary frequency (except, $[H_2B{=}CH_2]^- \cdots M^+$; M = K, Ca).

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The interaction energy (IE) can be evaluated from the difference between the energy of the complex and the sum of energies of the π-systems and M^{n+}

$$\text{IE} = E(\text{complex}) - [E(M^{n+}) + E(\pi\text{-systems})].$$

The calculated interaction energies were corrected for basis set superposition errors (BSSE), which were computed for all calculations using the counterpoise correction method of Boys and Bernardi [13].

All electronic structure calculations have been performed using the Gaussian 2003 program [14].

The population analysis has also been performed by the natural bond orbital method [15] at the B3LYP/6-311++G(*d*,*p*) level of theory using the NBO program [16] under the Gaussian 2003 program package.

The AIM methodology is applied to analyze the electron density and its corresponding Laplacian at the critical point π-systems···M^{n+} contact at the B3LYP/6-311++G(*d*,*p*) level. The topological analyses have been performed with the AIM 2000 program [17] using the B3LYP /6-311++G(*d*,*p*) wave functions as input.

RESULTS AND DISCUSSION

Energetic aspects. Table 1 presents the computed energies, relative energies, interaction energies (IEs), BSSE and corrected IEs for the complexes of M^{n+} ($M^{n+} = Li^+$, Na^+, K^+, Be^{2+}, Mg^{2+}, and Ca^{2+}) with π-systems: $[HB{\equiv}CH]^-$, $[H_2B{=}CH_2]^-$, and $[C_5BH_6]^-$.

Table 1

Calculated energy (Hartree), *interaction energy* (kcal/mol), *BSSE* (kcal/mol), *corrected interaction energy* (kcal/mol), *and π-system distortion energy* (kcal/mol) *for* HC≡BH···M^{n+}, $H_2C{=}BH_2$···M^{n+}, *boratabenzene*$^-$···M^{n+} (M = *alkaline metals*, *alkaline earth metals*) *complexes by the* B3LYP *method with the* 6-311++G(*d*,*p*) *basis set*

Interaction	*E*	IE	BSSE	IE^{corr}	π-System distortion
HC≡BH(1)	–64.117	—	—	—	—
(1)···Li^+	–71.651	–156.06	0.25	–155.81	0.63
(1)···Na^+	–226.421	–135.96	0.34	–135.61	0.48
(1)···K^+	–664.062	–115.20	0.19	–115.01	0.54
(1)···Be^{2+}	–78.535	–480.13	0.31	–479.82	10.66
(1)···Mg^{2+}	–263.940	–365.22	0.38	–364.84	2.59
(1)···Ca^{2+}	–741.498	–298.08	0.25	–297.83	4.40
$H_2C{=}BH_2$(2)	–65.378	—	—	—	—
(2)···Li^+	–72.907	–153.29	0.23	–153.06	1.46
(2)··· Na^+	–227.676	–132.27	0.48	–131.79	0.66
(2)···K^+	–665.317	–111.80	0.24	–111.55	0.57
(2)···Be^{2+}	–79.765	–460.90	0.41	–460.49	11.40
(2)···Mg^{2+}	–265.188	–357.21	0.50	–356.72	3.58
(2)···Ca^{2+}	–742.740	–286.24	0.29	–285.95	3.94
Boratabenzene (3)	–219.090	—	—	—	—
(3)···Li^+	–226.627	–158.31	0.69	–157.62	0.49
(3)···Na^+	–381.386	–130.86	0.96	–129.90	0.40
(3)···K^+	–819.032	–113.63	0.48	–113.16	0.29
(3)···Be^{2+}	–233.544	–502.68	0.80	–501.88	3.98
(3)···Mg^{2+}	–418.908	–362.21	1.04	–361.16	2.25
(3)···Ca^{2+}	–896.477	–301.86	0.60	–301.26	1.21

Table 2

Bond distances (M···C, CB in Å) *for* HC≡BH···M^{n+}, H_2C=BH_2···M^{n+} *and* (M···C1, BC1, C1C2, C2C3 *in* Å) *for boratabenzene*$^{-}$···M^{n+} (M = *alkali metals*, *alkaline earth metals*) *complexes by the* B3LYP *method with the* 6-311++G(*d*,*p*) *basis set*

Cation	HC≡BH···M		H_2C=BH_2···M		Boratabenzene^{-}···M^{n+}				
	r(M···C)	*r*(CB)	*r*(M···C)	*r*(CB)	r_{cov}(M)[a]	*r*(M···B)	*r*(BC1)	*r*(C1C2)	*r*(C2C3)
—	—	1.325	—	1.457		—	1.514	1.399	1.405
Li^+	1.980	1.327	1.969	1.458	1.230	2.280	1.521	1.404	1.412
Na^+	2.346	1.329	2.434	1.471	1.540	2.619	1.521	1.405	1.409
K^+	2.701	1.326	2.877	1.460	2.030	3.003	1.518	1.402	1.408
Be^{2+}	1.569	1.387	1.634	1.576	0.890	1.963	1.540	1.419	1.426
Mg^{2+}	2.042	1.356	2.139	1.528	1.360	2.332	1.542	1.419	1.416
Ca^{2+}	2.228	1.352	2.575	1.460	1.740	2.669	1.529	1.406	1.414

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[a] r_{cov}(B) = 0.82, C = 0.77, Ref. G.L. Miessler and D.A. Tarr, *Inorganic Chemistry*, 3d ed., Prentice-Hall International, Inc. Englewood Cliffs, N.J., 2004, Page 45.

It can be seen that IE values increase with increasing atomic number of metals. On the other hand, these values decrease in M^+ complexes. Investigating the magnitude of IE^{corr}, it can be found that the cation size and charge are influential factors determining the strength of the binding interaction in these systems.

The distortion energy of the π-system within the complexes has been listed in Table 1. These values present that the π-system is more distorted in M^{2+} complexes.

Structures. Table 2 presents the CB, CC, and M···C bond lengths in the π-system and π-system complexes. It is well established that the B≡C and B=C bonds could be elongated as a result of the M^{n+}···π-system. Obviously, the CC and CB bond lengths of boratabenezene complexes are all between the double bond length of H_2C=CH_2 (1.33 Å), $[H_2B{=}CH_2]^-$, and the single bond length of H_3C—CH_3 (1.53), $[H_3B{=}CH_3]^-$ (1.65 Å). The bond lengths in the cyclic structure provide the structural criteria of aromaticity. As shown in Table 2, the CC and CB bond lengths in the cycles are shorter than the sum (1.54, 1.64 Å) of the covalent radii of the atoms. The CB and CC bond lengths in cyclic structures indicate the existence of delocalization. The M—B bond lengths in pyramidal structures are longer than the sum of the covalent radii of the corresponding metal atoms and a boron atom, indicating that the portion of covalent bonds in relatively small. The covalent radii for metal atoms, boron, and carbon have been presented in Table 2.

Atoms in molecules analysis. The analysis of the electron density by means of Bader′s methodology (AIM) provides useful tools to confirm the presence of π-system…metals interactions. Table 3 lists the values of ρ and $\nabla^2\rho$ of the π-system complexes and the π-system at the B3LYP/6-311++G(*d*,*p*) level. It contains the electron densities at the bond critical points of π-system…M bonds.

Different features of the analysis of electron densities obtained in the AIM framework are summarized as follows:

1. For all complexes, the analysis of the electron density as well as the Laplacian at a bond critical point (BCP) is interesting. It can be easily observed that for each HBCH···M^{n+} and H_2BCH_2···M^{n+} interaction, there exists a bond path linking the metal atom with carbon of the B=C bond accompanied by BCP (Fig. 1). On the other hand, there is a bond path linking the metal atom with boron of the B=C bond in the H_2BCH_2···Li^+ interaction

2. The plots of ρ(B=C) *versus* *r*(B=C) are shown in Fig. 2. As can be seen, a linear relationship is shown between the B=C bond lengths and the electron density of B=C.

Table 3

Electron densities ρ (e/a_0^3) *and Laplacians* $\nabla^2\rho$ (e/a_0^5) *for* (a) $HC{\equiv}BH\cdots M^{n+}$, (b) $H_2C{=}BH_2\cdots M^{n+}$, (c) *boratabenzene*$^-\cdots M^{n+}$ (M = *alkali metals*, *alkaline earth metals*) *complexes by the* B3LYP *method with the* 6-311++G(*d*,*p*) *basis set*

M	ρC≡B	$\nabla^2\rho$	ρM…Cation	$\nabla^2\rho$	M	ρCCP(3,+3)	ρCCP(3,+1)
		(a) $HC{\equiv}BH\cdots M^{n+}$				(c) Boratabenzene	
Li	0.2426	0.3090	0.0380	0.1914	Li^+	0.0165	0.0222
Na	0.2422	0.3239	0.0283	0.1306	Na^+	0.0113	0.0200
K	0.2421	0.3393	0.0256	0.0857	K^+	0.0094	0.0200
Be^{2+}	0.2421	–0.1789	0.1129	0.4649	Be^{2+}	—	—
Mg^{2+}	0.2421	0.0974	0.0525	0.2331	Mg^{2+}	0.0201	0.0212
Ca^{2+}	0.2448	0.3393	0.0660	0.1858	Ca^{2+}	0.0160	0.0204
		(b) $H_2C{=}BH_2\cdots M^{n+}$					
Li	0.2018	0.0565	0.0334(C), 0.0312(B)	0.2176(C), 0.1708(B)			
Na	0.2006	0.0156	0.0263	0.1088			
K	0.2038	0.0294	0.0224	0.0650			
Be^{2+}	0.1654	–0.1047	0.1025	0.3592			
Mg^{2+}	0.1835	–0.0454	0.0468	0.1682			
Ca^{2+}	0.2063	0.0048	0.0470	0.1082			

3. It is interesting that for all $[HBCH]^-\cdots M^{n+}$ and $[H_2BCH_2]^-\cdots M^{n+}$ contacts analyzed here the Laplacians ($\nabla^2\rho$) of M···C are positive, implying the typical closed-shell type of the interaction in the complexes.

4. In addition, for all complexes the positive values of $\nabla^2\rho$ of the π-system…metals interactions are gradually decreasing with the atomic number of metals. Namely, the π-system…metals interaction

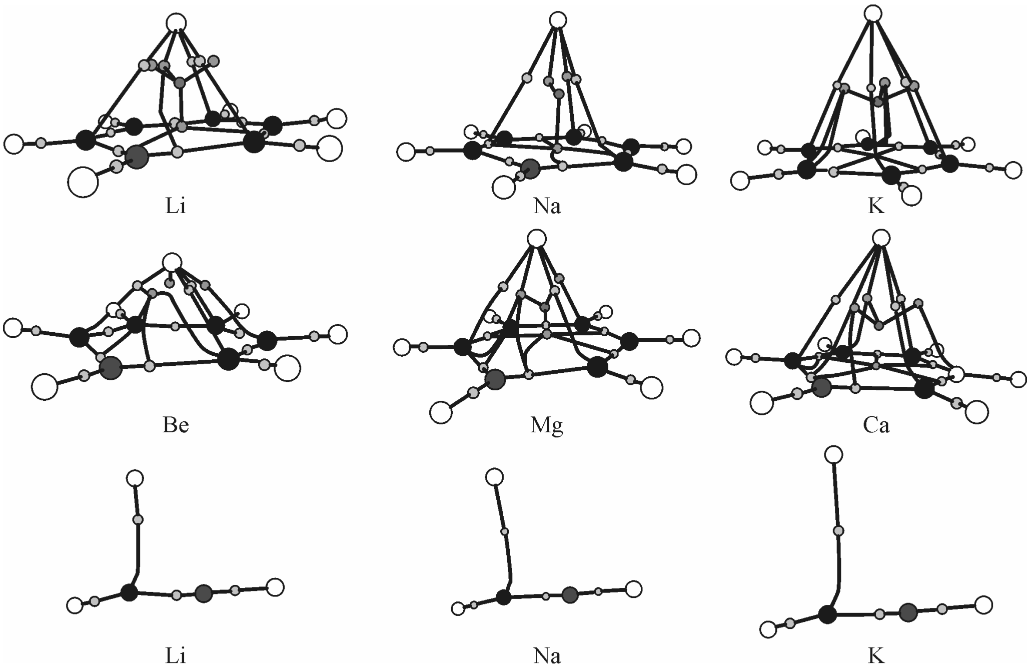

Fig. 1. Optimized structures for the interaction of metals with boratabenzene

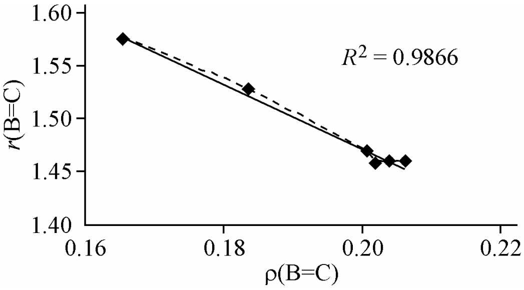

Fig. 2. Linear correlation between the electron density at BCP and the B=C bond length in $H_2C{=}BH_2\ldots M^{n+}$ complexes

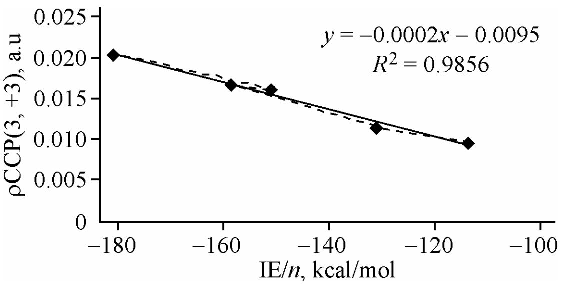

Fig. 3. Correlation between the IE/n (n = metal oxidation number) and density at CCP for boratabenzene…M^{n+} (except M = Be)

becomes weaker and weaker, and this is in good agreement with the calculated interaction energy sequence.

5. Calculations show the formation of a cage critical point (CCP, ρ(3,+3) along the line connecting the cation with the center of the ring upon complexation (except M = Be). Fig. 3 illustrates the correlation between IE/n (n = metal oxidation number) and the density at CCP for the boratabenzene$\cdots M^{n+}$ (except: M = Be), which shows the following equation:

$$\rho(3,+3) = -0.0002\left(\frac{\mathrm{IE}}{n}\right) - 0.0095 \qquad n = 1 \text{ or } 2; \qquad R^2 = 0.9856.$$

Natural population analysis. Natural bond orbital analysis stresses the role of the 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. For each donor NBO(i) and acceptor NBO(j), the stabilization energy $E(2)$ associated with electron delocalization between the donor and acceptor is estimated as

$$E^{(2)} = -q_i \frac{(F_{i,j})^2}{\varepsilon_j - \varepsilon_i},$$

where q_i is the orbital occupancy, ε_i, ε_j are the diagonal elements, and F_{ij} is the off-diagonal NBO Fock matrix element. The results of the second-order perturbation theory analysis of the Fock matrix at the B3LYP/6-311++G(d,p) level of theory are collected in Table 4.

For the $[HB{\equiv}CH]^{-}\cdots M^{n+}$ and $[H_2B{=}CH_2]^{-}\cdots M^{n+}$ interactions, the most of the charge transfer energies reported in Table 4 are related to the dominant interaction between π(BC) of donor species and $n^*(1)(M)$ (except M = Be, Mg). However, in the boratabenzene$\cdots M^{n+}$ interactions, the most of the charge transfer energies are related to the dominant interaction between $n^*(1)$B of donor species and $n^*(1)$Be (except M = Mg). Furthermore, the net charge transfer is evaluated from the π-system to M^{n+} (Table 4), indicating the π-system…M^{2+} interaction being stronger than that with M^+. On the other hand, these results show that most interactions between the π-system and M^+ are more ionic than those with M^{2+}, with some back transfer from the π-system to M^{n+}. For metal atoms, with increasing atom number the positive charge is mainly located over the metals atoms. These results are compatible with IEs and AIM calculations.

One of the prevailing notions is that the binding of these cations to various π-systems can be explained by charge transfer [18, 4] (Table 4). It is therefore interesting to examine the charge

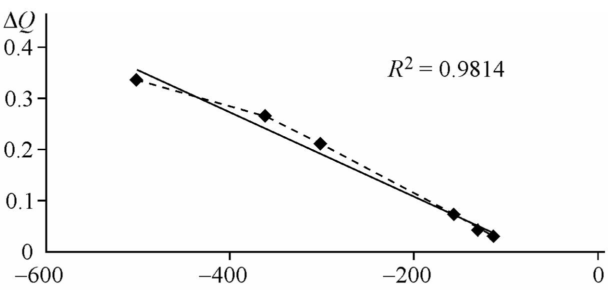

Fig. 4. Correlation between IE and charge transfer in the boratabenzene…M^{n+} complex

Table 4

Results of the second-order perturbation theory analysis of the Fock matrix within the NBO *basis* (E^2 *energy values for the* π*-system*→*metal donor-acceptor interactions in* kcal/mol) *and the natural population analysis* (NPA) *for* $HC{\equiv}BH\cdots M^{n+}$, $H_2C{=}BH_2\cdots M^{n+}$, *boratabenzene*$^-\cdots M^{n+}$ (M = *alkali and alkaline earth metals*) *complexes by the* B3LYP *method with the* 6-311++G(*d,p*) *basis set*

Interaction	Donor→acceptor	E^2	M	Interaction	Donor→acceptor	E^2	M
$(1)\cdots Li^+$	πBC→n^*(1)Li	14.66	0.924	$(2)\cdots Be^{2+}$	σB—C→RY*(1)Be	4.51	1.567
$(1)\cdots Na^+$	πBC→n^*(1)Na	14.46	0.879	$(2)\cdots Mg^{2+}$	σB—C→RY*(1)Mg	1.85	1.414
$(1)\cdots K^+$	πBC→n^*(1) K	7.64	0.930	$(2)\cdots Ca^{2+}$	πBC→n^*(1)Ca	1.07	1.731
$(1)\cdots Be^{2+}$	πBC→ RY*(1)Be	23.00	1.656	$(3)\cdots Li^+$	n^*(1) B→n^*(1)Li	3.66	0.928
$(1)\cdots Mg^{2+}$	πBC→ RY*(1)Mg	8.89	1.532	$(3)\cdots Na^+$	n^*(1) B→n^*(1)Na	18.05	0.956
$(1)\cdots Ca^{2+}$	πBC→n^*(1)Ca	31.25	1.739	$(3)\cdots K^+$	n^*(1) B→n^*(1) K	4.33	0.967
$(2)\cdots Li^+$	πBC→n^*(1) Li	7.51	0.929	$(3)\cdots Be^{2+}$	n^*(1) B→n^*(1)Be	44.19	1.667
$(2)\cdots Na^+$	πBC→n^*(1) Na	19.24	0.840	$(3)\cdots Mg^{2+}$	π(C5—C6)→n^*(1)Mg	17.19	1.734
$(2)\cdots K^+$	πBC→n^*(1) K	9.66	0.908	$(3)\cdots Ca^{2+}$	n^*(1) B→n^*(1)Ca	13.37	1.792

transfer ΔQ evaluated using the NBO method. It is found that the interaction energies of the boratabenzene$\cdots M^{n+}$ complex correlate with ΔQ, as shown in the following equation:

$$\Delta Q = -0.0008\ \mathrm{IE} - 0.0537 \qquad R^2 = 0.9814$$

However, no correlations can be found between charge transfers and IEs for $[HB{\equiv}CH]^-\cdots M^{n+}$ and $[H_2B{=}CH_2]^-\cdots M^{n+}$ complexes.

CONCLUSIONS

In the present theoretical study, the interactions of $[HB{\equiv}CH]^-$, $[H_2B{=}CH_2]^-$, and the boratabenzene anion with alkali and alkaline earth metals have been investigated. The calculations suggest that the cation size and charge are two influential factors that affect the nature of the interaction. The results of NBO and AIM analyses can be summarized as follows:

1. Both AIM and NBO calculations as well as the obtained IEs suggest that the interaction between M^{n+} and the π-system results in the ionic interaction.
2. In the interaction between M^{n+} and π-systems, the density at the $M^{n+}\cdots B$ critical point is a useful measurement for the interaction strength.
3. When the boratabenzene anion interacts with metals, IEs correlate well with charge transfers.

These results provide valuable information for estimating the interaction of $[HB{\equiv}CH]^-$, $[H_2B{=}CH_2]^-$, and the boratabenzene anion with alkali and alkaline earth metals.

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