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Probing the Strength Changes in C−H and C−C Bonds for Cation/*π* Complexes

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The interaction of cation/benzene complexes (cation = Na^+, Li^+, K^+) was calculated by using the density functional theory (DFT). The calculated results suggested that the C−H bonds were strengthened and the C−C bonds were weakened in cation/benzene complexes in comparison to that in free benzene. This conclusion was confirmed by the changes in the stretching frequencies. The redistribution of the charges and the rehybridization analysis of the C−H and C−C bonds gave a further understanding. Similar phenomena have also been found in cation/perfluorobenzene, cation/naphthalene, cation/toluene, and cation/aniline systems.

1. Introduction

The cation/π interactions such as Li^+/π and Na^+/π have been extensively investigated over the last several years.[1] This strong attractive noncovalent interaction is an important driving force in molecular recognition, drug action, and protein folding.[2] Both experimental[3] and theoretical[4] studies have been carried out on cation/π interactions, and have provided valuable insights into their nature. Theoretical methods have been demonstrated to be powerful tools for studying such interactions at the atomic and electronic levels. Quantum chemical methods are therefore widely accepted as being complementary to experimental measurements on cation/π complexes.[5] Though a number of papers concerned the cation/π interaction, to the best of our knowledge, few works studied the C−H bonds in the cation/π complex. Actually, the investigation of C−H provided significant information in determining the shapes, properties, and functions of the molecules. For example, a wavenumber shift of the CH stretching band gives an insight into the molecular interaction and attracted keen interest in recent years.[6] In particular, the shift to higher wavenumber ("blue shift") of the ν_{C-H} band has been studied both experimentally and theoretically.[7] The cation/π interaction has been observed in many biological systems such as the binding site acetylcholine esterase and alkylamine dehydrogenase.[1] Investigation of C−H and C−C properties in the cation/π complexes may help us to understand the physical and chemical properties of biological systems. In what follows, we showed the strength changes in C−H and C−C bonds induced by the cation/π interactions.

2. Methods of Calculation

Benzene (B), perfluorobenzene (FB), naphthalene (N), toluene (T), and aniline (A) were chosen as model molecules of π and Li^+, Na^+, and K^+ as cation to investigate the contribution of the cation/π interaction to the strength changes in C−H and C−C bonds. The geometry of cation/B complexes was gradiently optimized at B3LYP/6-31G*, B3LYP/6-31++G**, and B3LYP/6-311++G(2d, 2p) levels of theory by using the Gaussian 03 program.[8] No symmetry constrains have been imposed in the optimizations. The cation/FB, cation/N, cation/T, and cation/A complexes are optimized directly at the B3LYP/6-311++G(2d, 2p) level. Atoms in molecules (AIM) and natural bond orbital (NBO) calculations were run on the optimized configurations. The AIM analysis was performed with the AIM2000 program.[9] Topological properties of the electron density at the bond critical points (BCP) were characterized at the B3LYP/6-311++G(2d, 2p) level. The hybridization analysis as well as the atomic charges were calculated by the NBO method[10] at the B3LYP/6-311++G(2d, 2p) level. The aromaticity indices based on magnetism (NICS) were calculated by using the GIAO-B3LYP method with the corresponding basis set.[11] The negative values of the absolute shielding (estimated in the center of the ring) were obtained for benzene, perfluorobenzene, naphthalene, toluene, and aniline.

TABLE 1: Calculated Binding Energies, Gibbs Free Energies, Enthalpies (kcal/mol), and Entropies (J/mol) for the Cation/B (B = benzene) Complexes

methods	parameters	Li_B	Na_B	K_B
B3LYP/6-31G(d)	ΔE	−40.44	−27.14	−18.21
	$\Delta E + \delta$BSSE	−40.49	−27.17	−18.25
	ΔH	−41.03	−27.73	−17.93
	ΔG	−33.27	−20.31	−10.97
	ΔS	−26.14	−24.98	−23.45
B3LYP/6-31++G(d,p)	ΔE	−35.62	−23.01	−15.16
	$\Delta E + \delta$BSSE	−35.59	−23.11	−15.22
	ΔH	−36.21	−23.60	−15.03
	ΔG	−28.33	−16.33	−8.28
	ΔS	−26.53	−25.04	−22.72
B3LYP/6-311++G(2d,2p)	ΔE	−37.59	−23.01	−15.83
	$\Delta E + \delta$BSSE	−37.54	−23.10	−15.86
	ΔH	−37.59	−23.60	−15.67
	ΔG	−29.63	−16.28	−8.70
	ΔS	−26.78	−24.65	−23.44

3. Results and Discussion

3.1. Strength Changes in C−H and C−C Bonds. Geometry optimizations of Li_B, Na_B, and K_B complexes were performed by using density functional theory with various basis sets. All frequency calculations for the three optimized geometries gave no imaginary frequencies, suggesting that they are all true energy minimum structures (Figure 1). The binding energies, Gibbs free energies, enthalpies, and entropies obtained at three theoretical levels are summarized in Table 1. According

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TABLE 2: C−H or C−F Frequency Parameters, Calculated Binding Energies, and Gibbs Free Energies (kcal/mol) for Cation/π Complexes[a]

	complexes	ν^{as}	$\Delta\nu^{as}$	ΔE	ΔG
cation/B	B	3161.33			
	Li_B	3195.16	33.83	−37.59	−29.63
	Na_B	3182.04	20.71	−23.01	−16.28
	K_B	3174.01	12.68	−15.83	−8.70
cation/FB	FB	1333.74			
	Li_FB	1375.56	41.82	−7.37	−0.41
	Na_FB	1359.23	25.49	−0.20	5.14
	K_FB	1350.03	16.29	1.32	9.67
cation/N	N	3162.64			
	Li_N	3184.88	22.24	−39.59	−32.20
	Na_N	3176.40	13.76	−25.27	−18.64
	K_N	3171.45	8.81	−17.12	−10.85
cation/T	T	3158.85			
	Li_T	3185.05	26.20	−39.24	−32.81
	Na_T	3175.91	17.06	−24.35	−18.67
	K_T	3169.68	10.83	−15.88	−10.62
cation/A	A	3158.65			
	Li_A	3183.50	24.85	−43.77	−36.23
	Na_A	3175.06	16.41	−28.42	−21.56
	K_A	3169.19	10.54	−19.77	−13.24

[a] Calculated at the B3LYP/6-311++G(2d,2p) level, ν^{as} means asymmetric stretching, $\Delta\nu^{as} = \nu^{as}_{cation/\pi} - \nu^{as}_{\pi}$, B = benzene, FB means perfluorobenzene, N means naphthalene, T means toluene, and A means aniline.

TABLE 3: Natural Population Analysis for Cation/B Complex (Calculated at the B3LYP/6-311++G(2d,2p) Level)

	C	H	cation	NCT[a]	$NCT_{(H\rightarrow C)}$[b]
B	−0.2022	0.2022			
Li_B	−0.2389	0.2449	0.9638	−0.0362	−0.0367
Na_B	−0.2320	0.2352	0.9809	−0.0191	−0.0298
K_B	−0.2253	0.2278	0.9850	−0.0150	−0.0231

[a] Net charge transferred from benzene to cation. [b] Net charge transferred from H atom to C atom.

to Table 1, the predicted binding energies are not very sensitive to the basis sets used, as can be inferred from complex Li_B, only 1∼2 kJ/mol difference when calculated at the basis from B3LYP/6-31++G** to B3LYP/6-311++G(2d,2p). The corresponding values at the three different theoretical levels are similar to the literature data.[12]

Changes in bond length and shift in bond stretching frequency of C−C and C−H bonds in benzene caused by complexation with Li^+, Na^+, and K^+ are summarized in Figure 1 and Table 2. The elongation of the C−C bonds in alkaline earth metal ions/π complexes had been reported by Jiang et al. at the B3LYP/6-31G* level.[13] As indicated in Figure 1, at our B3LYP/6-31++G(2d,2p) level, the greatest change comes from the Li_B complex, in which the C−C bond length increases 0.0073 Å, and the corresponding values for the Na_B and K_B complexes are 0.0061 and 0.0005 Å, respectively. This elongation showed a weakening of the strength of the C−C bond.

In the C−H···Y (Y is an electronegative atom and has a lone pair of electrons or π electrons) blue shift hydrogen bonds, normally, the C−H bonds are contracted. The CH bond contraction and an increase of the CH stretch frequency (blue shift) are the most important features of traditional blue shift hydrogen bonds.[14] The ΔR_{CH} (the length changes in C−H bonds) of traditional blue shift hydrogen bonds are always in the 0.001 Å grade.[14] The contraction of the R_{CH} in the cation/π complexes is very small (Figure. 1). For example, ΔR_{CH} for K_B, Na_B, and Li_B complexes is −0.0001, −0.0005, and −0.0007 Å at the B3LYP/6-311++G (2d,2p) level, respectively. Normally, the hydrogen atom connects with the Y atom in the C−H···Y blue shift hydrogen bonds. However, the hydrogen atoms do not connect with the cation directly in the cation/π complexes. To reveal the C−H changes, the spectroscopy and electronic density changes in the C−H have been analyzed in detail in the following.

The C−H stretching frequencies (ν^{as} means asymmetric stretching) showed a systematic blue shift (the CH frequency shifted to high wavenumber) in the cation/π complexes. For example, at the B3LYP/6-311++G(2d,2p) level, the blue-shifted extent of the ν^{as}_{CH} for K_B, Na_B, and Li_B complexes are 12.68, 20.71, and 33.83 cm^{-1}, respectively. A gross linear trend was found between the C−H blue-shifted extent and binding Gibbs free energies, where the increase of the C−H blue-shifted extent was associated with an increase of the absolute binding Gibbs free energies (Figure. 2a).

The electron density (ρ_{BCP}) correlates with the strength of an atomic interaction.[15] The $\rho_{BCP(C-C)}$ significantly decreased in K_B, Na_B, and Li_B, indicating that the C−C bonds weakened in the cation/B complexes (Figure 1). For example, the$\rho_{BCP(C-C)}$ in free benzene is 0.3131 e/au^3, while the corresponding values are 0.3086, 0.3093, and 0.3105 e/au^3 for Li_B, Na_B, and K_B complexes, respectively. Conversely, the $\rho_{BCP(C-H)}$ apparently increased in K_B, Na_B, and Li_B complexes. The $\rho_{BCP(C-H)}$ in free benzene is 0.2900 e/au^3, while the corresponding values are 0.2942, 0.2931, and 0.2922 e/au^3 in Li_B, Na_B, and K_B complexes, respectively. The ρ_{BCP} analysis of the C−H and C−C bonds confirmed that the C−H bonds strengthened and the C−C bonds weakened in the cation/B complexes.

3.2. Charges Transfer Analysis. The natural bond orbital (NBO) analysis was performed at the B3LYP/6-311++G(2d,2p) level to reveal the role of intra- and intermolecular electron transfer within the complexes. The Natural population analysis

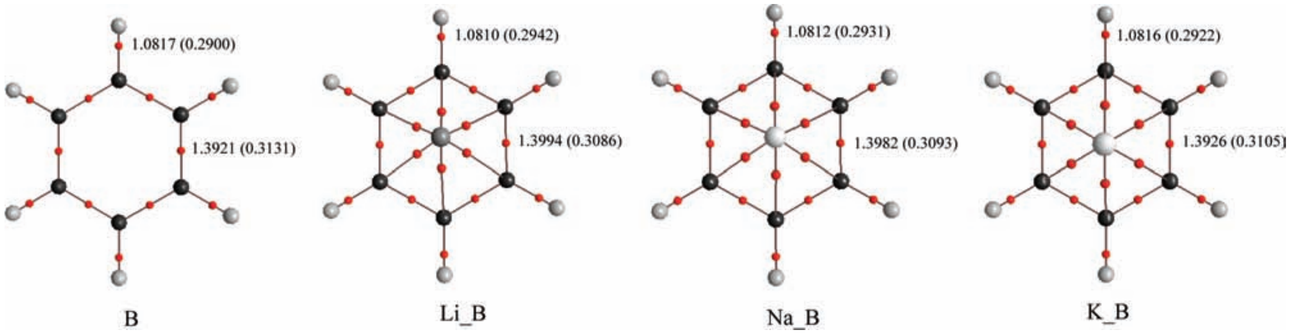

Figure 1. The bonds length and the electron density values (in the bracket) of the cation/B complexes (the bond lengths are in Å, the electron densities are in e/au^3).

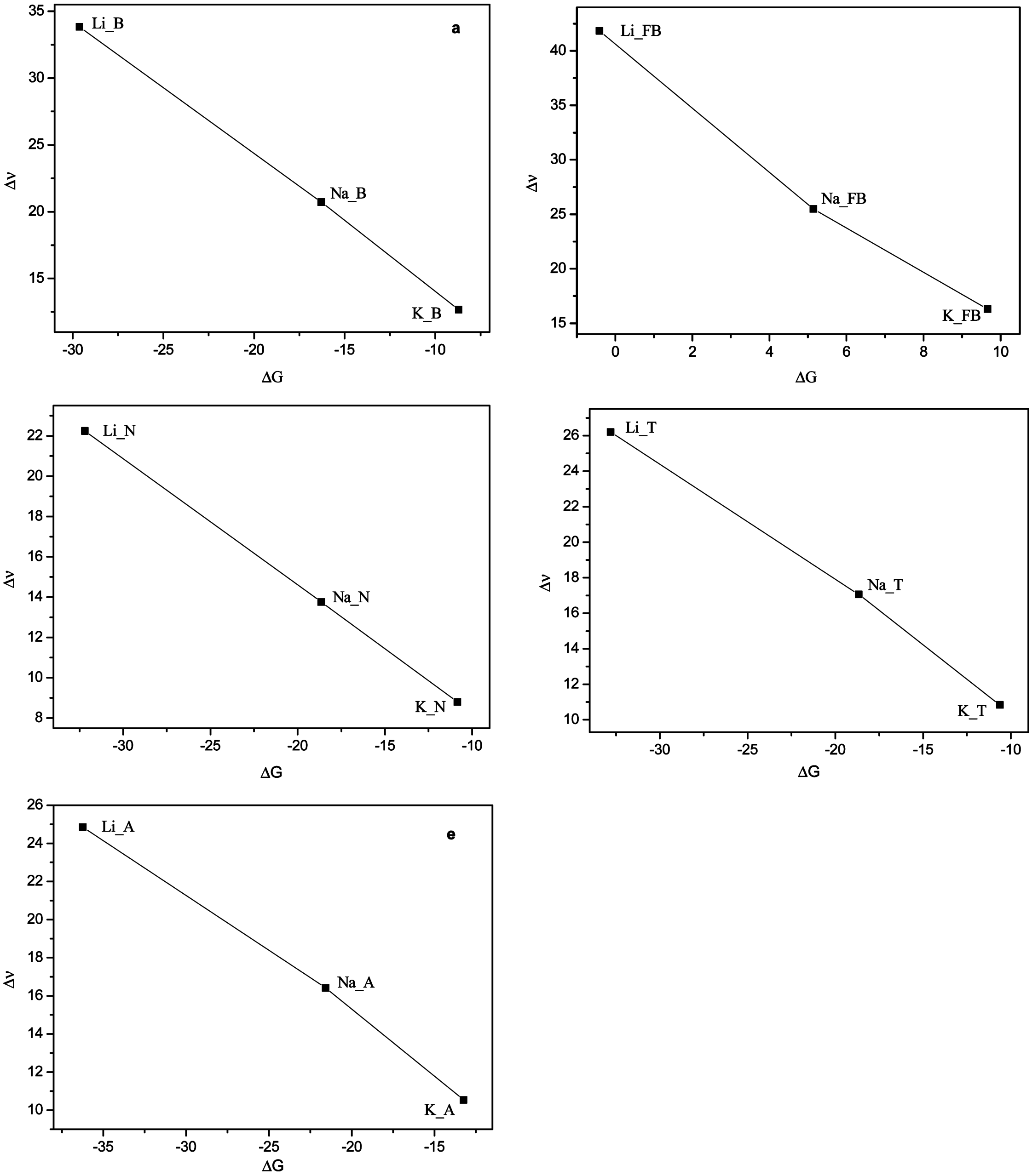

Figure 2. Linear trend between the C−H (or C−F) blue-shifted extent and binding Gibbs free energies.

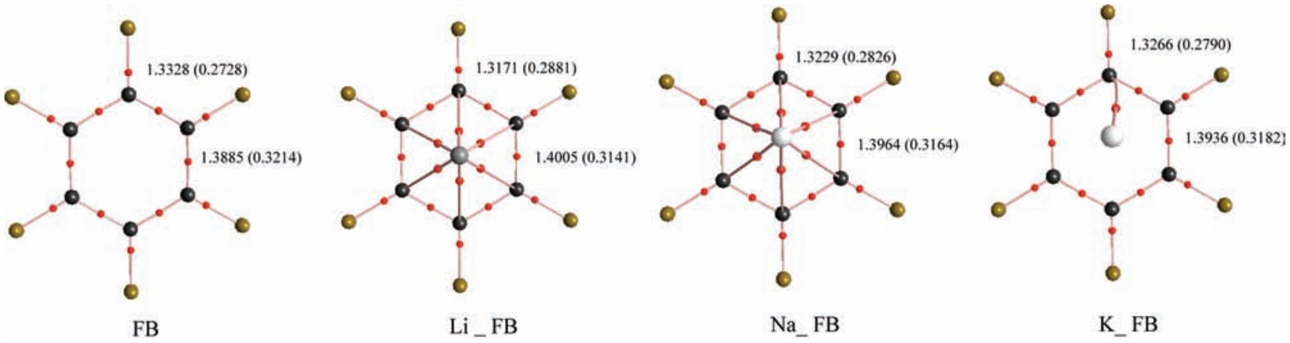

Figure 3. The principal structure parameters and the electron density values of the cation/FB complexes (the bond lengths are in Å, the electron densities are in e/au^3).

(NPA) for cation/B complexes is listed in Table 3. When benzene is connected with a cation, the C atoms in benzene are more negative, and the H atoms are more positive than that in the monomer. The polarity of the C−H in cation/π complexes is greater than that in free benzene. The net charge transfer (NCT) is more significant in the cation/B system than that in the traditional blue-shifted hydrogen bonds systems. The NCT for the hydrogen bond $F_2N-H\cdots OH_2$ is −0.0126 eV;[16]

TABLE 4: NBO Analysis of the C−C and C−H Bonds for Cation/B (Calculated at the B3LYP/6-311++G(2d,2p) Level)[a]

		C_{A1}	C_{A2}	α_1	α_2	s-character (%)
B	σ_{CC}	0.7071		1.80		35.7
	σ^*_{CC}	0.7071	−0.7071	1.80		35.7
	σ_{CH}	0.7863	0.6178	2.52	0.00	28.4
	σ^*_{CH}	0.6178	−0.7863	2.52	0.00	28.4
Li_B	σ_{CC}	0.7071		1.85		35.1
	σ^*_{CC}	0.7071	−0.7071	1.85		35.1
	σ_{CH}	0.7894	0.6138	2.36	0.00	29.8
	σ^*_{CH}	0.6138	−0.7894	2.36	0.00	29.8
Na_B	σ_{CC}	0.7071		1.83		35.3
	σ^*_{CC}	0.7071	−0.7071	1.83		35.3
	σ_{CH}	0.7863	0.6178	2.41	0.00	29.3
	σ^*_{CH}	0.6178	−0.7863	2.41	0.00	29.3
K_B	σ_{CC}	0.7071		1.82		35.5
	σ^*_{CC}	0.7071	−0.7071	1.82		35.5
	σ_{CH}	0.7840	0.6207	2.44	0.00	29.1
	σ^*_{CH}	0.6207	−0.7840	2.44	0.00	29.1

[a] C_{A1} and C_{A2} are the polarization coefficients, a_1 and a_2 are percentage of the NBO on p and d hybrids.

however, the NCT is −0.0362 eV in the Li_B complex (Table 3). It worth mentioning that the total amount of charge transferred from benzene to the cation is not a significant contributor to the change in charges of atoms in benzene. The change in charges of the atoms in benzene comes primarily from the charge redistribution within benzene rather than that from charge transfer. For example, in the free benzene, the NPA charges for the C atoms and H atoms are −0.2022 and 0.2022 eV, respectively. The same figures are −0.2389 and 0.2449 eV, respectively, while in the Li_B complex. The $NCT_{\pi\rightarrow cation}$ (net charge transferred from benzene to cation) is −0.0362 eV, even though all the charges transferred from the H atom, each H atom contributed only −0.00603 eV charge. The $NCT_{H\rightarrow C}$ (net charge transferred from C atom to H atom) is −0.0367 eV, which is more significant than the $NCT_{\pi\rightarrow cation}$. On the basis of the analysis of the above, we can therefore conclude that the intramolecular electron transfer (redistribution) rather than the intermolecular electron transfer significantly affected the C−H strengthening and C−C weakening. In other words, the positive charge of the cation induced the polarization of the C−H bonds, there is a simple redistribution of the charges within the benzene.

3.3. Rehybridization Analysis. The rehybridization of the C−H and C−C bonds in the cation/π complexes allows a better understanding of the C−H and C−C bond changes. According to the natural bond orbital analysis, the C−C and C−H bonding orbital and antibonding orbital can be displayed as shown below:

$$\sigma_{CC} = C_{A1}(sp^{\alpha_1}d^{\alpha_2})_C + C_{A1}(sp^{\alpha_1}d^{\alpha_2})_C$$
$$\sigma^*_{CC} = C_{A1}(sp^{\alpha_1}d^{\alpha_2})_C + C_{A1}(sp^{\alpha_1}d^{\alpha_2})_C$$
$$\sigma_{CH} = C_{A1}(sp^{\alpha_1})_C + C_{A1}(sp^{\alpha_1})_H$$
$$\sigma^*_{CH} = C_{A1}(sp^{\alpha_1})_C + C_{A1}(sp^{\alpha_1})_H$$

where C_{A1} and C_{A2} are the polarization coefficients, α_1 and α_2 are percentage of the NBO on each hybrid, and sp and spd are the hybrid labels showing the sp-hybridization (percentage of s-character, p-character, etc.) and spd-hybridization (percentage s-character, p-character, d-character, etc.) of each natural atomic hybrids. The above parameters of the cation/B complexes are listed in Table 4. Hybridization of the C−C bond is sensitive to the cation and changes from $sp^{1.8}$ to $sp^{1.85}$ (i.e., from 35.7%

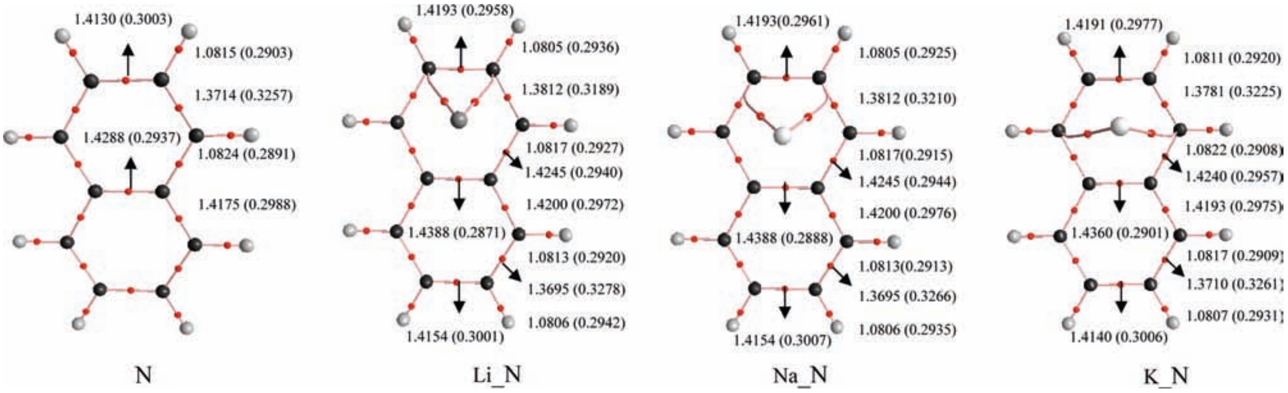

Figure 4. The principal structure parameters and the electron density values of the cation/N complexes (the bond lengths are in Å, the electron densities are in e/au^3).

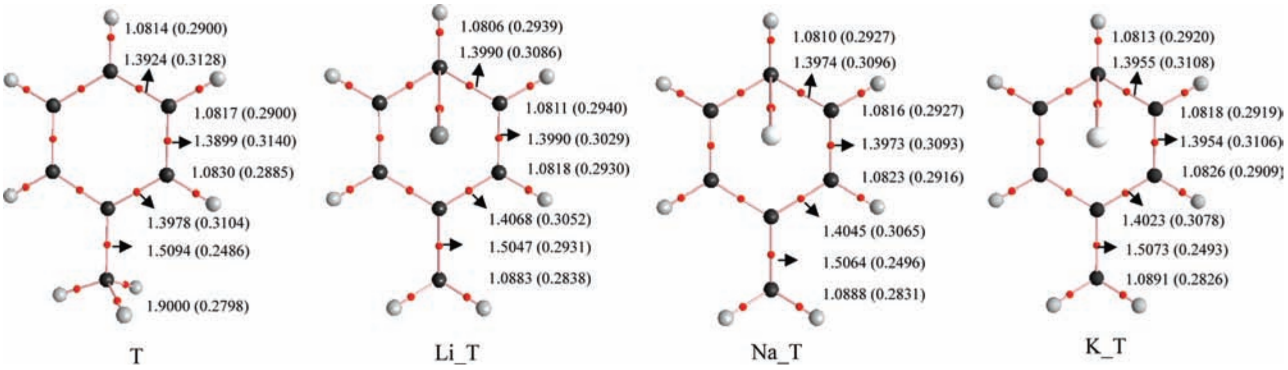

Figure 5. The principal structure parameters and the electron density values of the cation/T complexes (the bond lengths are in Å, the electron densities are in e/au^3).

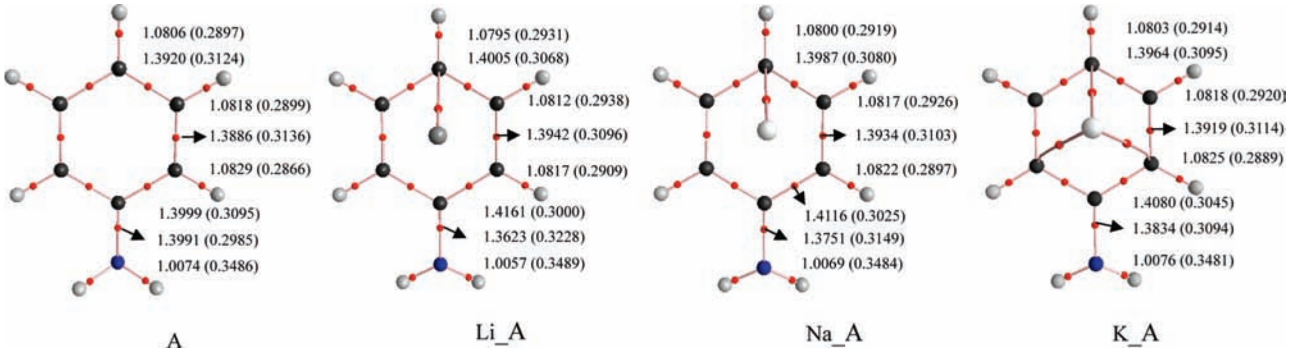

Figure 6. The principal structure parameters and the electron density values of the cation/A complexes (the bond lengths are in Å, the electron densities are in e/au^3).

to 35.1% s-character) in different cation/π complexes (Table 4). The s-characters of C−C bonds decreased with the increase of the cation size, indicating that with the strengthening of the cation/B interaction, the C−C bond has been weakened. Hybridization of the C−H bond is also sensitive to the cation ion and changes from sp$^{2.52}$ to sp$^{2.09}$ (i.e., from 28.4% to 29.8% s-character). Opposite to the C−C bonds, the s-characters of C−H bonds increased with the increase of the cation ion size, which means that with the strengthening of the cation/B interaction, the C−H bond has been strengthened.

According to the reports of Jiang et al.,[13] no significant change is observed in lengths of the C−H bonds for alkaline earth cation/π interactions. We then investigated alkaline earth cation/B interactions at the B3LYP/6-31++G(2d,2p) level. Although the calculated results indicated a slight elongation of the length of C−H in alkaline earth cation/B complexes, the $\nu^{as}{}_{CH}$, AIM, and NBO parameters also reinforced the C−H bonds strengthened and the C−C bonds weakened in Be_B, Mg_B, and Ca_B complexes (see Tables S1 to S3 in the Supporting Information).

3.4. Effect of Various Aromatic Rings Systems. To examine the effect of various aromatic rings systems, cation/FB, cation/N, cation/A, and cation/T were also investigated. The aromaticity indices based on magnetism (NICS) for benzene, perfluorobenzene, naphthalene, toluene, and aniline are −7.577, −18.132, −8.056, −7.560, and −7.414 (calculated at the B3LYP/6-311++G(2d,2p) level), respectively. On the basis of the NICS values the following conclusion was drawn: the aromaticity decreases in the order aniline < toluene < benzene < naphthalene < perfluorobenzene. Changes in frequencies, bond lengths, binding energies, and electron densities of cation/FB, cation/N, cation/T, and cation/A are shown in Table 2 and Figures 2−6. At the B3LYP/6-311++G(2d,2p) level, the weakening of the C−C bonds and the strengthening of the C−H (or C−F in cation/FB) bonds were found in all cation/π complexes just like the cation/B systems. The blue-shifted extent of C−H bonds in cation/N was the smallest among all the examined systems, although the aromaticity of naphthalene is larger than that of benzene, toluene, and aniline (Table 2). For example, the $\nu^{as}{}_{CH}$ in Li_N is 22.24 cm^{-1}, while the corresponding values are 33.83, 26.20, and 24.85 cm^{-1} in Li_B, Li_T, and Li_A, respectively. No obvious relationship was found between the aromaticity of the π systems and the blue-shifted extent.

4. Conclusion

In conclusion, the C−H (or C−F) strengthening and C−C weakening induced by the cation/π interaction was demonstrated in this paper. The same Natural population analysis (NPA) for cation/π complexes indicates that intramolecular rather than intermolecular electron transfer significantly affected the C−H strengthening and C−C weakening. Rehybridization analysis of the C−C and the C−H bonds suggested that the decreasing of the s-character in C−C bonds and the increasing of the s-character in C−H bonds might be responsible for the weakening of the C−C bonds and the strengthening of the C−H bonds in the cation/π complexes. In the same π system, the blue-shifted extent increased with the increase of the binding Gibbs free energies. Similar phenomena existed in different aromaticity π systems, while no linear relationship was found between the aromaticity and the blue-shifted extent.

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Supporting Information Available: List of Cartesian coordinates and parts of the principal parameters for the cation/π complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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