Is the Cation/π Interaction in Alkaline-Earth-Metal Dication/Benzene Complexes a Covalent Interaction?

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The interaction energies of the alkaline-earth-metal dication/benzene complexes (dication = Mg^{2+} and Ca^{2+}) were calculated at the MP2 (the second-order Møller−Plesset calculation) level using the 6-311G** basis set. The electrostatic and induction energies were calculated with the distributed multipoles and distributed polarizabilities model. Induction is mainly responsible for the very strong attractive interaction in these complexes. Electrostatic energies are considerably smaller than the induction energies. The complexes have significant attraction, even if the cations are well separated from the benzene, which indicates that short-range (covalent) interactions are not the major source of the attraction and that long-range interactions (induction and electrostatic interactions) are mainly responsible for the attraction. The calculations of benzene under an electric field show that the electric field produced by the dication is a cause of the C−C bond elongation in the alkaline-earth-metal dication/benzene complexes.

Introduction

The cation/π interaction is the strong attractive interaction between the cation and π system. Detailed information on the cation/π interaction is important for many fields of chemistry from molecular biology to material design. The cation/π interaction is an important driving force in molecular recognition processes in biological and artificial systems.[1−20] The interaction between a cation and graphite is important for the development of battery materials.[21] Although many experimental studies have been reported on the cation/π interaction, it is still difficult to confirm the origin of the attraction by experimental measurements only. Several ab initio molecular orbital calculations have been reported on the alkali-metal cation/benzene complexes.[10,12,22−24] Recently reported calculations show that electrostatic interaction and induction are the major sources of the attraction in the alkali-metal cation/benzene complexes and that the induction is mainly responsible for the large binding energies of the Li^+ and Na^+ complexes.[24]

On the other hand, only a few studies were reported on the alkaline-earth-metal dication/π complexes. Recently reported ab initio calculations of alkaline-earth-metal dication/benzene complexes show that these complexes have very strong attraction.[25−28] The sizes of the binding energies are close to those of normal chemical bonds. The origin of the strong attraction in the alkaline-earth-metal dication/benzene complexes has been a controversial issue. The large induction energy in the Li^+ and Na^+ complexes[24] suggest that the induction energy is significantly large in the alkaline-earth-metal dication/benzene complexes, as the induction energy is proportional to the square of the electric field produced by the cation.[29] This means that the alkaline-earth-metal dication/benzene complexes have 4 times larger induction energies than the alkali-metal cation/benzene complexes, if the complexes have the same cation/benzene distance. Jiang and co-workers also reported that the induction energies of the alkaline-earth-metal dication/benzene complexes (dication = Be^{2+}, Mg^{2+}, and Ca^{2+}) are very large.[25] In a more recent paper, however, they concluded that the interaction in the alkaline-earth-metal dication/benzene complexes was in nature a chemical bonding, and they called it the cation−π bond.[28] Although they found that the nonelectrostatic term (difference between the total interaction energy and electrostatic energy) is significantly large, they did not mention the importance of the induction to the attraction. They carried out molecular orbital component analysis and concluded that the orbital interactions (covalent interactions) between the dication and benzene form a cation−π bond. Liu and co-workers calculated the atomic charges by electrostatic potential fitting and found that a large charge transfer occurred in the alkaline-earth-metal dication/benzene complexes.[27] They also carried out molecular orbital analysis and concluded that the large nonelectrostatic term should be attributed to the charge-transfer interaction in the complexes. These groups reported that covalent (orbital or charge-transfer) interactions are important for the attraction in the alkaline-earth-metal dication/benzene complexes. However, the alkaline-earth-metal dication/benzene complexes would have large induction energies. Induction (a noncovalent interaction) is another candidate of the major source of the attraction.

Is the major source of the strong attraction in the alkaline-earth-metal dication/benzene complexes covalent or noncovalent? The interaction energies of the complexes would depend on the intermolecular distance. This dependence provides essential information to answer the question. Covalent interactions (short-range interactions) arise at distances where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance. On the other hand, induction (a noncovalent interaction) is a long-range interaction. The energies of long-range interactions behave as some inverse power of distance.[29] Therefore, noncovalent interactions still exist even when the molecules are well separated. Unfortunately, however, the intermolecular

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distance dependence of the interaction energies of the alkaline-earth-metal dication/benzene complexes was not reported. We have calculated the interaction energies of the Mg^{2+} and Ca^{2+} complexes with changing intermolecular separation to study the intermolecular distance dependence. We have also calculated the electrostatic and induction energies and have compared them to the total interaction energies to discuss the roles of these terms for the attraction in these complexes. In addition, we have discussed the effects of the electric field produced by the cation on the C−C bond elongation in the alkaline-earth-metal dication/benzene complexes.

Computational Method

The Gaussian 98 program[30] was used for the ab initio molecular orbital calculations to evaluate the total interaction energy. The basis sets implemented in the Gaussian program were used. Electron correlation was accounted for at the MP2[31,32] and CCSD(T) (coupled cluster calculations with single and double substitutions with noniterative triple excitations) levels.[33] The geometries of the complexes were optimized at the MP2/6-311G** level. The basis set superposition error (BSSE)[34] was corrected for all calculations with the counterpoise method.[35] The total interaction energy (E_{total}) was calculated at the MP2/6-311G** level, if not otherwise noted. Distributed multipoles[29,36] up to the hexadecapole on all atoms were obtained from MP2/6-311G** wave functions of an isolated benzene using CADPAC version 6.[37] The electrostatic and induction energies of the complexes were calculated with ORIENT version 3.2.[38] The electrostatic energies of the complexes were calculated as the interactions between the charge of the cation and the distributed multipoles of benzene. The induction energies were calculated as interactions of the polarizable sites with the electric field produced by the cation.[39,40] Anisotropic polarizabilities $\alpha_{xx} = \alpha_{yy} = 14$ au and $\alpha_{zz} = 7$ au were put on the carbon atoms of the benzene ring (the z-axis is parallel to the 6-fold axis).[24]

Results and Discussion

Effects of the Basis Set and Electron Correlation. The interaction energies of the Mg^{2+}/benzene and Ca^{2+}/benzene complexes were calculated using several basis sets. The MP2/6-311G** level optimized geometries were used for the calculations (Figure 1).[41] The calculated HF and MP2 interaction energies are summarized in Table 1. The effects of the basis set on the calculated interaction energies of these complexes are not large as in the case of the interaction energies of alkali-metal cation complexes.[24] Tan et al. and Cheng et al. also calculated the interaction energies of the two complexes. Although they used different basis sets, the calculated interaction energies of these complexes are close to those obtained in this work.[25,27] The effects of electron correlation correction are not large. The HF interaction energy of the Mg^{2+} complex is slightly larger (more negative) than the corresponding MP2 interaction energy. On the other hand, the MP2 interaction energy of the Ca^{2+} complex is slightly larger than the HF interaction energy as shown in Table 1. The effects of electron correlation beyond MP2 are negligible. The calculated MP2/6-311G** level interaction energies of the Mg^{2+} and Ca^{2+} complexes (−109.9 and −73.7 kcal/mol, respectively) are very close to the CCSD(T)/6-311G** interaction energies (−109.2 and −71.5 kcal/mol, respectively). Due to the good performance of the MP2/6-311G** level calculations, we have carried out all the following calculations at the MP2/6-311G** level.

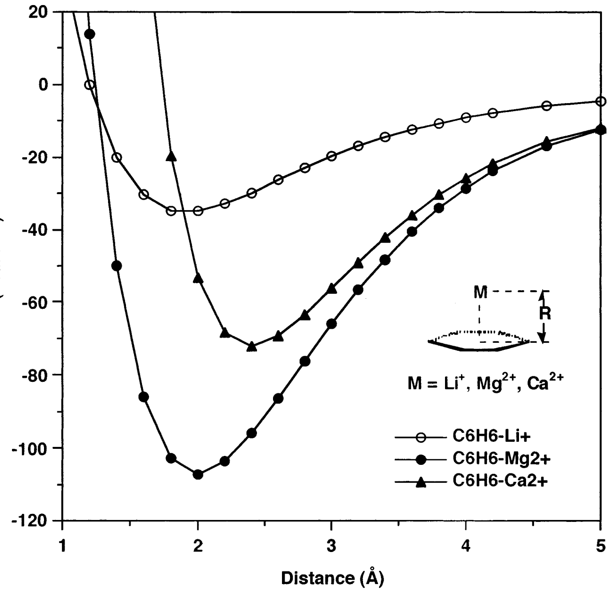

Figure 1. MP2/6-311G** level interaction energies of the cation/benzene complexes. The cation is on the 6-fold axis of the benzene.

TABLE 1: Calculated Interaction Energies of Mg^{2+}/Benzene and Ca^{2+}/Benzene Complexes[a]

basis set	Mg^{2+}	Ca^{2+}	basis set	Mg^{2+}	Ca^{2+}
HF/6-31G*	−119.8	−67.2	MP2/6-31G*	−115.9	−66.7
HF/6-311G*	−117.0	−73.4	MP2/6-311G*	−112.3	−76.1
HF/6-311G**	−116.8	−72.8	MP2/6-311G**	−109.9	−73.7
HF/6-311++G**	−116.6	−73.0	MP2/6-311++G**	−109.4	−73.8
HF/6-311G(2d,2p)	−121.5	−76.7	MP2/6-311G(2d,2p)	−114.1	−78.5
HF/6-311G(3d,3p)	−121.9	−78.2	MP2/6-311G(3d,3p)	−114.4	−80.6
CCSD/6-311G**	−110.0	−71.6	MP3/6-311G**	−110.4	−72.2
CCSD(T)/6-311G**	−109.2	−71.5			

[a] Energies in kilocalories per mole. The geometries optimized at the MP2/6-311G** level were used. BSSE-corrected interaction energies.

TABLE 2: Calculated Geometries and Energies of Cation/Benzene Complexes[a]

cation	$M^{+}-C$[b]	M^{+}−centroid[c]	E_{total}[d]	E_{es}[e]	E_{ind}[e]
Li^{+} [f]	2.340	1.869	−35.4	−18.7	−46.9
Na^{+} [f]	2.803	2.425	−21.3	−14.8	−21.0
K^{+} [f]	3.137	2.805	−17.0	−11.9	−12.8
Rb^{+} [f]	3.461	3.165	−13.9	−9.2	−8.4
Cs^{+} [f]	3.690	3.414	−12.1	−7.9	−6.4
Mg^{2+}	2.419	1.958	−109.9	−37.8	−162.4
Ca^{2+}	2.751	2.361	−73.7	−31.2	−91.2

[a] Distances in angstroms and energies in kilocalories per mole. [b] Distance between the cation and carbon atoms of benzene. [c] Distance between the cation and the centroid of benzene. [d] Calculated total interaction energy at the MP2/6-311G** level. [e] Electrostatic and induction energies. See the text. [f] Reference 24.

Origin of Attraction in Mg^{2+} and Ca^{2+} Complexes. The electrostatic and induction energies of the Mg^{2+} and Ca^{2+} complexes at the potential minima are shown in Table 2. The electrostatic energies (E_{es}) of the Mg^{2+} and Ca^{2+} complexes (−37.8 and −31.2 kcal/mol, respectively) are considerably smaller than E_{total} (−109.9 and −73.7 kcal/mol, respectively). The E_{es} values are 34% and 42% of E_{total}, respectively.[42] This indicates that the nonelectrostatic term (the difference between E_{total} and E_{es}) is significantly important for the attraction in these complexes. Liu and co-workers also reported the importance of the nonelectrostatic term.[27] They concluded that the nonelectrostatic term should be attributed to charge transfer. However, these complexes have very large induction energies.

The calculated induction energies (E_{ind}) of these complexes are -162.4 and -91.2 kcal/mol, respectively. The very large induction energies indicate that induction is the main component of the nonelectrostatic term and that it is not possible to estimate the size of the charge-transfer energy only from the size of the nonelectrostatic term. The large induction energies indicate that the benzene is strongly polarized in the complexes, and this polarization would be the cause of the charge transfer reported by Liu et al.[27]

The E_{ind} values of the Mg^{2+} and Ca^{2+} complexes are significantly larger than the E_{es} values (-37.8 and -31.2 kcal/mol, respectively). The E_{es} values of these complexes are only 23% and 34% of the E_{ind} values, respectively. On the other hand, the E_{es} values of the three alkali-metal cation complexes are 40−93% of the E_{ind} values. Apparently, the very large induction energies of the Mg^{2+} and Ca^{2+} complexes are the cause of the large E_{total} of these complexes. The amount of the induction energy is proportional to the square of the electric field.[29] The magnitude of the electric field produced by a cation is approximately proportional to R^{-2} (R is the distance from the cation). Therefore, E_{ind} is approximately proportional to R^{-4}. The short intermolecular distance in the Mg^{2+} complex (1.96 Å) is the cause of the huge E_{ind} of the Mg^{2+} complex.

The molecular polarizabilities of Mg^{2+} and Ca^{2+} are very small. The calculated polarizabilities of these dications at the HF/6-311G(3d) level are only 0.41 and 3.21 au, respectively. The polarizabilities of these dications are considerably smaller than that of methane (17.28 au). It has been reported that the estimated dispersion energy of the benzene/methane complex is -2.3 kcal/mol when the intermolecular distance R is 3.8 Å.[43] If we assume that the dispersion energy is approximately proportional to R^{-6}, we can estimate that the dispersion energy in the Ca^{2+}/benzene complex ($R = 2.361$ Å) is -7.4 kcal/mol from the polarizabilities of methane and Ca^{2+} and the dispersion energy in the benzene/methane complex. The estimated dispersion energy in the Mg^{2+}/benzene complex is -2.9 kcal/mol. The dispersion energies are much smaller than the electrostatic and induction energies, indicating that dispersion is not the major source of the attraction in these dication complexes.

The calculated interaction energy potentials of the Mg^{2+} and Ca^{2+} complexes are shown in Figure 1. The MP2/6-311G** level optimized geometry of isolated benzene was used for the calculations. The calculated potentials of Mg^{2+} and Ca^{2+} complexes show that significant attraction still exists, even if the cations are well separated from the benzene ($R > 4$ Å). The large attraction indicates that the major source of the attraction in these alkaline-earth-metal dication complexes is not a short-range (covalent) interaction ($E \approx e^{-\alpha R}$) such as charge-transfer or orbital interaction, but a long-range interaction ($E \approx e^{-n}$) such as electrostatic interaction and induction.

The electrostatic and induction energies of the Ca^{2+} complex were calculated with changing intermolecular distance. The calculated electrostatic and induction energies are compared with E_{total} as shown in Figure 2. The sum of E_{es} and E_{ind} is close to E_{total} when the intermolecular distance (R) is larger than 3.0 Å, which indicates that the electrostatic attraction and induction are the main components of the intermolecular interaction and other terms are not large when $R > 3.0$ Å. E_{total} is smaller (less negative) than the sum of E_{es} and E_{ind} when $R < 3.0$ Å. The exchange repulsion at the short intermolecular separation ($R < 3.0$ Å) would be the cause of the smaller E_{total}. The comparison of E_{total} and the sum of E_{es} and E_{ind} (Figure 2) does not suggest the existence of any specific attraction by short-range interactions (charge-transfer or orbital interaction) in the Ca^{2+}/benzene complex.

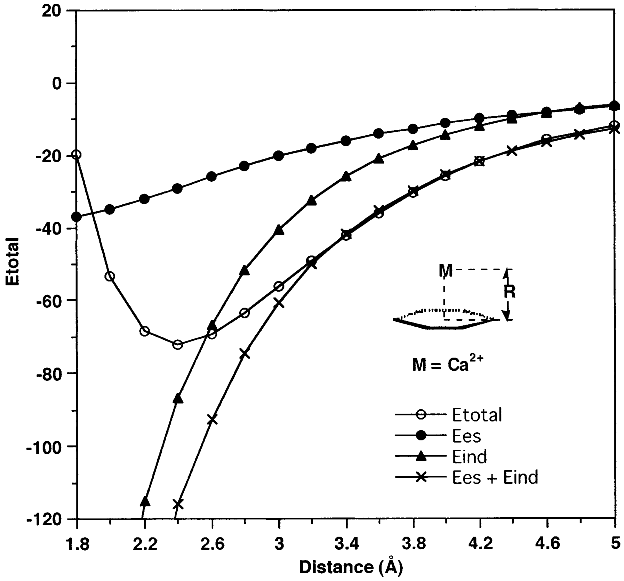

Figure 2. MP2/6-311G** level total interaction energy (E_{total}), electrostatic energy (E_{es}), and induction energy (E_{ind}) of the Ca^{2+}/benzene complex.

C−C Bond Elongation. A few ab initio calculations of the geometries of alkaline-earth-metal dication/benzene complexes have been reported.[25,27] Jiang and co-workers reported MP2/6-31G** level geometry optimizations.[25] The calculated C−C bond distances in the dication (Mg^{2+} and Ca^{2+}) complexes are slightly longer (0.022 and 0.014 Å, respectively) than that in the isolated benzene (1.396 Å). They reported that this elongation indicated the weakening of the strength of the C−C bond. Does this elongation suggest the formation of the covalent bond between the dication and carbon atoms of benzene?

We have calculated the energy of benzene with changing C−C bond distances to confirm this issue. The relative energies of benzene calculated at the MP2/6-311G** level are shown in Figure 3. The C−H bond distances are fixed at 1.086 Å. The benzene keeps D_{6h} symmetry. The calculated potential shows that the C−C bond stretching potential is not steep. The 0.02 Å elongations of the six C−C bonds only increase the energy of benzene as much as 1.4 kcal/mol. The large binding energy of the complexes would easily compensate this small deformation energy.

We have also calculated the C−C bond stretching potential under the electric field produced by Ca^{2+}. The $+2e$ charge ($1e = 1.602 \times 10^{-19}$ C) was put on the 6-fold axis of benzene. The distance between the centroid of the benzene and the charge is 2.36 Å, which corresponds to the intermolecular separation of the Ca^{2+}/benzene complex. The calculated C−C bond stretching potential is also shown in Figure 3. The comparison of the two potentials shows that the electric field increases the equilibrium C−C bond distances substantially. These calculations indicate that the electric field of the dication is a cause of the elongation of the C−C bonds and that the formation of the covalent bond between the cation and carbon atom is not the only possible cause of the C−C bond elongation.

Conclusion

Induction (polarization) is the major source of the attraction in the alkaline-earth-metal dication/benzene (dication = Mg^{2+} and Ca^{2+}) complexes. Electrostatic energies are considerably smaller (less negative) than induction energies. The electrostatic

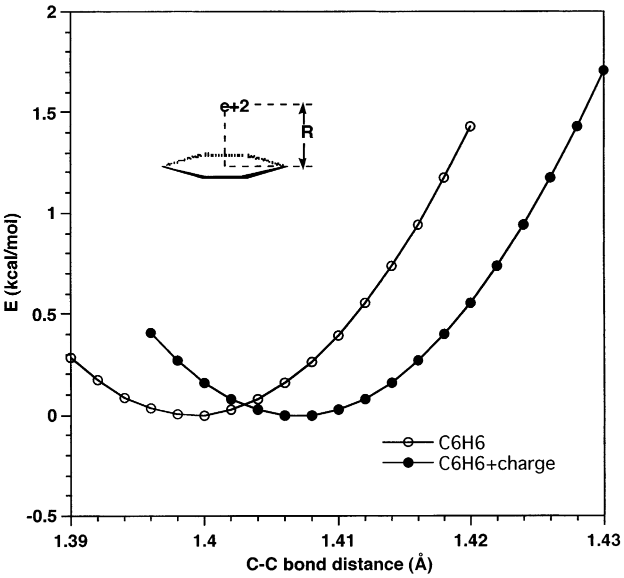

Figure 3. Relative energy of benzene with respect to the changes of the six C−C bond distances with and without a point charge, which represents the charge of Ca^{2+}. The energy of benzene was calculated at the MP2/6-311G** level. The distance between the point charge and the centroid of benzene is 2.36 Å. See the text.

energies (E_{es}) in these complexes are 23% and 34% of the induction energies (E_{ind}). The calculated intermolecular interaction energy potentials of these complexes show that substantial attraction still exists, even if the cations are well separated from the benzene. This shows that short-range (covalent) interactions are not the major source of the attraction in these complexes and that long-range interactions (induction and electrostatic) are mainly responsible for the attraction. The sum of E_{es} and E_{ind} of the Ca^{2+}/benzene complex is close to the calculated total interaction energy (E_{total}) when the intermolecular distance $R > 3.0$ Å. E_{total} is smaller than the sum of E_{es} and E_{ind} when $R < 3.0$ Å due to the exchange repulsion. The comparison of E_{total} and the sum of E_{es} and E_{ind} does not suggest the existence of any specific attraction by short-range interactions. Although the Mg^{2+} and Ca^{2+} complexes have very strong interaction (−109.9 and −73.7 kcal/mol, respectively) and their sizes are on the order of those of normal chemical bonds, covalent interaction is not the major source of the attraction in these complexes. The calculations of benzene in an electric field show that the electric field produced by a dication increases the equilibrium C−C bond distance of benzene substantially. This indicates that the formation of the covalent bond between the cation and carbon atom is not the only possible cause of the C−C bond elongation in the alkaline-earth-metal dication/benzene complexes.

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induction energies of the complex calculated using distributed multipoles are not largely different from those obtained by Cubero et al. as illustrated in ref 24.

(41) Vibrational frequency analysis shows that the optimized geometries correspond to the potential minima.

(42) The electrostatic energy of the Mg^{2+}/benzene complex (−47.6 kcal/mol) reported by Cheng et al. using atomic charges obtained by electrostatic potential fitting with the ChelpG scheme in ref 27 is substantially larger than the electrostatic energy reported in this work (−37.8 kcal/mol). It is well-known that point-charge models are crude approximations to estimate the electrostatic energy and sometimes have large errors. Reference 29 shows that the electrostatic energy obtained using distributed multipoles is more reliable. This would be the cause of the larger electrostatic energy reported in ref 27. Tan et al. compared the electrostatic energy from ChelpG charges and that from distributed multipoles in ref 25. The electrostatic energy from distributed multipoles (−37.43 kcal/mol) is very close to that obtained in this work. On the other hand, the ChelpG charges overestimated the electrostatic energy (−47.69 kcal/mol) as in the case of ref 27.

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