JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

Cation⊗3π: Cooperative Interaction of a Cation and Three Benzenes with an Anomalous Order in Binding Energy

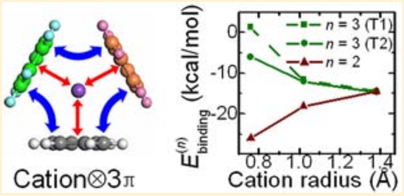
Manyi Duan,[†,‡] Bo Song,*[,‡] Guosheng Shi,[‡] Haikuo Li,[‡] Guangfu Ji,[†,§] Jun Hu,[‡] Xiangrong Chen,*[,†] and Haiping Fang*[,‡]

[†]School of Physics Science and Technology, Sichuan University, Chengdu 610064, P.R. China

[‡]Division of Interfacial Water and Laboratory of Physical Biology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, P.R. China

[§]National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang 621900, P.R. China

ABSTRACT: Cation−π or cation−π−π interaction between one cation and one or two structures bearing rich π-electrons (such as benzene, aromatic rings, graphene, and carbon nanotubes) plays a ubiquitous role in various areas. Here, we analyzed a new type interaction, cation⊗3π, whereby one cation simultaneously binds with three separate π-electron-rich structures. Surprisingly, we found an anomalous increase in the order of the one-benzene binding strength of the cation⊗3π interaction, with $K^+ > Na^+ > Li^+$. This was at odds with the conventional ranking of the binding strength which usually increases as the radii of the cations decrease. The key to the present unexpected observations was the cooperative interaction of the cation with the three benzenes and also between the three benzenes, in which a steric-exclusion effect between the three benzenes played an important role. Moreover, the binding energy of cation⊗3π was comparable to cation⊗2π for K^+ and Na^+, showing the particular importance of cation⊗3π interaction in biological systems.



INTRODUCTION

Noncovalent interactions play crucial roles in the structures, dynamic processes, and functions of microscale and nanoscale materials, and also for macroscopic materials.[1−9] Specifically, cation−π interactions are ubiquitous in chemistry, nanotechnology, physics, and biology, occurring in supermolecular assembly, molecular recognition, enzyme catalysis, drug delivery, and stability of protein structure,[10−17] and their properties have been extensively studied.[18−38]

In 1993, Kumpf and Dougherty[34] proposed a new interaction between an alkali metal cation (M^+) and two benzenes (Bz) (denoted as cation−π−π interaction) to form a complex of a cation sandwiched between two staggered, face-to-face benzene molecules (M^+⊗2Bz complex) based on quantum chemical methods calculations, which were later experimentally demonstrated.[27] In 2006, Reddy et al.[29] showed that the binding energy of the M^+⊗2Bz complex was stronger than the other possible configuration. Further, Gal et al.[35] reported that the aliphatic chain connecting two benzene rings was favored to sandwich a Li^+ cation between the two benzenes with the help of cation−π−π interaction. These results suggest that the cation will trigger a structural folding when the structure contains two aromatic subunits connected by a flexible atomic chain.

Structures rich in π-electrons (such as benzene, aromatic rings, graphene, and carbon nanotubes) are abundant in biological and other materials.[39−44] Lisy and his co-workers[32,45] performed a series of experiments showing competition of the cation−π interaction simultaneously with cation−dipole, π−hydrogen, and water−water hydrogen bonds. El-Shall et al.[46] determined the structures of the cluster cations $(C_6H_6)_n^+$ with $n = 2−6$ both experimentally and theoretically. They found a quasiplanar triangular structure for the benzene trimer ion. Recently, we demonstrated that cation−π interaction between Li^+ cation and carbon nanotubes was the key to the mechanism of Li intercalation in Li-based energy storage devices.[47] In those studies, the analysis was still based on the single cation−π interaction, although there observations focused on a cation surrounded by three or more π-electron-rich structures together with one or more water molecules. Thus, the experimental and simulation results are still far from being fully understood.

Herein, we analyze a new type of cooperative interaction, namely a cation⊗3π interaction, whereby one cation (Li^+, Na^+, and K^+ serving as examples) interacts simultaneously with three separate structures containing rich π-electrons (as a representative structure, we have used benzene), which is clearly different from the cation−π or cation−π−π interactions due to a steric-exclusion effect between the three benzenes. This cooperative interaction resulted in a stable triangular structure, ◬, characterized via one cation surrounded by three benzenes, termed the M^+⊗3Bz complex. Interestingly, we found that the increase in the order of the one-benzene binding strength (OBB-strength) of the cation⊗3π interaction with respect to the radii of the cations was the opposite of the order observed for the OBB-strength in the cation−π−π and cation−π

Received: March 26, 2012
Published: July 2, 2012

dx.doi.org/10.1021/ja302918t | J. Am. Chem. Soc. 2012, 134, 12104−12109

interactions. Explicitly, the OBB-strength of the cation⊗3π interaction increased, and the OBB-strength of the cation−π and cation−π−π interaction decreased, with respect to the cations ranging in order from Li^+, Na^+, to K^+. Here, the OBB-strength is the absolute value of the one-benzene binding energy (OBB-energy), which is the binding energy in a M^+⊗nBz complex between a single benzene and the residual stable M^+⊗(n-1)Bz complex. Moreover, the OBB-energies of the K^+⊗3π and Na^+⊗3π interactions were comparable to K^+⊗2π and Na^+⊗2π, respectively, while the OBB-energy of Li^+⊗3π was much weaker than Li^+⊗2π. Considering that the cation⊗3π interaction also occurs for other ions (such as the iron, copper, or cobalt cation), these findings are expected to have great applications in the design and self-assembly of carbon-based materials/devices, and in the understanding of biological systems.

■ METHODS

All of our calculations were performed by the second-order Møller−Plesset perturbation theory (MP2), as implemented in the Gaussian-09 package[48,49] with the 6-311++G(d,p) basis set of triple-zeta quality and including diffuse functions applied on all atoms, which has been widely used to study metal cation−π and π−π interactions.[50] Basis set superposition errors (BSSEs) were corrected by using the full counterpoise correction method.[51]

The initial structures consisted of three benzenes around one cation (K^+, Na^+, or Li^+), in which the three benzenes formed a triangle with the cation at the center of the triangle, and the cation rested over the hollow site of each benzene (△). The conformations shown in Figure 1 were obtained after relaxation.

■ RESULTS

The triangular structures after relaxation included two kinds of conformations (Figure. 1), namely, M^+⊗3Bz-T1 and M^+⊗3Bz-T2. In the two K^+-based structures, the cation was found at the hollow site of each benzene, with the three benzenes arrayed symmetrically around the cation, where the two upper overlapping benzenes perfectly aligned for the K^+⊗3Bz-T1 complex, and they overlapped with a 30° dislocation for K^+⊗3Bz-T2 (Figure 1G,H). The vertical distance between the cation and a benzene was denoted by $d_M(T)$ where M = K, Na, and Li, and T = T1 and T2. For d_K and d_{Na}, the distances were virtually the same for the T1 and T2 structures, ∼2.95 Å and 2.76 Å, respectively. However, in the Li^+-based complex, the two conformations Li^+⊗3Bz-T1 and Li^+⊗3Bz-T2 were clearly different. Li^+⊗3Bz-T1 was similar to K^+⊗3Bz-T1 with $d_{Li}(T1)$ = 2.63 Å. Li^+⊗3Bz-T2 showed a compact triangular structure (Figure. 1F), with the cation located above the bridge site of each benzene ring, although the three benzenes were still symmetrically arrayed about the cation, with $d_{Li}(T2)$ = 2.37 Å, the shortest of all the distances observed between any of the cations and the benzene.

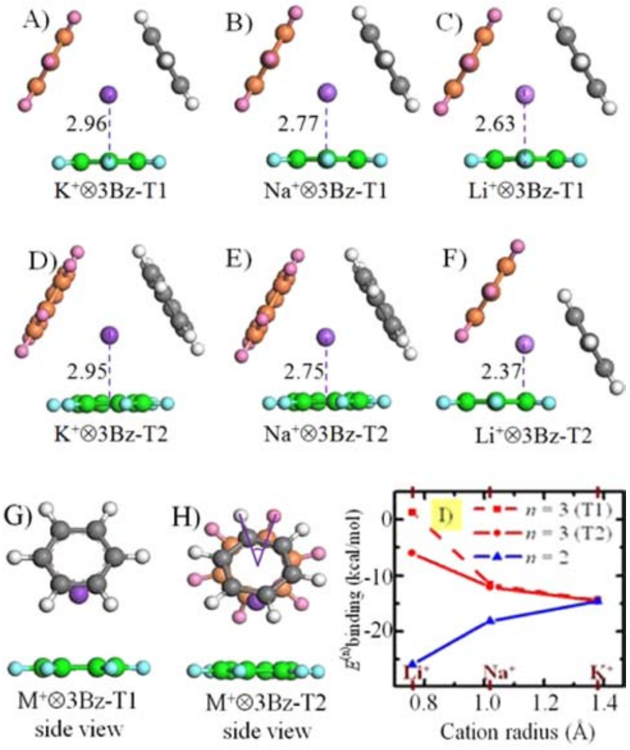


Figure 1. Relaxed conformations for the K^+⊗3Bz (A, D), Na^+⊗3Bz (B, E), and Li^+⊗3Bz (C, F) complexes. The labels T1 and T2 denote the first and the second kinds of structures, respectively. The large balls, small balls, and violet balls represent the carbon atoms, the hydrogen atoms, and the cation (K^+, Na^+, or Li^+). (A−F) Top view of conformations of M^+⊗3Bz, in which the vertical distance between the cation and the benzene is given in the unit of angstroms at the top views. (G) Side view of the T1 structures of the M^+⊗3Bz complex. (H) Side view of the T2 structures of the K^+⊗3Bz and Na^+⊗3Bz complexes. (I) One-benzene binding energy of the M^+⊗3Bz (T1, red dashed; T2, red solid) and M^+⊗2Bz (blue solid) complexes. The strength (the absolute value of the OBB-energies) for the cation⊗3π interaction of the M^+⊗3Bz complex increased in the order of Li^+ < Na^+ < K^+, whether they were in the structure T1 or T2, contrast with the normal order of the strength for the cation−π−π interactions of the M^+⊗2Bz complex which were ranked in the order Li^+ > Na^+ > K^+.

To study the stability of the M^+⊗3Bz complex, we examined the OBB-energy $E_{binding}$, defined by

$$E_{binding}(M^+ \otimes nBz) = E(M^+ \otimes nBz) - E(M^+ \otimes (n-1)Bz) - E(Bz) \quad (1)$$

with n = 2, 3. $E_{binding}(M^+ \otimes nBz)$ denotes the binding energy in a M^+⊗nBz complex between a single benzene and the residual stable M^+⊗(n − 1)Bz complex, which can describe the energy required to separate the benzene from the stable M^+⊗nBz complex and result in the M^+⊗(n − 1)Bz complex together with a free benzene. Here, $E(M^+ \otimes 3Bz)$ stands for the energy of the complex consisting of one cation and three benzenes with either of the stable structures, M^+⊗3Bz-T1 or M^+⊗3Bz-T2. $E(M^+ \otimes 2Bz)$ denotes the energy of the complex consisting of one cation and two benzenes with the most stable structure M^+⊗2Bz, namely the cation sandwiched between two parallel benzenes.[29] $E(M^+ \otimes Bz)$ indicates the energy of the cation−benzene interaction, while $E(Bz)$ denotes the energy of an individual benzene. We also calculated the OBB-energy $E_{binding}(M^+ \otimes 2Bz)$ for comparison.

Figure 1I shows the OBB-energies as a function of the radius of each cation. It is clear that the strength (the absolute value of the OBB-energies) of the cation⊗3π interaction increased in the order of Li^+ < Na^+ < K^+, whether they were in the structure T1 or T2. This is a surprising contrast to the normal order of the strength for the cation−π−π or cation−π interactions which are ranked in the order Li^+ > Na^+ > K^+.[27] Interestingly, $E_{binding}(K^+ \otimes 3Bz\text{-}T1)$ = −14.44 kcal/mol and $E_{binding}(K^+ \otimes 3Bz\text{-}T2)$ = −14.60 kcal/mol, very close to $E_{binding}(K^+ \otimes 2Bz)$ = −14.55 kcal/mol, showing that the K^+⊗3π interaction was comparable to K^+⊗2π. In contrast, for the Na^+ cation,

$E_{\text{binding}}(\text{Na}^+\otimes 3\text{Bz-T1}) = -11.58$ kcal/mol and $E_{\text{binding}}(\text{Na}^+\otimes 3\text{Bz-T2}) = -12.08$ kcal/mol, which were weaker than $E_{\text{binding}}(\text{Na}^+\otimes 2\text{Bz}) = -18.13$ kcal/mol. The energy difference between them was 6.55 kcal/mol for T1 and 6.05 kcal/mol for T2, corresponding to about 10−11 k_BT at a $T = 300$ K. Thus, $\text{Na}^+\otimes 2\text{Bz}$ is more stable than $\text{Na}^+\otimes 3\text{Bz}$. For Li^+, $E_{\text{binding}}(\text{Li}^+\otimes 3\text{Bz-T1}) = +1.31$ kcal/mol, denoting that $\text{Li}^+\otimes 3\text{Bz-T1}$ is much less stable than $\text{Li}^+\otimes 2\text{Bz}$. We thought that there was a barrier between $\text{Li}^+\otimes 3\text{Bz-T1}$ and $\text{Li}^+\otimes 2\text{Bz}$, so that the structure $\text{Li}^+\otimes 3\text{Bz-T1}$ still showed its stability during the relaxation. $E_{\text{binding}}(\text{Li}^+\otimes 3\text{Bz-T2}) = -6.00$ kcal/mol, which is much weaker than $E_{\text{binding}}(\text{Li}^+\otimes 2\text{Bz}) = -25.94$ kcal/mol, so that $\text{Li}^+\otimes 3\text{Bz}$ is obviously less stable than $\text{Li}^+\otimes 2\text{Bz}$. We note that both K^+ and Na^+ are important and abundant components in biological systems, while Li^+ is much rarer. The comparable OBB-energies between $\text{M}^+\otimes 3\text{Bz}$ and $\text{M}^+\otimes 2\text{Bz}$ for K^+ and Na^+ imply the importance of $\text{M}^+\otimes 3\text{Bz}$ in biological systems. Further, the value of $[E_{\text{binding}}(\text{K}^+\otimes 3\text{Bz}) - E_{\text{binding}}(\text{K}^+\otimes 2\text{Bz})] - [E_{\text{binding}}(\text{Na}^+\otimes 3\text{Bz}) - E_{\text{binding}}(\text{Na}^+\otimes 2\text{Bz})] \approx 10\ k_BT$ (for $T = 300$ K) also indicates the difference between K^+ and Na^+, which may be helpful to the understanding of differences in the behavior of K and Na cations, as in the K-ion channels in a biosystems.

Mechanism Underlying the Observations. To elucidate the mechanism underlying the difference of the behaviors between the $\text{K}^+\otimes 3\pi$, $\text{Na}^+\otimes 3\pi$, and $\text{Li}^+\otimes 3\pi$ interactions, and underlying their anomalous order, we analyzed the interaction of a single benzene in the $\text{M}^+\otimes n\text{Bz}$ complex and took the structure T2 to illustrate the idea. A benzene participates in two kinds of interactions: (1) the interaction of the benzene with the cation and (2) the interaction of the benzene with other benzenes in the complex.

We defined the cation−π interaction energy as $E^{(n)}_{\text{cation}-\pi} = E_{\text{cation}-n\pi} - E_{\text{cation}-(n-1)\pi}$ in the $\text{M}^+\otimes 3\text{Bz}$ complex ($n = 3$) and $\text{M}^+\otimes 2\text{Bz}$ complex ($n = 2$). $E_{\text{cation-}n\pi} = E(\text{M}^+\otimes n\text{Bz}) - E(\text{M}^+) - E(n\text{Bz})$ denotes the interaction between the cation and the remaining n benzenes. $E(n\text{Bz})$ is the energy of the n benzenes within the conformation of the $\text{M}^+\otimes n\text{Bz}$ complex in the absence of the cation. We thereby obtained the cation−π interaction energy of an individual benzene with the cation while taking into account the effect from the other benzenes in the complex. As shown in Table 1, the differences between $E^{(3)}_{\text{cation}-\pi}$ and $E^{(2)}_{\text{cation}-\pi}$ were +2.93 kcal/mol for K^+, +7.29 kcal/mol for Na^+, and +21.33 kcal/mol for Li^+. These values were positive, denoting that the cation−π interaction in the $\text{M}^+\otimes 3\text{Bz}$ complex is weaker than that in $\text{M}^+\otimes 2\text{Bz}$.

Table 1. Cation−π Interaction Energy ($E^{(n)}_{\text{cation}-\pi}$) and the π−π Interaction Energy ($E^{(n)}_{\pi-\pi}$) in the $\text{M}^+\otimes n\text{Bz}$ Complex[a]

$\text{M}^+\otimes 3\text{Bz}$	$E^{(n)}_{\text{cation}-\pi}$	$E^{(n)}_{\pi-\pi}$	$E^{(3,2)}_{\text{cation}-\pi}$	$E^{(3,2)}_{\pi-\pi}$
$\text{K}^+\otimes 3\text{Bz-T1}$	−11.53	−2.91	+2.95	−2.84
$\text{K}^+\otimes 3\text{Bz-T2}$	−11.55	−3.04	+2.93	−2.97
$\text{K}^+\otimes 2\text{Bz}$	−14.48	−0.07		
$\text{Na}^+\otimes 3\text{Bz-T1}$	−9.82	−1.75	+7.41	−0.85
$\text{Na}^+\otimes 3\text{Bz-T2}$	−9.94	−2.14	+7.29	−1.24
$\text{Na}^+\otimes 2\text{Bz}$	−17.23	−0.90		
$\text{Li}^+\otimes 3\text{Bz-T1}$	−0.74	+2.05	+22.87	+4.38
$\text{Li}^+\otimes 3\text{Bz-T2}$	−2.28	−3.71	+21.33	−1.38
$\text{Li}^+\otimes 2\text{Bz}$	−23.61	−2.33		

[a] $n = 3$ stands for the $\text{M}^+\otimes 3\text{Bz}$ complex, and $n = 2$ for the $\text{M}^+\otimes 2\text{Bz}$ complex. $E^{(3,2)}_{\text{cation}-\pi} = E^{(3)}_{\text{cation}-\pi} - E^{(2)}_{\text{cation}-\pi}$, and $E^{(3,2)}_{\pi-\pi} = E^{(3)}_{\pi-\pi} - E^{(2)}_{\pi-\pi}$. The energies are given in the unit of kcal/mol.

We then calculated the π−π interaction energy of a single benzene with respect to the other benzenes in the complex as $E^{(n)}_{\pi-\pi} = E_{n\pi} - E_{(n-1)\pi}$, with $E_{n\pi} = E(n\text{Bz}) - nE(\text{Bz})$. Here, $E(n\text{Bz})$ represents the energy of the n benzenes within the structure of the $\text{M}^+\otimes n\text{Bz}$ complex, but in the absence of the cation. The obtained values of the π−π interaction energy allowed us to evaluate the effect from the relative positions of the benzenes in the $\text{M}^+\otimes n\text{Bz}$ complex (see Table 1). Compared to the case of two-benzene stacking in the $\text{M}^+\otimes 2\text{Bz}$ complex, a benzene in $\text{M}^+\otimes 3\text{Bz}$ obtained an additional π−π energy from three-benzene stacking: −2.97 kcal/mol, −1.24 kcal/mol, and −1.38 kcal/mol for K^+, Na^+, and Li^+, respectively. The negative sign of these values denotes that the stacking interaction of an individual benzene with the other benzenes in the $\text{M}^+\otimes 3\text{Bz}$ complex is stronger than that in $\text{M}^+\otimes 2\text{Bz}$.

Now we can rewrite eq 1 as

$$E_{\text{binding}}(\text{M}^+ \otimes n\text{Bz}) = E^{(n)}_{\text{cation}-\pi} + E^{\{n\}}_{\pi-\pi}$$

The difference of the OBB-energy between the $\text{M}^+\otimes 3\text{Bz}$ and $\text{M}^+\otimes 2\text{Bz}$ complexes read

$$\Delta E^{(3,2)}_{\text{binding}} = (E^{(3)}_{\text{cation}-\pi} - E^{(2)}_{\text{cation}-\pi}) + (E^{(3)}_{\pi\text{-}\pi} - E^{(2)}_{\pi\text{-}\pi}) \tag{2}$$

which includes the difference due to the cation−π interaction (the first two terms) and due to the π−π interaction (last two terms). As shown in Table 1, $(E^{(3)}_{\text{cation}-\pi} - E^{(2)}_{\text{cation}-\pi})$ was always positive, meaning that the cation−π interaction in $\text{M}^+\otimes 2\text{Bz}$ always exceeded that in $\text{M}^+\otimes 3\text{Bz}$, while the negative values of $(E^{(3)}_{\pi-\pi} - E^{(2)}_{\pi-\pi})$ show that the π−π interactions in the $\text{M}^+\otimes 3\text{Bz}$ complexes (except for the unstable $\text{Li}^+\otimes 3\text{Bz-T1}$) are stronger than those in $\text{M}^+\otimes 2\text{Bz}$. Interestingly, we found that, for K^+, the energy difference from the π−π stacking interaction was −2.97 kcal/mol, and its absolute value was larger than the energy difference from the cation−π interaction (+2.93 kcal/mol). Thus, the OBB-energy in the $\text{K}^+\otimes 3\text{Bz}$ complex was a little stronger than that in $\text{K}^+\otimes 2\text{Bz}$. However, for Na^+, the energy difference from the π−π stacking interaction is −1.24 kcal/mol, and gives an absolute value smaller than the energy difference from the cation−π interaction (+7.29 kcal/mol). In this case, the OBB-energy of the $\text{Na}^+\otimes 3\text{Bz}$ complex was weaker than that in $\text{Na}^+\otimes 2\text{Bz}$. In the case of Li^+, the energy difference from the π−π stacking interaction (−0.138 kcal/mol) cannot readily offset the energy difference from the cation−π interaction (+21.33 kcal/mol). This discrepancy results in the OBB-energy of the $\text{Li}^+\otimes 3\text{Bz}$ complex being significantly weaker than that in $\text{Li}^+\otimes 2\text{Bz}$.

Why is the interaction between an individual benzene and the cation so different for Li^+, Na^+, and K^+ in the $\text{M}^+\otimes 3\text{Bz}$ complex as compared to $\text{M}^+\otimes 2\text{Bz}$? Clearly, the interaction of the cation with a benzene depends on the distance between them, and we usually can calculate the different equilibrium distances for the interactions in the different complexes. Interestingly, we found that the equilibrium distances in $\text{M}^+\otimes 2\text{Bz}$ were essentially the same as the values in $\text{M}^+\otimes\text{Bz}$ (Table 2), although we expected that the behavior of the interaction between the cation with a benzene in $\text{M}^+\otimes 2\text{Bz}$ might be different from $\text{M}^+\otimes\text{Bz}$ due to the presence of the second benzene. From this observation, we expected the equilibrium distance between the cation and the benzene in $\text{M}^+\otimes 3\text{Bz}$ would also resemble that in $\text{M}^+\otimes\text{Bz}$, but we found

Table 2. Cation−Benzene Distance (d_M) in the M^+⊗3Bz Complex to the M^+⊗2Bz and M^+⊗Bz Complexes

	M^+⊗3Bz (n = 3)			M^+⊗2Bz (n = 2)			M^+⊗Bz (n = 1)		
	K^+	Na^+	Li^+	K^+	Na^+	Li^+	K^+	Na^+	Li^+
d_M	2.96[a] 2.95[b]	2.77[a] 2.75[b]	2.63[a] 2.37[b]	2.93	2.53	2.00	2.90	2.50	1.91

[a] Data for the T1 structure of the M^+⊗3Bz complex. [b] Data for the T2 structure of the M^+⊗3Bz complex. The distance is given in the unit of Å.

that they were quite different (Table 2). Remarkably, the distances for $d_{Na}(M^+⊗⊗3Bz)$ and $d_{Li}(M^+⊗3Bz)$ were considerably larger than the corresponding distances for $d_{Na}(M^+⊗Bz)$ and $d_{Li}(M^+⊗Bz)$. In addition to the interaction of the cation with the benzenes, the interaction between the benzenes in M^+⊗3Bz also differed from that in M^+⊗2Bz and M^+⊗Bz. In considering M^+⊗3Bz, we assume that there are only three benzenes forming a triangular structure △ (as the structure T2 with the absence of the cation, see the inset in Figure 3) with a distance h between a benzene and the center of the triangle. The interaction energy $E_{3\pi} = E(3Bz) - 3E(Bz)$ of this structure may be expressed as a function of h (Figure 3). $E_{3\pi}$ reaches a minimum of −3.27 kcal/mol at h_m = 2.86 Å. Moreover, $E_{3\pi}$ increases very rapidly as h decreases from h_m. Clearly, h_m was much larger than $d_{Na}(M^+⊗Bz)$ and $d_{Li}(M^+⊗Bz)$. From Figure 3, we can see that $E_{3\pi}$ = 2.26 and 207.34 kcal/mol for $h = d_{Na}(M^+⊗Bz)$ = 2.50 Å and $h = d_{Li}(M^+⊗Bz)$ = 1.91 Å, respectively. These values of $E_{3\pi}$ for Na^+ and Li^+ in complex with a benzene were 5.53 kcal/mol, and 210.61 kcal/mol larger, respectively, than the minimal value of $E_{3\pi}$ at h_m. If we locate a cation at the center of this triangle, the three-benzene interaction (trying to make h closer to h_m) would compete with the cation−benzene interaction (trying to make h closer to d_M). However, $h_m > d_M(M^+⊗Bz)$ for M = Na and Li, resulting in steric exclusion between the three benzenes and making the cation−benzene distance smaller than h_m, but larger than $d_M(M^+⊗Bz)$. Because the distance between the cation M^+ (M = Na or Li) and a benzene is larger than $d_M(M^+⊗Bz)$ due to the steric-exclusion effect, the interaction of the cation M^+ with a benzene was weaker in M^+⊗3Bz as compared to the interaction in M^+⊗2Bz (and M^+⊗Bz). Thus, $E^{(3)}_{cation-\pi} - E^{(2)}_{cation-\pi}$ reached a value of +7.29 kcal/mol for Na^+ as shown in Figure 2. For Li^+, $E^{(3)}_{cation-\pi} - E^{(2)}_{cation-\pi}$ = +22.87 kcal/mol in the structure T1, which was so large that the structure with the Li^+ cation at the center of the triangle became unstable at room temperature. To achieve a stable structure, the relative positions of the three benzenes shifted so that the cation did not face the center of each benzene (the structure T2) as shown in Figure 1F. For K^+, $E^{(3)}_{cation-\pi} - E^{(2)}_{cation-\pi}$ = +2.93 kcal/mol, a very small value because the cation−benzene distance did not change much in M^+⊗3Bz, since this distance in M^+⊗Bz was only slightly larger than h_m. These factors resulted in the order of the OBB-strength of the cation⊗3π interactions to increase in the order $Li^+ < Na^+ < K^+$, as opposed to the OBB-strength of cation⊗2π and cation⊗π which decrease in the order $Li^+ > Na^+ > K^+$. For M^+⊗2Bz, it is clear that the steric-exclusion effect was very weak, because the π−π interaction between the two benzenes was very small since the distance between the two benzenes was two times greater than the cation−benzene distance. These factors led the OBB-strength in the M^+⊗2Bz to increase in the same order as M^+⊗Bz.

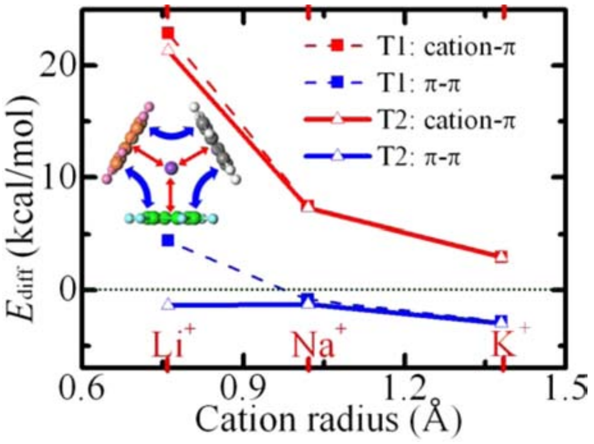


Figure 2. Differences in the interaction energy ($E^{(3)}_{cation-\pi} - E^{(2)}_{cation-\pi}$) of a single benzene with the cation between the M^+⊗3Bz and M^+⊗2Bz complexes (red curve), and the differences in the interaction energy ($E^{(3)}_{\pi-\pi} - E^{(2)}_{\pi-\pi}$) of a benzene with the other benzenes between the M^+⊗3Bz and M^+⊗2Bz complexes (blue curve). The dashed and solid curves denote the T1 and T2 structures, respectively. The inset indicates the schematic representation of the cation−π (red arrow) and π−π (blue arrow) interaction in M^+⊗3Bz, where the large balls, small balls, and violet balls stand for the carbon atoms, the hydrogen atoms, and the cation (K^+, Na^+, or Li^+), respectively.

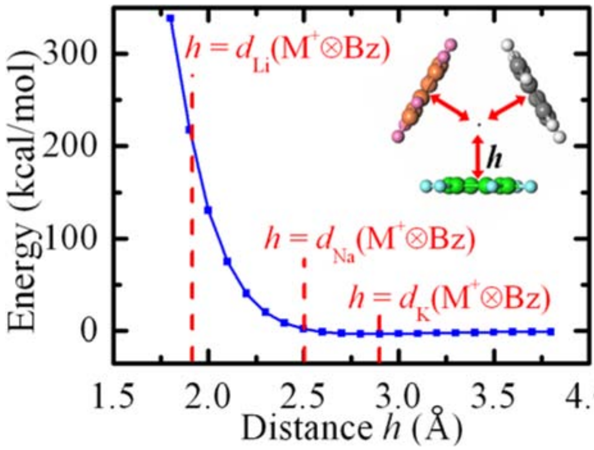


Figure 3. Interaction energy of a complex composed of only three benzenes forming a triangular structure (inset), as a function of their distance h to the center of the triangle structure of them.

Now, we considered the other potential structures consisting of one cation and three benzenes. The initial conformations with a sandwich core of one cation sandwiched between two benzene molecules were applied as follows: (A) the third benzene forming a triple stacked structure over the sandwich core in a parallel configuration; (B) the third benzene resting on the side of the sandwich core in a perpendicular configuration.

For the Li^+ ion, we obtained three stable structures, labeled by S1, S2, and S3 (see Figure 4). From the initial conformation A of the Na^+ and K^+ ions, there are two stable structures S1 and S2. However, from the initial conformation B, the sandwich-

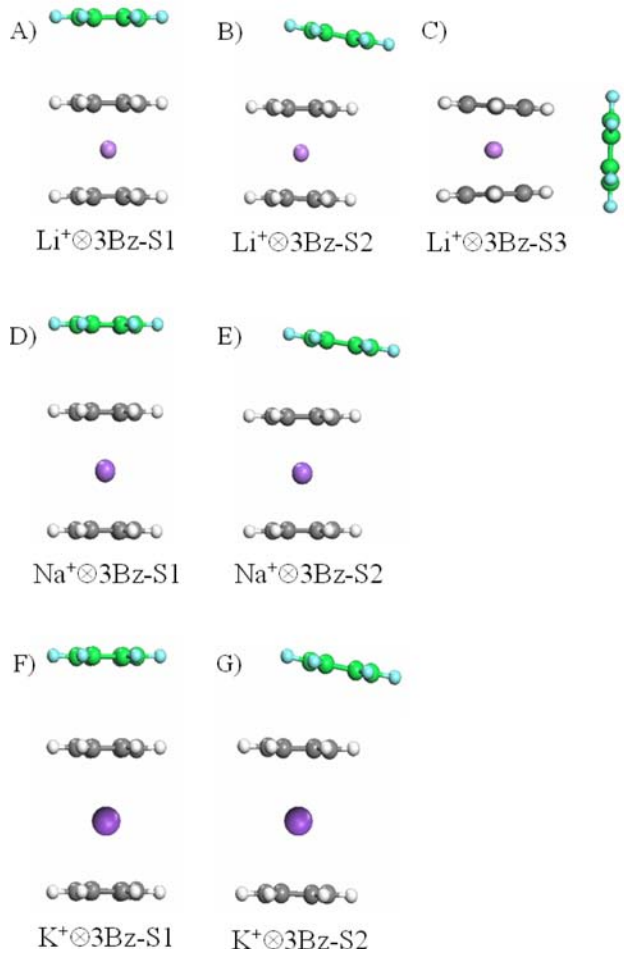


Figure 4. Relaxed conformations for the Li$^+$⊗3Bz (A–C), Na$^+$⊗3Bz (D, E), and K$^+$⊗3Bz (F,G) complexes with a core of one cation sandwiched between two benzene molecules. The large balls, small balls, and violet balls represent the carbon atoms, the hydrogen atoms, and the cation (K$^+$, Na$^+$, or Li$^+$).

core-based initial conformation of Na$^+$ and K$^+$ went to the triangular structures (T1 or T2) during the relaxation, which showed that the sandwich-core-based structures with the third benzene resting on the side of the core were not stable for Na$^+$ and K$^+$. From their OBB energies presented in Table 3, we can see that, for the Li$^+$ complex, the stability of the sandwich-core-based structures is comparable to the stability of the triangular structure Li$^+$⊗3Bz-T2, and is clearly stronger than the triangular structure Li$^+$⊗3Bz-T1. For Na$^+$ and K$^+$, the triangular structures are much more stable than the sandwich-core-based structures.

Table 3. One-Benzene Binding Energy of the M$^+$⊗3Bz Complexes[a]

M$^+$	M$^+$⊗3Bz -T1	M$^+$⊗3Bz -T2	M$^+$⊗3Bz -S1	M$^+$⊗3Bz -S2	M$^+$⊗3Bz -S3
Li$^+$	1.31	−6.0	−5.74	−7.01	−7.42
Na$^+$	−11.58	−12.08	−5.17	−6.37	
K$^+$	−14.44	−14.60	−5.16	−6.32	

[a] The energy is given in the unit of kcal/mol.

We notice here that El-Shall et al.[46] observed that the most stable structure of benzene tetramer cation $(C_6H_6)_4{}^+$ was the form of a pancake trimer stack core $(C_6H_6)_3{}^+$ with an additional neutral molecule resting against the side of the core, which is very similar to the Li$^+$⊗3Bz-S3 complex. Meanwhile, the most stable structure of the benzene hexamer cation $(C_6H_6)_6{}^+$ can be taken as a pancake trimer stack core $(C_6H_6)_3{}^+$ surrounded by other three benzene molecules, which form a triangle similar to the triangular structures of K$^+$⊗3Bz and Na$^+$⊗3Bz.

■ CONCLUSION

We analyze a new type of cooperative interaction, M$^+$⊗3π, which induced a stable triangular structure ◬ composed of a single cation and three benzenes. The cation⊗3π interaction has a comparable strength to the cation−π and cation−π−π interactions but different behavior, so that it is of the same importance with the cation−π and cation−π−π interactions, and can play a special role in many cases, particularly in biological systems. Explicitly, we found an unexpected increasing order of the OBB-energy of the cation⊗3π interaction with respect to the radii of the cations, Li$^+$ < Na$^+$ < K$^+$. In the case of cation−π and cation−π−π, for a cation with a larger radius, the distance between the cation and the benzene is greater which results in decreased binding strength (Li$^+$ > Na$^+$ > K$^+$).[27] The steric-exclusion effect between the three benzenes in M$^+$⊗3Bz makes the distance between the cation and a single benzene considerably different from the distance in M$^+$⊗Bz and M$^+$⊗2Bz, resulting in the odd behaviors of cation⊗3π with respect to cation−π and cation−π−π. This anomalous order increasing behavior of the cation⊗3π favors the preferential behavior of a cation directly surrounded by three benzenes as shown in earlier experiments,[32,45] although the physics behind the experimental observation may be more complicated since there are one or more water molecules involved. Moreover, the OBB-energy of the K$^+$⊗3π interaction was comparable to K$^+$⊗2π, and the OBB-energy of Na$^+$⊗3π was a little weaker than Na$^+$⊗2π, while the OBB-energy of Li$^+$⊗3π was much weaker than Li$^+$⊗2π. The observation that Li$^+$⊗2Bz is much more stable than Li$^+$⊗3Bz suggests a potential application for a selective self-assembly of bio/nanomaterials. In the case of biological molecules, there are abundant fragments that are rich in aromatic rings, and it is well-known that the behavior, including the aggregate behavior, of a protein in pure water can be very different from its behavior in phosphate buffer.[52] Moreover, the cooperative cation⊗3π interaction also occurs for other cations, such as iron, copper, or cobalt cation. Thus, our findings are expected to extend the understanding of the behavior of biological molecules, and may have many applications in the design of carbon-based materials/devices.

■ AUTHOR INFORMATION

Corresponding Author

bosong@sinap.ac.cn; xrchen@scu.edu.cn; fanghaiping@sinap.ac.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge Dr. Chunlei Wang and Yi Gao for their helpful discussions. This work was supported by the National Science Foundation of China (10825520, 11175230, and 11174214), the National Basic Research Program of China under Grant 2012CB932400 and 2011CB808201, Shanghai

Leading Academic Discipline Project (B111), the Knowledge Innovation Program of the Chinese Academy of Sciences, the Knowledge Innovation Program of SINAP, the National Key Laboratory Fund for Shock Wave and Detonation Physics Research of the China Academy of Engineering Physics (9140C671101110C6709), the Supercomputer Center of Chinese Academy of Sciences and the Shanghai Supercomputer Center of China.

REFERENCES

(1) Strmcnik, D.; Kodama, K.; van der Vliet, D.; Greeley, J.; Stamenkovic, V. R.; Markovic, N. M. *Nat. Chem.* **2009**, *1*, 466.
(2) Schulze, S.; Koster, S.; Geldmacher, U.; van Scheltinga, A. C. T.; Kuhlbrandt, W. *Nature* **2010**, *467*, 233.
(3) Berl, V.; Huc, I.; Khoury, R. G.; Krische, M. J.; Lehn, J. M. *Nature* **2000**, *407*, 720.
(4) Madueno, R.; Raisanen, M. T.; Silien, C.; Buck, M. *Nature* **2008**, *454*, 618.
(5) Reinhoudt, D. N.; Crego-Calama, M. *Science* **2002**, *295*, 2403.
(6) Muller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100*, 143.
(7) Koishi, T.; Yoo, S.; Yasuoka, K.; Zeng, X. C.; Narumi, T.; Susukita, R.; Kawai, A.; Furusawa, H.; Suenaga, A.; Okimoto, N.; Futatsugi, N.; Ebisuzaki, T. *Phys. Rev. Lett.* **2004**, *93*, 185701.
(8) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 19.
(9) Rocha, A. R.; Garcia-Suarez, V.; Bailey, S. W.; Lambert, C. J.; Ferrer, J.; Sanvito, S. *Nat. Mater.* **2005**, *4*, 335.
(10) Gallivan, J. P.; Dougherty, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 9459.
(11) Beene, D. L.; Brandt, G. S.; Zhong, W. G.; Zacharias, N. M.; Lester, H. A.; Dougherty, D. A. *Biochemistry* **2002**, *41*, 10262.
(12) Michau, M.; Caraballo, R.; Arnal-Herault, C.; Barboiu, M. *J. Membr. Sci.* **2008**, *321*, 22.
(13) Xiu, X. A.; Puskar, N. L.; Shanata, J. A. P.; Lester, H. A.; Dougherty, D. A. *Nature* **2009**, *458*, 534.
(14) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.
(15) Gromiha, M. M.; Santhosh, C.; Ahmad, S. *Int. J. Biol. Macromol.* **2004**, *34*, 203.
(16) Wintjens, R.; Lievin, J.; Rooman, M.; Buisine, E. *J. Mol. Biol.* **2000**, *302*, 395.
(17) Prajapati, R. S.; Sirajuddin, M.; Durani, V.; Sreeramulu, S.; Varadarajan, R. *Biochemistry* **2006**, *45*, 15000.
(18) Zhong, W. G.; Gallivan, J. P.; Zhang, Y. O.; Li, L. T.; Lester, H. A.; Dougherty, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 12088.
(19) Lenaeus, M. J.; Vamvouka, M.; Focia, P. J.; Gross, A. *Nat. Struct. Mol. Biol.* **2005**, *12*, 454.
(20) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85*, 1814.
(21) Gokel, G. W.; De Wall, S. L.; Meadows, E. S. *Eur. J. Org. Chem.* **2000**, *17*, 2967.
(22) Vijay, D.; Sastry, G. N. *Chem. Phys. Lett.* **2010**, *485*, 235.
(23) Amunugama, R.; Rodgers, M. T. *Int. J. Mass. Spectrom.* **2003**, *222*, 431.
(24) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.
(25) Guo, B. C.; Purnell, J. W.; Castleman, A. W. *Chem. Phys. Lett.* **1990**, *168*, 155.
(26) Reddy, A. S.; Sastry, G. N. *J. Phys. Chem. A* **2005**, *109*, 8893.
(27) Amicangelo, J. C.; Armentrout, P. B. *J. Phys. Chem. A* **2000**, *104*, 11420.
(28) Soteras, I.; Orozco, M.; Luque, F. J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2616.
(29) Reddy, A. S.; Vijay, D.; Sastry, G. M.; Sastry, G. N. *J. Phys. Chem. B* **2006**, *110*, 2479.
(30) Meadows, E. S.; De Wall, S. L.; Barbour, L. J.; Gokel, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3092.
(31) Mahadevi, A. S.; Sastry, G. N. *J. Phys. Chem. B* **2011**, *115*, 703.
(32) Beck, J. P.; Lisy, J. M. *J. Phys. Chem. A* **2011**, *115*, 4148.
(33) Nicholas, J. B.; Hay, B. P.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 1394.
(34) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708.
(35) Gal, J. F.; Maria, P. C.; Mo, O.; Yanez, M.; Kuck, D. *Chem.—Eur. J.* **2006**, *12*, 7676.
(36) Pless, S. A.; Millen, K. S.; Hanek, A. P.; Lynch, J. W.; Lester, H. A.; Lummis, S. C. R.; Dougherty, D. A. *J. Neurosci.* **2008**, *28*, 10937.
(37) Engerer, L. K.; Hanusa, T. P. *J. Org. Chem.* **2011**, *76*, 42.
(38) Wu, R. H.; McMahon, T. B. *J. Am. Chem. Soc.* **2008**, *130*, 12554.
(39) Dougherty, D. A.; Stauffer, D. A. *Science* **1990**, *250*, 1558.
(40) Roderick, S. L.; Chan, W. W.; Agate, D. S.; Olsen, L. R.; Vetting, M. W.; Rajashankar, K. R.; Cohen, D. E. *Nat. Struct. Biol.* **2002**, *9*, 507.
(41) Jacobs, S. A.; Khorasanizadeh, S. *Science* **2002**, *295*, 2080.
(42) Nielsen, P. R.; Nietlispach, D.; Mott, H. R.; Callaghan, J.; Bannister, A.; Kouzarides, T.; Murzin, A. G.; Murzina, N. V.; Laue, E. D. *Nature* **2002**, *416*, 103.
(43) Zuo, G.; Zhou, X.; Huang, Q.; Fang, H. P.; Zhou, R. H. *J. Phys. Chem. C* **2011**, *115*, 23323.
(44) Zhao, Y.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2813.
(45) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110*, 8429.
(46) Rusyniak, M. J.; Ibrahim, Y. M.; Wright, D. L.; Khanna, S. N.; El-Shall, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 12001.
(47) Song, B.; Yang, J. W.; Zhao, J. J.; Fang, H. P. *Energy Environ. Sci.* **2011**, *4*, 1379.
(48) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(49) Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 1784.
(50) Frontera, A.; Quinonero, D.; Costa, A.; Ballester, P.; Deya, P. M. *New. J. Chem.* **2007**, *31*, 556.
(51) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(52) Shi, J. H.; Lua, S. X.; Tong, J. S.; Song, J. X. *Biochemistry* **2010**, *49*, 3887.