

Counterion Effects on the Cation– π Interaction between Alkaline Earth Cations and Benzene

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Systematic theoretical calculations were performed on the interactions between benzene and a variety of MX^+ cations ($\text{M} = \text{Be}^{2+}$, Mg^{2+} , and Ca^{2+} ; $\text{X} = \text{H}^-$, F^- , Cl^- , OH^- , SH^- , CN^- , NH_2^- , and CH_3^-) in order to expand the scope of the cation– π interaction. It was found that the basis set and electron correlation effects on the geometry optimization and energy calculation were small. Therefore, the chosen method of this study, MP2/6-311++g(2d,2p)/MP2/6-31+g*, should be sufficiently reliable. Using this method, it was found that the cation– π interaction between benzene and a naked alkaline earth cation is much stronger than the prototypical benzene–alkali cation interaction. In comparison, when a counterion is introduced into the complex, the $\text{C}_6\text{H}_6\cdots\text{MX}^+$ interaction is very similar to the benzene–alkali cation in many aspects. Further analyses indicated that electrostatic interaction is the major driving force for $\text{C}_6\text{H}_6\cdots\text{Li}^+$ and $\text{C}_6\text{H}_6\cdots\text{Na}^+$ complexes, whereas large charge transfer occurs in $\text{C}_6\text{H}_6\cdots\text{Be}^{2+}$ and $\text{C}_6\text{H}_6\cdots\text{Mg}^{2+}$ complexes. Electrostatic interaction was also found to be an important driving force for $\text{C}_6\text{H}_6\cdots\text{MgX}^+$ and $\text{C}_6\text{H}_6\cdots\text{CaX}^+$. However, electrostatic interaction only accounts for a minor portion of $\text{C}_6\text{H}_6\cdots\text{BeX}^+$ interaction.

1. Introduction

Cation– π interaction refers to the noncovalent attraction between a cation (e.g., Li^+ , Na^+ , K^+) and a π molecule (e.g., benzene).¹ Its strength is often comparable to the interaction between a cation and traditional ligands including water, alcohols, and amines. As a result, the cation– π interaction plays an important role in the field of molecular recognition.

A detailed understanding of the cation– π interaction is clearly valuable. Therefore, many studies have been performed on the cation– π interaction between alkali or ammonium cations and aromatic compounds including benzene, naphthalene, and heterocycles.² Sometimes, less common cations such as Mg^+ , Al^+ , Ca^+ , Cr^+ , Fe^+ , and Mo^+ were also considered in the study of the cation– π interaction.³

We are interested, however, in the cation– π interaction of alkaline earth cations (e.g., Mg^{2+} , Ca^{2+}). We believe that such interaction should be important for the biochemical systems (e.g., ribozyme and ion channels) where both the alkaline earth cations and the π compounds are abundant. We also anticipate that such interaction can be useful in the design and synthesis of supramolecular complexes.

Nevertheless, we do not think that it is appropriate to use the $\text{M}^{2+}-\pi$ ($\text{M} = \text{Be}$, Mg , or Ca) complexes to model the cation– π interaction of alkaline earth cations. One reason is that the lowest unoccupied molecular orbital (LUMO) of M^{2+} is much lower than the highest occupied molecular orbital (HOMO) of many π systems. Therefore, a gas phase $\text{M}^{2+}-\pi$ complex is possibly not held together by the noncovalent forces only. In addition, it is hard to imagine a complex between a

neutral π compound and a naked M^{2+} cation in the condensed phase without any participation of a counteranion.

In agreement with our opinion, Dunbar recently proposed the use of MX^+ ($\text{X} =$ counterion) in the study of cation– π interaction of alkaline earth cations.⁴ On the basis of radiative association kinetic studies, he indeed found appreciable binding energies of MX^+ ($\text{M} = \text{Mg}$, Ca , or Sr and $\text{X} = \text{Cl}$ or Br) to benzene and mesitylene.⁴ This pioneer study prompted us to disclose our own results about the counterion effect on the interaction between benzene and alkaline earth cations.^{5,6}

2. Methods

All of the calculations were done using GAUSSIAN 98.⁷ The alkaline earth cations including Be^{2+} , Mg^{2+} , Ca^{2+} and counterions including H^- , F^- , Cl^- , OH^- , SH^- , CN^- , NH_2^- , and CH_3^- were considered in the study.

Geometry optimization was done using the MP2(full)/6-31+g* method from a face-centered initial structure without any constraint. After optimization, frequency calculation was done on each optimized complex using MP2/6-31+g* to verify that the geometry was a real minimum without any imaginary frequency.

The binding energy was determined from the difference between the total energy of the $\text{C}_6\text{H}_6\cdots\text{MX}^+$ complex and the sum of the total energies of MX^+ and benzene at the MP2/6-311++g(2d,2p) level. Zero point energy (ZPE) correction was calculated using MP2/6-31+g* (unscaled). Basis set superposition errors (BSSE) were estimated for the interaction energies with the full counterpoise technique using MP2/6-311++g(2d,2p).⁸

3. Results and Discussion

3.1. Method and Basis Set Effects on the Geometry Optimization. Using $\text{C}_6\text{H}_6\cdots\text{BeF}^+$, we examined the method (MP2 and B3LYP) and basis (6-31+g*, 6-311++g**,

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TABLE 1: Method and Basis Effects on the Geometry of C₆H₆...BeF⁺ Complex

| method | ΔZPE (kcal/mol) | BSSE (kcal/mol) | ΔE (kcal/mol) ^a | Be ²⁺ –F [–] (Å) | Be ²⁺ –centroid (Å) | C–C (Å) | C–H (Å) |
|-----------------------|--------------------|--------------------|-------------------------------|---|-----------------------------------|------------|------------|
| MP2/6-31+g* | 3.7 | 9.4 | –93.3 | 1.397 | 1.481 | 1.411 | 1.087 |
| MP2/D95V++(d,p) | 3.5 | 12.0 | –90.0 | 1.394 | 1.501 | 1.416 | 1.085 |
| MP2/6-311++g** | 3.7 | 10.5 | –89.7 | 1.379 | 1.508 | 1.412 | 1.086 |
| MP2/6-311++g(2d,2p) | 3.6 | 5.1 | –89.8 | 1.374 | 1.533 | 1.408 | 1.080 |
| MP2/D95++g(2d,2p) | 3.5 | 5.9 | –92.0 | 1.377 | 1.512 | 1.414 | 1.083 |
| B3LYP/6-31+g* | 2.2 | 1.2 | –95.6 | 1.384 | 1.522 | 1.410 | 1.086 |
| B3LYP/D95V++(d,p) | 1.9 | 3.0 | –97.0 | 1.383 | 1.527 | 1.413 | 1.087 |
| B3LYP/6-311++g** | 2.1 | 2.6 | –92.8 | 1.376 | 1.526 | 1.406 | 1.084 |
| B3LYP/6-311++g(2d,2p) | 2.1 | 1.6 | –92.7 | 1.368 | 1.538 | 1.404 | 1.081 |

^a The interaction energy (ΔE) at every level of calculation was corrected with BSSE and ΔZPE obtained at the same level of theory. ΔZPE is the zero-point energy correction.

TABLE 2: Interaction Energies between Benzene and MF⁺ Cations Calculated Using Different Theoretical Methods (kcal/mol)^a

| M ²⁺ | | Be ²⁺ | Mg ²⁺ | Ca ²⁺ |
|-----------------|-----------------|------------------|------------------|------------------|
| HF | 6-31+g* | –92.9 | –59.3 | –34.2 |
| | 6-311++g** | –92.6 | –59.1 | –33.8 |
| | 6-311++g(2d,2p) | –92.3 | –60.5 | –34.5 |
| | 6-311++g(3d,3p) | –92.7 | –61.1 | –35.4 |
| B3LYP | 6-31+g* | –93.9 | –58.7 | –35.1 |
| | 6-311++g** | –91.1 | –57.6 | –33.2 |
| | 6-311++g(2d,2p) | –91.0 | –58.6 | –33.2 |
| | 6-311++g(3d,3p) | –91.6 | –58.7 | –34.0 |
| | D95V++(d,p) | –96.0 | <i>b</i> | <i>b</i> |
| | D95++g(2d,2p) | –93.8 | <i>b</i> | <i>b</i> |
| MP2 | 6-31+g* | –93.3 | –57.2 | –34.4 |
| | 6-311++g** | –89.4 | –55.1 | –34.3 |
| | 6-311++g(2d,2p) | –89.5 | –56.6 | –36.0 |
| | 6-311++g(3d,3p) | –90.3 | –56.8 | –37.4 |
| | D95V++(d,p) | –92.8 | <i>b</i> | <i>b</i> |
| | D95++g(2d,2p) | –91.4 | <i>b</i> | <i>b</i> |
| MP4 | 6-31+g* | –93.2 | –57.1 | –34.1 |
| CCSD | 6-31+g* | –93.3 | –57.5 | –34.2 |

^a The interaction energy (ΔE) at every level of calculation was corrected with BSSE and ΔZPE obtained at the same level of theory. MP2/6-31+g* optimization geometry was used throughout this Table.

^b D95V and D95 basis sets are not available for Mg and Ca.

6-311++g(2d,2p), D95V++(d,p), and D95++(2d,2p)) effects on the accuracy of geometry optimization. The results are shown in Table 1.

TABLE 3: Geometries and Interaction Energies of C₆H₆...MX⁺ Complexes Calculated Using MP2/6-311++G(2d,2p)//MP2/6-31+g*

| M ²⁺ | | H [–] | F [–] | Cl [–] | OH [–] | SH [–] | CN [–] | NH ₂ [–] | CH ₃ [–] | |
|------------------|--|----------------|----------------|-----------------|-----------------|-----------------|-----------------|------------------------------|------------------------------|-------|
| Be ²⁺ | ΔE ^a | –213.8 | –86.4 | –89.5 | –87.2 | –77.4 | –79.8 | –98.9 | –74.7 | –76.7 |
| | M–X ^b | | 1.318 | 1.397 | 1.791 | 1.413 | 1.894 | 1.640 | 1.503 | 1.678 |
| | M–centroid ^b | 1.277 | 1.465 | 1.481 | 1.478 | 1.521 | 1.492 | 1.440 | 1.514 | 1.498 |
| | C–C ^b | 1.424 | 1.410 | 1.411 | 1.410 | 1.409 | 1.410 | 1.411 | 1.409 | 1.409 |
| | C–H ^b | 1.091 | 1.087 | 1.087 | 1.087 | 1.087 | 1.087 | 1.088 | 1.087 | 1.087 |
| | q(C ₆ H ₆) ^c | 1.331 | 0.786 | 0.810 | 0.445 | 0.725 | 0.649 | 0.889 | 0.458 | 0.718 |
| Mg ²⁺ | ΔE | –108.6 | –47.4 | –56.6 | –55.5 | –52.2 | <i>d</i> | –57.6 | –49.2 | –42.3 |
| | M–X | | 1.681 | 1.753 | 2.151 | 1.769 | | 2.016 | 1.882 | 2.071 |
| | M–centroid | 1.960 | 2.129 | 2.069 | 2.072 | 2.082 | | 2.073 | 2.104 | 2.151 |
| | C–C | 1.419 | 1.410 | 1.411 | 1.411 | 1.410 | | 1.411 | 1.410 | 1.409 |
| | C–H | 1.090 | 1.088 | 1.088 | 1.088 | 1.088 | | 1.088 | 1.088 | 1.088 |
| | q(C ₆ H ₆) | 0.680 | 0.405 | 0.420 | 0.353 | 0.390 | | 0.375 | 0.394 | 0.293 |
| Ca ²⁺ | ΔE | –73.8 | –33.9 | –36.0 | –38.3 | –35.9 | <i>d</i> | –40.0 | –33.3 | –31.8 |
| | M–X | | 2.059 | 2.051 | 2.491 | 2.064 | | 2.382 | 2.218 | 2.462 |
| | M–centroid | 2.472 | 2.610 | 2.558 | 2.551 | 2.559 | | 2.547 | 2.578 | 2.622 |
| | C–C | 1.411 | 1.407 | 1.407 | 1.407 | 1.407 | | 1.407 | 1.407 | 1.406 |
| | C–H | 1.090 | 1.088 | 1.088 | 1.088 | 1.088 | | 1.089 | 1.088 | 1.088 |
| | q(C ₆ H ₆) | 0.451 | 0.232 | 0.251 | 0.318 | 0.229 | | 0.325 | 0.260 | 0.262 |

^a kcal/mol. ^b In Ångstroms. ^c Mulliken charges on benzene in the complex obtained at MP2/6-311++g(2d,2p) level. These charges should not be used for modeling but will give the information about trends required here. ^d We failed in getting these complexes optimized.

According to Table 1, the structures of C₆H₆...BeF⁺ optimized using MP2 with different basis sets are fairly close to each other. The differences between MP2/6-31+g* and higher level method results for the Be–F bond length, Be–centroid distance, C–C bond length, and C–H bond length are 0.00–0.02, 0.02–0.05, 0.001–0.005, and 0.001–0.007 Å, respectively. These small differences are consistent with the previous studies on cation–π complexes, where it was found that the basis set effects on the optimized geometries were not large.^{2,9} Therefore, use of MP2/6-31+g* in geometry optimization is adequate.

B3LYP optimizations give slightly different results as compared to MP2. The Be–F bond length from B3LYP is about 0.01 Å shorter than from MP2, whereas the Be–centroid distance from B3LYP is about 0.02 Å longer than from MP2. The basis set effect on B3LYP optimization is also very small.

3.2. Method and Basis Set Effects on the Interaction Energy Calculation. To obtain a more accurate interaction energy of the C₆H₆...MX⁺ complex, one may need to use a higher level method than MP2/6-31+g* to do single-point calculations. Therefore, we examined the method and basis set effects on the calculated interaction energy. The results are shown in Table 2.

According to Table 2, the interaction energies calculated using different methods are fairly close to each other. In particular, the electron correlation effect on the interaction energy calculation is very small. Using the 6-31+g* basis set, the interaction energies of C₆H₆...MF⁺ calculated at the HF, MP2, MP4, and CCSD levels are 92.9, 93.3, 93.2, and 93.3 kcal/mol for Be,

59.3, 57.2, 57.1, and 57.5 kcal/mol for Mg, and 34.2, 34.4, 34.1, and 34.2 kcal/mol for Ca.

The small method and basis set effects on energy calculation are consistent with previous studies of alkali cation-benzene complexes, where very small changes were found in the interaction energies when more extensive treatment of electron correlation (e.g., MP4, CCSD(T)) and considerably more flexible basis sets (e.g., aug-cc-pVTZ) were used instead of MP2/6-311+g*.⁹ The small electron correlation effect also indicates that the dispersion contribution to the interaction energy is small. Therefore, MP2/6-311++g(2d,2p)/MP2/6-31+g* appears to be adequate for the energy calculation.¹⁰

The difference between the B3LYP and MP2 results on $C_6H_6 \dots MF^+$ interaction energies is also found to be small, i.e., 1–2 kcal/mol. Given the fact that none of the existing functionals describes the London dispersion energy,¹¹ this observation also indicates that the dispersion contribution to the $C_6H_6 \dots MX^+$ interaction is small.

All MP2 methods predict that the ZPE correction is about 3–4 kcal/mol. This correction is about 1/20–1/30 of the total interaction energy. BSSE correction, on the other hand, is dependent on the basis set, a larger basis set having a smaller BSSE. At the MP2/6-311++g(2d,2p) level, BSSE is about 1/10–1/20 of the total interaction. As a result, ZPE and BSSE corrections are fairly small in the present calculations.

3.3. Geometry and Interaction Energy of $C_6H_6 \dots M^{2+}$ and $C_6H_6 \dots MX^+$ Complexes. In Table 3 are shown the geometries and interaction energies of $C_6H_6 \dots MX^+$ complexes calculated using MP2/6-311++g(2d,2p)/MP2/6-31+g*. According to Table 3, $C_6H_6 \dots M^{2+}$ (M = Be, Mg, Ca) complexes are stable in the gas phase (real minima), which do not decompose spontaneously to benzene radical cation and M^+ . In the complexes, the cation-centroid distances (1.277 Å for Be, 1.960 Å for Mg, and 2.472 Å for Ca) exhibit a steady increase as the size of the cation increases. These distances are considerably smaller than the corresponding ones for alkali cation-benzene complexes (2.340 Å for Li, 2.803 Å for Na, and 3.137 Å for K).⁹ On the other hand, the interaction energies of $C_6H_6 \dots M^{2+}$ complexes (213.8 kcal/mol for Be, 108.6 kcal/mol for Mg, and 73.8 kcal/mol for Ca) are considerably larger than those for the corresponding alkali cation-benzene complexes (35.4 kcal/mol for Li, 21.3 kcal/mol for Na, and 17.0 kcal/mol for K).⁹

Addition of counterions significantly lowers the interaction energies between alkaline earth cations and benzene. In fact, the interaction energies of $C_6H_6 \dots MX^+$ complexes are about one-half of $C_6H_6 \dots M^{2+}$ complexes. The cation-centroid distances in $C_6H_6 \dots MX^+$ complexes (~ 1.5 Å for Be, ~ 2.1 Å for Mg, and ~ 2.6 Å for Ca) are larger than those for the $C_6H_6 \dots M^{2+}$ but close to those for benzene-alkali cation complexes. In addition, in $C_6H_6 \dots MX^+$ complexes, the structure of benzene is only slightly changed as compared to the geometry of free benzene. This can be demonstrated by the small deformation energies calculated using MP2/6-311++g(2d,2p) (energy difference between benzene using its geometry in the complex and benzene using its free geometry), for instance, 1.1 kcal/mol for $C_6H_6 \dots BeF^+$, 0.5 kcal/mol for $C_6H_6 \dots MgF^+$, and 0.4 kcal/mol for $C_6H_6 \dots CaF^+$.

It should be mentioned that the interaction energies of $C_6H_6 \dots MgCl^+$ and $C_6H_6 \dots CaCl^+$ have been measured by Dunbar to be $59.0-62.3 \pm 9.3$ and 42.9 ± 6.4 kcal/mol, respectively.⁴ In comparison, our theoretical values (55.5 and 38.3 kcal/mol) fall within the error bars of the experimental results.¹² Thus, the agreement between the experiment and the theory is good.

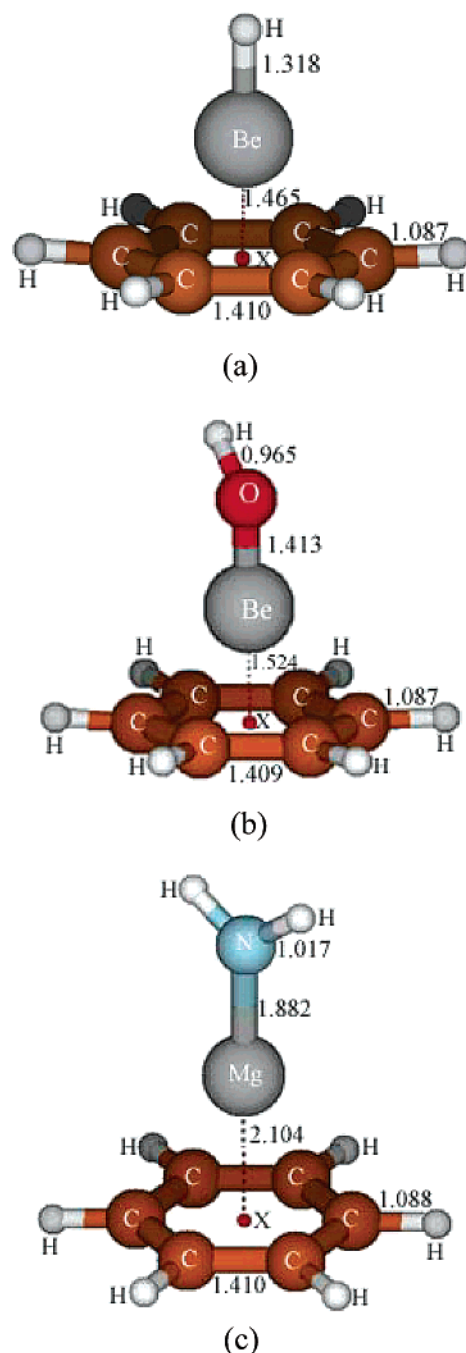


Figure 1. MP2/6-31+g*-optimized (a) $C_6H_6 \dots BeH^+$, (b) $C_6H_6 \dots BeOH^+$, and (c) $C_6H_6 \dots MgNH_2^+$ complexes.

3.4. Counterion Effects on the $C_6H_6 \dots MX^+$ Interaction. Counterions affect $C_6H_6 \dots MX^+$ interactions in geometry as well as in interaction energy. Although in the geometry optimization, no constraint is used, the optimized structures for $C_6H_6 \dots MH^+$, $C_6H_6 \dots MF^+$, $C_6H_6 \dots MCl^+$, and $C_6H_6 \dots MCN^+$ have C_{6v} symmetry. $C_6H_6 \dots MOH^+$, $C_6H_6 \dots MSH^+$, and $C_6H_6 \dots MNH_2^+$ complexes, on the other hand, have C_s symmetry. $C_6H_6 \dots MCH_3^+$ is C_{3v} .

The magnitudes of $C_6H_6 \dots MX^+$ interaction energies decrease roughly in the order $CN^- > F^- \approx Cl^- > SH^- > OH^- > H^- > NH_2^- > CH_3^-$. This should be compared to the order of the gas phase proton affinities of the counterions calculated using CCSD(T)/6-311++g(d,p): Cl^- (342.5 kcal/mol) < CN^- (358.1 kcal/mol) < SH^- (363.2 kcal/mol) < F^- (379.7 kcal/mol) < OH^- (402.0 kcal/mol) < H^- (410.1 kcal/mol) < NH_2^- (416.9

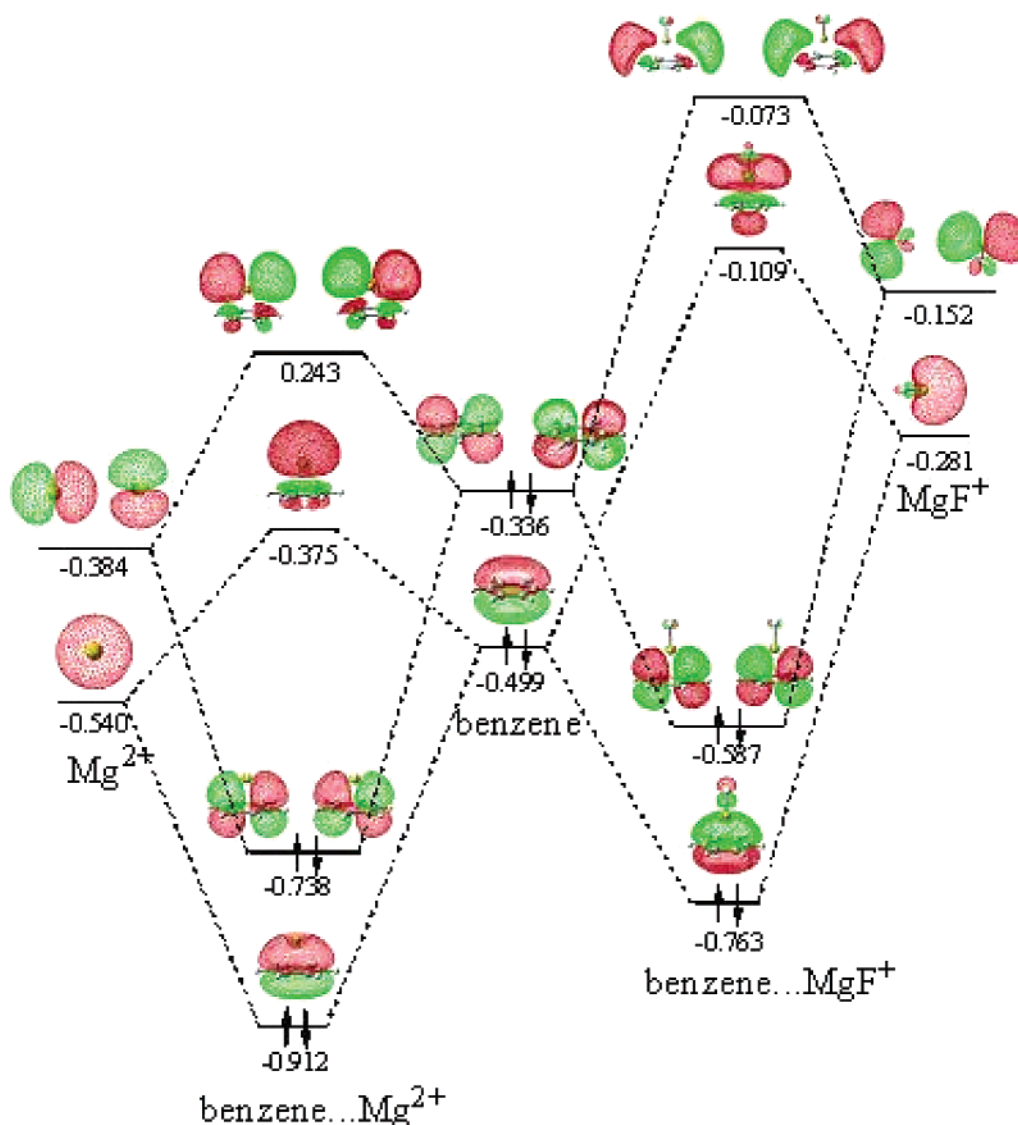


Figure 2. Molecular orbital interactions involved in benzene...Mg²⁺ and benzene...MgF⁺ complexes. The number below each line indicates the energy level of the orbital (hartree).

kcal/mol) < CH₃⁻ (429.4 kcal/mol). Therefore, when X⁻ is a stronger base, the C₆H₆...MX⁺ interaction is weaker.

One may propose on the basis of the above correlation that the charge-transfer interaction should be the cause of the counterion effect, i.e., a stronger base X⁻ makes M²⁺ a poorer acceptor and, therefore, the C₆H₆...MX⁺ interaction weaker. However, it is found that C₆H₆...MX⁺ interaction energies do not correlate with the amount of Mulliken charge transfer (See Table 3) from benzene to MX⁺. In fact, when one performs a linear regression of the C₆H₆...MX⁺ interaction energy against the transferred charge, the correlation coefficient is only about 0.50. This indicates that the charge-transfer interaction cannot be used to account for the observed counterion effects.

On the other hand, it is found that the interaction energies correlate well with the M-centroid distances (*R*) as shown in the following equations:

$$\Delta E_{\text{BeX}} = -512.0 + 288.1 R \quad (r = 0.93) \quad (1)$$

$$\Delta E_{\text{MgX}} = -404.7 + 168.4 R \quad (r = 0.97) \quad (2)$$

$$\Delta E_{\text{CaX}} = -249.7 + 83.1 R \quad (r = 0.86) \quad (3)$$

The slopes are positive, which means that longer M-centroid distance disfavors C₆H₆...MX⁺ interaction. Quadrupole-point charge interaction between the benzene and the cation may result in this correlation.¹³ Point charge-induced dipole interaction may also result in this correlation.¹⁴ Separation of these interactions is hard.

3.5. Electrostatic Interaction in C₆H₆...MX⁺ Complexes.

Kollman suggested that electrostatic interactions account for about 60% of total interaction energy in the ethylene-Li⁺ complex.¹⁵ Dougherty also suggested that for most aromatic systems, electrostatic interactions between an ion and the quadrupole moment of an aromatic make major contributions to the cation- π interaction.¹ Herein, we calculated the strength of the electrostatic interaction involved in the cation- π complexes of benzene with Li⁺, Na⁺, Be²⁺, Mg²⁺, BeF⁺, and MgF⁺. We used the point charge model as described earlier.¹⁶ The results are shown in Table 4.

According to Table 4, the electrostatic interaction energy for the Li⁺ or Na⁺ complex (20.8 or 19.0 kcal/mol) is over 50% of the total cation- π interaction energy (38.3 or 28.0 kcal/mol). Therefore, electrostatic interaction is indeed the major driving force leading to the complex formation. Na⁺ has a slightly

TABLE 4: Electrostatic Interaction Energies Calculated Using a Point-Charge Model with CHelpG Charges Using MP2/6-311++G(2d,2p)^a

| cation | charge on M (au) | charge on F (au) | electrostatic interaction energy (kcal/mol) |
|------------------|------------------|------------------|---|
| BeF ⁺ | 0.617 | -0.490 | -13.2 |
| MgF ⁺ | 0.943 | -0.591 | -25.8 |
| Li ⁺ | 0.611 | | -20.8 |
| Na ⁺ | 0.724 | | -19.0 |
| Be ²⁺ | 0.782 | | -37.5 |
| Mg ²⁺ | 1.230 | | -47.6 |

^a For more details about ChelpG charges, see ref 16. CHelpG charges are not available for K and Ca.

smaller electrostatic interaction than Li⁺ because C₆H₆...Na⁺ has a larger centroid-metal distance.

In comparison, the electrostatic interaction energy for the Be²⁺ or Mg²⁺ complex (37.5 or 47.6 kcal/mol) is twice as large as that for Li⁺ or Na⁺. This clearly is caused by the fact that Be²⁺ or Mg²⁺ are divalent. However, as compared to the total interaction energy (213.8 kcal/mol for Be²⁺, 108.6 kcal/mol for Mg²⁺), the electrostatic interaction accounts for considerably less than 50% of the total. This should be attributed to the large charge transfer in the complexes. In fact, in the C₆H₆...Be²⁺ complex, the cation only carries a charge of +0.782e, not much larger than Li⁺ in C₆H₆...Li⁺ (+0.611e). Also, because Be²⁺ causes larger charge transfer, the electrostatic interaction energy for the Be²⁺ complex is actually about 10 kcal/mol smaller than that for the Mg²⁺ complex despite the fact that the Mg²⁺...benzene distance is larger than the Be²⁺ case.

The electrostatic interaction in C₆H₆...Be²⁺ is calculated to be 13.2 kcal/mol. This value is significantly smaller than that for Li⁺ or Na⁺ complexes, possibly also caused by the large charge transfer. As compared to the total interaction energy (93.3 kcal/mol), electrostatic interaction apparently is only a minor driving force for the complex formation.

Nevertheless, for C₆H₆...MgF⁺, the electrostatic interaction energy is calculated to be 25.8 kcal/mol. This value is slightly larger than that for the Li⁺ or Na⁺ complexes, presumably because the centroid-metal distance in C₆H₆...MgF⁺ is slightly shorter than the Li⁺ or Na⁺ cases. Because the electrostatic interaction accounts for 40% of the total interaction energy (59.3 kcal/mol), the electrostatic interaction is also an important driving force for the interaction between MgX⁺ (and presumably CaX⁺) and π systems.

3.6. Molecular Orbital Interactions. The difference between C₆H₆...MX⁺ and C₆H₆...M²⁺ interactions can be further revealed by the molecular orbital analyses. (Figure 2).

According to Figure 2, benzene uses its a_{2u} and e_{1g} bonding orbitals to interact with the empty s and p (or σ^* and π^* antibonding) orbitals of the cation. For the C₆H₆...Mg²⁺ complex, the empty s and p orbitals have lower energy than the filled a_{2u} and e_{1g} orbitals of benzene. Therefore, strong orbital interactions occur in this complex. Nevertheless, it should be mentioned that according to Figure 2 electron transfer does not occur from the filled orbital of benzene to Mg²⁺. Therefore, the C₆H₆...Mg²⁺ complex is thermodynamically stable, not decomposing automatically to benzene radical cation and Mg⁺.

In comparison, for the C₆H₆...MgF⁺ complex, the empty σ^* and π^* antibonding orbitals have higher energy than the filled orbitals of benzene. As a result, orbital interactions for this complex are not very strong. It should be mentioned that similar orbital energies (i.e., LUMO of cation is higher than HOMO of π systems) are also seen for C₆H₆-alkali cation complexes.^{6a}

Therefore, use of MX⁺ is more appropriate in the study of cation- π interactions.

4. Conclusion

Expecting that the cation- π interactions of alkaline earth cations would be important for diverse fields, we performed systematic theoretical studies on the cation- π interactions between benzene and MX⁺ cations (M = Be, Mg, and Ca; X = H⁻, F⁻, Cl⁻, OH⁻, SH⁻, CN⁻, NH₂⁻, and CH₃⁻). The major findings include the following.

(i) The basis set and the electron correlation effects on the geometry optimization and energy calculation are small for C₆H₆...MX⁺ complexes. Therefore, theoretical methods such as MP2/6-311++g(2d,2p)//MP2/6-31+g* are sufficiently reliable for the calculation.

(ii) The cation- π complex between benzene and a naked alkaline earth cation is stable, but the interaction is much stronger than the prototypical benzene-alkali cation complexes. Therefore, consideration of counterion is necessary in the study of the benzene-alkaline earth cation interactions.

(iii) The counterion significantly modulates the C₆H₆...MX⁺ interaction so that many properties of a C₆H₆...MX⁺ complex are close to those for the prototypical benzene-alkali cation complexes.

(iv) Electrostatic interaction is the major driving force for the C₆H₆...Li⁺ and C₆H₆...Na⁺ complexes. Electrostatic interaction is also an important driving force for C₆H₆...MgX⁺ and C₆H₆...CaX⁺. However, electrostatic interaction only accounts for a minor portion of the C₆H₆...BeX⁺ interaction.

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(10) It should be mentioned that recent calculations on alkali cation–benzene complexes showed that the difference between the interaction energy obtained by very large basis set and that obtained with a medium size basis set could be as large as 1–4 kcal/mol. Thus, interaction energies obtained using our finally chosen method, MP2/6-311++g(2d,2p)/MP2/6-31+g*, may also have an error of 1–4 kcal/mol. For more, see Feller, D.; Dixon, D. A.; Nicholas, J. B. *J. Phys. Chem. A* **2000**, *104*, 11414.

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(12) It should be mentioned that Dunbar's experimental values might be overestimated. For example, in the same study where they studied the $C_6H_6...MgCl^+$ and $C_6H_6...CaCl^+$ complexes, they obtained a binding energy of 1.61 eV for $Mg(\text{benzene})^+$ complex. However, another reliable literature value for the same complex is 1.39 eV, which was measured by Armentrout's group with the threshold CID approach.⁴

(13) The counterion may affect the electrostatic interaction between benzene as a quadrupole and cation as a point charge. According to the quadrupole–point charge interaction model, if we fix the quadrupole and the point charge, the interaction energy (ΔE) should correlate with $1/R^3$, i.e., $\Delta E = k/R^3 + a$. As a result, a small change in the M–centroid distance, dR , should cause a change of interaction energy $d\Delta E$ obeying the following equation $d\Delta E = -3k/R^4 \cdot dR$. Because the M–centroid distance is roughly the same when M is the same, the counterion effects should correlate with R .

(14) We thank one of the reviewers for pointing out this important problem.

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